Environmentally Acceptable Alternatives To Existing Primary Explosives

Replacements for lead azide, lead styphnate and tetrazene

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NSWC-IH, Indian Head, MD USA
Green Energetics – Why?

Environmental:

>95% of all shooting, missile launches and explosions within the military or police force are done exclusively for training purposes in “friendly” areas.

In addition to the energetic materials themselves, one has to consider the materials used in manufacture, use and decommissioning/disposal of these materials in friendly areas.

Lead azide (LA) and lead styphnate (LS) are two widely used materials responsible for dangerously high levels of lead found at some firing ranges. Clean-up of heavy metal waste is extremely costly.

Safety:

**NAVSEA Instruction 8020.3A** (1986) – Limits use of LA in Navy ordnance – in non-hermetic systems LA may generate hydrazoic acid, a gas which can migrate and react to form unstable copper azide - fatalities have occurred.

Regulatory:

**Executive Order 12856** (1993) – Issued to reduce/eliminate procurement of hazardous substances and chemicals by federal facilities. Included directives to use acquisition programs encouraging new technologies and building markets for environmentally friendly products.

**EPA (TSCA)** – frowns on the use of lead, mercury, barium and other heavy metals as well as perchlorate.

National Security:

There is currently **NO** U.S. Manufacturer of LA - ~ 1 ton/year is used for military items all of which comes from a diminishing stockpile produced in the 1950-60’s and which has age related issues.

LS has only limited industry availability as it is made for captive use only by military/commercial ammunition facilities.
Lead Styphnate:
Major ingredient in stab and percussion primers, used as ignition element in hot-wire devices – high pressure output

*PSEMC has synthesized/evaluated 13 different compounds in effort to find a replacement for LS*

KDNP appears suitable as a drop-in replacement and offers high performance

**KDNP was approved as safe and suitable for service use and qualified for weapons development in Feb2009**

Lead Azide:
Most well known of the energetic inorganic azides, used widely in detonators/primers to initiate secondary explosives

- RD1333 – Most sensitive/high performance, 98.7% with carboxymethylcellulose added to control particle characteristics
- PVA – Also high performance, 96% with polyvinyl alcohol as crystal modifier
- DLA – Least sensitive/best for safety/handling, 93% with dextrin crystal modifier (spherical)

Attempts to replace have been ongoing for 3 decades and include CP, CICP, BNCP, DXN-1, cyanuric triazide

*PSEMC has synthesized/evaluated 33 different compounds in effort to find a drop-in replacement for RD1333*

- DBX-1 appears suitable as a drop-in replacement and offers advantages over RD1333

PSEMC was awarded (with NSWC-IH and LANL) an R&D 100 award for work leading up to DBX-1 and KDNP.

Tetrazene:
Explosive high nitrogen material used for sensitization of a variety of priming compositions (mil/com ammunition)

Tetrazene is a high nitrogen material containing no heavy metals but has low hydrolytic and thermal stability

Extremely impact and friction sensitive.

*PSEMC is currently involved, under contract with ONR, in a project to find a high stability replacement*

- Iso-DTET has sensitivity equivalent to tetrazene with high thermal and water stabilities
KDNP is based on KDNBF and has a similar structure but KDNBF is a Jackson-Meisenheimer adduct while KDNP is a true salt. Difference apparent when considering DSC temperatures.

4,6-Dinitro-7-hydroxybenzofuroxan, salt MDNP

Potassium dinitrohydroxy hydrobenzofuroxan KDNBF
Jackson-Meisenheimer adduct
Well known material introduced 1950’s

DSC exo 271°C
DSC exo 217°C
KDNP (4,6-dinitro-7-hydroxybenzofuroxan, potassium salt) is currently prepared via a 2-step process. A recrystallization step allows full control of particle size and tailoring for specific use (bridgewire vs. primer). Other synthetic methods for preparation are currently being evaluated at PSEMCA and NSWC-IH.

Like LS, KDNP is a fast deflagrating material with good thermal stability and safe handling characteristics.

KDNP has been evaluated vs. LS successfully in a variety of applications including:
- CCU-63 Impulse Cartridge – in a bridgewire slurry mix
- TOW Missile Initiator Units – pressed onto bridgewire
- PVU-12/A Percussion Primers – a component of primer mix (with tetrazene)
- RSCB – as consolidated/unconsolidated output
- Various pressure-time (closed bomb) tests – has higher impetus, equivalent ignition time and faster rise time vs. LS

KDNP will easily ignite common propellants (Black Powder, BKNO₃, Red Dot, HiTemp, etc).

