GrIMEx: Development of a Novel, Green IM Comp B Replacement

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BAE SYSTEMS
INSPIRED WORK

Acknowledgements

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BAE SYSTEMS INSPIRED WORK	**BAE SYSTEMS** Dr. Jacob Morris, Dr. Neil Tucker, Dr. Sarah Headrick, Jim Phillips, Brian Alexander, Matt Hathaway, Dr. Jeremy Headrick, Robyn Wilmoth, Kelly Guntrum, Chris Long, Dr. Tess Kirchner -Synthesis, Formulation and Testing

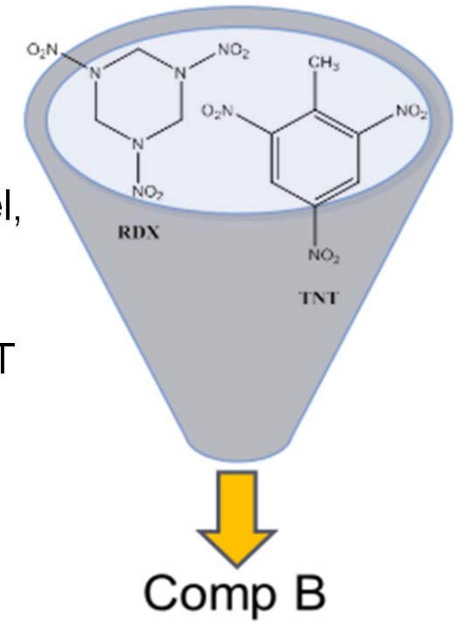
GrIMEx (Green IM Explosive)

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.

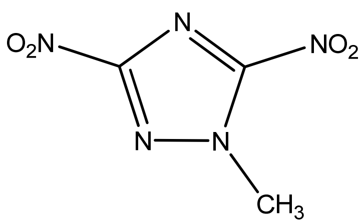
Performance:

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

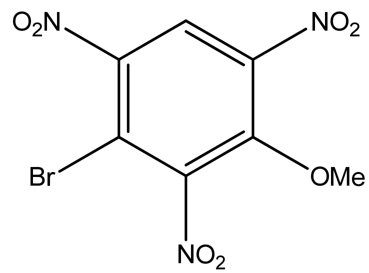
IM Test:	Fast Heating	Slow Heating	Bullet Impact	Fragment Impact	Sympathic Reaction	Shaped Charge Jet Impact
Passing Criteria	V	V	V	V	III	III
120mm (Comp B)	II	I	I	I	(I)*	(I)*

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

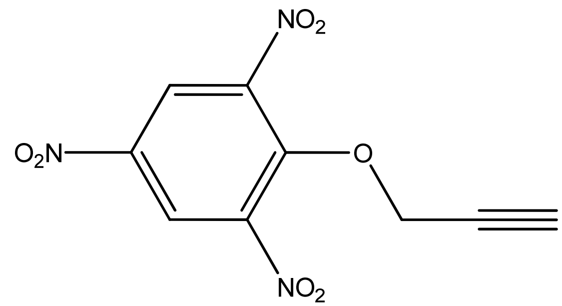
Potential TNT replacements



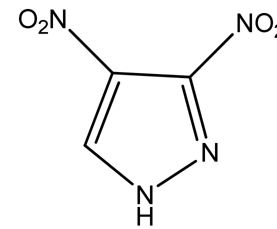
DNMT



TNBA



PiPE

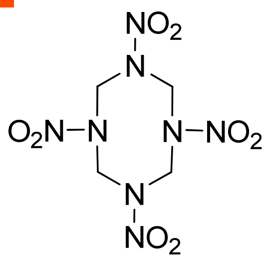


DNP

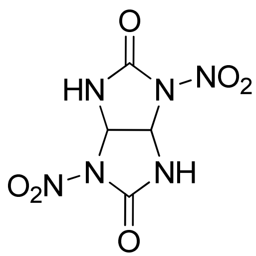
Compound		Pros	Cons
DNMT	✗	Close to Comp B performance, Insensitive	Low synthetic yields, Use of methylhydrazine
PiPE	✗	TNT performance, Predicted insensitivity	Starting material toxicity, insufficient characterization
TNBA	✓	Reasonable maturity, Insensitive, One synthetic step	Effect of Bromide atom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

