Synthesis, Formulation, and Testing of 3,4-DNP

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Melt-Pour Ingredient Objectives

Ingredient Development Overview

- Identify and Prepare New Melt Pour Ingredients with ~Comp B Performance
- Evaluate Using Small Scale Safety and Performance Testing
- Evaluate Scalability of Synthesis
- Evaluate Formulation Characteristics

Selection Criteria

- Melting Point in Desired Range (80-110 ^{o}C)
- Sufficiently High Density /Performance
- Ease of Preparation
- Scalability
- Environmental / Handling Issues

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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 in personnel, and is a possible human carcinogen.
  - RDX has also become an environmental contaminant of concern

Performance

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

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

Analytical Requirements

Properties	*Method*	*Minimum*	*Maximum*
Density (g/cm^3)	Gas Pycnometry	1.7	-
Exotherm Onset	DSC	150°C	-
Thermal Stability	VTS (48h@100°C)	-	2 cc/g
Purity	Chromatography (GC or HPLC) or NMR	95%	-
Det. C-J Pressure	Calculated by Cheetah 7.0	30 GPa	-
Detonation Velocity	Calculated by Cheetah 7.0	8.0 km/s	-

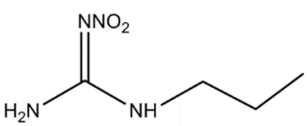
Additional Data Requirements:

- Sensitivity (Impact, Friction, ESD)
- Heat of Formation
- Compatibility (DSC or VTS)

Melt-Pour Candidates

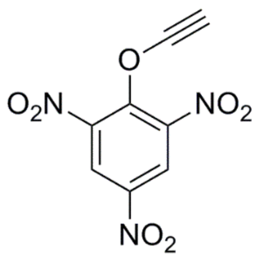
Issues Encountered:

Performance

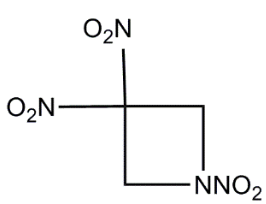


PrNQ

Toxicity / Vapor Pressure

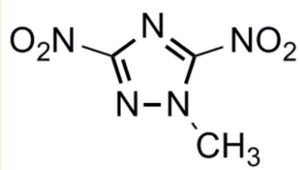


PiPE

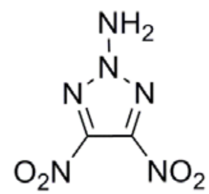


TNAZ

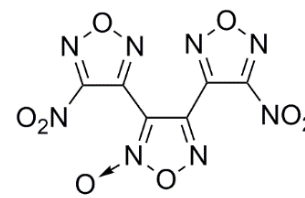
No. of Synthetic Steps / Reaction Conditions



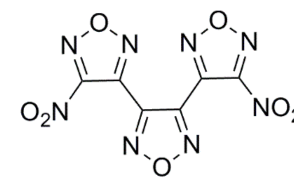
MDNT



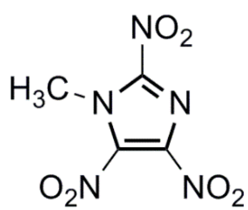
DNAT



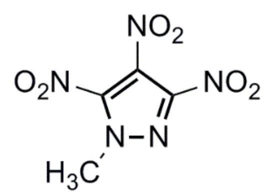
BNFF (DNTF)



