MTNI-Based Replacement for Comp B in a Printed Grenade (WP18-1203)

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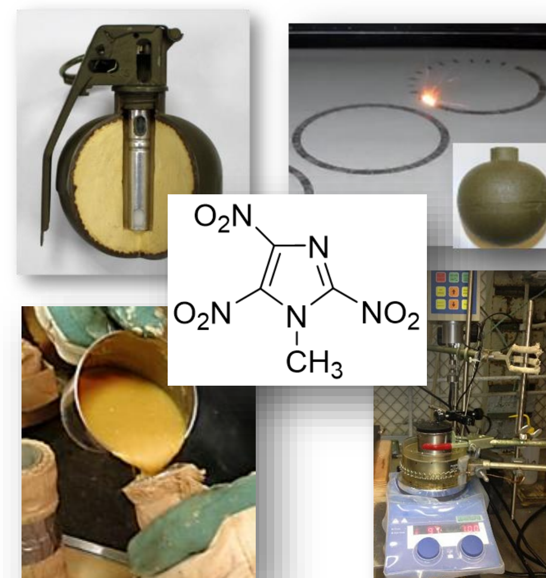
Objective

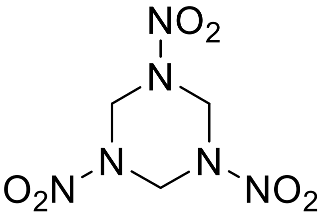
Develop an environmentally/ toxicologically-acceptable melt-pour explosive formulation and warhead system capable of replacing Comp B in a printed precision, tailored-fragmentation hand grenade.



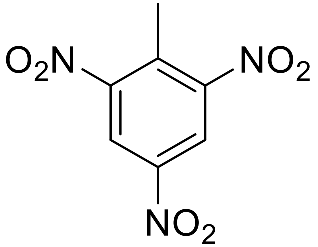
Environmental/Toxicological Justification

- Comp B: common melt-pour explosive formulation traditionally used in many Army munitions since WWII (contains TNT & RDX)
- **TNT (2,4,6-trinitrotoluene):**
  - Toxic occupational health hazard (EPA RfD = 5 x 10^{-4} mg/kg/day)
  - Group C (possible human) carcinogen
  - Hazardous Waste: "red water" & "pink water"
- **RDX (1,3,5-trinitro-1,3,5-triazacyclohexane):**
  - Mobile groundwater contaminant
  - Group C (possible human) carcinogen
  - Toxicity to nervous system if inhaled or ingested in large amounts (EPA RfD = 3 x 10^{-3} mg/kg/day)

TNT/RDX-contaminated runoff at Blue Grass Army Depot washout facility (2010)



