LA-UR- 11-05724

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Title: Melt Castable Formulations Containing DAAF as Replacements for Comp B

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Intended for: SERDP Scientific Board Meeting
Oct 12-14, Arlington VA

Los Alamos NATIONAL LABORATORY EST.1943

Melt-Castable Formulations Containing DAAF as Replacements for Comp B

Abstract

This project has the objective to replace Comp B with a formulation that contains Diaminoazoxyfurazan (DAAF) and a melt castable explosive. The value of DAAF is its green synthesis, insensitivity to common insults and performance. The melt castable portion will be chosen from explosives with low melting point, environmentally sensible synthesis, long-term sustainability, and acceptable stability in storage, non-polluting residue after explosion, or acceptable consumption during detonation. This proposal includes newer materials where the synthesis is still being developed. Down-selection will be made with environmental impact in mind.

We feel confident a formulation with lesser environmental impact and equal or greater performance to Comp B can be found among the explosives identified in this proposal. Explosive research is critical for the future of munitions, and advances in new materials with an added focus on environmental stewardship is visionary.

Melt Castable Formulations Containing DAAF as Replacements for Comp B

Project WP-2209

Elizabeth Francois
Los Alamos National Laboratory

Brief to the Scientific Advisory Board
October 12, 2011

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Performers

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Los Alamos National Lab, Los Alamos, NM
Specialist in Chemical Synthesis

Dr. Mark Johnson and Dr. William Eck

USAPHC
Providing expertise in toxicology of new compounds

Mr. Philip Samuels

ARDEC, Picatinny, NJ
Providing expertise in Melt Casting and Transition to DoD

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Problem Statement

- **COMP B contains environmentally unfriendly constituents.**
  - **TNT: Presents health and environmental concerns. Considered an Emerging Contaminate by the EPA.**
  - **RDX: Water contaminant around munitions depots. Presents health concerns.**
- **Comp B is widely used in munitions.**
  - **60/81/120mm Mortar**
  - **105mm M1 and 155mm M107 Artillery**
- **A replacement formulation is needed that:**
  - **Is Melt Castable**
  - **Performs as well or better than Comp B**
  - **Is Insensitive, can pass IM testing**
  - **Utilizes Environmentally Acceptable Synthesis**
  - **Low Environmental Impact**

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Technical Objective

- Replace Comp B with a formulation that contains Diaminoazoxyfurazan (DAAF) and a low melting point explosive.
- Low melting point explosive will be chosen with environmentally sensible synthesis in mind.
- All constituents will be chosen with safety in mind.
- All Constituents will be chosen with performance in mind.

To paraphrase

Objectives: Green, Safe, Fast

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Technical Background: To be like Comp B…

Comp B:

RDX (crystalline explosive)

TNT (Low Melting Point Explosive)

D_v = 7.8 km/s

Our Replacement:

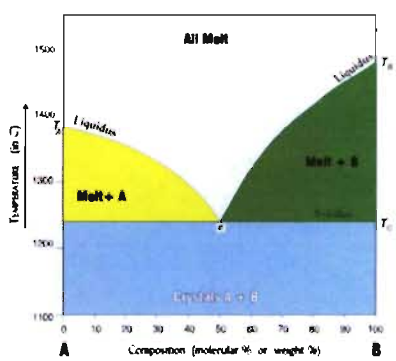
Crystalline explosive

- DAAF
  - MP 255°C
  - Insensitive
  - Performs well

Low Melting Point Explosive

- AN/Urea
- TNAZ
- DNMT
- BNFF
- NTMTs

Technical Background: Melt-Castable Explosives



Comp B is a melt cast.

So must the replacement.

Melt Cast offers challenges in composition, microstructure, melting point (eutectic), etc.

- Pick Formulation based on performance?
- Pick Formulation based on melting point, vapor pressure reduction, microstructure etc..
- Develop phase diagram for each formulation to address microstructure AND performance

Technical Background: Why DAAF?

