Melt-pour Explosive Formulations Development Featuring TNBA

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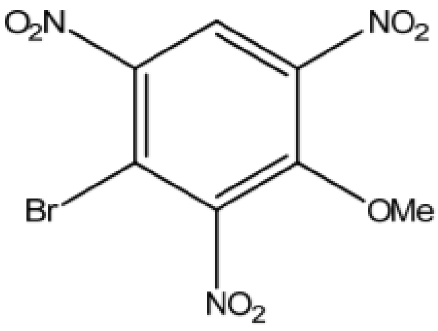
Briefing Outline

- TNBA Background
- TNBA Synthesis and Formulation Efforts
- Preliminary Sensitivity and Performance Testing
- Results and Conclusion
- Path Forward
- Acknowledgements

TNBA Background – The GrIMEX Program

- TNBA (2,4,6-Trinitro-3-bromoanisole) selected as an ingredient candidate from the Green IM Comp B Replacement Program, GrIMEX (presented previously at 2015 and 2016 IMEMTS)
- GrIMEX program objectives
  - Develop environmentally acceptable synthesis methods to produce environmentally sustainable, insensitive secondary explosives as alternatives to cyclotrimethylenetrinitramine (RDX), 2,4,6-trinitrotoluene (TNT), and ammonium perchlorate (AP)
  - Develop novel formulations utilizing the alternative materials to replace Composition B (without RDX and NTO)
- TNBA selected as one of the candidates to replace TNT due to its higher energy and relatively low melting point
  - Suitable for existing LAP infrastructure



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TNBA Background – Toxicology Assessment

- Toxicology Assessment performed in accordance with the United States Army Public Health Center (USAPHC) Phased Approach concept ASTM E-2552-08
- TNBA is no worse than TNT as a melt-ingredient

Compound	Oral	Inhalation	Dermal	Ocular	Reproduction/ Development	Mutagenicity	Comments
TNBA	Moderate	Low	Moderate	Low	Moderate	High	
PiPE	High	Low	Moderate	Low	Moderate	Low	Possible carcinogen
DNMT	Low	Low	Moderate	Low	Low	High	
DNP	Moderate	Low	Moderate	Low	Low	High	
TNT	Moderate	Low	Moderate	Moderate	Low	High	Suspect human carcinogen

TNBA Background – Performance Comparison

	TNT replacements		
	TNBA	DNP	TNT
Impact Sensitivity, cm	(Naval) 79.43	55.0	88
Impact Sensitivity (RDX Std.), cm	23.3	39.0	
Friction Sensitivity, N	70.0	246.0	216
Friction Sensitivity (RDX Std.), N	144.0	164.0	
ESD, J	0.2900	0.2625	> 0.25
Detonation velocity (m/s)	6571	8251	7180
Detonation pressure (GPa)	23.98	29.24	20.02
V/V0 7.20	-5.87	-7.93	-5.42
Oxygen balance	-44.72	-30.37	-73.96
Density, g/cm^3	1.948	1.773	1.654
Melting Point °C	97	87	
Heat of Formation (kJ/mol)	18.88	120.5	-63.2

TNBA Background – BAE Systems IRAD Program

- BAE Systems IRAD program to develop TNBA melt-cast formulations
  - Unlike the GrIMEX program, there is no restriction on HE filler selection
- Program Strategy
  - Leveraging the improved performance aspect of TNBA, the new TNBA melt-pour formulations can potentially out-perform existing candidates containing 2,4-Dinitroanisole (DNAN)
  - Direct replacement of DNAN in IMX formulations
    - IMX-104 (DNAN/RDX/NTO)
    - PAX-48 (DNAN/HMX/NTO)
  - Preliminary formulation effort to assess IM response in comparison to baseline candidates
- Relatively new and continuing effort

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TNBA Background – BAE Systems IRAD Program

- TNBA was selected due to:
  - Robust/mature chemistry
  - Insensitive compare to TNT
  - One Synthetic Step
  - Higher performance than DNAN
  - Relatively cheap to produce
  - Similar thermal properties to existing melt-pour formulations – suitable for processing at current LAP facilities
- TNBA had been successfully scaled up to Pilot and Full Production Scale Manufacture
  - Batch size ranging from 300 – 2,000 lbs.

