GrIMEx: Development of a Novel, Green IM Comp B Replacement (Abstract 22217)

IMEMTS 2019 (Session 2B)

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Non Export Controlled per PS-2019-DR-1226

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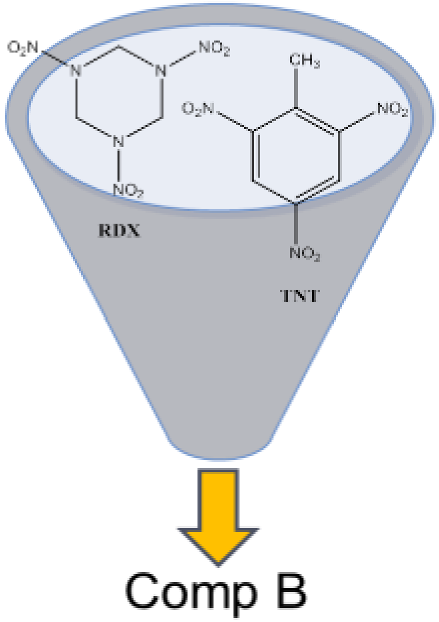
GrIMEx (Green IM Explosive)

Technology Focus

- To develop a novel IM Comp B replacement formulation containing novel, environmentally favorable TNT and RDX replacements.

Research Objectives

- The design and development of new synthesis routes for novel TNT and RDX replacements candidates that will be (relative to TNT or RDX):
  - Less sensitive to unplanned stimuli
  - Of comparable performance
  - Less toxic
  - Made through environmentally acceptable routes
- The design and development of new melt-pour Comp B replacement candidates that will be:
  - More IM-compliant than Comp B
  - Less toxic
  - Of comparable performance



What's Wrong with Comp B?

Environmental:

- DoD utilizes a large amount of Comp B in artillery and mortar rounds
- RDX and TNT have known toxicity concerns and contaminate soil and groundwater
  - RDX has become an undesirable component of new munitions formulations because it causes neurological effects (i.e. convulsions) in personnel, and the U.S. EPA lists RDX as a possible human carcinogen.
  - RDX has also become an environmental contaminant of concern because of residues from its use in munitions and from manufacturing.

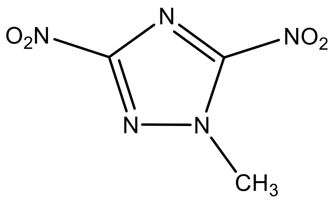
Performance:

- Comp B does not meet current IM (Insensitive Munitions) requirements mandated by DoD
- Both RDX and TNT contribute to the lack of IM compliance

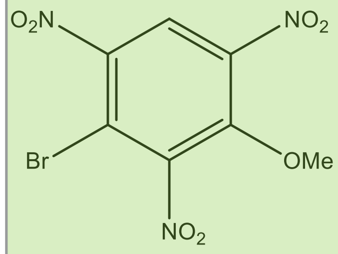
IM Test:	Fast Heating	Slow Heating	Bullet Impact	Fragment Impact	Sympathetic Reaction	Shaped Charge Jet Impact
Passing Criteria	V	V	V	V	III	III
120mm (Comp B)	II	I	I	I	(I)*	(I)*

VI	V	IV	III	II	I
No Sustained Reaction	Burn	Deflagration	Explosion	Partial Detonation	Detonation

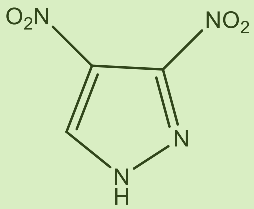
Background: Potential TNT Replacements



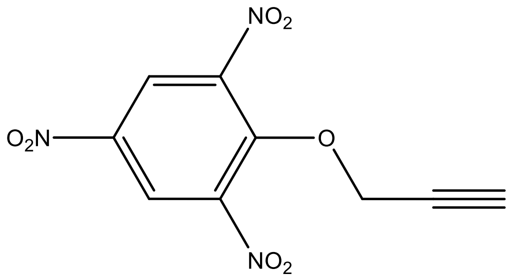
DNMT
Mp: 95C
Impact: 154 cm (2.5 kg wt)
Density: 1.7 g/cc
VOD: 7850 m/s (exp)
Pcj: 23.3 (exp)



TNBA
Mp: 95C
Density: 1.95 g/cc
VOD: 7300 m/s (calc'd)



