Energetic Ingredients Research for the FREEDM Program

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F.R.E.E.D.M. Organization

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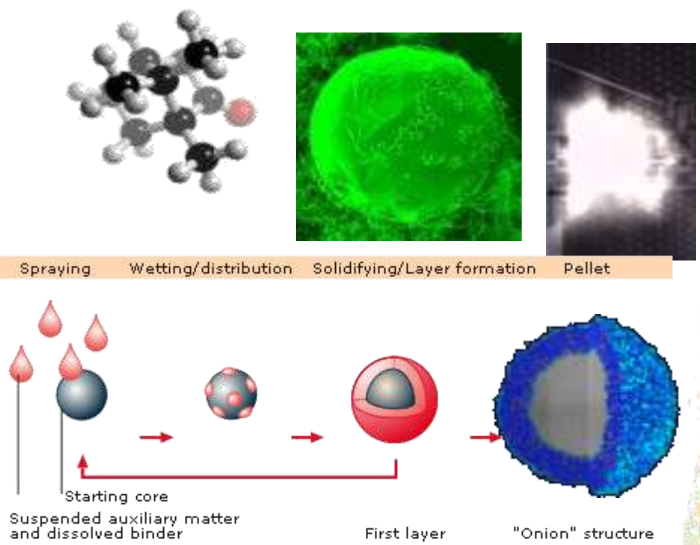
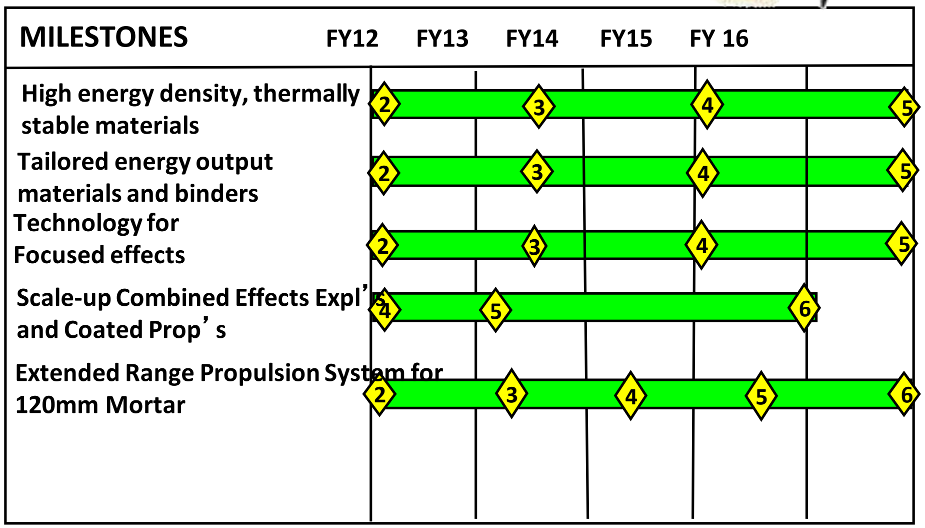
    John O' Reilly, Paul Anderson, Dick Beyer, Brian Roos, Greg Drake
    - **F.L.I.G.H.T**
      Further, Lighter Insensitive Greater Hits on Target
    - **F.E.A.R.D**
      Focused Effects with Adaptive Response Delivered

- **Propulsion**
- **ANCER**
- **Ignition**
- **Nano**
- **Synthesis**
- **Formulation**
- **Processing**
- **M&S**

Future Requirements of Enhanced Energetics for Decisive Munitions



Schedule & Cost



Purpose

Provide insensitive, green energetic materials, enabling the capability to increase the lethality, range, precision, and utility of munitions while providing focused and variable effects through tailored energy release.

