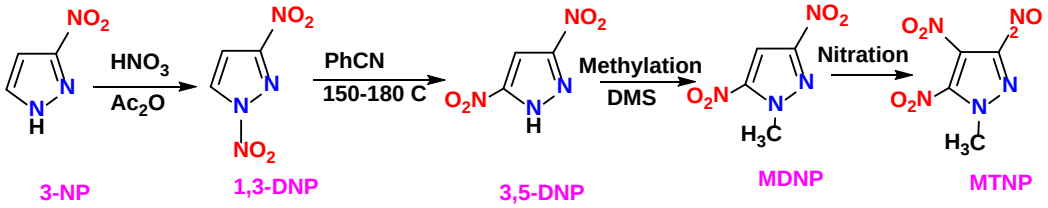
Characterization of MTNP (1-methyl-3,4,5-trinitro-1,2-pyrazole)

Philip Samuels*, Dr. Reddy Damavarapu, Henry Grau, Dr. Kimberly Spangler, Dr. Kelley Caflin, Erik Wrobel
U.S. Army ARDEC
Energetics, Warheads, and Manufacturing Technology Directorate
Picatinny Arsenal, New Jersey 07806
Email: philip.j.samuels2.civ@mail.mil; Phone: 973-724-4064

ABSTRACT

The Ordnance Environmental Program (OEP) from RDECOM has recently funded synthesis efforts evaluating new green synthesis routes to produce both RDX and TNT replacements. MTNP (1-methyl-3,4,5-trinitro-1,2-pyrazole) is a low melting energetic compound. Recently, MTNP has shown promise in terms of a relatively simple synthesis route. ARDEC has characterized this compound from lab scale batches for safety testing.
Thermo-chemical codes such as Cheetah and Jaguar were used to predict the Gurney energy for this high energy material. MTNP was reported in literature using pyrazole, chloro pyrazole and Methyl Pyrazole as starting materials. Our approach involves commercially available 3-Nitropyrazole as starting compound and its synthetic transformation to MTNP as outlined in the following scheme.



Small scale safety testing was completed, including impact, friction and electrostatic discharge testing. The crystal density was determined by pycnometry and the thermal stability was accessed via DSC, isothermal weight loss, and vacuum thermal stability (<2 cc gas/48hrs at 100°C). MTNP has proven to be compatible with most energetics and metals. This paper will discuss the synthesis, thermal, sensitivity and analytical results of pure MTNP.

Introduction

In modern ordnance there is a strong requirement for explosives having good thermal stability, impact insensitivity and explosive performance. However, these requirements are somewhat mutually exclusive. Those explosives having good thermal stability and impact insensitivity exhibit poorer explosive performance and vice versa. TNT has been the mainstay of melt-castable formulations. Among the TNT-based compositions known for making melt-cast explosives, Composition B (TNT/RDX/Wax) is one of the more widely known and practiced. As widely acknowledged in the art, however, melt-cast explosives compositions such as Composition B have several drawbacks. In order to overcome the above-mentioned problems with the existing melt-cast explosive formulations and to meet the U. S. DoD requirements for future high performance munitions systems, it is critical to develop other promising candidates, which possess properties superior to TNT, in an environmentally benign manner. A number of

polynitroazoles have been reported in the literature that are thermally stable, have higher densities and, in some cases, outstanding insensitivity characteristics. Use of a higher density polynitroazole such as 1-Methyl 3,4,5-trinitropyrazole (MTNP) as the melt-cast matrix replacement for TNT would not only result in a formulation with higher performance but also, by virtue of its higher power contribution, allow for a lower added energetic solids fill resulting in lower sensitivity to unplanned stimuli. MTNP was selected for evaluation as a promising new low melting energetic ingredient under the RDECOM Ordnance Environmental Program. It has a crystal density of 1.82 g/cc @ 25 C (measured, Xray).

Synthesis of MTNP has been reported in literature in different approaches: Direct and sequential nitration of Methyl pyrazole, Synthesis of 3,4,5-trinitropyrazole followed by N-methylation, Nitrolysis of 1-Methyl triiodopyrazole, and Nitration of 1-Methyl 3,5-dinitropyrazol. This effort focused on the N nitration of 3-NP as was used in the literature.