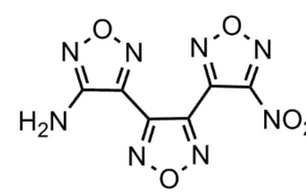
LLM-172



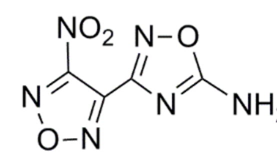
MTNI



MTNP

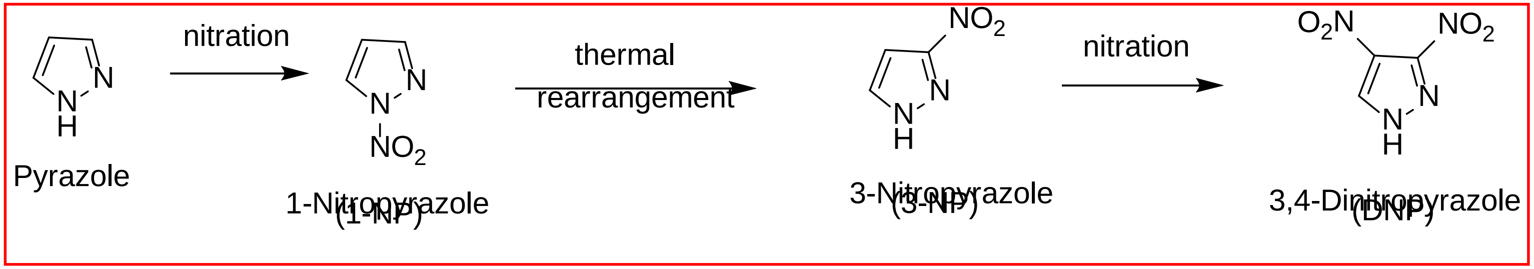


LLM-175



LLM-201

3,4-DNP Overview



DNP Advantages

- Insensitive to impact, friction, ESD
- Performance exceeding Comp-B
- Inexpensive starting materials
- High yielding, 1-step synthesis
- Chemistry can be readily scaled at HSAAP

Property	Comp. B	DNP
Melting Point (°C)	80	87
Density (g/cm^3)	1.68	1.79
Exotherm Onset (°C)		276
VOD (m/s)	7960	8115
Detonation Pressure (GPa)	29.2	29.4
Oxygen Balance (%)	-43.0	-30.4
Impact Sensitivity $h_{50\%}$ (cm)	75	147

DNP Sensitivity

Impact

Sample	Holston Short Impact (cm)	Navy Impact (cm)
DNP (Purified)	>80	94.8
RDX Standard	42.8	21.9

Friction

Sample	Friction (N)
DNP (Purified)	246
RDX Standard	164

ESD

Sample	ESD (J)
DNP (Purified)	0.26
RDX Standard	0.03

✓ DNP less sensitive than RDX

VTS Compatibility

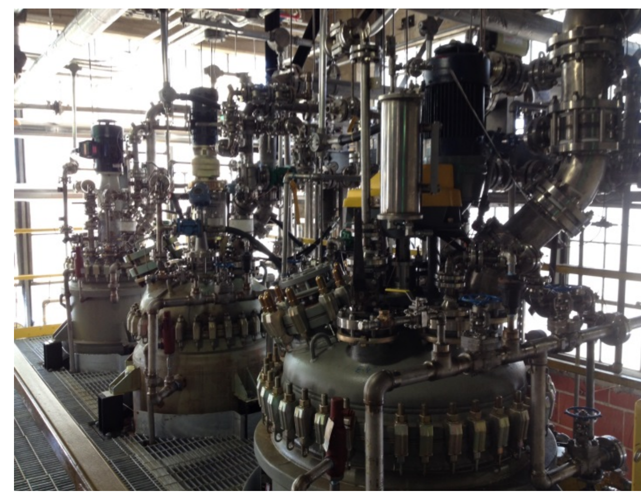
	Neat	RDX	HMX	NTO	LLM-105	HK-56	DNGU	Aluminum	Carbon Steel
DNP	---	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass

- VTS Compatibility by STANAG 4147 Test 1B:
  - 2.5 g of DNP mixed with 2.5 g other ingredients
  - Total gas evolved after 40 hrs at 100 ^{o}C must be less than 5 cc of neat material
- **All materials were compatible as tested**

DNP – Pilot Plant

- Process scaled from lab to pilot plant at Holston
- Process:
  - Mixed acid nitration of 3-NP to DNP
  - Solvent recrystallization
  - Isolated and dried
- Total Yield: **>300 lbs**
- Material for further formulation/testing at BAE Systems and ARDEC

Purity	Nitrate wt%	Sulfate wt%
>99.5%	<0.02	<0.02



USPHC Toxicity Testing

- Early DNP Testing from USPHC:
  - Ames Salmonella Assay: Positive
  - Mouse Micronucleus Test: Negative

USAPHC Phased Approach Testing (ASTM E-2552-08)