Products

- Higher energy density multi-purpose IM explosives for anti-armor and blast-frag warhead applications
- Extended range propulsion system prototypes
- Novel processing and precision coating techniques for highly efficient progressive charges
- Energetic technologies for focused & tailored energy release on target
- Novel materials to enable and compliment next generation IM initiation and ignition systems

Payoff:

Faster (high density) FOB setup and extended range (better propellant) protection against multiple targets (tailored and focused effects) with more rounds (IM) readily available to the call for fire (IBD/HD)

BAE SYSTEMS
INSPIRED WORK

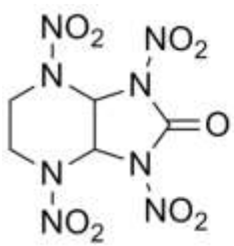
Energetic Ingredients Synthesis

Dr. Jacob Morris (BAE Systems)

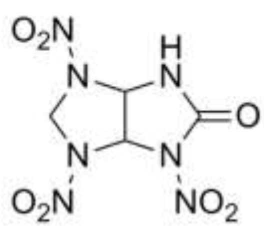
Holston Army Ammunition Plant

Ingredient Downselect

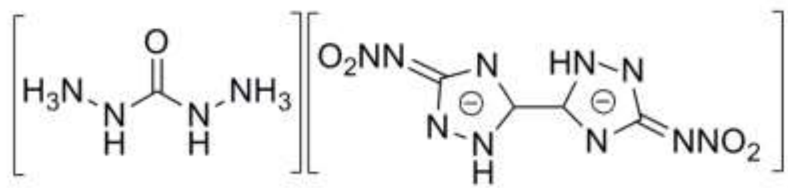
- A goal of the FREEDM program is to develop energetic ingredients for use in novel formulations that will be IM compliant Octol and PBXN-9 replacements.
- Program looked to develop the chemistry of ~10 energetic ingredients at Holston
- Highlighted compounds:



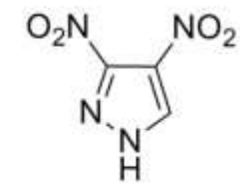
TNABN



HK-55



CBNT



DNP

Compound	Pros	Cons
TNABN	High density, good performance	Conflicting sensitivity information
HK-55	High density, good performance	Conflicting sensitivity information
CBNT	Good density, good performance	Material not mature
DNP	Melt-pour candidate with Comp-B performance	Availability of starting material

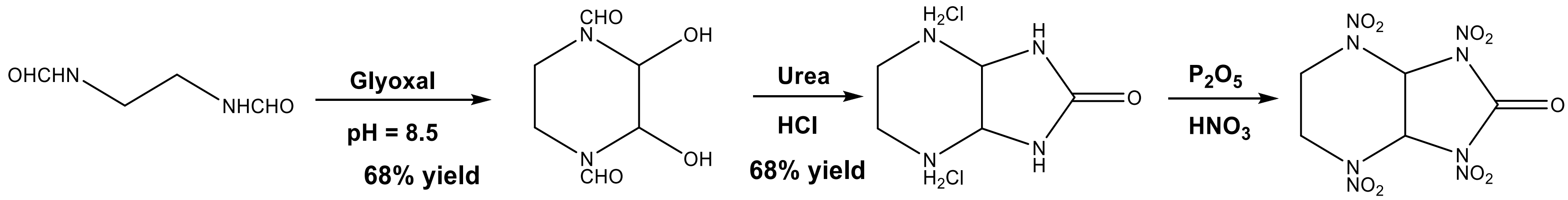
Analytical Requirements

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 collected includes:

- Sensitivity (Impact, Friction, ESD)
- Crystal Morphology (SEM)
- Heat of Formation (Calculated or Measured)
- Compatibility (DSC or VTS)

TNABN (K-56) Overview



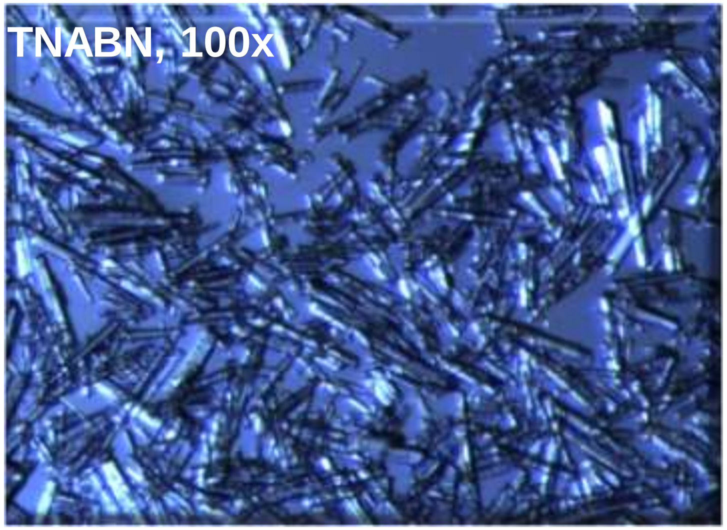
- TNABN is a relatively new high-explosive with calculated performance between RDX and HMX
- Conflicting information about impact sensitivity data in the literature
- TABN synthesized on the lab-scale in a two-step process from ethylene bisformamide
- TNABN was synthesized from TABN directly or through HK-56 intermediate
  - Both routes produce TNABN in high yield and purity