✓ = Ingredient moving forward in program

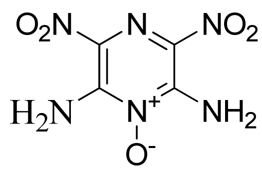
Potential RDX replacements



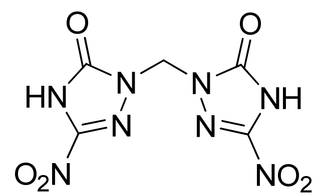
HMX



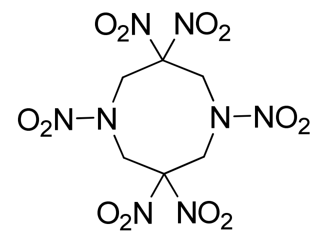
DNGU



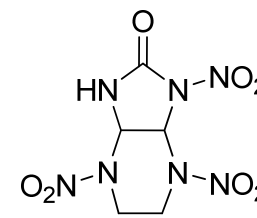
LLM-105



BiNTO



HCO

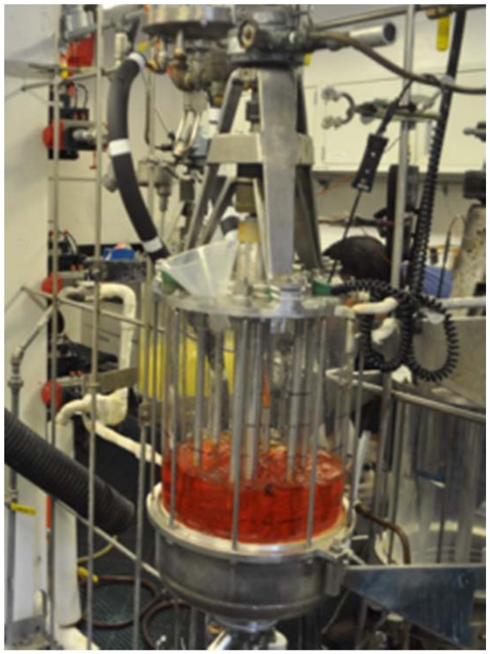


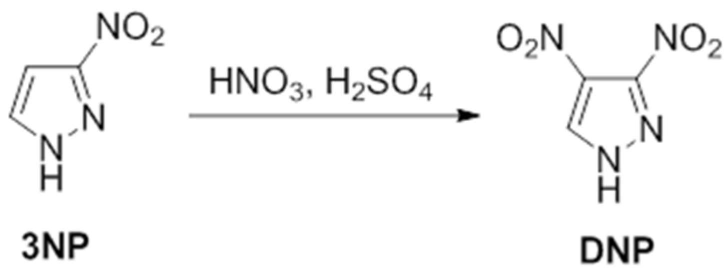
HK-56

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, particle morphology
LLM-105 ✓	Insensitive, good performance	particle morphology and size
BiNTO ✗	Reduced water solubility, NTO as starting material	Unconfirmed performance, material unstable
HCO ✗	Similar to TNAZ, High density	Laborious synthesis
HK-56	Potential for low-cost and sensitivity	Unconfirmed performance, immature synthesis route

✓ = Ingredient moving forward in program

DNP Synthesis

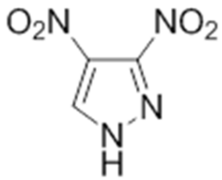




- DNP (3,4-dinitropyrazole) is technically mature, and has been consistently synthesized on the 5 lb scale with 65% crude yield and 99.9% HPLC purity but with ~5% remaining acids.
- With new purification process, yield increased to ~52%. Purity was greater than 99% by HPLC. Sulfate content was less than 0.02%.
- Previous purification methods involved extractions and vacuum. Current efforts are focused on isolation and purification processes amenable to scale-up.

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

DNP Skin Sensitization Potential

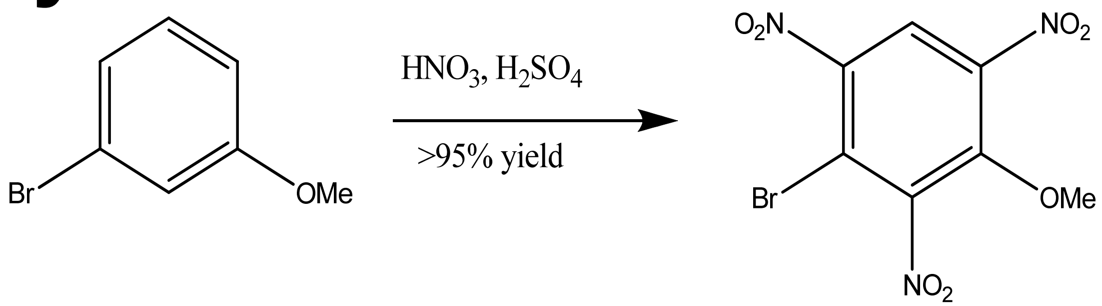


DNP

- DNP sample was sent to USAPHC for Dermal Testing
- "DNP was found to elicit a low-to-mild hapten formation response by DPRA (direct peptide reactivity assay). Analysis of cysteine alone produces a mild response (percent depletion of peptide), but when coupled with data for the lysine-containing peptide chain (percent depletion of peptide), the overall response is considered to be low. 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. Alternatively, further *in vivo* sensitization testing could be conducted if development of the compound is continued."