- Properties:
  - Green Synthesis- no hazardous waste
  - Similar shock sensitivity to HMX
  - Similar impact sensitivity to TATB
  - Yellow crystalline solid
  - Very thermally stable- Does not DDT (deflagration to detonation transition)

- Uses
  - Booster: PBXN-7 Replacement
  - Booster PBXW-14 replacement
  - IHE C-4 type explosive
- Successes
  - 2 pollution Prevention awards, 2008, 2009
  - R&D 100 best invention for 2009 award
  - Continuous Process developed by NSWC-IHDIV for simplified synthesis 2010

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Technical Background: DAAF compared to benchmarks TATB and RDX

	DAAF	TATB	RDX
Density	1.747 g/cc	1.93 g/cc	1.816 g/cc
H_{50} on Type 12 DWI apparatus	>320 cm	>320 cm	25.5 cm
Friction	>36 kg	>36 kg	20.8 kg
Spark	0.0625 J	0.25 J	0.025 J
Detonation Velocity at 96.5 % TMD	7.93 km/s	7.62 km/s	8.54 km/s
CJ Pressure at 96.5 % TMD	306 kbar	259 kbar	337 kbar

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Brief History of DAAF

1981
Interesting high nitrogen molecules discovered
DAAF, DAAZF, ANF

1999-2000
DAAF patented, testing results published. Insensitive like TATB, but with enhanced performance. HMX-like shock sensitivity, small critical diameter

2005 -2007
Problems with DAAF synthesis, particle size, performance, and waste make it unpopular

2007
Novel synthesis of DAAF developed, all previous problems fixed

2009
Renewed interest in molecule, funding broadens significantly. Interest in filling in knowledge gaps.

DAAF booster project transitioned to 6.3 through JIMTP. Other uses sought through SERDP

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Technical Background: Requirements

DAAF

Low Melting Point Explosive

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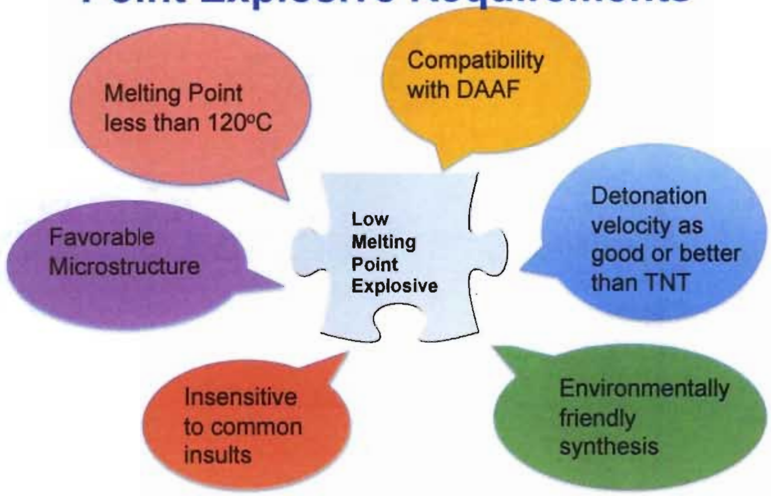
Technical Background: Low Melting Point Explosive Requirements



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Technical Background: Low Melting Point Explosives of Interest and Why

- AN/U Eutectic: A fertilizer and an explosive. MP 80-100°C
- TNAZ: Great Performance, at a price. Favorable synthesis. MP 101°C
- DNMT: Similar performance to Comp B, more insensitive. Scaled up and ready to use. MP 95°C
- BNFF: A new molecule, high performing, synthesis needs optimization. MP 112°C
- NTMTs: a new family of molecules possibly with extremely high performance. All safety characteristics unknown.