Property	RDX	HMX	TNABN
Density (g/cm^3)	1.82	1.91	1.97
ΔH_f (kJ/mol)	92.6	104.8	70.31
Det. Pressure (GPa)	35.2	39.6	38.12
Det. Vel (m/s)	8850	9320	9015
Impact H_{50} (cm)	26		>80

TNABN

- Multiple crystallizations completed:
  - All batches yield crystalline needles
- TNABN has impact sensitivity much lower than RDX (closer to PETN)
- Needle-like form of TNABN crystals may contribute to sensitivity

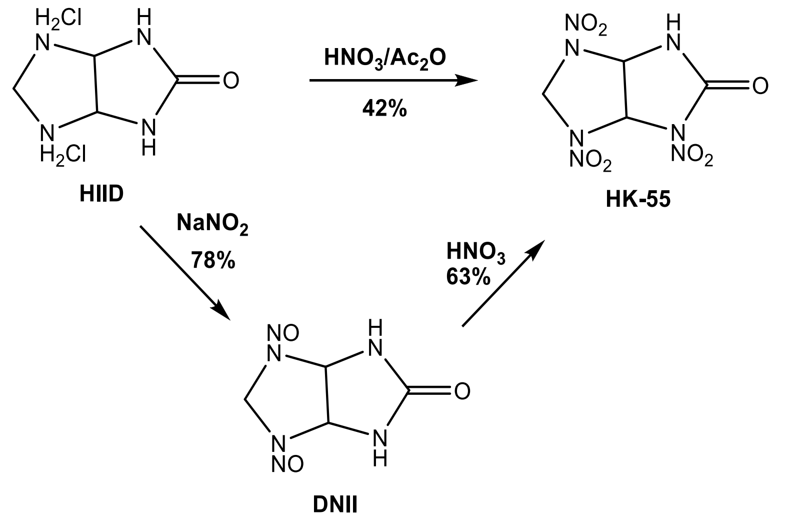
Material	Holston Impact (cm)	BAM Friction (N)
TNABN	20	132.4
Class 5 RDX	51.25	134.2



TNABN dropped from program due to poor sensitivity

HK-55 Overview

- HK-55 is a structural analogue of TNABN with RDX performance
- HIID precursor synthesized on the lab-scale in a two-step reaction from methylene bisformamide
- HK-55 synthesized via two known routes:
  - One-step of nitration HIID using HNO_3/Ac_2O (Scale up concerns)
  - Two-step nitrosation/nitration reaction through DNII using $NaNO_2$ and HNO_3