Experimental

Scanning Electron Microscopy (SEM)

SEM images were obtained using a JEOL JCM 5700 tungsten filament scanning electron microscope using palladium/gold-coated samples in high vacuum mode as shown in Figure 1.

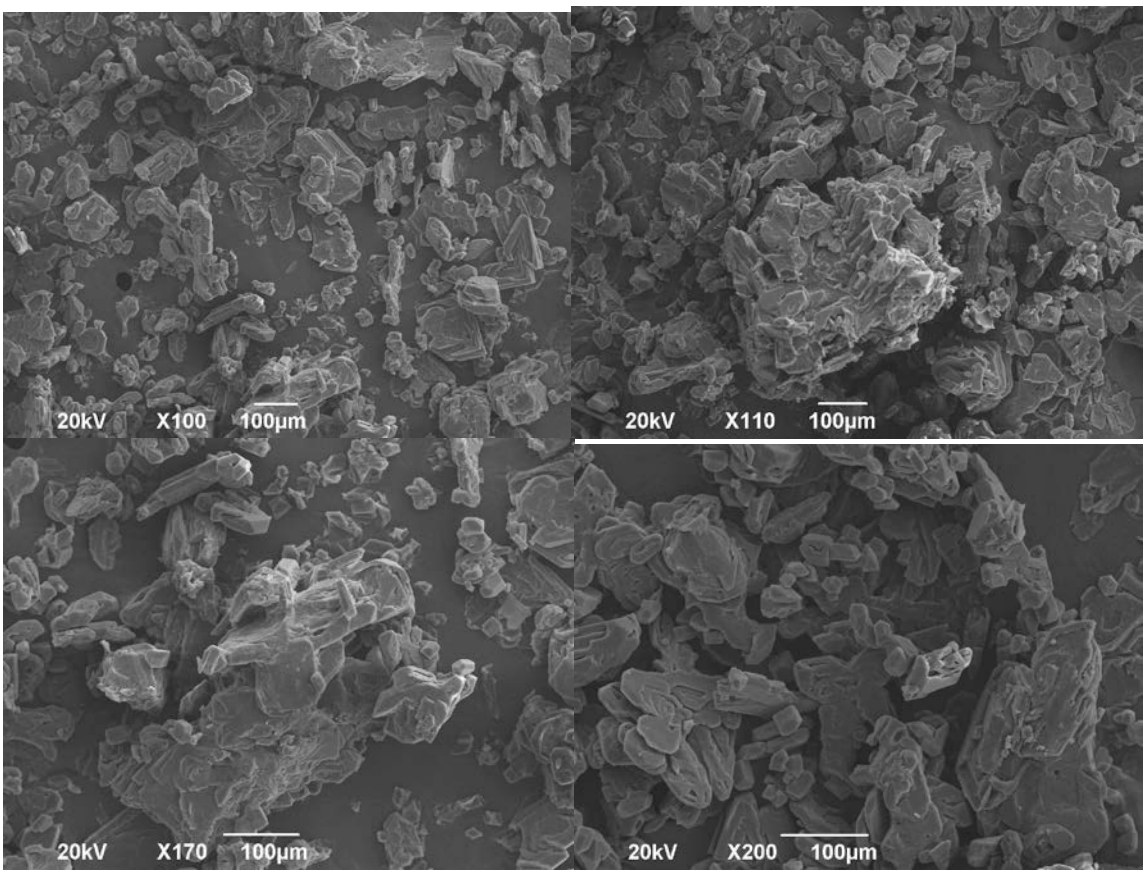


Figure 1. SEM images of MTNP

Differential Scanning Calorimetry (DSC)

The DSC was performed according to AOP-7, US 202.01.020 or STANAG 4515 where 20 mg MTNP was subjected to a heating rate of 10 °C/min until decomposition of the sample occurred. The sample endotherm(s), exotherm(s), onset temperature(s), and peak temperature(s) are recorded. MTNP exhibited a melting point of 91.25 °C, exotherm onset at 225.06 °C, and an exotherm peak temperature at 252.16 °C as shown in Figure 2. By comparison, RDX exhibited an exotherm onset at 210 °C, and an exotherm peak temperature at 241 °C.[1]