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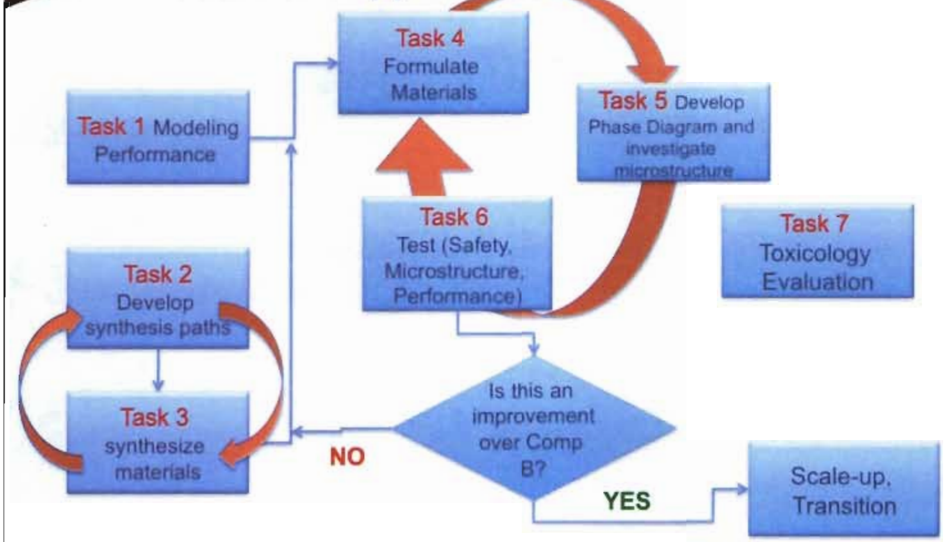
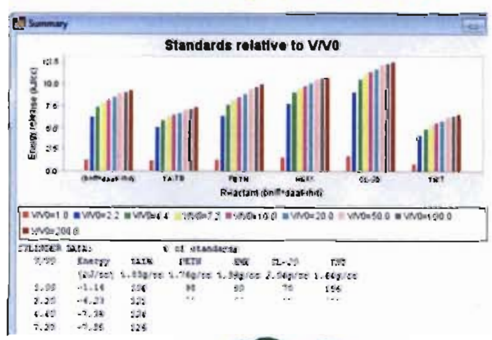
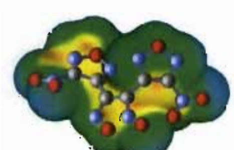
Technical Approach



Technical Approach: Modeling (Task 1)

- Cheetah 6.0 is used to model performance of ingredients and formulations.
- Good way to estimate performance, cannot predict safety characteristics
- Using calculations performed with software developed by Dr. Betsy M. Rice we can predict Enthalpy of Formation and Density for new molecules but not melting point.





BNFF
ρ (g/cc) = 1.914
ΔH_f (kcal/mol) = 148.2
O-N bond ~ 1.46 A

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Technical Approach: Develop Synthesis Paths (Task 2)

- Finding a target molecule is only part of the battle.
- The synthesis path to the molecule needs development with focus towards environmental stewardship.
- Existing molecules of interest with sub-optimal environmentally conscious synthesis need improvement.
- Once synthesis paths found and optimized, scale up can occur.

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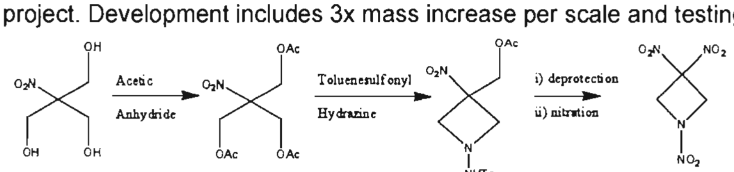
Technical Approach: Synthesize Materials (Task 3)

- Materials of interest will be synthesized in quantities up to 500g under this project. Development includes 3x mass increase per scale and testing.



Commercially available starting material

TNAZ

- Scale-up and improve large scale purification of BNFF
- Complete characterization and scale-up of known NTMTs
- Synthesize and characterize unreported but desirable NTMTs
- Measure physical properties for Quantitative Structure Activity Relationships (QSARs): How transportable is the molecule in the environment? Provide data to PHC

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Technical Approach: Formulation (Task 4)

- Based on Modeling, formulations of interest will be chosen.
- 2g batches will be made to address compatibility.
- 10g samples of each will be made and safety tested.
- Binary phase diagrams of each formulation will be made to evaluate the microstructure and eutectic.
- Formulations will be scaled up to 500g batches
- Safety testing is repeated to investigate scaling effects.
- Melt-castability will be investigated and optimized

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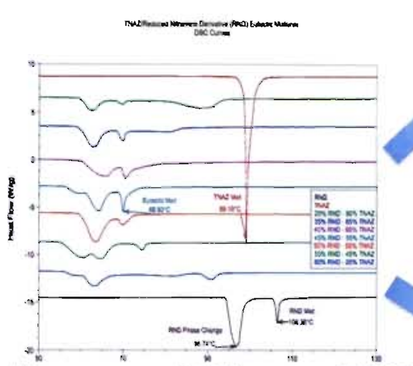
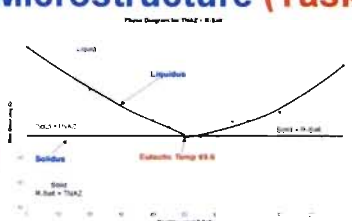
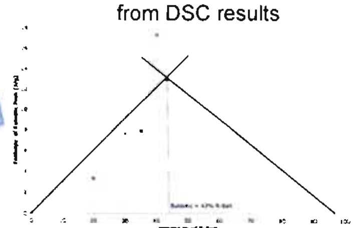
Technical Approach: Develop Binary Phase Diagram and Investigate Microstructure (Task 5)