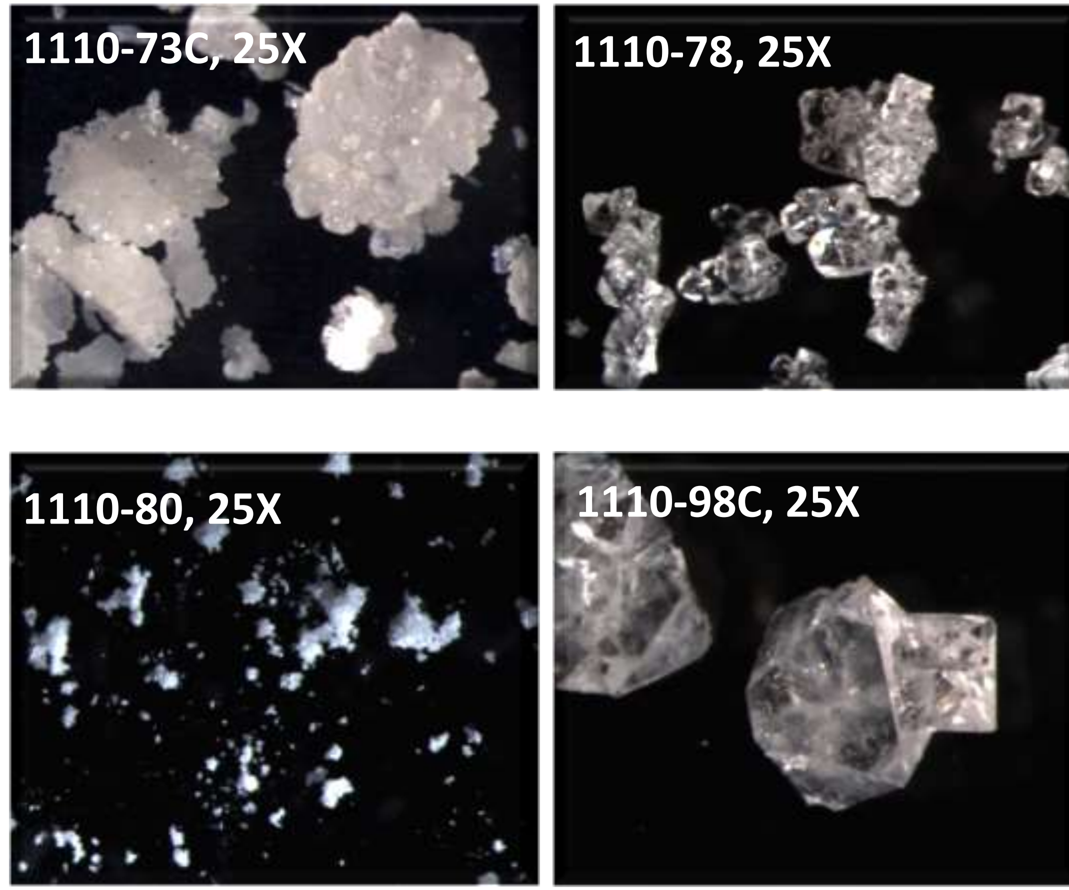


Property	RDX	HMX	HK-55
Density (g/cm^3)	1.82	1.91	1.91
Det. Pressure (GPa)	35.2	39.6	-
Det. Vel (m/s)	8850	9320	8631
Impact H_{50} (cm)		32	61

HK-55 Crystallizations

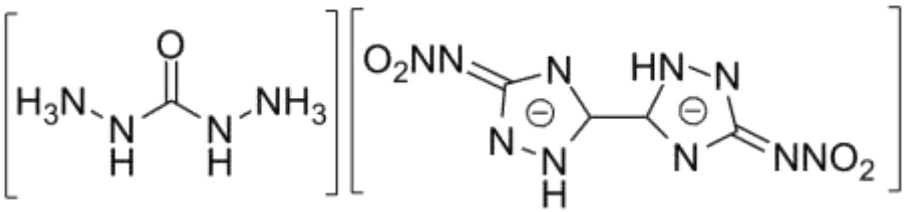
Sample #	Holston Impact (cm)
1110-73C	~25
1110-78	~20-25
1110-86	~20
1110-81	~20-25
1110-86#2	~20
1110-91C	~20-25
1110-94C	~20-25
1110-101	~15-20

- Crystallizations completed using various conditions
  - High purity material for all batches
- Purities determined by NMR and/or HPLC
- Impact testing performed on eight samples
  - Most have PETN-like sensitivity



HK-55 dropped from program due to poor sensitivity

CBNT Overview



CBNT

Carbonic dihydrazidinium bis[3-(5-nitroimino-1,2,4-triazolate)]