RDX

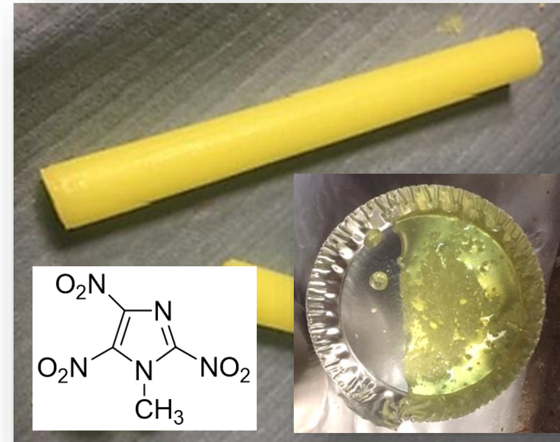


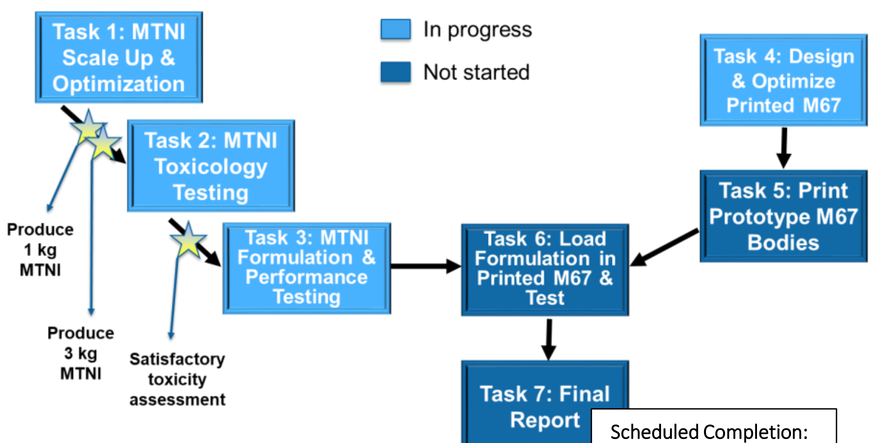
TNT

Technical Approach

- Two-pronged effort:
  1. Develop & characterize alternate Comp B formulation (including initial toxicity/environmental assessment)
  2. Develop prototype of printable M67 hand grenade body and evaluate performance with new explosive fill
- Replacement of Comp B focused on "new" explosive compound, MTNI (1-methyl-2,4,5-trinitroimidazole)
- Laser Powder Bed Fusion (L-PBF) approach to printing grenade body

MTNI: Melt-castable explosive



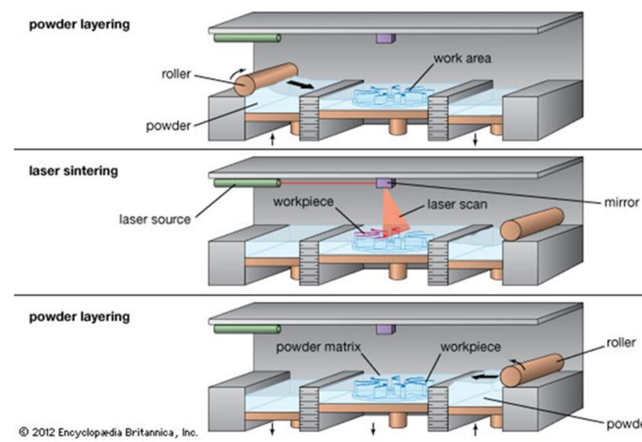


Scheduled Completion: April 2021*

*Will likely be delayed due to COVID-19

M67 Grenade:

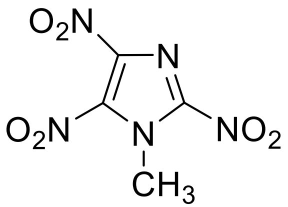
L-PBF Printing Process:



Technical Approach: MTNI (1-methyl-2,4,5-trinitroimidazole)

- First reported in 1970's by Russian chemists and later re-investigated by both South Korea and US Army CCDC AC
- Explosive Performance: MTNI outperforms Comp B in many key explosive performance parameters and is comparable in sensitivity
- Toxicological: only existing data prior to project start was TOPKAT computer modeling
  - Predicted low acute toxicity for oral, inhalation, and dermal exposure
  - May pose moderate occupational hazard: skin sensitization and ocular irritation

Material	Melt Pt.(°C)	DSC (°C)	Density (g/cm³)	Detonation Velocity (km/s)	Detonation Pressure (kbar)	Gurney (km/s)	Impact (cm)	Frict. (N)
MTNI	86	280	1.77	8.17	321*	2.96*	32.7	232
Comp B	80	202	1.71	7.8-8.0	275-280	2.65-2.76	38.3	324
TNT	80	300	1.65	6.7-6.9	188	2.42	108	240