DNP
Mp:87C
Density: 1.77 g/cc
VOD: 8251 m/s



PiPE
Mp: 100C
Density (calc): 1.61 g/cc
VOD: 6950 m/s (calc'd)

Compound	Pros	Cons
DNMT	Close to Comp B performance, Insensitive	Low synthetic yields, Use of methylhydrazine
PiPE	TNT performance, Predicted insensitivity	Immature synthetic route, insufficient characterization
TNBA	Reasonable maturity, Insensitive, One synthetic step	Density unknown, Effect of Bromide atom on performance unknown
DNP	> Comp B performance, synthesis already developed	Acidic proton?

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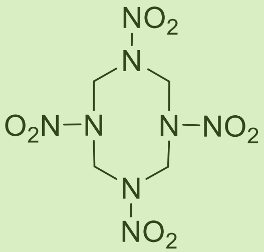
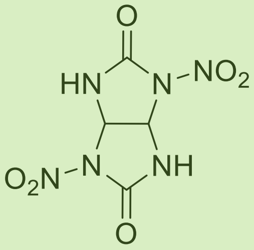
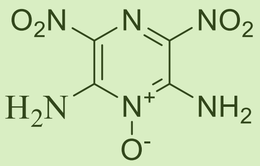
Background: Potential RDX Replacements



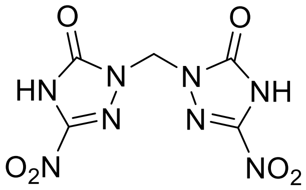
HMX



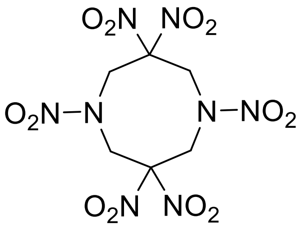
DNGU



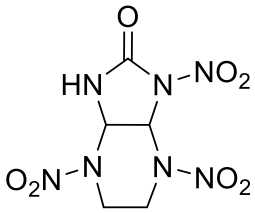
LLM-105



BiNTO



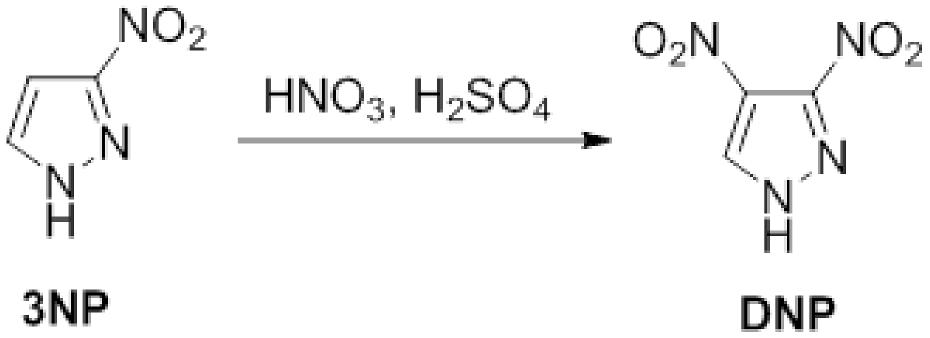
HCO



HK-56

Compound	Pros	Cons
HMX	Less toxic and env. persistent than RDX, Higher power than RDX	Slightly more sensitive than RDX
DNGU	Low sensitivity, inexpensive	Unconfirmed performance
LLM-105	Insensitive, good performance	3-step synthesis, particle morphology
BiNTO/NANTO	Reduced water solubility, NTO as starting material	Unconfirmed performance and synthetic data
HCO	Similar to TNAZ, High density	Unconfirmed synthetic route
HK-56	Potential for low-cost and sensitivity	Unconfirmed performance, sensitivity and particle size issues