	Oral	Inhalation	Dermal	Ocular	Reproduction/ Development	Mutagenicity
DNMT	Low	Low	Moderate	Low	Low	High
DNP	**Moderate**	**Low**	**Moderate**	**Low**	**Low**	**High**
TNT	Moderate	Low	Moderate	Moderate	Low	High
RDX	Moderate	Unknown	Low	Low	Low	Moderate

Compound	Green algae	Daphnia	Fish	Earthworms	Transport	Persistence	Bioaccumulation
TNBA	Moderate	Low	Low	Unknown	Low	High	Low
PiPE	Low	Low	Low	Unknown	Low	High	Low
DNMT	Low	Low	Low	Unknown	High	High	Low
DNP	Low	Low	Low	Unknown	High	High	Low
TNT	Low	Low	Moderate	High	Moderate	High	Low

- No unusual DNP environmental toxicity issues

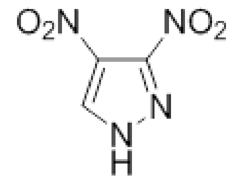
Results-Ingredient Testing (ARL)

- Ingredients were sent to Army Research Lab for Kow, Koc, water solubility, and vapor pressure testing:

Sample	VP (torr; estimated) 25°C	70°C	100°C	$\Delta H_{vap\ (est)}$ kJ/mol
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

- ✓ DNP has lower vapor pressures than TNT
- ✓ Soluble in water but low tendency to bioconcentrate in aquatic life.

DNP Dermal Testing



DNP

- “DNP was found to elicit a low-to-mild hapten formation response by DPRA (direct peptide reactivity assay). Thus, DNP is found to be **mildly sensitizing** by analysis with DPRA.”
- “The mild reaction by DPRA indicates that exposure to DNP in an occupational setting should be considered **generally safe with appropriate precautions**. Sensitization to the compound could potentially occur over an extended period of exposure, but with adequate PPE, this can be mitigated. The DPRA is best analyzed in conjunction with additional in vitro skin sensitization assays and in correlation with in silico analysis of the physical and chemical properties in order to accurately predict its sensitizing potential.”
- “DNP was found to elicit a positive reaction for both sensitization markers in the THP-1 monocytic leukemia cell line, a dendritic cell surrogate. Both CD54 and CD86 expression levels were increased as a result of 24-hour exposure to DNP. Thus, **DNP is a sensitizer according to the h-CLAT test**.”-(Toxicology Study No. S.0024589d-15)
- BAE is requiring R&D personnel to **wear Tyvek suits and full-face respirators** while handling DNP in heated, molten phase and when handling solid DNP outside of adequate ventilation and engineering controls (i.e. hood).

Proper Engineering Controls and PPE for safe handling

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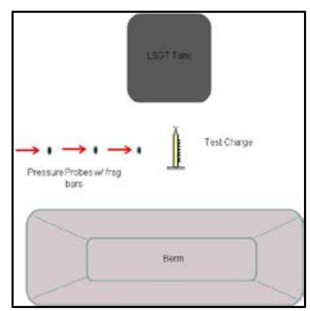
DNP Performance Testing

DNP Explosive Performance Testing:

- Rate Stick / Plate Dent (ARDEC)
- Critical Diameter (BAE Systems)
- Shock Overpressure (BAE Systems)
- LSGT (BAE Systems)



Performance Rate-Stick / Plate-Dent

- Detonation velocity and pressure of DNP tested
- DNP pressed to a density of 1.75 g/cc
- Results compared to Comp. B and DNMT

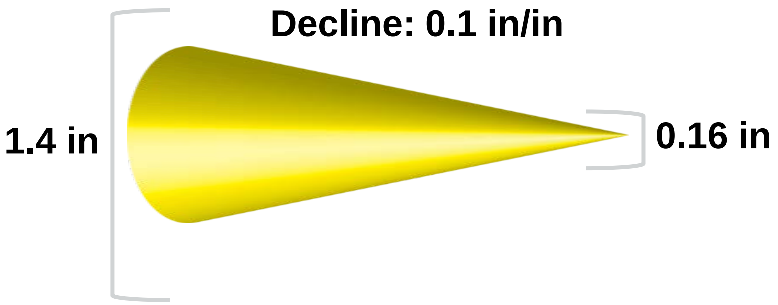
	Pressure (Calc) GPa	Pressure (Exp.) GPa	VOD (Calc) m/s	VOD (Exp.) m/s
DNP	29.1	30.2	8,246	8,115
DNMT	27.5	24.8	7,710	7,800
Comp. B	26.1	27.6	7,900	8,018