PSEMCA completed Compound Qualification Testing on KDNP per NAVSEAINST 8020.5C in 2008. PSEMCA and NSWC-IH are currently working alternate syntheses/MANTECH scale-up projects KDNP.
From: Commander, Naval Sea Systems Command

Subj: QUALIFICATION OF KDNP PRIMARY EXPLOSIVE

Ref: [a] NAVSEAINST 8020.5C of 5 May 00
(b) Technical Manual SWO10-AG-ORD-010

Encl: (1) NAVSUREWARCENDIV Indian Head ltr 8020 Ser E216/12 of 14 Apr 08

1. KDNP (potassium 5, 7-dinitro-[2, 1, 3]-benzoxadiazol-4-olate 3-oxide) is a new primary explosive developed as a possible replacement for lead styphnate. KDNP has the potential for use in a wide range of explosive component applications and offers significant improvements in its environmental characteristics.

2. Based on the technical data provided in enclosure (1), the Naval Sea Systems Command hereby qualifies KDNP as a primary explosive in accordance with the requirements of reference (a). Qualification does not imply Final (Type) Qualification. Final (Type) Qualification requires further testing and approval in accordance with reference (a).

3. To date, KDNP has only been synthesized in small batch sizes. It is reasonable to expect that some changes in purity and morphology may be encountered when the synthesis is scaled up to production level batch sizes, possibly affecting sensitivity or performance properties. These possible changes must be investigated during any subsequent Final (Type) Qualification process.

4. For Commander, Naval Surface Warfare Center, Indian Head Division: Request incorporate KDNP into reference (b) identifying it as safe and suitable for service use and qualified for weapon development.

Laura M. Desimone
By direction

“KDNP is a green replacement for lead styphnate”

“Naval Sea Systems Command hereby qualifies KDNP as a primary explosive in accordance with the requirements of NAVSEAINST 8020.5C”

“Request incorporate KDNP into SWO10 identifying it as safe and suitable for service use and qualified for weapons development.”
DBX-1 Background

Composition:
\[
\text{Na}_2 \cdot \text{Cu}
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{array}
\begin{array}{c}
\text{NO}_2 \\
\text{NO}_2 \\
\text{NO}_2 \\
\text{NO}_2
\end{array}
\cdot 2 \text{H}_2\text{O}
\]

Four nitrotetrazoles are complexed with Cu(II)

This material has lower output compared to LA - dead presses at high loading pressures

*Terrible* particle habit/morphology

Attempts to reduce Cu(II) to Cu(I) with hydrazine gave crude DBX-1 (Sept 05’)
Attempts substitute water with coordinating ligand (carbohydrazide) (Nov 05’)
(Dr. Al Stern – NSWC-IH)

**Modifications of these studies led to discovery of DBX-1**

LANL-Proceedings of the National Academy of Sciences DOI: 10.1073/pnas.0600827103
Use of conventional laboratory techniques & equipment…

Starting materials added at front end

Unusual reaction – brown slurry to crystals

*variable crystallization induction periods*

DBX-1 isolated ~1 hour

Have evaluated variations – ratios, heating, acid etc.
Green Energetics – DBX-1

EL3C098A

Optical

77x

SEM

1000x

EL3C106A

77x

150x
Analysis of DBX-1:

- **5-Nitrotetrazolate content:**
  
  UV-Vis analysis of NaOH extract:
  
  NT: 65.30 (257nm, pH ~8.0); Theory 64.22 (1:1, 5-NT:Cu)

- **Estimated Copper Content:**
  
  Residue (assumed to be Cu$_2$O) from UV analysis:
  
  Cu: 35.06; Theory: 35.78
  
  (Filtered solution from NaOH treatment was slightly blue before dilution, slight loss of Cu)

- **Electrolytic Copper Content**
  
  Platinum cathode 35.60%

- **Density:** (He pycnometry) 2.59g/cm$^3$, (X-ray) 2.58g/cm$^3$
## Green Energetics – DBX-1

### DBX-1 Sensitivity Testing

**Essentially Equivalent to Lead Azide**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>DSC (20°C/minute)</th>
<th>IMPACT (J) (Ball Drop)</th>
<th>FRICTION (Small BAM)</th>
<th>DENSITY (g/cc)</th>
<th>High Res TGA Onset of Wt. Loss</th>
<th>ESD (LEESA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset</td>
<td>Peak</td>
<td>No Fire</td>
<td>Low Fire</td>
<td>TMD</td>
<td></td>
</tr>
<tr>
<td>DBX-1</td>
<td>329°C</td>
<td>337°C</td>
<td>0g</td>
<td>10g</td>
<td>2.59 (Cu)</td>
<td>260 ºC</td>
</tr>
<tr>
<td>LA (RD1333)</td>
<td>332°C</td>
<td>341°C</td>
<td>0g</td>
<td>10g</td>
<td>4.80 (Pb)</td>
<td>166 ºC</td>
</tr>
</tbody>
</table>