▪Proper Engineering Controls and PPE for safe handling

TNBA Synthesis

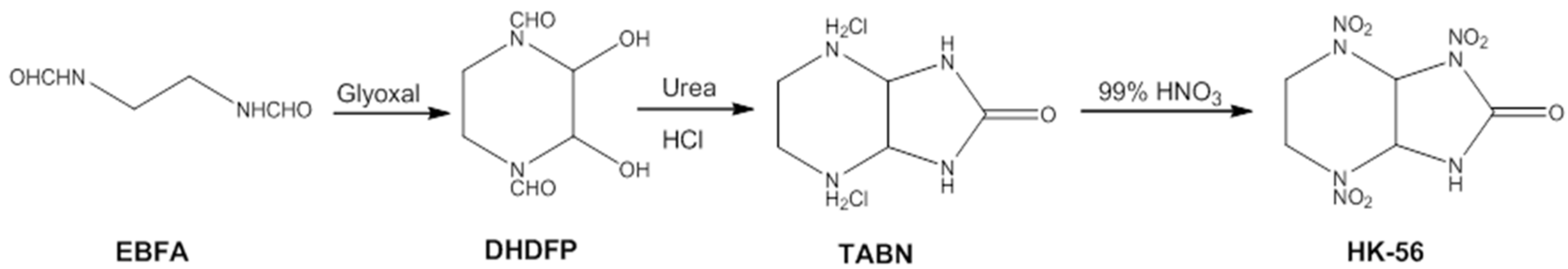


TNBA

- Synthesis route is one step nitration
  - Crystalline solid precipitates from reaction in high yield
- **Robust Process:**
  - Many nitrations have been performed
  - 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)

▪**Technical Maturity:** Minimal **optimization** needed. Need to get preliminary performance testing to verify detonation velocity.

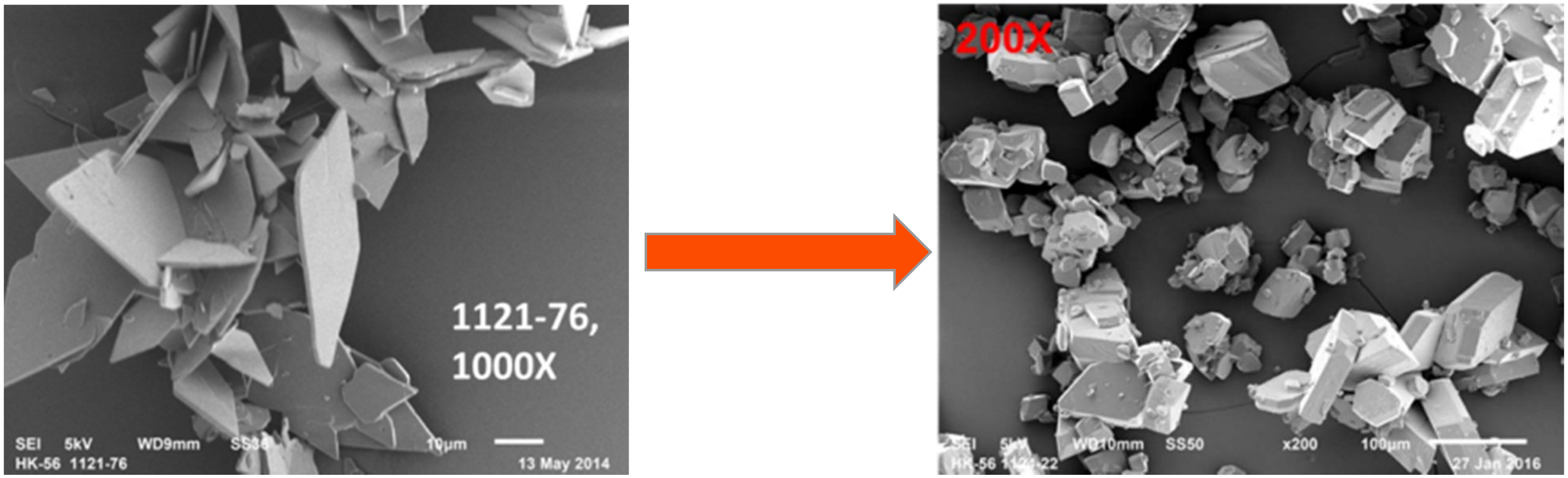
HK-56 Synthesis



- Simple condensation to DHDFP (yields of 68%)
- TABN reaction completed up to the 2 L scale (yields of 50-70%)
- HK-56 yields of ~40%
- A total of 1 lb of HK-56 has been synthesized.