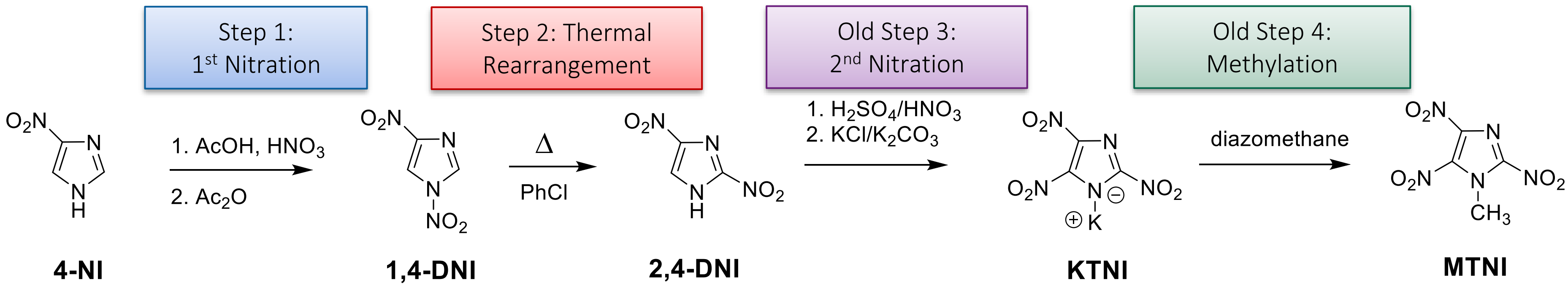


MTNI

Technical Approach: MTNI Synthesis

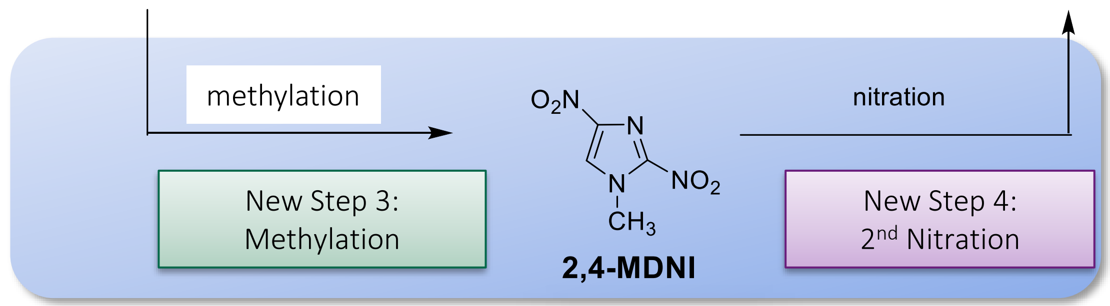
Key goal: produce 3 kg or more of MTNI to support subsequent tasks

Original synthesis (Cho et al, *J. Heterocycl. Chem.* **2002**, *39* (1), 141-147):



Improved CCDC AC route:

Damavarapu et al, US Patent 7,304,164 B1, **2007**.
Duddu et al, *Synthesis*, *17*, **2011**, 2859-2864.



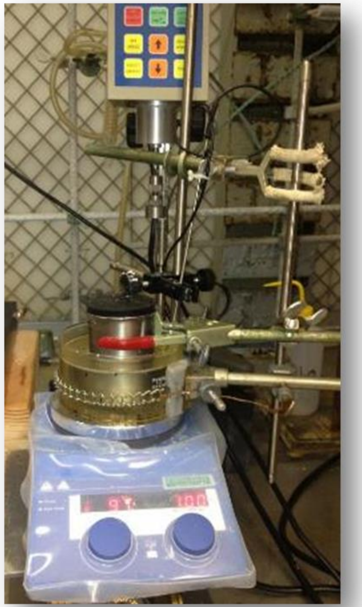
Mettler Toledo EasyMax Workstation & in situ IR probe

Grams → Kilograms

20 L reactor

Technical Approach: MTNI Formulation & Evaluation

- MTNI requires formulation with binders/additives to achieve desired properties: IM behavior, molten viscosity, no cracking, mechanical properties, etc.
- Theoretical calculations show that even diluting MTNI with 5% wax should still have comparable performance to Comp B
- Investigate various polymers based on previous CCDC Armaments Center successes