Critical Diameter Testing

- Critical Diameter was determined by pouring conical charges of DNP into a split-mold
- Cone Parameters:
  - Maximum Diameter: 1.4 Inches
  - Minimum Diameter: 0.16 Inches
  - Declining Angle: 0.1 Inches per Inch
- Charges set on aluminum plate (16” x 6” x 0.5”)
- **Critical diameter <0.16 inches**
  - Propagation through length of explosive

DNP w/ #8 Detonator

Witness Plate

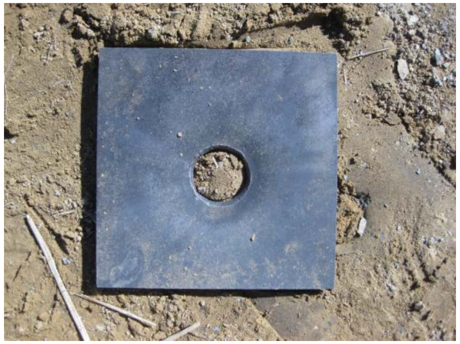


Large-Scale Gap Testing – DNP

- DNP poured into 6” steel tubes (~0.5 lbs of material, 96% TMD)
- Heated tubes required to obtain quality pours:
  - No Visible Cracking/Crystalline Domains
- Steel Witness Plate used to provide a clear go/no-go indication:
  - Calculated 50% Go/No-Go point based upon firings

DNP: 193-195 cards (22.8-22.2 kbar)

Comp B: 215-225 cards (17.9-16.2 kbar)

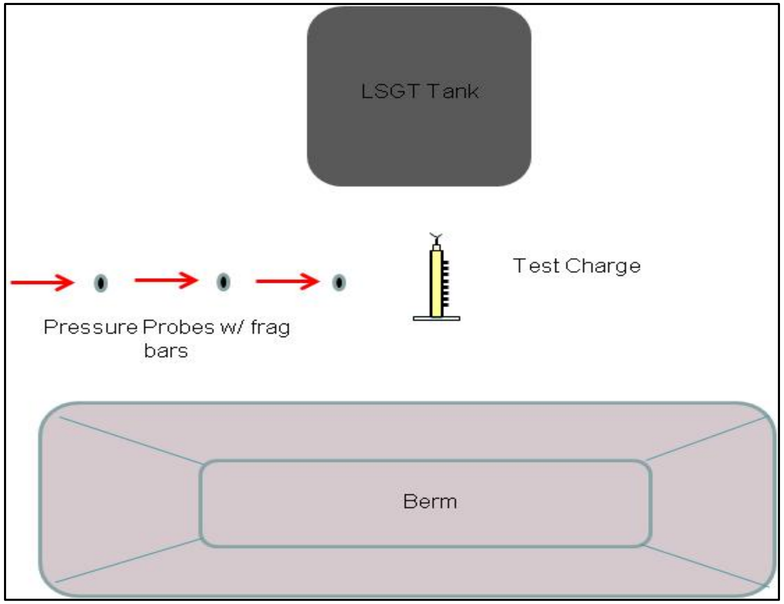


Shock Overpressure Testing

- Degree of damage to surroundings related to:
  - Shock Overpressure
  - Shock Duration
  - Peak Impulse

- Ovepressure measured by Piezotronic pressure probes
  - Oriented axially at 5,10, and 15 ft

- DNP poured into tubes:
  - Sample size: 0.5 lbs
  - Density: 1.67 g/cc



Shock Overpressure Testing

- Comparison testing shows that DNP is an extremely powerful explosive
- Better performance than current melt-pour explosives
- Performance close to LX-14 (95.5% HMX)

Shock Overpressure (Psi)

	5 ft	10 ft	15 ft
DNP	30.8	6.5	3.3
Comp. B	27.7	6.3	3.1
IMX-104	28.1	6.1	3.2
PBXN-7	27.5	6.4	3.2
LX-14	31.7	6.4	3.3