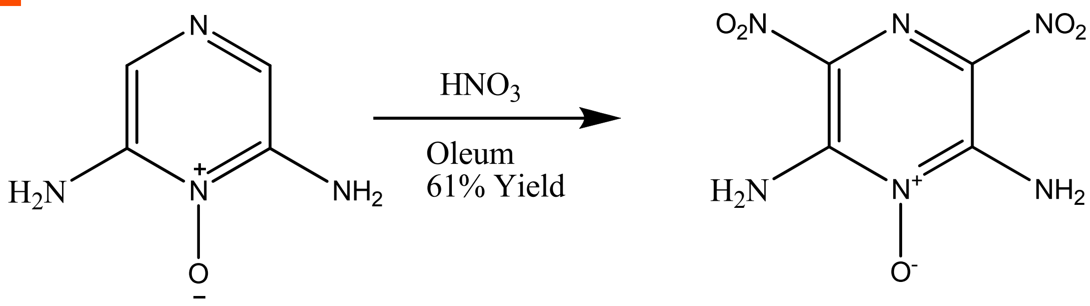
- Particle size and shape of the HK-56 will be important for future formulation activities
  - HK-56 particle shape appears promising (no needles)
  - Particle size was originally approximately 5-10 microns

HK-56 Particle Improvements



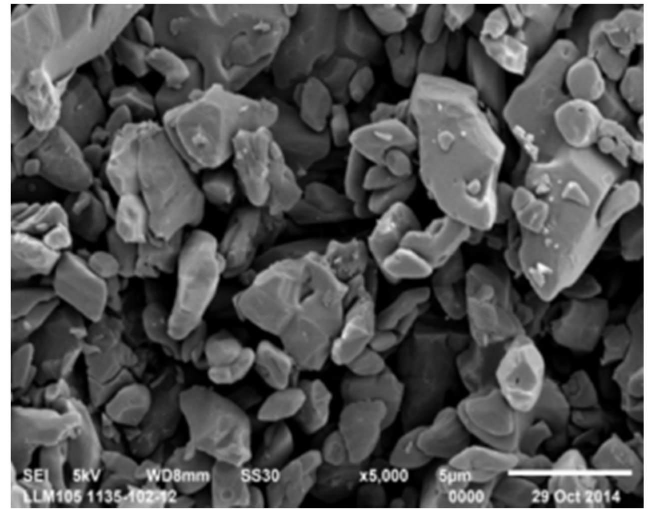
- Through a novel reaction quenching method, the particle size grows and the particle shape improves.
  - This method allows the HK-56 to crystallize slowly.
  - This yields crystals that are more cubic.
- Average particle size is about an order of magnitude larger than original process material

LLM-105 Synthesis



DAPO

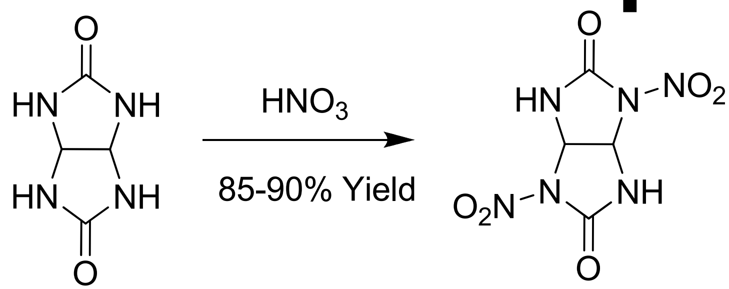
LLM-105



- Final stir in LLM-105 formation complicated by significant foaming.
- Off-gassing suggests consumption of the product or intermediates.
- Reduced HNO_3 loading and a reduced final stir temperature provides a modest yield improvement (4-5%).
- The reduced HNO_3 loading and reduced final stir temperature also results in less troublesome headspace foaming.
- Extensive robustness testing revealed reduced oleum loading and extended final stir temperatures above 30 ºC as the only two major concerns affecting yield.

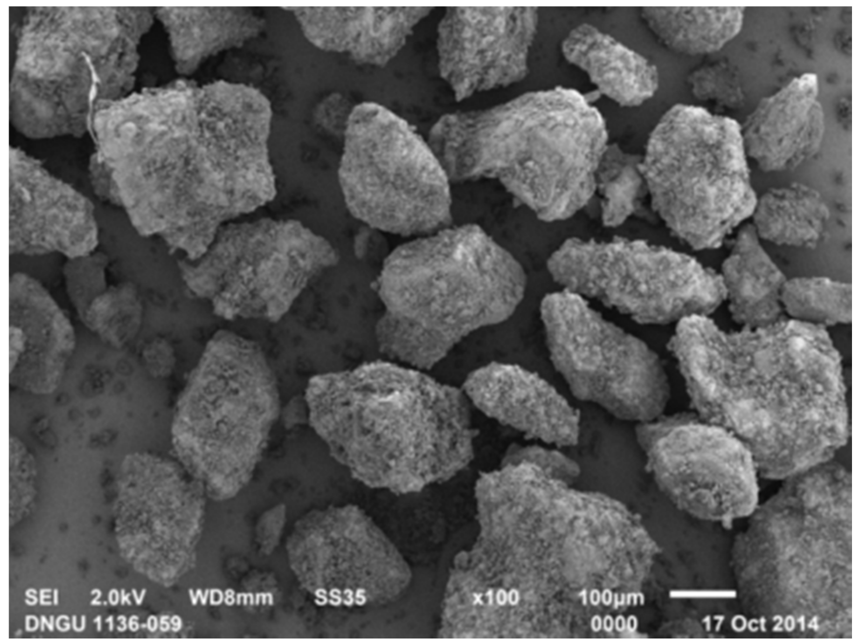
▪**Technical Maturity:** Robust synthesis process. Particle size is rather small.