Lab-scale melt-pour setup

Theoretical Performance Calculations:

Formulation	Density (g/cm^3)	Pressure (GPa)	Det Velocity (km/s)	Cylinder Energy (kJ/cm^3)	Total Detonation Energy (kJ/cm^3)
Comp B	1.73	27.4	7.91	2.81	9.0
MTNI:wax (95:5)	1.69	27.7	7.89	2.86	9.1

All listed properties calculated at 100% Theoretical Maximum Density (TMD)

Technical Approach: Print Design Optimization Strategy

3D Modeling

Printing

Load with Comp B (baseline) & x-ray inspect

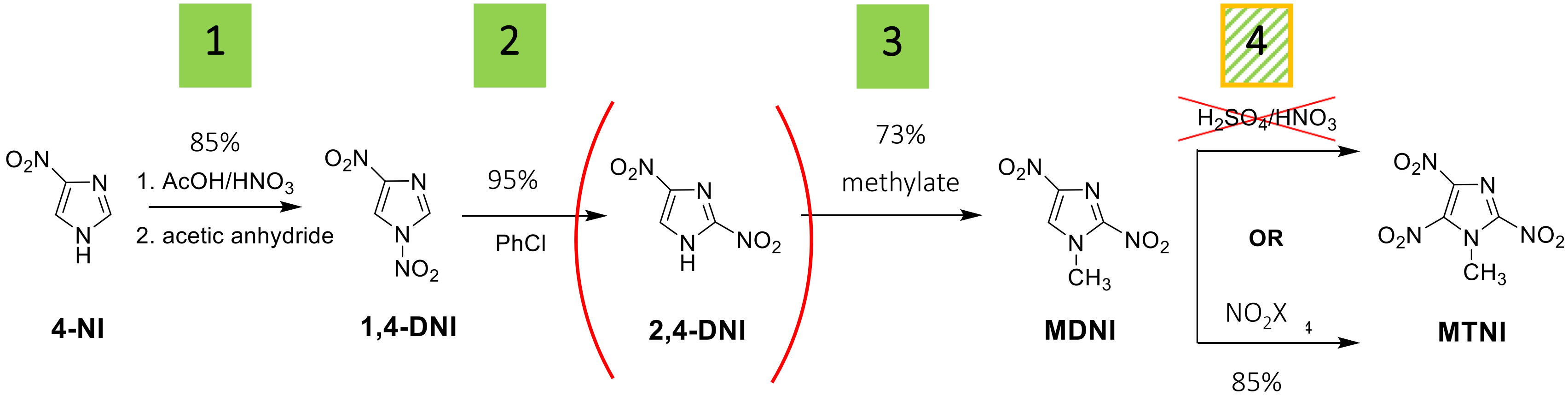
Machine & Assemble with Fuze

Detonate & Evaluate Fragmentation

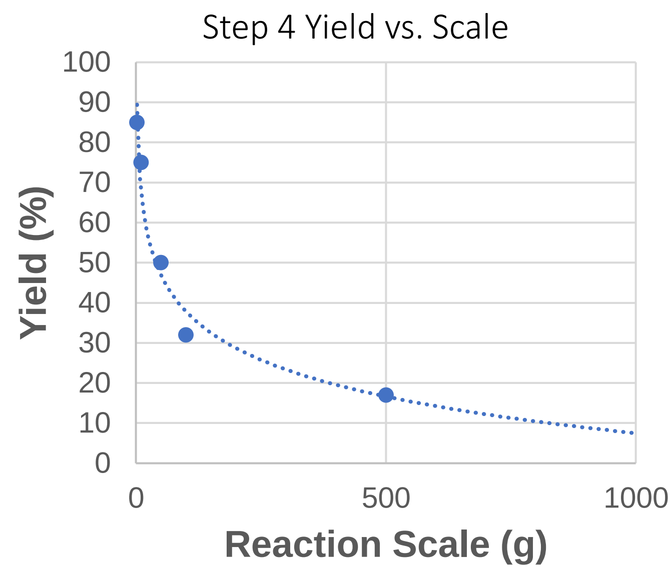
1. Saw Dust Test (fragment shape/size distribution)