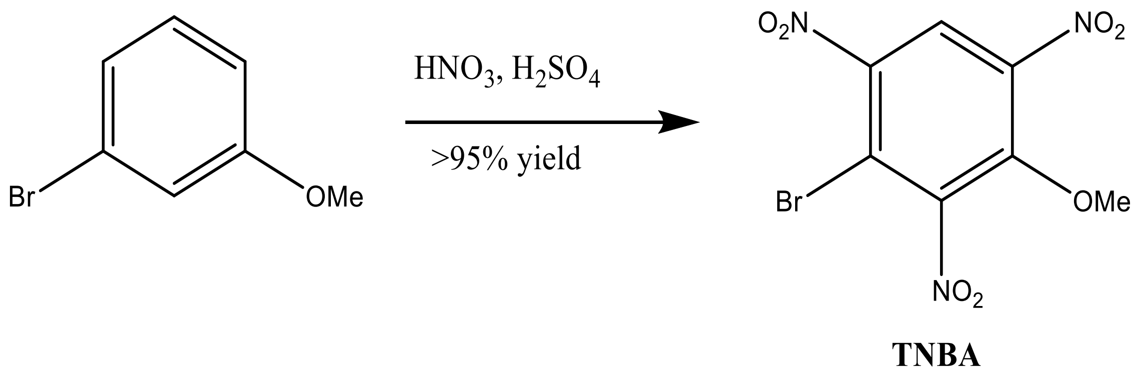
DNP Synthesis



- DNP (3,4-dinitropyrazole) is technically mature, and has been consistently synthesized on lab and pilot scale at Holston with >50% yield and 99.5% HPLC.
- Nitrate and Sulfate content is typically less than 0.02%.
- Previous purification methods involved extractions and vacuum. The efforts of this project were focused on isolation and purification process improvements to be amenable to affordable scale-up.

Technical Maturity: Solid synthesis route, isolation and purification needs work

TNBA Synthesis

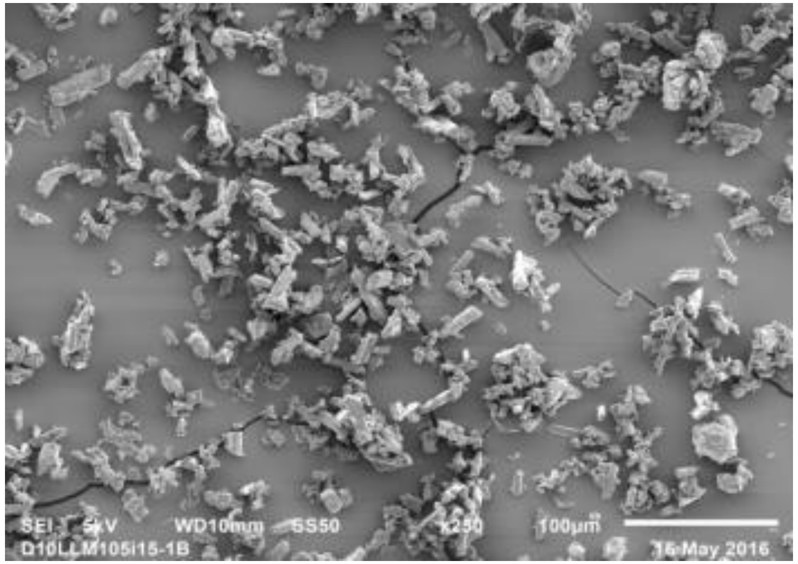


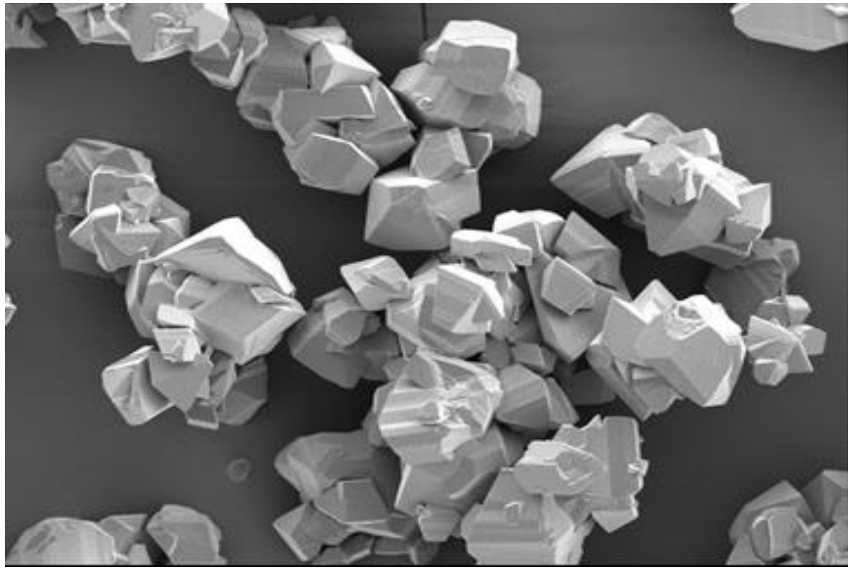
- Synthesis route is one step nitration
  - Crystalline solid precipitates from reaction in high yield
- **Robust Process:**
  - Pilot plant produced ~80 lbs in one batch
  - Yields ranged from 96.5% to 100%
  - Purity ranged from 98.69% to 99.92%
  - Simple recrystallization yields over 90% return
  - 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)