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.
- Higher temperature final stir contributes to larger particle size growth.
  - >100 microns
- Purity is typically greater than 99%.
- Residual acid is typically ~0.1%.



▪**Technical Maturity:** Larger particles generated with novel nitration process .

VTS Compatibility

	NEAT	TNBA	DNMT	PiPE	DNP	DNGU	LLM-105	HK-56	HMX
NEAT		0.5273	0.785	2.8188	2.6083	0.4744	0.4348	0.2857	0.0699
TNBA	0.5273					0.4569	0.7201	0.4146	0.2323
DNMT	0.785					------	0.5184	0.1175	------
PiPE	2.8188					1.5223	1.7547	------	1.3033
DNP	2.6083					2.0563	1.6351	0.2971	------
DNGU	0.4744	0.4569	------	1.5223	2.0563		0.6147	0.4653	------
LLM-105	0.4348	0.7201	0.5184	1.7547	1.6351	0.6147		------	0.3372
HK-56	0.2857	0.4146	0.1175	------	0.2971	0.4653	------		0.226
HMX	0.0699	0.2323	------	1.3033	------	------	0.3372	0.226	

- STANAG 4147 Test 1B states that when 2.5 grams of material A is mixed with 2.5 grams of material B, the total gas evolved after 40 hrs at 100° C must be less than 5 cc in order to be deemed compatible.
- **All materials were compatible as tested.**

Comparative Data

	TNT replacements					RDX replacements				
	TNBA	DNMT	PiPE	DNP	TNT	DNGU	LLM-105	HK-56	FEM-HMX	RDX
SEM	√	√	√	√		√	√	√	√	
Impact, cm	(Naval) 79.43	>85	56.7	55.0	88	(Naval) 112.20	50.0	35.0	30.7	45
Impact Std, cm	23.3	45.0	50.8	39.0		16.7	39.0	42.5	-	
Friction, N	70.0	166.0	>360	246.0	216	>360	>360	>360	183.5	144
Friction Std, N	144.0	142.7	144.0	164.0		164.0	164.0	-	-	
ESD, J	0.2900	0.0425	0.2113	0.2625	>0.25	0.0366	0.0366	0.0829	0.1050	<0.25
particle size	0	0	0	0		120	4	20	5	
det velocity	6.571	7932	6.929	8251	7180	8878	8667	8628	9246	8862
det pressure	23.98	25.97	21.96	29.24	20.02	35.64	32.72	32.82	37.19	33.46
V/V0 7.20	-5.87	-7.05	-5.91	-7.93	-5.42	-8.33	-7.56	-8.49	-9.66	-9.01
Oxygen balance	-44.72	-32.35	-80.85	-30.37	-73.96	-27.57	-37.02	-37.52	-21.61	-21.61
Density, g/cm3	1.948	1.66	1.612	1.773	1.654	1.941	1.881	1.85	1.91	1.816
melt temp	97	97	100	87		0	0	0	0	
heat of formation	18.88	122.8	227.4	120.5	-63.2	-41.54	-13	100.6	75	70

- This data was used in the downselect process for ingredients.
- Performance data was calculated using Cheetah 7.0.

Overview of Completed Tox Work

- Toxicology Assessment being performed in accordance with USAPHC Phased Approach concept ASTM E-2552-08
- Profiles completed for 13 candidate compounds
- Recommendations included Ames testing, aquatic toxicity testing, and biodegradation testing

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
DNGU	High	Moderate	Moderate	Low	Moderate	Low	
LLM-105	High	Moderate	Moderate	Moderate	Moderate	High	Possible carcinogen
DADNP	Low	Low	Moderate	Low	Low	High	
NANTO	Low	Low	Moderate	Moderate	Low	High	
HNDO	High	Low	Moderate	Moderate	Moderate	Low	
BNTO	Low	Low	Moderate	Moderate	Low	Unknown	
BiNTO	Low	Low	Moderate	Moderate	Low	High	
HK-56	High	Low	Low	Low	Moderate	High	
RDX	Moderate	Unknown	Low	Low	Low	Moderate	Carcinogenicity only observed in female mice.