Run DSC on various compositions to determine eutectic melt temperature



Generate binary phase diagram from DSC results



Calculate eutectic composition from melt enthalpies

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Technical Approach: Testing (Task 6)

- This task has two parts:
  - ♦ Safety testing
  - ♦ Performance testing

Electro-Static Discharge testing on PETN

DAAF rate stick

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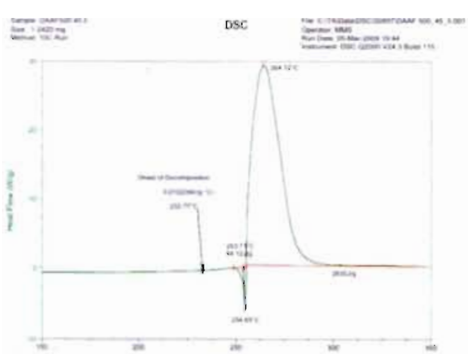
Technical Approach: Safety Testing

- Required for every subsequent step.
- Consists of
  - ♦ Drop Weight Impact
  - ♦ Electro-Static Discharge
  - ♦ Friction
  - ♦ Vacuum Stability
  - ♦ Differential Scanning Calorimetry



Typical DSC of DAAF showing purity and melt.

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Technical Approach: Performance Testing- Rate Stick and Detonation Curvature

- Small scale test yielding 3 important pieces of information.
  - Detonation Velocity
  - Detonation front curvature
  - Diameter effects
- Uses tiny amount of material (< 2g per test)
- Easy to field
- Yields high fidelity data

Front curvature rate stick test on DAAF

BNFF curvature results on 1/8" diameter pellet

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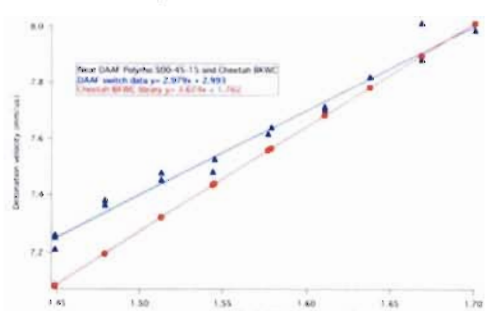
Technical Approach: Performance Testing- PolyRho

- Quintessential HE performance test
- Gives Detonation Velocity as a function of density
- Allows evaluation of Cheetah model over wide range of densities.
- Can include microstructural effects (voids, crystal size etc.)



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Technical Approach: IHE Gap Test

- Tests an explosives' sensitivity to shock
- Large database on DoD materials exists and allows meaningful comparison
- Matching shock sensitivity allows drop in replacement.
- Economical: Uses only 11g per shot
- Test series is 8 shots

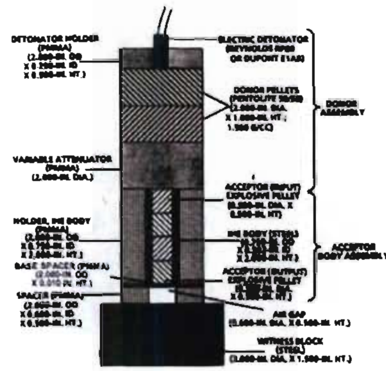

Figure 3. IHE Gap Te st Configuration with Spacer Modification

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Technical Approach: Toxicology Evaluation

Task 7

- QSARs (Quantitative Structure Activity Relationships) computer modeling based on physical measurement for material transport in the environment
- DAAF will be evaluated by the PHC for toxicity starting as early as possible.
- Testing to encompass *In Vitro* and *In Vivo* tests and will progress over the duration of the project

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Scale-up/ Transition

- Formulations considered favorable will be scaled up to the kilo-scale.
- Melt-casting evaluation and consultation will be provided by ARDEC.
- Transition to JIMTP 6.2 or 6.3 will be sought to evaluate formulation in munitions.