Technical Maturity: Minimal **optimization** necessary, performance testing needed

LLM-105 Recrystallization

- Typical LLM-105 process affords small particles (10-20 microns)
  - Difficult to formulate in melt cast without some coarse particles
- LLM-105 was recrystallized using process developed under separate project by LLNL, Nalas Engineering and BAE Systems.
- Process affords improved, larger crystals that will aid in formulation processing and maintain IM.





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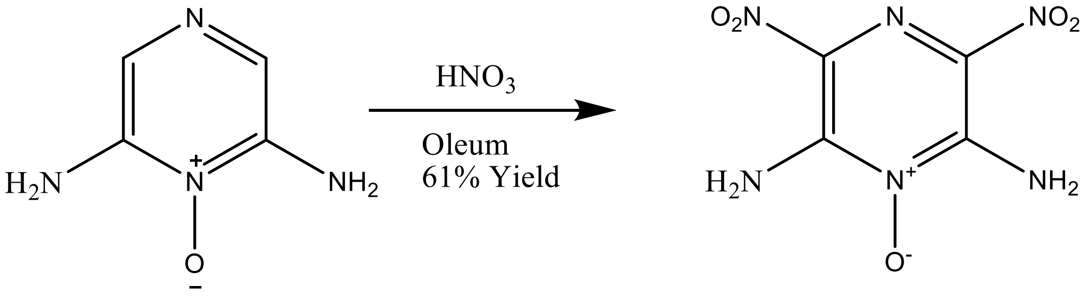
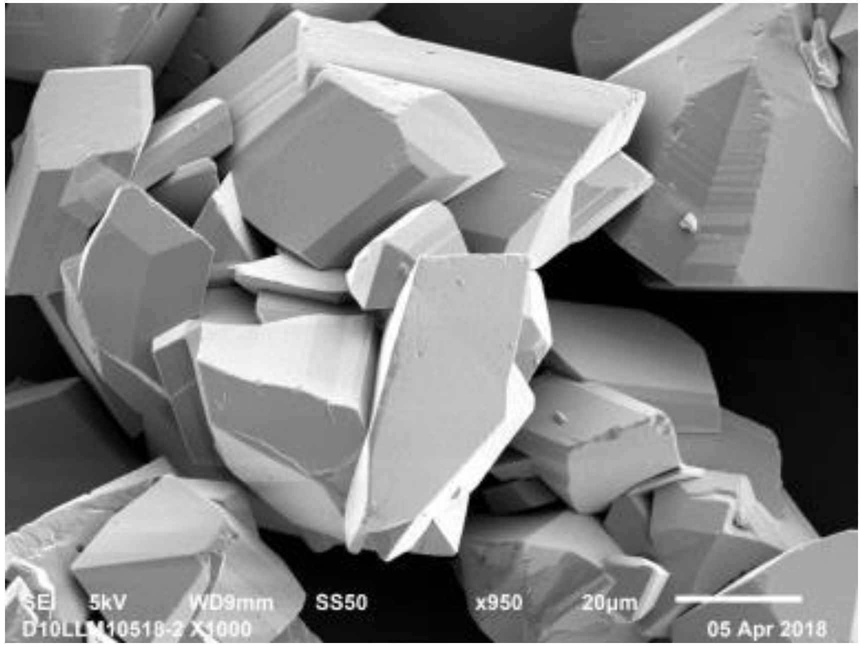
LLM-105 Synthesis- Larger Particles



DAPO

LLM-105



- LLM-105 was also synthesized using process developed under separate project by LLNL, Nalas Engineering and BAE Systems.
- New process avoids recrystallization step
- Produced ~25 lbs in one batch in pilot plant