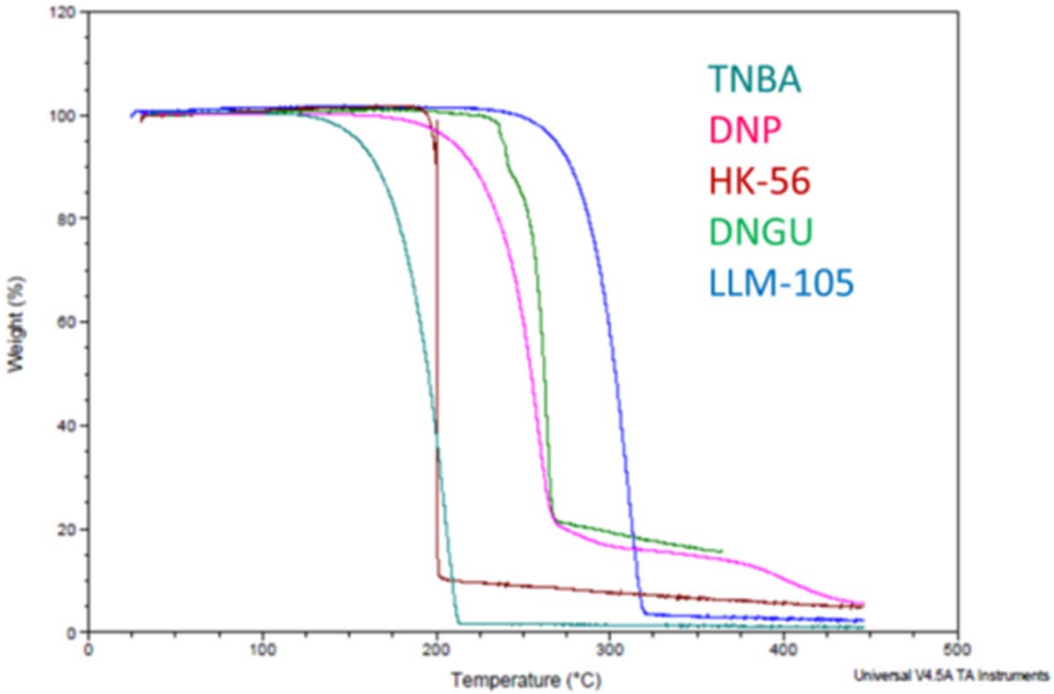
Overview of Completed Eco-Tox Work

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
[redacted]							
DNGU	Low	Low	Low	Low	High	High	Low
LLM-105	Low	Low	Low	Unknown	High	High	Low
HNDO	Low	Low	Low	Low	High	High	Low
BNTO	Low	Low	Low	Unknown	High	High	Low
BiNTO	Low	Low	Low	Unknown	High	High	Low
DADNP	Low	Low	Low	Unknown	High	High	Low
NANTO	Low	Low	Low	Unknown	Moderate	High	Low
HK-56	Low	Low	Low	Unknown	High	High	Low
RDX	Low	Low	Low	Unknown	Moderate	High	High (plants)

- Tox and Eco-Tox indicate likely differences between candidates.
- PiPE, DNGU, and HCO could be least toxic candidates
- TNBA, PiPE, DNGU, and HCO could have least Eco-toxicity

Vapor Pressures

Sample	VP (torr; estimated) 25°C	70°C	100°C	ΔH$_{vap}$ (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



- Ingredients were sent to Dr. Rose Pesce-Rodriguez at ARL for Kow, Koc, water solubility and vapor pressure testing.
- DNP and TNBA have lower vapor pressures than TNT:
  - Good news for melt-pour materials

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Melt Kettle

- BAE has traditionally used a melt kettle for melt pour formulations development that operates with approximately 500 grams of material (vessel on left).
- With new ingredients in limited supply, we cannot afford to experimentally formulate at this scale.
- Therefore, BAE designed and fabricated a melt kettle capable of formulating 50 gram batches in an effort to consume less of the precious novel materials (vessel on right).