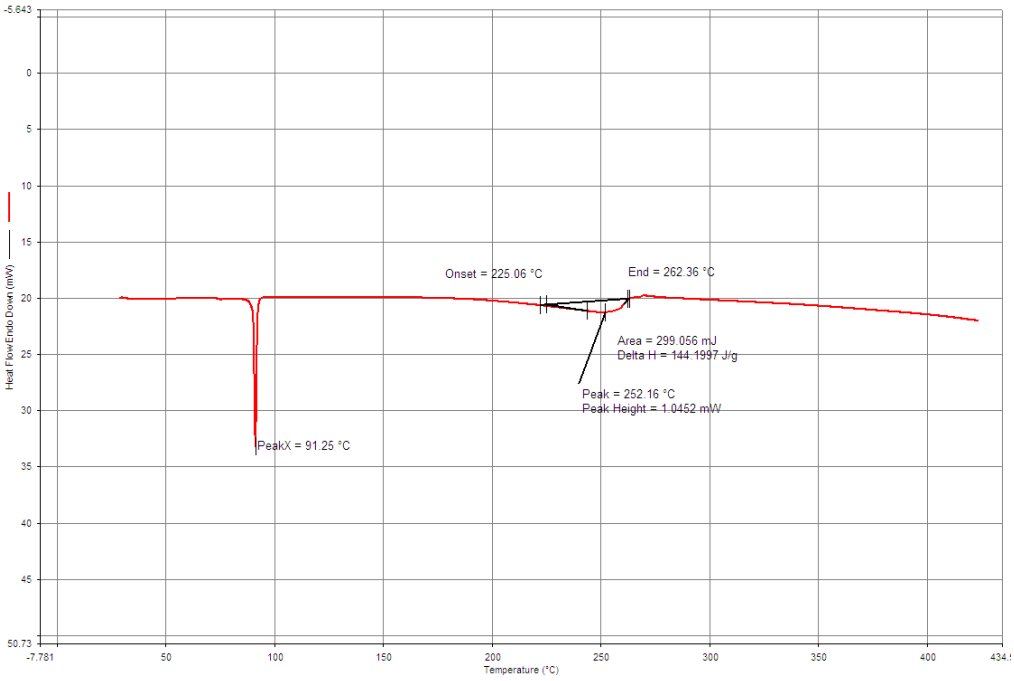


Figure 2. DSC Scan of MTNP

Critical Temperature Determination

Critical temperature determination is a type of thermal stability testing and is defined as the lowest constant surface temperature at which a given material of a specific shape and size will catastrophically self-heat. Experimental data obtained from a Differential Scanning Calorimeter (DSC) is used to determine various kinetic parameters associated with a given chemical reaction or decomposition. Table 1 shows the summary of the thermal properties attained for MTNP.

Critical Temperature Calculations using Frank-Kamenetski (F-K) equation

$$T_C = \frac{E_a / R}{\ln\left[\frac{a^2 \rho Q A E_a}{T_C^2 \lambda \delta R}\right]}$$

Self-heating requirements defined in AOP-7 provide the acceptance criteria for this test are as follows: An explosive should have a critical temperature greater than 82C for a given geometry and size. According to military specifications the average calculated critical temperatures for MTNP (238.7C) as shown in Table 2 exceed the minimum value of 82C for explosive material.[1]

Table 1. Thermal Properties of MTNP

Variable	Description	Unit	Value	Comment
E_a	Activation Energy	cal/mol	21426.94	Variable heating rate data from DSC
R	Gas constant	cal/mol.K	1.707	
a	geometry dimension	Cm	6.123	For 1-LCO
ρ	Density	g/cm^3	1.7057	Gas pycnometer
Q	heat of self-heating rx	cal/g	500	(%wt)
A (Z)	pre-exponential factor	1/sec	4.08E+05	From variable heating rate data from DSC
λ	thermal conductivity	cal/cm.sec.C	0.007	30 deg C
δ	shape factor	geometry dependent	2	for cylinder

Table 2. Critical Temperature of MTNP

T_c (K)	T_c (K)	T_c (C)
Initial Guess (K)	Calculated value	Converted
400	501.7918315	228.6418315
501.7918315	511.0555737	237.9055737
511.0555737	511.8179538	238.6679538
511.8179538	511.8801791	238.7301791
511.8801791	511.8852545	238.7352545
511.8852545	511.8856684	238.7356684
511.8856684	511.8857022	238.7357022
511.8857022	511.8857049	238.7357049
511.8857049	511.8857052	238.7357052
511.8857052	511.8857052	238.7357052
511.8857052	511.8857052	238.7357052
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DSC Compatibility

DSC Analysis: Compatibility of MTNP with Al, O-ring, A2 steel, 304/316 steel, brass, copper, HMX, FOX-7 and NTO.