Technical Maturity: Robust synthesis process, reproducible particle size

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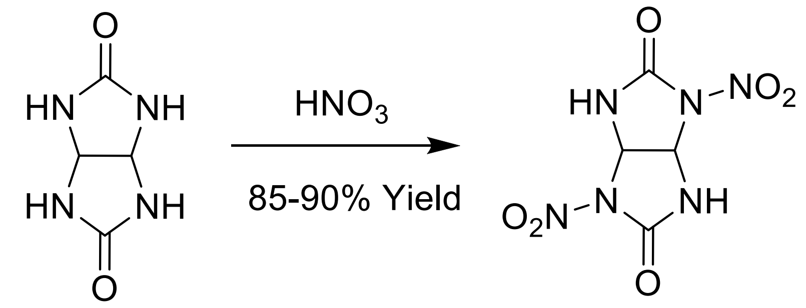
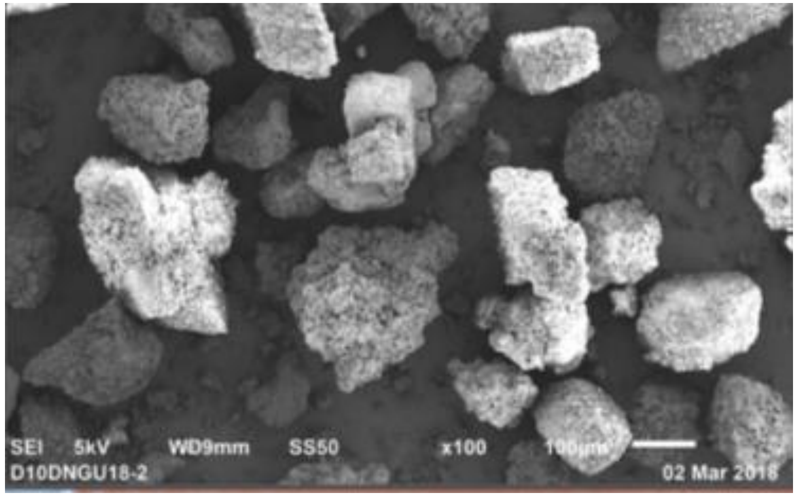
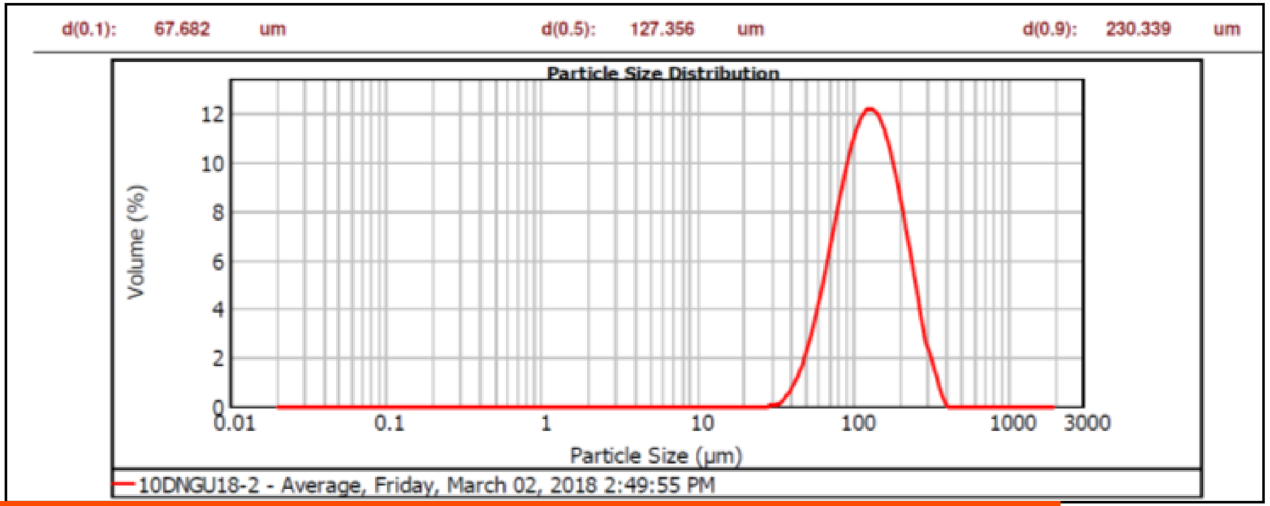
DNGU Particle Size Development



glycoluril **DNGU**





- Previous process afforded small particle size DNGU
  - <10 microns
- Specific nitration conditions needed to promote desired particle size growth
  - >100 microns
- ~200 lbs in one batch in pilot plant
- Purity typically >99%
- Residual acid typically <0.1%