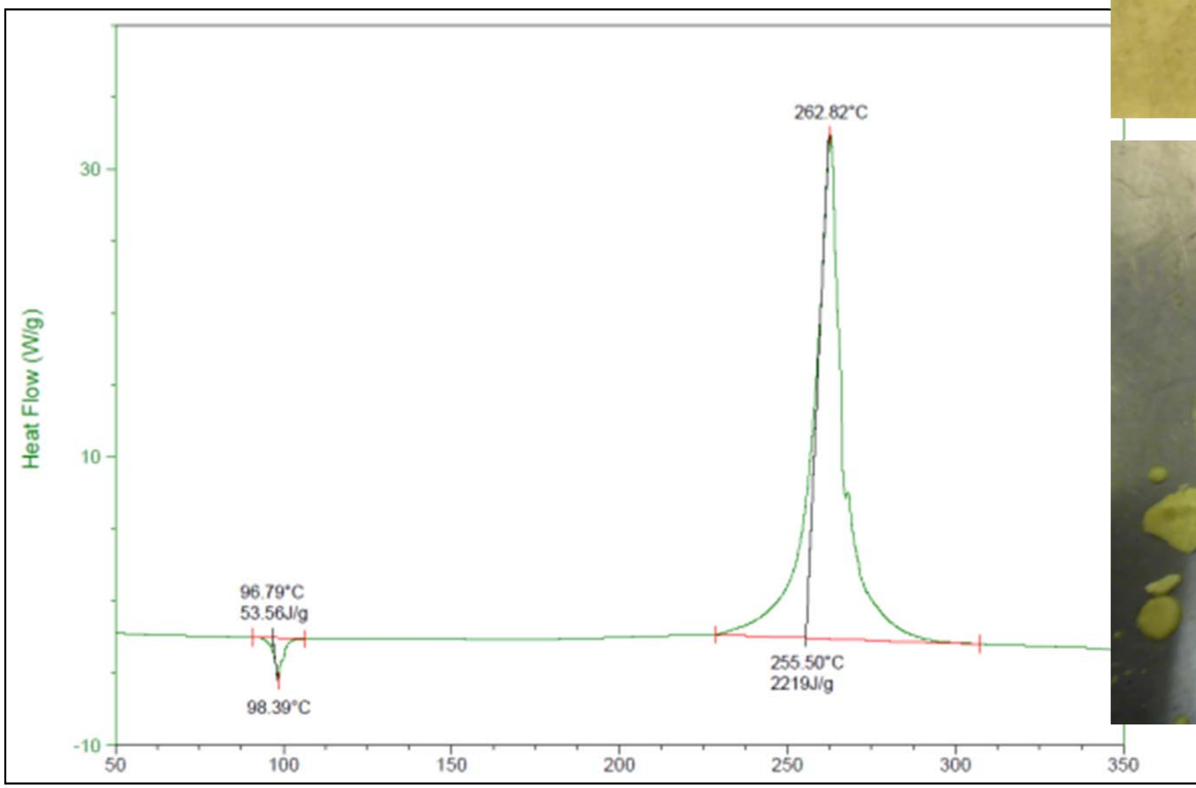
GrIMEx Performance Calculations & Sensitivity Data

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

Formulation	Pcj (Cheetah 7.0)	V/Vo (7.20) (Cheetah 7.0)	Impact	Friction
TNBA/DNGU/HFEM	24.876	-6.78	45	331
TNBA/HMX/HFEM	31.800	-8.40	26	331
DNP/DNGU/LLM105/HFEM	31.301	-7.97	82*	322
DNP/DNGU/HFEM	32.757	-8.28	33	346
DNP/DNGU/LLM105	32.088	-8.05	35	328
Comp B	27.028	-7.55	38	150