Test Description:
Perform compatibility testing in accordance to STANAG 4147 ED.2. This standard testing procedure measures the thermal transitions and decomposition of explosives, test materials and their mixtures. A DSC for each individual explosive, test material and mixture shall be run in duplicate. Explosives and test materials are mixed in a 1:1 (w/w) ratio. Samples are heated at a rate of 5°C/min from room temperature to 300°C or more for each sample. The reactivity (compatibility) is then determined by comparing the decomposition profiles of the individual components to the mixture.[2]

Instrument: Perkin Elmer DSC 4000 with Autosampler with nitrogen purgeTemperature Profile: 30-320°C at 2°C/min, Nitrogen Flow Rate: 20mL/min

Criteria:
Shifts in the peak temperature of the decomposition of the explosive are examined. A shift in this peak temperature indicates an interaction between the explosive and test material. If the peak shifts towards a lower temperature, this indicates the presence of the test material has accelerated the decomposition of the explosive. If two explosive materials are tested together, the exotherm peaks for both explosives are examined for any occurring shifts.

Based on test results, which were conducted in accordance with the defining criteria of STANAG 4147 ED.2, MTNP is incompatible with NTO, FOX-7, HMX and O-ring (Vacuum Thermal Stability testing required). MTNP is compatible with Al. MTNP requires VTS testing with brass and 304/316 stainless steel to determine compatibility due to the appearance of a new exotherm. VTS testing is also needed with copper (Figure 3) and A2 Steel due to earlier onset of the decomposition (around 250°C). VTS testing was completed with copper as shown in Table 3 in which MTNP/Copper combination passed this test.

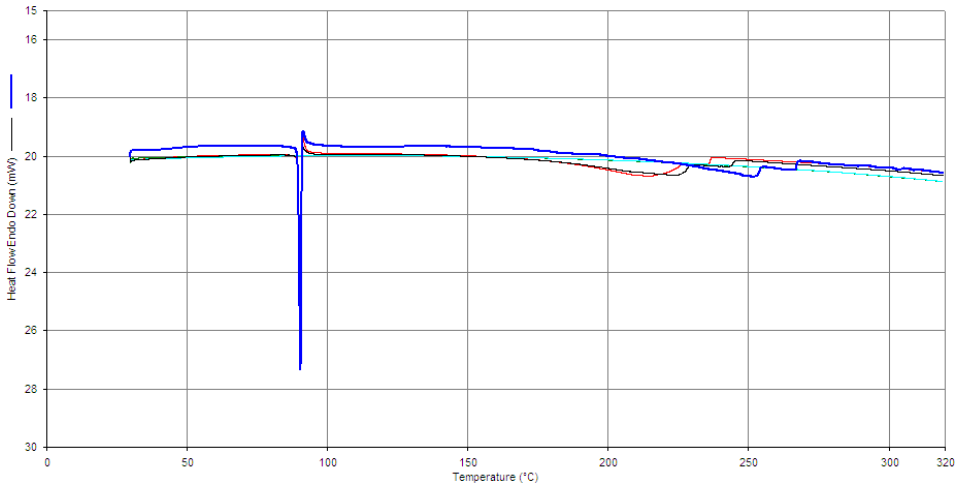

Figure 3. DSC of MTNP and Copper

Table 3. Vacuum Thermal Stability Results for MTNP & Copper

1:1 ratio	Reactivity of mix (ml)	Result
MTNP & copper	negligible	Pass

SENSITIVITY TESTS

Electrostatic Sensitivity (ESD)

The Electrostatic Discharge Sensitivity Test (AOP-7, 201.03.001) determines the energy threshold required to ignite explosives by electrostatic stimuli of varying intensities. The MTNP did not react in 20 trials at 0.051 Joule as shown in Table 4.[1]