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Year 1 Project Plan

• Model Material Characteristics and Performance	$50K
• Synthesize Materials	$149K
• Make Formulations	$120K
• Develop Phase Diagrams of formulations	$90K
• Safety Test Formulations	$60K
• EHA Development by the PHC	$15K
	TOTAL $489K

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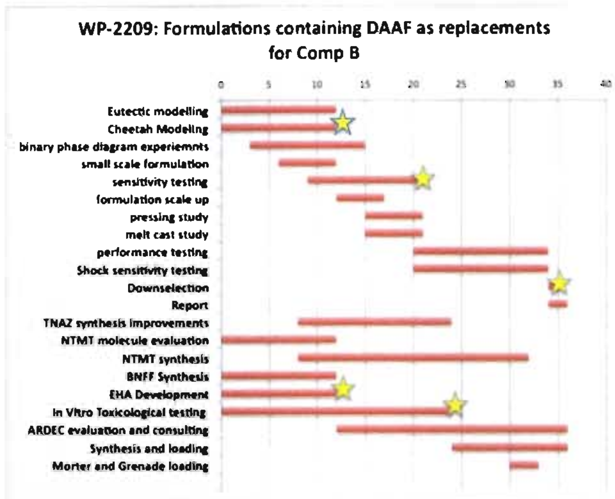

☆ Go/No go on toxicology: If DAAF is unacceptably toxic, project needs rethinking
Formulations too sensitive will not be selected
Formulations that are modeled with unfavorable performance will not be selected

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Project Funding

$K	SERDP	DOE Campaign 2	Joint Munitions Program
Year 1	489	50	50
Year 2	487	50	50
Year 3	476	50	50
Total	1452	150	150

Campaign 2 Is DOE match to JMP
JMP is DoD centric HE development fund

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Deliverables

- Novel synthesis methods on several energetic materials.
- A new melt-cast formulation(s) with unique and interesting properties
- A new eutectic and microstructure evaluation method
- Toxicology information on DAAF- Useful to all DoD
- Final report outlining methodology, results, downselection and transition.
- New knowledge of what makes a good melt cast.
- 2 undergrad students involved, excellent experience!
- Peer reviewed articles

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Backup Slides

Responses to peer review or program office comments

Supporting material to be used in response to anticipated SAB questions

Transition Plan

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Acronyms

ANF	AminoNitroFurazan
AN/U	Ammonium Nitrate/Urea
BNFF	Bis(nitrofurazanyl)furoxan
Comp. B	Compound B (RDX/TNT explosive)
DAAF	Diaminoazoxyfurazan
DAAZF	Diaminoazofurazan
DDT	Detonation to Deflagration Transition
DSC	Differential Scanning Calorimetry
HMX	Her Majesty's Explosive
IM	Insensitive Munition
JIMTP	Joint Insensitive Munitions Technology Program
MP	Melting Point
NTMT	N-TrinitroMethyl-Triazole
QSAR	Quantitative Structure-Activity Relationship
RDX	Royal Detonating eXplosive
TATB	TriAmino Trinitro Benzene
TNAZ	TriNitroAZetadine
TNT	TriNitro Toluene

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Reviewer Comments

Comment: In the testing section performance and shock initiation (SDT) has been covered, but more thought should be given to testing the material in confined burning test to examine DDT.

Response: A fair amount of cook-off testing has been performed on DAAF. We have shown in extremely highly confined tests, DAAF does not DDT. We feel this is a paramount feature for any potential IHE. However the formulations that come out of this project will need to be evaluated in either VCCT or our DDT test. This will be evaluated in year two or three.

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Reviewer Comments

Comment: More details about the criteria for down selecting materials would have improved the proposal, or even indicating how many materials are going to be down selected.

Response: If I use the same approach I used in a JIMTP PBXN-7 replacement project it would go like this:

1) Safety test everything, do not use this alone to downselect but choices in material characteristics (particle size etc.) can be made based on these results.

2) Test all formulations for detonation velocity and shock sensitivity. These results will factor into the down selection. A drop in replacement for Comp B will be sought which requires similar shock sensitivity.

3) Cook-off can be used to strongly separate materials. DAAF never reacts violently EXCEPT when mixed with RDX. This was used in the past to not select any formulations with RDX in them. Some similar selection tool may become obvious in this project.