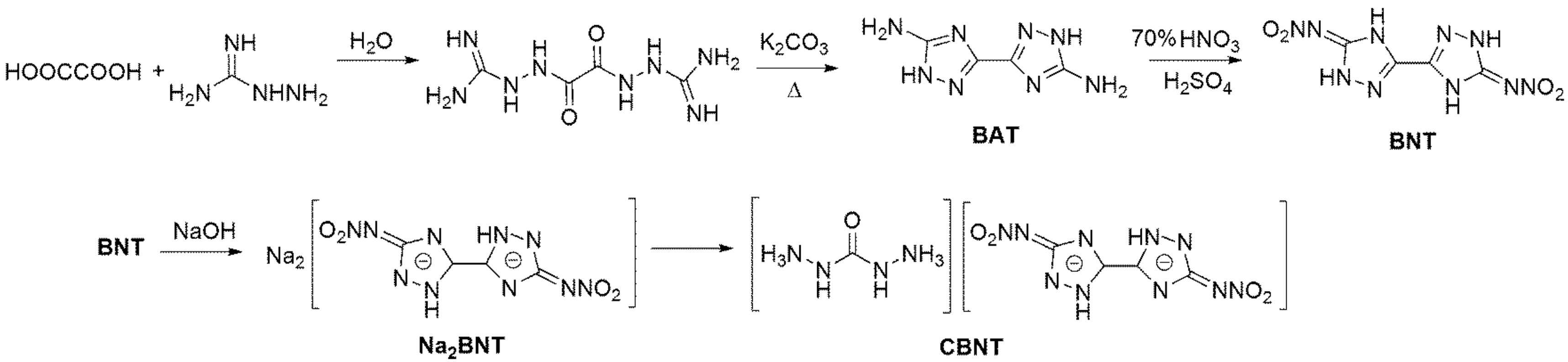
- The amine salts of BNT (bis[3-(5-nitroimino-1,2,4-triazolate)]) are insensitive high-explosives with RDX/HMX performance
- Compounds first reported by Jean'ne Shreeve group at the U. of Idaho (2010)[1]
- CBNT downselected as initial target based upon performance, density and sensitivity

Property	RDX	HMX	CBNT
Density (g/cm^3)	1.82	1.91	1.95
ΔH (kJ/mol)	92.6	104.8	47.2
Det. Pressure (GPa)	35.2	39.6	36
Det. Vel (m/s)	8850	9320	9399
Impact H_{50} (cm)	26		>80

Ref. 1: Wang, R.;Xu, H.; Guo, Y.; Sa, R.; Shreeve, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 11904.

CBNT Synthesis

Original Process (5-steps):

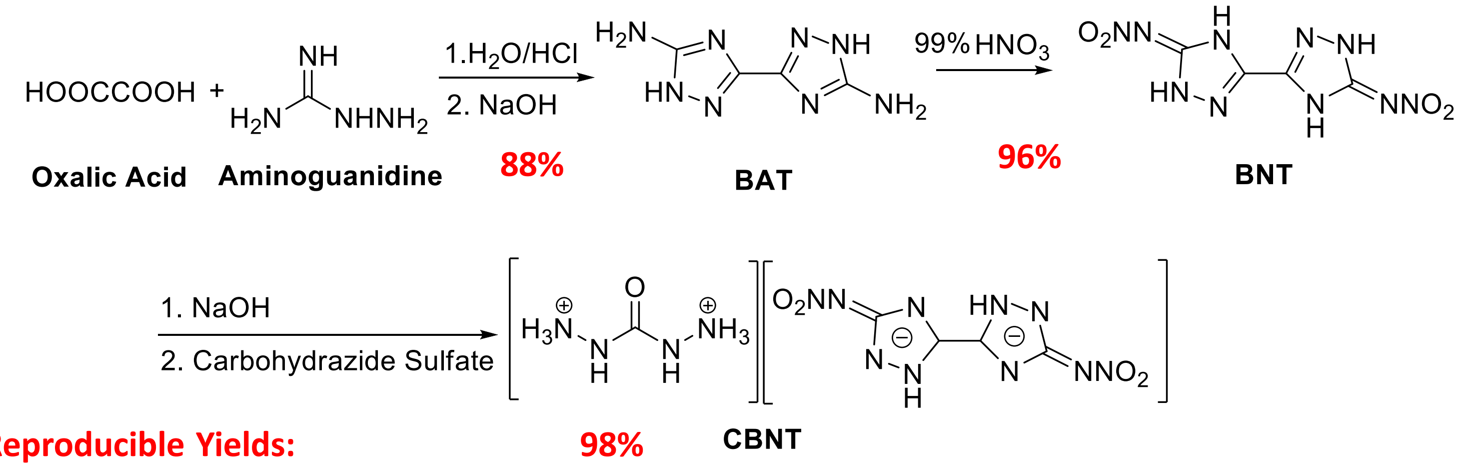


Original synthesis showed promise, but there were some issues:

- Attempts to synthesize BAT by this process failed
- Undesirable exotherm observed with nitration of BAT in 70% nitric/sulfuric acid
- Na_2BNT only isolated upon letting the solution sit for a few days
- Na_2BNT has high solubility in water, giving a low yield