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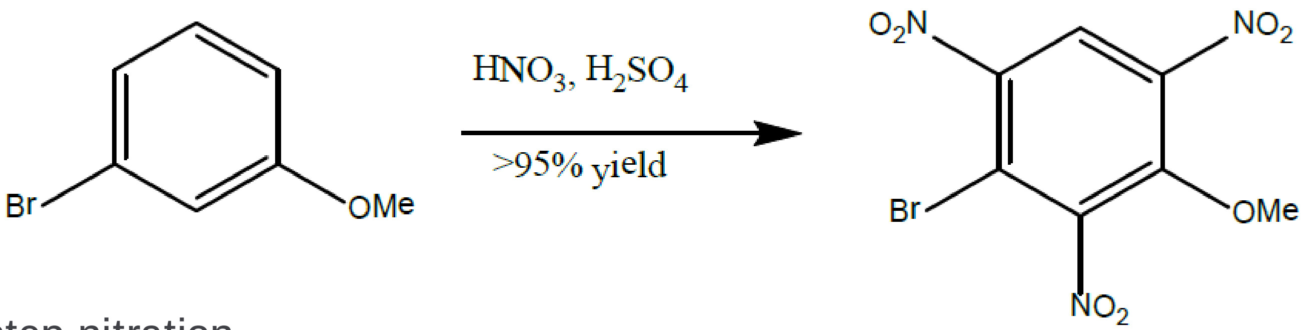
TNBA Synthesis

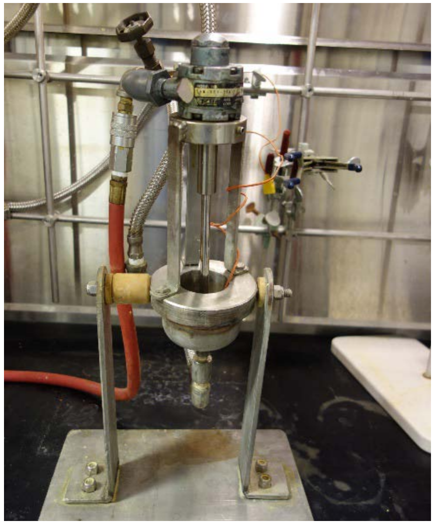


TNBA
$C_7H_4BrN_3O_7$
Mol. Wt.: 322.03

- Synthesis route is one step nitration
  - Crystalline solid precipitates from reaction in high yield
- Robust Process:
  - Many nitrations have been performed (lab and pilot scale)
  - Yields ranged from 96.5% to 100%
  - Purity ranged from 98.69% to 99.92%
- Preliminary data show TNBA has a shock sensitivity (NOL LSGT) of 164 cards
  - TNT is usually ~ 130 cards
  - Could be due to high degree of crystallinity, may improve with solid fills added (or better casting)

TNBA Formulation Efforts (1)

- Use TNBA as a replacement for DNAN in IMX-104 (RDX/NTO) and PAX-48 (HMX/NTO)
  - Increased performance of new TNBA candidates expected
- Initial formulation screening using 50 grams melt kettle to evaluate viscosity (ease of pouring)
- Attempted to maximize solids loading level to maintain high performance
- As the melting point of TNBA is higher, the processing temperature is more effective at >100°C
- Promising candidates were scaled to 500 grams batch
  - Physical assessment of viscosity
  - Samples for hazard and thermal analysis
- Final candidates were cast into tubes for limited LSGT and plate dent firing



50 grams melt-kettle

1-gallon melt-kettle

TNBA Formulation Efforts (2)

- Direct replacement of DNAN with TNBA, same solids ratio
- Initial compositions:
  - TNBA-IMX104 (~32% TNBA / 68% solids)
  - TNBA-PAX48 (~35% TNBA / 65% solids)
- Both candidates exhibited very high viscosities – more TNBA was needed, plus increase in processing temperature
- Final candidates (considered as processable for melt-pour)
  - TNBA-IMX104 (~ 41% TNBA / 59% solids)
  - TNBA-PAX48 (~ 44% TNBA / 56% solids)
- Thermal and Hazard Analysis conducted

Candidate	Melting (°C)	DSC Peak Max (°C)	Impact (cm) RDX Std. = 16.2 cm	BAM Friction (N)	ESD (J) RDX Std. = 0.0888 J
TNBA-IMX104	97.3	235.5	59.57	314.0	> 9.4875
TNBA-PAX48	98.8	242.5	49.17	270.0	> 9.4875

TNBA Formulations Sensitivity Testing

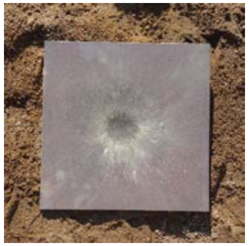
- Limited NOL LSGT conducted on both candidates (3 shots)
  - Shock sensitivity a good indication on the overall IM properties in confined environment

Candidate	Shot 1	Shot 2	Shot 3	50% Card Gap	Pressure (kbar)
TNBA-IMX104	150 Cards (NO GO)	125 Cards (GO)	137.5 Cards (GO)	137.5 -150.0 Cards	38.9 – 45.1
TNBA-PAX48	150 Cards (NO GO)	125 Cards (GO)	137.5 Cards (NO GO)	125.0 – 137.5 Cards	45.1 – 48.8