Technical Maturity: Larger particles generated with improved nitration process

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Ingredient Vapor Pressure Testing (ARL)

- Ingredients sent to Dr. Rose Pesce-Rodriguez at ARL for physical properties testing
- DNP and TNBA have lower vapor pressures than TNT
    - Desired for melt-pour materials

Sample	VP (torr; estimated) 25°C	70°C	100°C	$\Delta H_{vap\ (est)}$ kJ/mol
LLM-105	8.50×10^{-16}	9.15×10^{-13}	50.4×10^{-10}	163.8
DNGU	2.54×10^{-13}	2.06×10^{-10}	5.40×10^{-08}	151.2
HK-56	1.52×10^{-12}	1.13×10^{-09}	2.35×10^{-07}	147.3
DNP	2.42×10^{-11}	1.57×10^{-08}	2.72×10^{-06}	141.4
TNBA	1.59×10^{-07}	6.66×10^{-05}	3.08×10^{-03}	121.7
TNT*	5.50×10^{-06}	2.31×10^{-03}	5.77×10^{-02}	114.1
RDX*	3.30×10^{-09}	2.76×10^{-06}	9.92×10^{-05}	127.1
HMX*	3.01×10^{-15}	3.14×10^{-11}	4.37×10^{-09}	174.7

USA PHC Microtox Study

Compound	Microtox EC_{50} (mg/L) (Mean ± SEM)			Hazard Categories (USFWS 1984)	Hazard Classes (OECD 2001)
	5 min	15 min*	30 min		
HK-56	4.090 (± 1.066)	1.569 (± 1.057)	0.9574 (± 1.056)	Moderately Toxic	Acute Toxicity II (toxic to aquatic life)
TNBA	3.805 (± 1.903)	5.890 (± 1.183)	6.211 (± 1.224)		
LLM-105	7.473 (± 1.040)	5.948 (± 1.034)	5.241 (± 1.039)		
DNP	18.44 (± 1.097)	13.16 (± 1.092)	10.42 (± 1.104)	Slightly Toxic	Acute Toxicity III (harmful to aquatic life)
DNGU	236.9 (± 1.169)	210.8 (± 1.150)	179.7 (± 1.184)	Practically Nontoxic	----

GrIMEx Performance Calculations Data: Early Efforts

- TNBA + DNGU (+ FEM HMX): Lowest cost Comp B replacement
- DNP + FEM-HMX + LLM-105: High performance
  - LLM-105 may help with cook off IM response

Formulation	Pcj (Cheetah 7.0)	V/Vo (7.20) (Cheetah 7.0)	Impact (cm)	Friction (N)
TNBA/DNGU/HFEM	24.88	-6.78	45	331
TNBA/HMX/HFEM	31.80	-8.40	26	331
DNP/DNGU/LLM105/HFEM	31.30	-7.97	82	322
DNP/DNGU/HFEM	32.76	-8.28	33	346
DNP/DNGU/LLM105	32.09	-8.05	35	328
Comp B	27.03	-7.55	38	150

DNP Formulations

- Fairly easy to get high solids loadings in DNP
- Due to high performance of DNP, LLM-105 was replaced with DNGU
  - A high amount of DNGU can be added
  - DNGU helps lower potential costs
  - DNGU helps lower shock sensitivity without sacrificing performance

Formulation	Composition	Shock Sensitivity (cards)	Detonation Velocity (m/s)	Pcj (Jaguar)	Gurney 7 Vol (Jaguar)
OSX-15	DNP/DNGU/HMX	119	8600	31.3	2.78
Comp B	TNT/RDX (40:60)	240	8000	26.4	2.81

TNBA Formulations

- Difficult to get high solids loadings
  - Need high concentration of crystalline ingredients to drive performance
- Due to low performance of TNBA, DNGU was dropped and crystallized LLM-105 was added
- Also evaluated TNBA/HMX formulation
  - Predicted higher energy than Comp B