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Reviewer Comments

Comment: Both PI's are young scientists with strong backgrounds and credentials. However, assistance from more senior researchers experienced with synthesis, formulation, and testing of explosives is desired. The proposed cooperative efforts with JMP (D. Chavez) seem to be important for the success of this proposal.

Response: Phil Leonard is also funded through the JMP and both PIs work closely with Davis Chavez.

Comment: The team is strong in synthesis, performance, modeling, and formulation. The team seems weak in industrial chemical engineering experience and support.

Response: There are opportunities to involve more chemical engineering in years two and three. LANL has limited scale-up capability but may seek outside help as the need arises.

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Backup Slides

Provide any additional technical supporting information that may help in answering SAB questions

EXAMPLE:

- Supporting data from previous or preliminary work
- Details on specific techniques or instruments to be used

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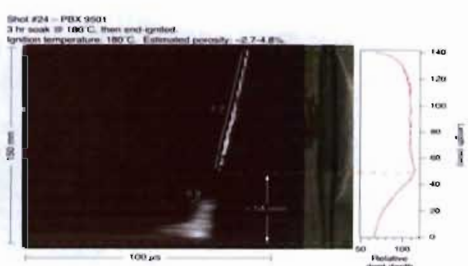
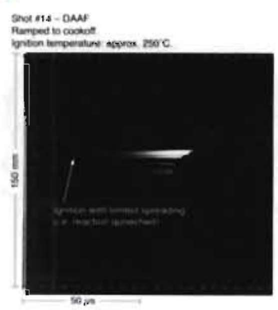
Heavily confined cook-off test





- Conventional HE (e.g. PBX 9501) has been observed to react violently
  - Fast convective burns
  - Thermal explosions (cookoff)
  - Deflagration-to-detonation transition (DDT)
- **Ideally, an insensitive HE will not cook off violently**

Testing Approach: Heavy confinement

- Isolation from boundary effects
- Worst case scenario
- Case is a diagnostic

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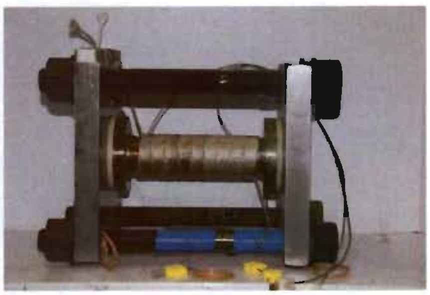
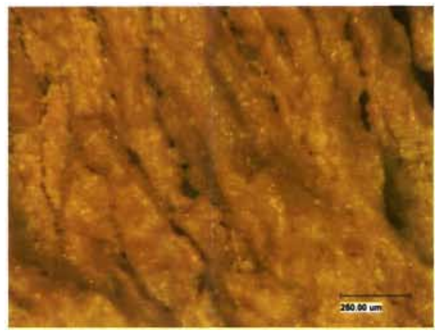
Super- Heavily confined cook off test

Pipe bomb configuration where DAAF was completely confined and molten DAAF could not escape. How would this effect violence?

Evidence of surface melting on recovered DAAF. Violence low, no DDT.





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Transition Plan

DoD already likes DAAF. In a recent JIMTP review comment stated "LOVE DAAF!! Good transition potential and a prime example of something going from DOE to DoD." This should help anything coming out this project be accepted and transitioned.

ARDEC and LANL plan to submit a JIMTP proposal to continue testing and scale-up, assuming success with this project, in FY13 or 14.

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Performance Testing

- Rate Stick – Detonation Velocity
- Front Curvature
- Polyrho
- IHE Gap Test

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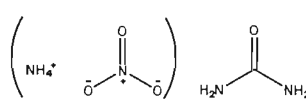
Ammonium Nitrate/ Urea



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Ammonium Nitrate

- Worlds most common mining explosive component (oxidant)
- No sensitivity to impact, friction, spark, shipped as DOT 5.1 oxidizer
- Also a common fertilizer
- Unused in military explosives due to hygroscopicity

Urea

- A high nitrogen fuel most commonly used as plant food
- Millions of tones produced per year

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AN/U Eutectic

- At mixtures between 50/50 and 80/20 AN/U forms a eutectic with a melting phase between 80-100 C
- Explosive properties similar to ANFO
- Very insensitive
- Non-ideal explosive behavior
- Water sensitive (deadening)

W.H. Rinkenbach, *Cast Ammonium Nitrate and Urea.* U.S. Patent 2817581, **1955.**
H.F. Scott, *Deicer Composition.* U.S. Patent 3630913, **1971.**

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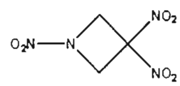
TNAZ: Trinitroazetadine



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TNAZ

- Developed by Swiss/Russians as a low-melt high-brisance explosive.
- Synthesis has been shortened dramatically with emphasis on reduced waste.
- Not currently used by US forces due to vapor pressure however co-melt studies on TNAZ/DNAZ reduced volatility significantly.
- Sensitivity similar to RDX.