DNP Formulations

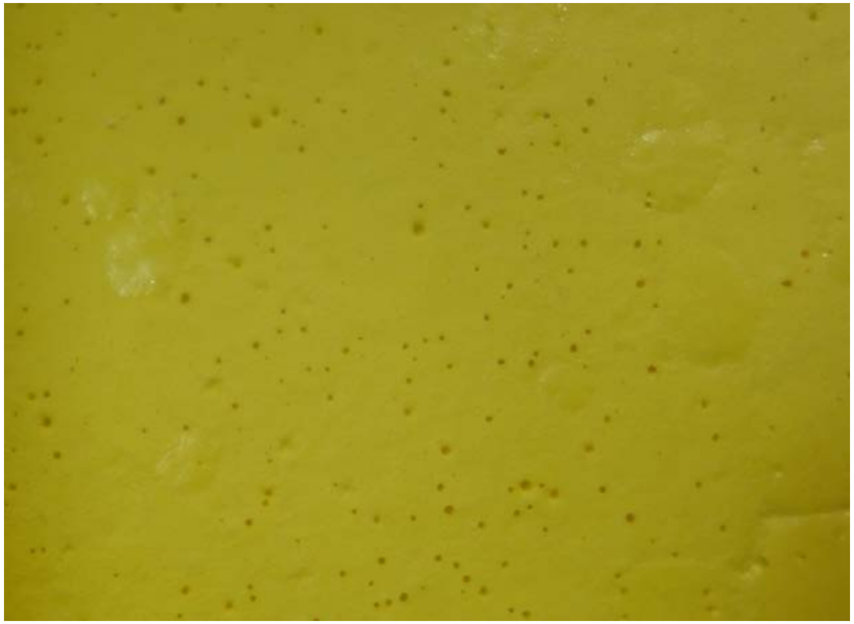
- Octol Replacement
- IMX-101/104 Replacement
- DNP w/ New IM Ingredients

Octol Replacement

	Density (g/cc)	Pressure (GPa)	Det. Velocity (km/s)	Estimated Gurney
DNP:HMX (50:50)	1.84	33.4	8.65	2.95
Octol (25:75)	1.83	32.4	8.57	2.89

- Ability to get high solids loading with molten DNP
- 40-60% HMX gives similar performance as Octol (Type 1)
- Use of FEM/Nano HMX would help reduce shock sensitivity

New IM Ingredients Formulations



Composition	Pcj (Cheetah 7.0)	V/Vo(7.20) (Cheetah 7.0)	ERL Impact, cm	BAM Friction, N
DNP/DNGU/LLM-105	31.0	-7.78	82	328
Comp. B	27.0	-7.55	38	150

New IM Ingredients Formulations

- Fairly easy to get high solids loadings in DNP
- Due to high performance of DNP, LLM-105 was replaced with DNGU:
  - High DNGU solids loading
  - DNGU helps lower potential costs,
  - DNGU helps lower shock sensitivity
  - “Coarse” grade DNGU can be balanced by normal “fine” grade DNGU or FEM HMX.

Formulation	Composition	Pcj (Jaguar)	Gurney 7 vol (Jaguar)	ERL Impact, cm	BAM Friction, N
OSX-15	DNP/DNGU/HMX	31.3	2.78	50.6	277.2
Comp B	TNT/RDX (40:60)	26.4	2.81	38	150

Conclusion and Path Forward

- Synthesis:
  - Scalable synthesis route: DNP currently synthesized on pilot-scale
  - >300-lbs of DNP synthesized to date
  - Optimization of purification/recrystallization currently ongoing
  - Inexpensive / High-Yield Process

- Formulation:
  - Formulation efforts are just beginning
  - DNP has Comp. B performance: Formulations could have explosive performance greater than Octol

- Testing:
  - Additional Explosive Testing (BAE Systems/ARDEC)
  - Formulation Testing (BAE Systems)
  - Weapons Testing (ARDEC)

Great Potential as the Next-Generation Melt-Pour Base

Acknowledgements

	US ARMY – ARDEC / ARL Anthony DiStasio, Kate Maier, Phil Samuels, Omar Abbassi, Paul Anderson, Dr. Rose Pesce-Rodriguez - Program Funding (FREEDM) and DNP Development Efforts
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