CBNT Optimization

BAE Modified Process (3-steps):



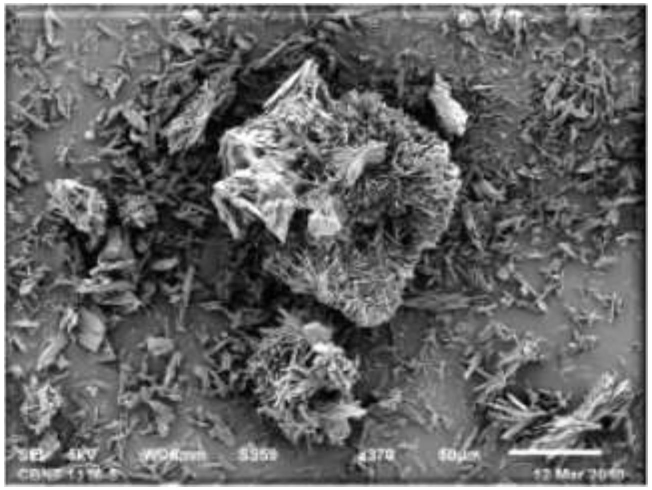
Current Reproducible Yields:

- Modified process to reduce steps and improve yield
- Initial and final steps use a one-pot process
- 99% nitric acid for nitration (Increased Yield and Purity)
- Na_2BNT is no longer isolated
- CBNT matches literature IR and DSC (T_d= 220 ^oC)
- Confirmed compound by HPLC-MS

CBNT

CBNT Advantages

- Very insensitive to impact, friction, ESD
- HMX performance
- Inexpensive starting materials
- High yielding, 3-step synthesis
- Chemistry can be readily scaled at HSAAP



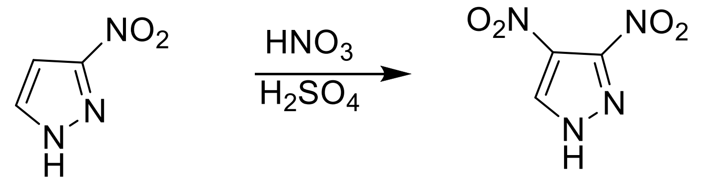
SEM of CBNT Crystals 370x

Path Forward

- >500-g of CBNT has been produced by BAE Systems
- Scale-up of process to kg scale
- Formulation effort with CAB and other binders
- Critical diameter and performance testing
- Particle size and shape modification

CBNT shows great promise as a new energetic ingredient

3,4-DNP Overview



3-Nitropyrazole (3-NP)

3,4-Dinitropyrazole (DNP)

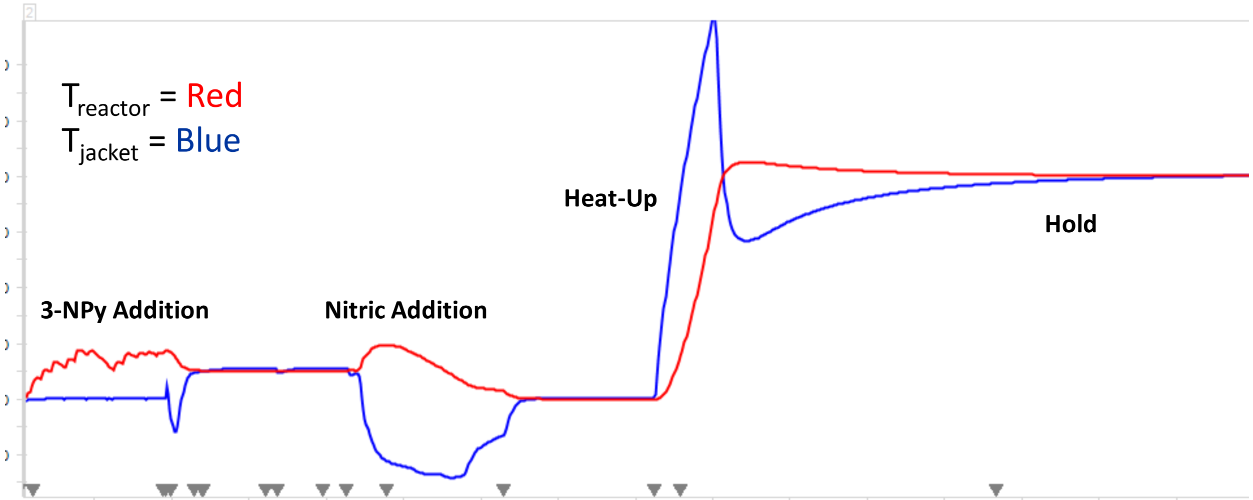
- DNP is an IM melt-pour base with performance greater than Comp. B
- Low-cost: synthesized from 3-NP in one-step reaction
- Lab-scale synthesis of DNP has been developed previously at BAE Systems and ARDEC
- Current program involves scale-up and IM explosive testing of DNP