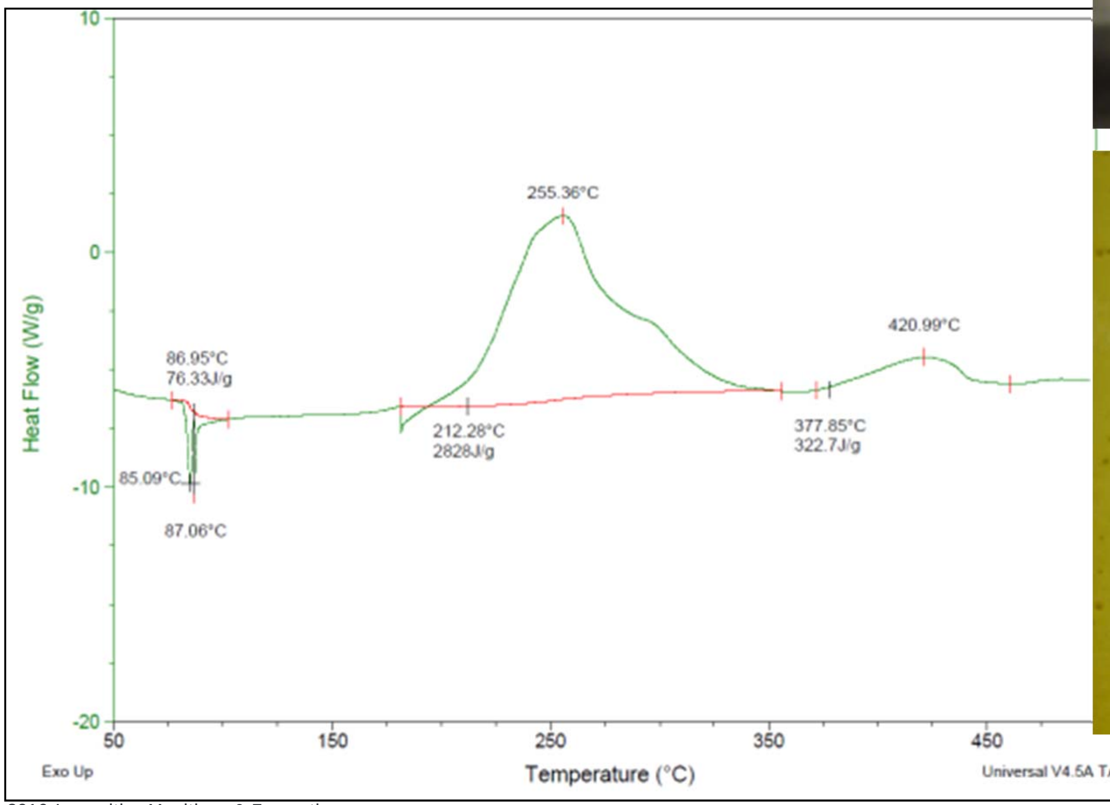
TNBA Formulations

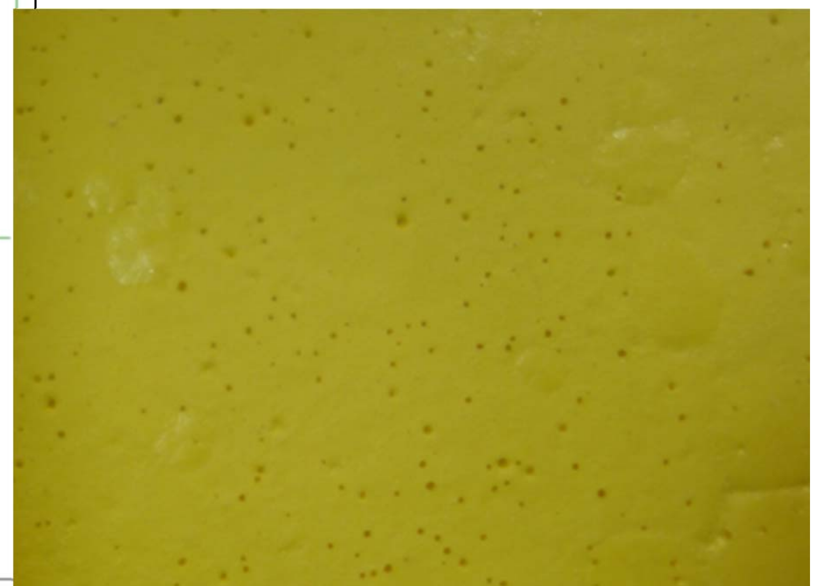
- TNBA/DNGU/HMX formulation shows:
  - Sharp melting point
  - Exothermic decomposition for DNGU remains unchanged



DNP Formulations

- DNP/LLM-105/HMX mixture shows:
  - ♦ sharp melting point
  - ♦ New exothermic decomposition appears >400° C, (interesting phenomenon)





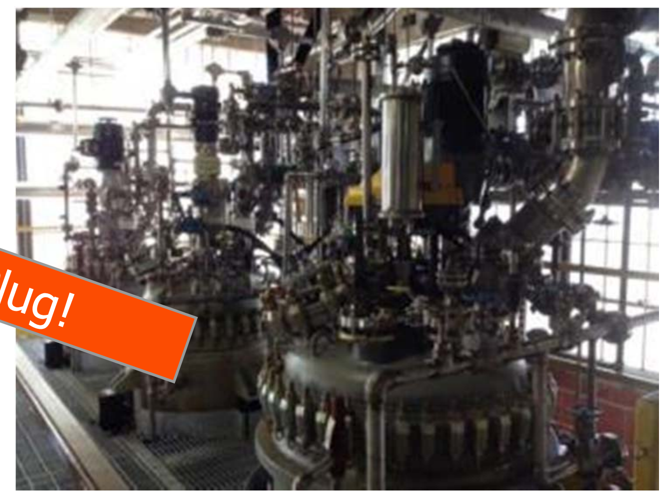
GrIMEx Formulations Progress

- DNP:
  - 45-50% solids loading (low melt viscosity)
  - Seems to be an irritant (need good engineering controls and PPE)
  - Cools slowly causing possible settling issues
- TNBA:
  - Current challenge: lower solids loading (<40%)
  - Achieved 34% TNBA formulation using multiple HMX classes
  - Might obtain improved results with better inputs

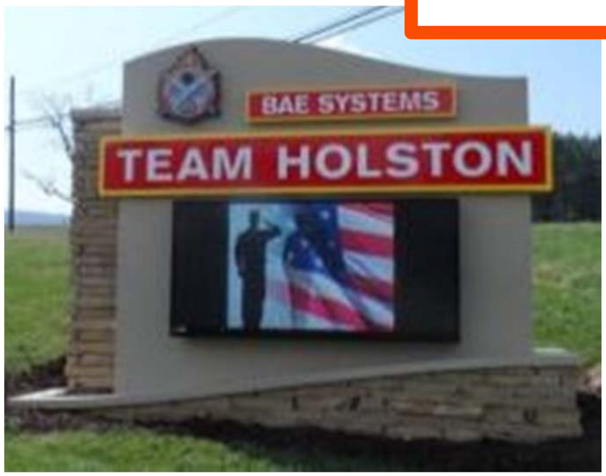
Conclusions

- Lots of interesting synthesis development work
- Down-select has helped us focus on ingredients and target formulations
- We are looking forward to scaling up ingredients and further toxicity evaluations
- BAE Systems has commissioned a pilot plant at Holston which should better enable the scale up of these new materials
- **End goal of an affordable, environmentally friendly, IM Comp B replacement is in sight.**

Shameless Plug!



Questions?



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