Formulation	Composition	Shock Sensitivity (cards)	Detonation Velocity (m/s)	Pcj (Jaguar)	Gurney 7 Vol (Jaguar)
OSX-16	TNBA/LLM-105/HMX	173	8600	25.2	2.50
OSX-17	TNBA/HMX	219	7870	28.4	2.70
Comp B	TNT/RDX (40:60)	240	8000	26.4	2.81

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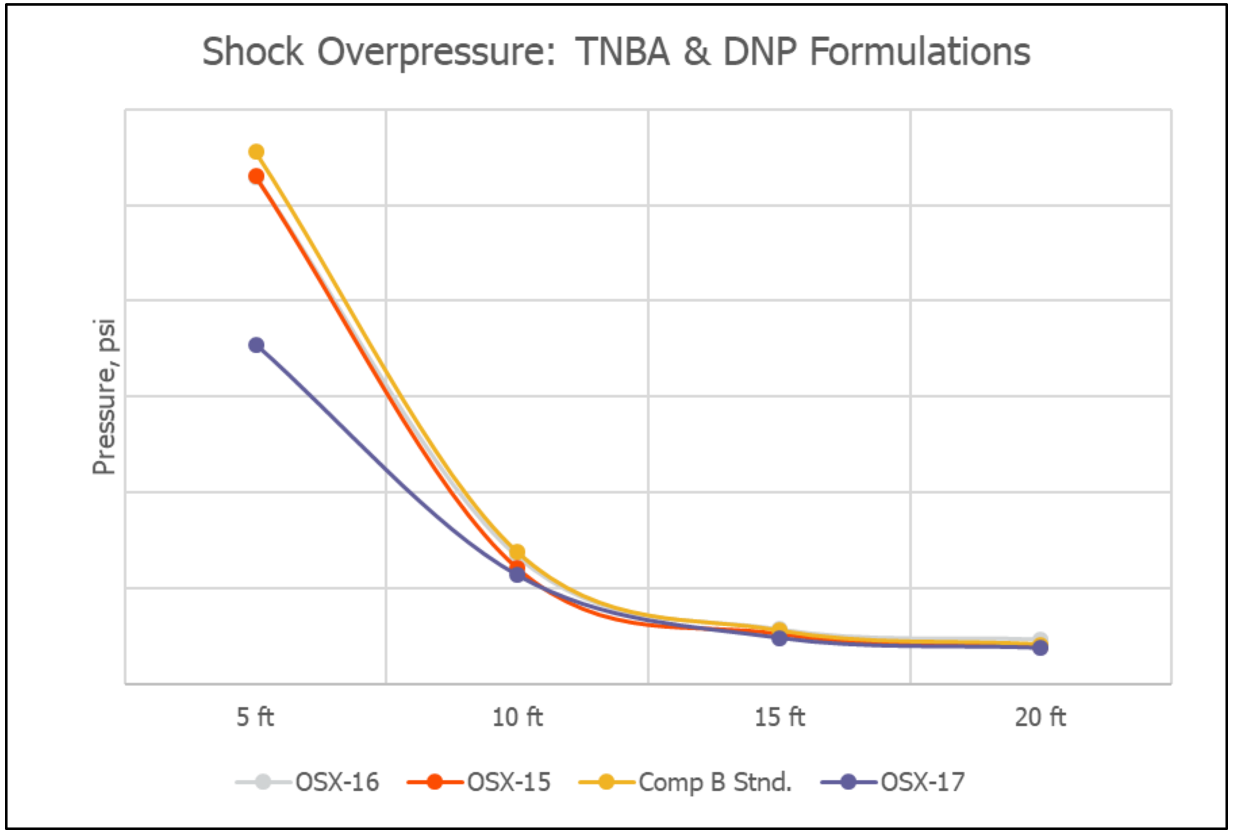
Blast Pressure Results