M.D. Coburn; M.A. Hiskey; T.G. Archibald, *Scale-up and Waste Minimization of the Los Alamos Process for 1,3,3-trinitroazetidine.* Waste Management, *17*, **1997,** p. 143.
D.S. Watt; M.D. Cliff, *TNAZ Based Melt-Cast Explosives: Technology Review and AMRL Research Directions,* DSTO-TR-0702

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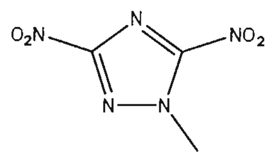
DNMT: Dinitromethyltriazole



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DNMT

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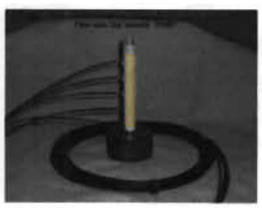
- Low-melt explosive, MP = 95°C
- Insensitive to impact, friction and ESD; passes vacuum stability test.
- No known environmental hazards
- Performance similar to Comp B (7.87 vs. 7.8 km/s)
- Similar shock sensitivity to Comp B.
- Scaled up at Holston.
- Undergoing toxicology study.



H.P. Burchfield; D.K. Gullstrom, US Patent 3054800, *3,5-Dinitro-1,2,4-triazoles*, **1962**.
P. Samuels; S. K. Singh; A. DiStasio; R. Damavarapu; E. Rivera; B. Fishburn, "Characterization of Melt Cast Materials," Technical Report ARAET-TR-08005, **2008**

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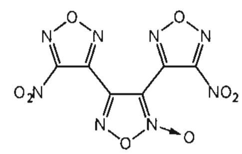
BNFF: Bis(nitrofurazanyl)furoxan



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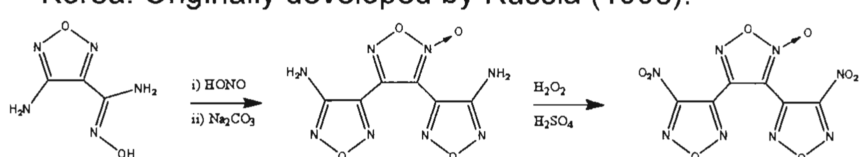
BNFF

- High density (1.91) high brisance explosive (9km/s, 37 GPa at TMD)
- Melting point 112 C
- Lower vapor pressure than TNAZ
- Synthesis optimization still under study by US, China, S. Korea. Originally developed by Russia (1998).



C.H. Lim; T.K. Kim; K.H. Kim; K. Chung; J.S. Kim, *Synthesis and Characterization of Bisnitrofurazanofuroxan*, Bull. Korean Chem. Soc. *Vol. 31*, 2010, p. 1400.

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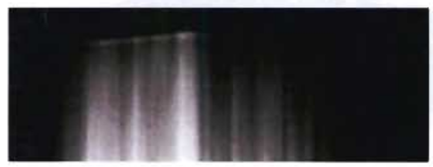
BNFF curvature and detonation velocity

- Pressed density:1.80g/cc (94.7% TMD)
- Detonation velocity: 8.516 km/s +/- 0.01
- Wave profile very flat, shows very little curvature.
- Expect critical diameter to be small.

Rate stick/front curvature configuration



Resulting front curvature

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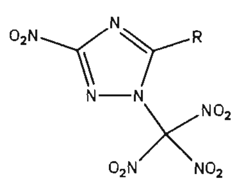
NTMT: N-trinitromethyltriazoles



R = NH_2, NO_2, I, Cl

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NTMTs

- High oxygen – overoxidized
- Currently under study by Russian chemists as high energy density organic oxidizers
- Low melting
- Sensitivity and performance unknown
- Significant performance enhancement probable
- Environmental aspects unknown

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