Repeat as needed to optimize

Results to Date: MTNI Synthesis



- **Step 1**: successfully scaled up to ~1.5 kg scale
- **Step 2 & 3**: can be combined due to elimination of need to isolate and purify 2,4-DNI; reached 0.5 kg scale
- **Step 4**: Nitronium salt-based procedure is most effective, though difficult to get past 50 g scale
  - 1 kg deliverable for MTNI achieved
  - 3 kg deliverable: over 2 kg of MDNI waiting for conversion pending outcome of toxicity testing
  - Investigating advanced mixing methods to improve yield



Results to Date: MTNI Formulation

- Safety screenings carried out first
  - Vacuum thermal stability testing (VTS) with stainless steel and other common metals
  - Impact, friction, ESD sensitivity; no issues, showing Comp B-like behavior
- Initial melt studies (5 g scale) studied qualitative melting & cooling behavior
  - Brookfield viscosity data obtained for pure MTNI as function of temperature→ material flows within acceptable parameters
- Successfully melt-cast pure MTNI into 0.5" diameter rate sticks to obtain piezopin-based detonation velocity data
  - Detonation velocity measured at 95% theoretical maximum density (TMD): **8.108 +/- 0.054 km/s** (verifies previous data)

An initial MTNI melting study sample

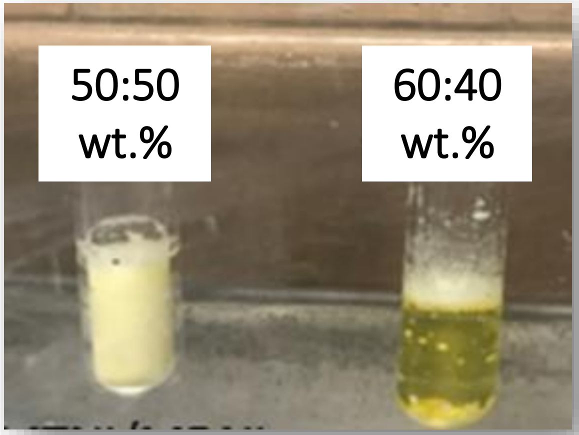
0.5" rate stick cast from pure MTNI

MTNI Formulation Results: Solids Investigation

- Investigated the addition of energetic solids to enhance mechanical strength
- Initial promising result with “Compound A”→ material found to be soluble in MTNI up to 50-70 wt. % and suggested eutectic[1] behavior
  - Performed cloud-point studies with various temperatures to determine optimal pouring temperature
  - Favorable sensitivity data (less impact sensitive)
  - Vacuum thermal stability testing (VTS) was less promising: failed or nearly failed

Vacuum Thermal Stability (VTS) of MTNI with “Compound A”:

	Total gas evolution (mL)	Reactivity / gram for 5g sample	Result
MTNI	0.6	0.12	pass
COMPOUND A	1.51	0.3	pass
MTNI/A 50:50 Physical Mix	9.7	1.94	Passes (barely)
MTNI/A 60:40 Physical Mix	10.2	2.04	fail
MTNI/A 60:40 Melted	9.7	1.94	Passes (barely)



[1] A mixture of 2+ components which (at certain stoichiometric ratios) inhibit the crystallization process of one another, resulting in a system which melts sharply below the melting point than any of the individual components

MTNI Formulation Results: Binder studies

- Multiple wax additives investigated (including biosourced materials)
  - Only one (Wax "A") passed VTS testing
- Investigated solidification behavior of Wax A in various ratios with MTNI (1, 5, and 10 wt. %)
- Down-selected 1 wt.% formulation with Wax A for now
- Initial impact sensitivity screen shows substantial improvement vs. pure MTNI
- In progress: cast formulation into rate sticks & machine for detonation velocity, detonation pressure, and critical diameter assessments