Low temperature weight loss for lead azide due to trace oxygen present in TGA system
An apparent disadvantage of lead azide compared to DBX-1
For DDT processes, explosive output increases with loading pressure until a maximum is reached then explosive output decreases (dead pressing). Not the case with LA OR DBX-1.
Green Energetics – DBX-1

DBX-1 DSC

DSC

File: DSC\Mike WEL30\EL30094A-1.002
Operator: Williams
Run Date: 30-Jul-2008 10:12
Instrument: DSC Q2000 V24.2 Build 107

Heat Flow (W/g)

Temperature (°C)

50 100 150 200 250 300 350

333.01 °C

325.91 °C

1963 J/g
Green Energetics – DBX-1

DBX-1 DSC Comparison

Heat Flow (W/g)

-25 25 75 125

Temperature (°C)

0 50 100 150 200 250 300 350 400

Universal V3.0G TA Instruments

NaNT
DXN-1
BNCP
Na$_2$Cu(NT)$_4$-(H$_2$O)$_2$

DBX-1

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Green Energetics – DBX-1

High Resolution TGA

- 181.80°C
- 233.56°C
- 248.15°C
- 256.97°C

Weight (%)

Temperature (°C)

- DBX-1 early
- DBX-1 late
- Lead azide RD-1333
- Silver azide Costain method

litharge

air in purge?
RD1333/DBX-1 Stability Comparison (High Temperature)

Weight loss after 24hr @ 181°C (358°F):
RD1333: 14.57%
DBX-1: 0%

Green Energetics – DBX-1

Oven Input: 25%RH/ambient air

Green: Before heat treatment
Blue: After heat treatment
Compound Qualification 8020.5C Project

Test procedures called out in MIL-STD-1751 (NATO AOP-7)

60g of DBX-1 prepared and crossblended in appropriate solvent age material at 70°C and ambient humidity for 1 year
Investigate safety characteristics (impact, friction, DSC, ESD)
    at T=0, T=6mo. and T=12mo. + “normally aged” at T=12mo.
Run hot wire initiation tests (P12 units, constant current and cap. discharge) at each time compare to RD1333
Investigate compatibility with various bridgewires/metal/secondary explosives
Priming ability test (RDX, DBX-1 as in MIL-STD-1751)

Additional Testing:

Prepare 104477-202 detonators with LA “normal” and DBX-1 transfer charges for comparison
Prepare NOL-130 primer mix with both DLA and DBX-1 and perform side by side safety tests
Investigate a variety of chemical properties (hygroscopicity, solubility, density, etc.)

PSEMC Internal R&D:

Extensive work on the temperature capability of DBX-1 vs. RD1333 in oil patch hardware
60.2g - 20 lots (3-4g ea.) of DBX-1 were prepared and evaluated (DSC, FTIR, photomicrograph) for acceptability
18 of these were crossblended while IPA moist
4 lots/15g each – unaged (T=0), aged 6 months @ 70C, aged 12 months @ 70C and “aged” 12 months at ambient temp/ 31% RH.

Repeated strong confinement to confirm crossblend’s output properties
Green Energetics – DBX-1

Molecular Formula: \( C_2Cu_2N_{10}O_4 \)
Molecular weight: 355.20
Heat of Explosion: 911.59 cal/gm
Density by pycnometry: 2.59 g/cc, (2.58 g/cc x-ray)
Oxygen balance: 0% (to Cu)
-9.01% (to \( Cu_2O \))
-18.02% (to CuO)
Solubility: next slide
Particle size: (EL3O094 crossblend) 10-40 \( \mu \)m
Ignition temperature via hot stage: 1sec 356ºC
5sec 351ºC
10sec 345ºC
X-ray structure: at right
Heat of formation: 67.08 cal/gm
Vacuum Stability: 0.025g 100ºC 48hrs: 0.470 mL/gram
Thermal Conductivity: free powder 29.5ºC: 0.03 W/mK
Hygroscopicity:

<table>
<thead>
<tr>
<th>Hygroscopicity at 25ºC</th>
<th>Large Particle (EL3C106A) ~110um</th>
<th>Small Particle (EL3O009B)~20 um</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hrs @ 31% RH</td>
<td>0.01%</td>
<td>0.02%</td>
</tr>
<tr>
<td>72 hrs @ 31% RH</td>
<td>0.05%</td>
<td>0.07%</td>
</tr>
<tr>
<td>7 days @ 31% RH</td>
<td>0.07%</td>
<td>0.07%</td>
</tr>
<tr>
<td>24 hrs @ 74% RH</td>
<td>0.03%</td>
<td>0.03%</td>
</tr>
<tr>
<td>72 hrs @ 74% RH</td>
<td>0.03%</td>
<td>0.05%</td>
</tr>
<tr>
<td>7 days @ 74% RH</td>
<td>0.03%</td>
<td>0.06%</td>
</tr>
</tbody>
</table>

Damon Parrish, NRL
DBX-1 Stability/Solubility in IPA and Water

DBX-1 slowly dissolves and decomposes to 5-nitrotetrazolate when put in direct contact with water. Observed by ultraviolet absorption spectroscopy at 256nm. Pronounced for small particle DBX-1 samples. The residual undissolved solids were determined to be unaffected DBX-1 as demonstrated by FTIR and DSC.