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

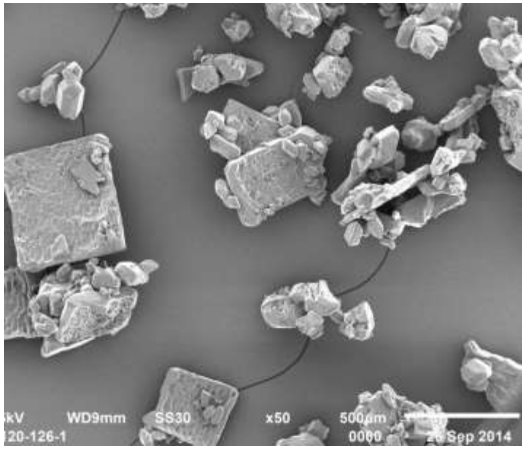
Performance Rate-Stick / Plate-Dent

	Pcj, calc. (GPa)	Pcj, exp. (GPa)	Energy out, calc. (cal/cc)	VOD, exp. (Km/s)
DNP	28.8	29.4	1961	8.104
DNMT	25.4	23.3	1739	7.850
Comp B	27.7	~27.6	1837	~7.960

5-Gallon Synthesis of DNP



DNP Reaction on 2-L RC-1 Scale



- Process successfully scaled to 2-L RC-1 then 5-gallon scale
- **15-lbs of DNP produced** (5-gallon scale)
- DNP formulation efforts are currently ongoing

DNP Path Forward

Model DNP Formulation:

	Density (g/cc)	Pressure (GPa)	Det. Velocity (m/s)	Energy of Det. (kJ/cc)
DNP:RDX (60:40)	1.80	31.5	8,460	9.7
PBXN-9	1.6	30.3	8,450	9.4

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

Path Forward

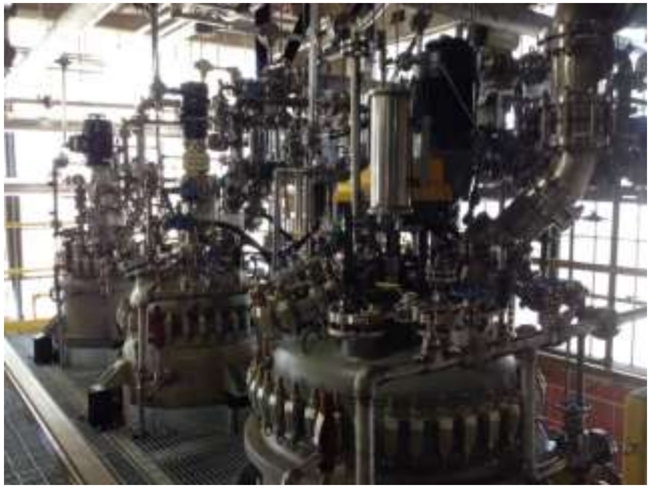
- Process is ready for pilot-plant scale-up
- Formulation efforts are currently ongoing
- Formulations are predicted to have exceptional IM and performance characteristics

DNP Shows Great Potential as a New Melt-Pour Base

Pilot Plant Transition

BAE Systems Energetics Pilot Plant

- 50-, 100-, 200-Gallon glass-lined reactors
- Better transition from lab scale to Production Facilities
- Commissioning completed Fall 2013
- Several ingredients successfully produced (military and commercial):
  - Class 1 NTO, PrNQ, NONA, TATB, DNMT, Granular IMX-104
- Ongoing upgrades to capabilities:
  - Sub-ambient chiller system (2014)
  - Stainless-steel filter press (2014)
  - Vacuum system (2015)
  - 100- and 400-gallon formulation stills (2015)



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BAE SYSTEMS

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