- Limited LSGT results more shock sensitivity than DNAN based baseline (~ 120 cards, 50.1 kbar) which is expected
- Still significantly less shock sensitive than Composition B (~ 200 cards, 20.7 kbar)
- Both candidates should have similar shock sensitivity properties – full LSGT firing (8-12 shots) can confirm

NOL LSGT Set Up

"GO" Witness Plate



"NO GO" Witness Plate

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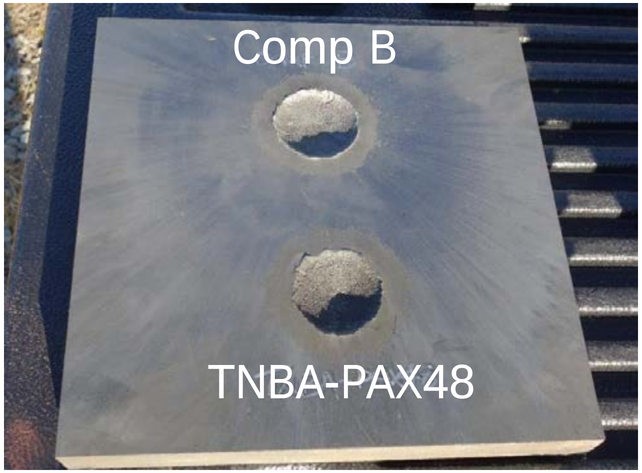
TNBA Formulations Performance Testing (1)

- Compare relative performance of candidates against IMX-104 and Composition B
  - Unconfined LSGT charge (~ 250 g) with no Pentolite booster placed on 10” × 10” × 1” witness plate
  - Dent on witness plate quantified using 3D Scanning Technique
  - Pressure probes @ 5, 10 and 15 feet from test charge
    - Shock Overpressure
    - Peak Impulse Pressure

TNBA Formulations Performance Testing (2)

- Plate Dent Comparison

Candidates	Visual Dent Observation	3D Scanning Result	
TNBA-IMX104	Larger than IMX-104	125% of IMX-104	93.7% of Comp B
TNBA-PAX48	Larger than IMX-104; Same size as Comp B	134% of IMX-104	100% of Comp B



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TNBA Formulations Performance Testing (3)

- Detonation Pressure Comparison
  - Normalized against IMX-104 baseline

Candidates	Shock Overpressure			Peak Impulse Pressure		
	@ 5 ft.	@ 10 ft.	@ 15 ft.	@ 5 ft.	@ 10 ft.	@ 15 ft.
IMX-104	1.00	1.00	1.00	1.00	1.00	1.00
TNBA-IMX104	1.32	1.20	1.07	1.27	1.32	1.25
TNBA-PAX48	0.97	1.10	1.18	0.95	1.89	1.26

  - Overall, the detonation pressures of the candidates are 20-30% higher than the baseline of IMX-104

Results / Conclusion

- Base on limited LSGT firing, both TNBA candidates exhibited good shock sensitivity (50% card gap = 150 cards or less).
- Performance comparison from Plate Dent and Det. Pressure suggested both TNBA candidates will out-perform existing DNAN-based IM explosives (IMX-104/PAX-48)
- From the limited available data, TNBA had proven to be a worthy melt ingredient candidate to replace DNAN in the current family of IM Melt Cast explosive
  - Robust chemistry at all scales
  - Readily available / CONUS manufacturing
  - Improvement in performance over existing IM melt-cast explosives (plate dent/det. pressure)
  - Adequate IM properties
  - Similar thermal characteristics of end product to current IM melt-cast explosive (no new investment required on LAP operations

Path Forward

- Continuation of the current IRAD program to further develop these TNBA formulation candidates:
  - Complete full Large Scale Gap Test on both TNBA formulation candidates
  - Optimize formulations base on efflux viscosity and degree of settling
  - Conduct in-depth, instrumented determination of explosive performances
    - Detonation Velocity & Pressure
    - Disc Acceleration eXperiment (DAX)
    - Cylinder Expansion (CYLEX)
  - Preliminary exudation / accelerated aging study
    - Mass loss / irreversible growth
- Formulation efforts involving novel energetic fillers already planned in the SERDP Green IM Explosive (GrIMEX) Program
- More to report at the IMEMTS 2019

Summary

- TNBA has shown great potentials to be used in a family of new IM melt-cast explosives
- TNBA can be manufactured in production quantities (robust process at HSAAP)
- TNBA melt-cast explosives can be processed with existing manufacturing equipment at LAP facilities
- TNBA melt-cast explosives exhibited good IM properties and performance matching or greater than existing baseline (IMX-104 / PAX-48), confirming that TNBA is a suitable replacement for DNAN as the melt ingredient
- Further IM and Performance improvement can be expected from further formulation optimization efforts
- Potential product TRL higher than other high-performance IM melt-cast explosives (e.g. DNP based)
    - Great stop-gap improvement to current DNAN based explosives

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