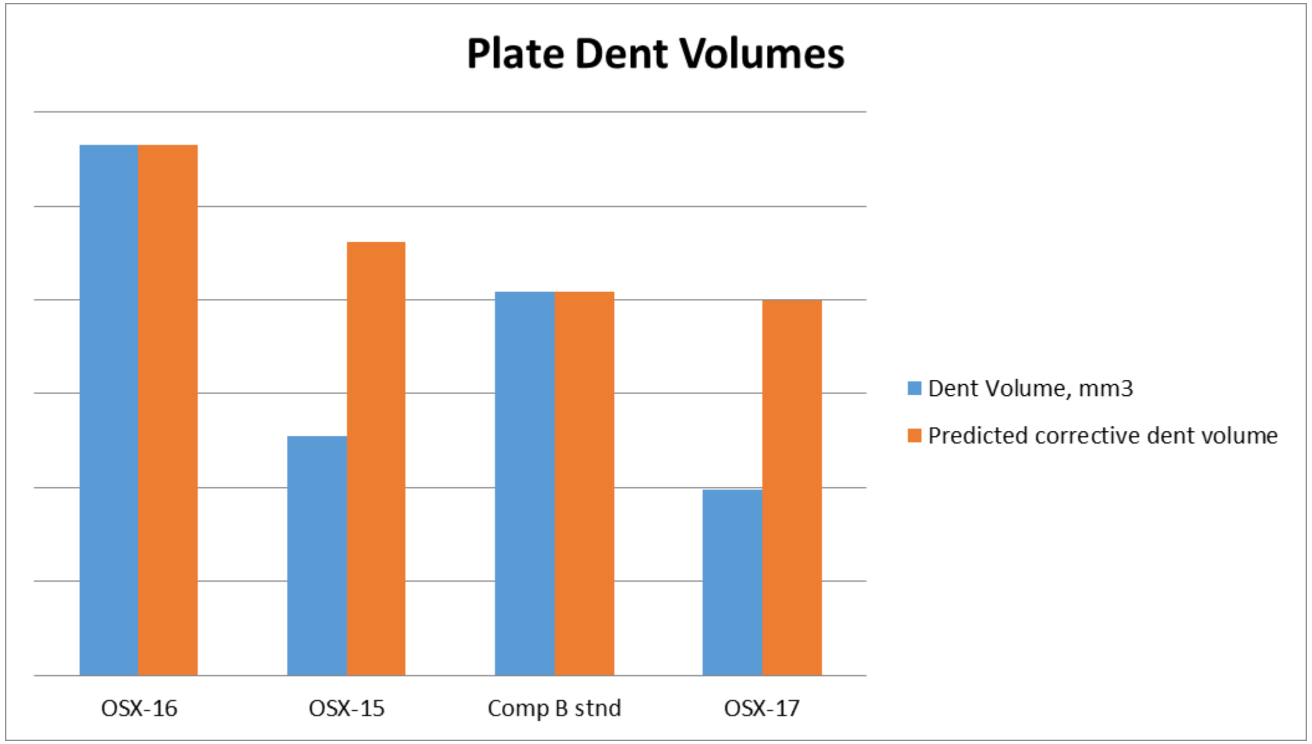


- Pressure measured at 5,10,15 & 20 ft from detonation
- OSX-15 and OSX-16 performed as expected
- OSX-17, however, showed much lower performance
    - Not expected as this formulation has a high amount of HMX

Formulation	Composition
OSX-15	DNP/DNGU/HMX
OSX-16	TNBA/LLM-105/HMX
OSX-17	TNBA/HMX
Comp B	TNT/RDX (40:60)

Plate Dent Results

- Raw data shows lower plate dent results for OSX-15 and OSX-17
- This plate dent difference may be due to lower TMDs of the tested charges versus the typical value for Comp B
- Predicted plate dent results for 98% TMD is shown
- OSX-16 yielded the largest plate dent, larger than that of Comp B



Formulation	Composition
OSX-15	DNP/DNGU/HMX
OSX-16	TNBA/LLM-105/HMX
OSX-17	TNBA/HMX
Comp B	TNT/RDX (40:60)

Conclusions

- **OSX-15**: DNP, DNGU, FEM HMX
  - Most environmentally favorable ingredients
  - Best explosive performance, matching or exceeding Comp B in the tests performed in this project
  - Best IM properties with a LSGT shock sensitivity of 119 cards; a 50% reduction of Comp B
- **OSX-16**: TNBA, LLM-105, FEM HMX
  - Good explosive and IM performance, close to Comp B
  - Lowest cost TNT replacement and the most thermally stable RDX replacement.
- **OSX-17**: TNBA and HMX
- HMX-based which currently poses minimal risks in the environment and is an affordable, mature product
- Good explosive performance
- Shock sensitivity was not improved over Comp B, presumably due to large particles of HMX in the mixture
- Currently the cheapest of the 3 to manufacture

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Acknowledgements

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Thank you