1:1 ratio of MTNI:binder	Reactivity of mix (mL)	Result
Wax A	negligible	pass
Wax B	> 10	fail
Wax C	> 10	fail
Wax D	> 10	fail
Wax E	7.95	fail
Wax F	9.94	fail

Formulation Characterization Progress

Task	Purpose
Thermochemical calculations (Jaguar, Cheetah)	Provides starting point to begin formulation work
Pouring/casting studies	Determine pourability and mechanical strength of cooled material on lab-scale (no cracking, pulling away from container walls, etc.)
Sensitivity Tests (impact/friction/ESD)	Verify safe handling of formulation
Critical Diameter Test	Assess performance potential in small items
Detonation Velocity & Pressure Testing	Common measurement of explosive performance
Cylinder Expansion (Cylex) Testing	Assesses "metal pushing" ability of formulation (ability to shatter metal casing into lethal fragments)
IHE Gap Test	Assess shock sensitivity of formulation (key IM/safety test)
Henkin Test	Assess stability at extreme temperatures (common test for melt-cast)
Slow Cook-off Test	Assess stability under prolonged high temperatures (IM test)
6 and 12 month Aging Studies	Assess long term stability of formulation

Results: In Vitro Toxicity Testing

- In vitro testing completed by Army Public Health Center (APHC)
  - Toxicity assessment report approved by APHC Publication Management Division (PMD) and now published
- Concerning results for aquatic toxicity in particular
- APHC recommended additional in vivo testing to confirm aquatic toxicity predictions
  - Nitroimidazoles (e.g. MTNI) are known anti-microbial substances; in vitro Microtox® test is bacteria-based
- APHC local sub-contractor carrying out short term in vivo assays: daphnia and fathead minnow (48-96 hr duration)
  - Testing delayed due to COVID-19 and administrative delays
- Results of assays will inform final toxicity assessment Go/No-Go deliverable

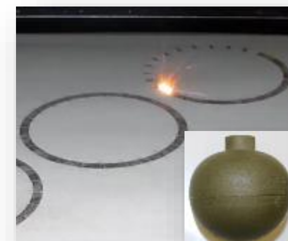
Compound	Genotoxicity (Ames Test)	Skin Sensitization (Human Cell Line Activation, h-CLAT)	Acute Mammalian Toxicity (confidence)	Acute aquatic toxicity (Microtox®)
MTNI	positive	positive	III (low)	I
TNT	positive	negative	IV (high)	II

Results: Printed Grenade

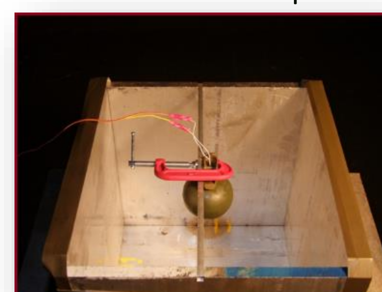
- Two grenade prototype designs printed using L-PBF 3D printers
  - Each prototype loaded with Comp B, analyzed by x-ray, machined for fuze wells, functioned, and fragment analyzed.
- Of the two prototypes, one was a relatively good match for the existing M67 fragmentation behavior
- Two new variations based on best prototype designed and printed
  - Will be loaded with Comp B and evaluated as before with fragment analysis; best performer will be down-selected for loading with final MTNI formulation.

3D Modeling

Printing



Mini-Arena Test Setup



Lessons Learned and Next Steps

- MTNI synthesis path optimized, though yield of final nitration step needs improvement
- MTNI melt-castability and explosive performance meet expectations; initial formulation developed with wax additive
- Concerning aquatic toxicity observed in in vitro studies; in vivo studies underway to further investigate
- Initial printed grenade prototypes performed well with Comp B baseline; optimized prototypes now being evaluated

Acknowledgements

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