Impact Sensitivity Test

The ERL, Type 12 impact tester, utilizing a 2 ½ kg drop weight, was used to determine the impact sensitivity of the sample. The drop height corresponding to the 50% probability of initiation is used to measure impact sensitivity. The ERL, Type 12 Impact Test Method is described in STANAG 4489 Ed.1 “Explosives, Impact Sensitivity Tests”. All impact tests were conducted using 180A garnet sandpaper and the test procedures given in AOP-7, 201.01.001. Bruceton method of statistical analysis was used to determine the 50% point of 54.1 cm for MTNP.[1]

Friction Sensitivity Test

The Large BAM Friction Test Method is described in AOP-7, 201.02.006, "BAM Friction Test". A sample of MTNP was placed on the porcelain plate. The porcelain pin was lowered onto the sample and a weight was placed on the arm to produce the desired load. The tester was activated and the porcelain plate was reciprocated once to and fro. The results are observed as either a reaction (i.e. flash, smoke, and/or audible report) or no reaction. Testing is begun at the maximum load of the apparatus (360 N) or lower if experience warrants it. If a reaction occurs in ten trials, the load is reduced until no reactions are observed in ten trials. MTNP did not react in 10 trials at 360 N.[1]

Table 4. MTNP Safety Test Results Compared to RDX, DNP, and TNT

Molecule	Impact (cm)	BAM Friction (N)	ABL ESD (J)
MTNP	54.1	No Reaction in 10 trials @ 360N	Reacted @ 0.063J, did not react in 20 trails @ 0.051J
RDX Class I Type II	18	Reacted @ 216N, did not react in 10 trials at 192N	Reacted @ 0.063J, did not react in 20 trails @ 0.051J
RDX Class V Type II	>100	Reacted @ 324N, did not react in 10 trials at 288N	Reacted @ 0.051J, did not react in 20 trails @ 0.040J
DNP	>100	No Reaction in 10 trials @ 360N	Reacted @ 0.063J, did not react in 20 trails @ 0.051J
TNT	88.3	Reacted @ 240N, did not react in 10 trials at 216N	Did not react in 20 trials @ 0.25J (Old Test Method)

Theoretical Calculations

Jaguar thermo-chemical code was utilized for determining the performance of MTNP and comparing it to other low melting energetic and crystalline compounds as shown in Table 5. MTNP is an attractive compound due to its high density and metal pushing capability for a low melting energetic compound.

Table 5.

Explosive	Formula	Density	DH_f	Det Vel	C-J P	Gurn Vel(3)	Gurn Vel(7)	OB
		g/cm^3	kJ/mol	km/s	GPa	km/s	km/s	%
DNAN	C7H6N2O5	1.546	-186.5	6.14	14.8	1.88	2.10	-96.9
3,4 DNP	C3H2N4O4	1.791	120.5	8.31	30.9	2.63	2.86	-30.4
MTNP	C4H3N5O6	1.82	4.53	8.36	31.1	2.59	2.82	-25.8
PrNQ	C4H10N4O2	1.335	-217.3	6.45	14.4	1.95	2.10	-120
TNT	C7H5N3O6	1.654	-63	6.89	19.8	2.20	2.43	-74.0
RDX	C3H6N6O6	1.816	70	8.76	34.8	2.73	3.01	-21.6
HMX	C4H8N8O8	1.905	75	9.09	38.7	2.76	3.04	-21.6

Conclusions

The synthesis team performed a literature search and analyzed the reported methods for isolating MTNP. The team identified suitable methods and made attempts to synthesize MTNP in one pot process from pyrazole. MTNP was prepared using sequential nitration processes. Safety and Handling as well as thermal testing has been completed on MTNP to date. The next step is to develop a scale up process to produce sufficient material for shock sensitivity and performance testing. Future work consists of continuing to investigate alternative nitrating agents, process improvements, and incorporation of multiple nitro groups in one process.

References

1. AOP-7: Manual of Data Requirements and Tests for the Qualification of Explosive Materials for Military Use. Edition 2 Version 2
2. STANAG 4147 ED.2 Chemical Compatibility of Ammunition Components with Explosives (Non-Nuclear Applications