Increased 2-propanol content suppresses the decomposition of DBX-1 with neat 2-propanol having no reactive effect.
### Friction Testing – Julius Peters small BAM

<table>
<thead>
<tr>
<th>CANDIDATE</th>
<th>NO-FIRELEVEL (gms)</th>
<th>MIN. FIRE LEVEL (gms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBX-1, T=0 months</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>DBX-1, T=6 months</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>DBX-1, T=12 months</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>DBX-1, T=12 months (un-aged)</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>DBX-1, previous contract</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>RD1333</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

### Impact Testing – Ball Drop Instrument

<table>
<thead>
<tr>
<th>CANDIDATE</th>
<th>IMPACT (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBX-1, T=0 months</td>
<td>0.036±0.012</td>
</tr>
<tr>
<td>DBX-1, T=6 months</td>
<td>0.042±0.003</td>
</tr>
<tr>
<td>DBX-1, T=12 months</td>
<td>0.038±0.013</td>
</tr>
<tr>
<td>DBX-1, T=12 months (un-aged)</td>
<td>0.037±0.004</td>
</tr>
<tr>
<td>DBX-1, previous contract</td>
<td>0.040±0.010</td>
</tr>
<tr>
<td>RD1333</td>
<td>0.089±0.054</td>
</tr>
</tbody>
</table>

### ESD Testing - LEESA

<table>
<thead>
<tr>
<th>CANDIDATE</th>
<th>MINIMUM FIRE LEVEL (μJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBX-1, T=0 months</td>
<td>12</td>
</tr>
<tr>
<td>DBX-1, T=6 months</td>
<td>12</td>
</tr>
<tr>
<td>DBX-1, T=12 months</td>
<td>12</td>
</tr>
<tr>
<td>DBX-1, T=12 months (un-aged)</td>
<td>12</td>
</tr>
<tr>
<td>DBX-1, previous contract</td>
<td>12</td>
</tr>
<tr>
<td>RD1333</td>
<td>6.75</td>
</tr>
</tbody>
</table>

**DBX-1 8020.5C Results**
Green Energetics – DBX-1

DBX-1 DSC Aging Samples
20°C/min

DBX-1 Aging Results (DSC)

- EL3R078A T=12 Months (aged)
- EL3R0100A T=12 Months (unaged)
- EL3R025A T=6 Months
- EL3O111A T=0 Months
## Green Energetics – DBX-1

### Hot Wire Initiation Test on DBX-1 per 8020.5C

<table>
<thead>
<tr>
<th>Material</th>
<th>Aging</th>
<th>Bridge</th>
<th>Constant Current</th>
<th>Cap. Discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tophet C</td>
<td>Mean (amps)</td>
<td>AF 99.9% (amps)</td>
</tr>
<tr>
<td>RD1333</td>
<td>0.001</td>
<td>0.299±0.009</td>
<td>0.326</td>
<td>0.272</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>0.132±0.008</td>
<td>0.157</td>
<td>0.108</td>
</tr>
<tr>
<td>DBX-1</td>
<td>T=0</td>
<td>0.001</td>
<td>0.252±0.017</td>
<td>0.304</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>0.106±0.005</td>
<td>0.121</td>
<td>0.092</td>
</tr>
<tr>
<td>DBX-1</td>
<td>T=6 m</td>
<td>0.001</td>
<td>0.244±0.010</td>
<td>0.276</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>0.105±0.005</td>
<td>0.120</td>
<td>0.090</td>
</tr>
<tr>
<td>DBX-1</td>
<td>T=12 m</td>
<td>0.001</td>
<td>0.228±0.014</td>
<td>0.272</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>0.106±0.007</td>
<td>0.127</td>
<td>0.086</td>
</tr>
<tr>
<td>DBX-1</td>
<td>Controlled</td>
<td>0.001</td>
<td>0.246±0.028</td>
<td>0.332</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>0.110±0.007</td>
<td>0.131</td>
<td>0.090</td>
</tr>
</tbody>
</table>

30 unit Bruceton run with P-12 units (BuOrd Drawing 1386180) loaded with 20mg of test material
Constant Current Bruceton: current applied for 10s in steps of 10mA, current constant to ±2%
Capacitor Discharge Bruceton: used 0.1 OR 1.0 mfd capacitor and 0.3 log unit voltage steps

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Green Energetics – DBX-1

Priming Ability Test on DBX-1 per 8020.5C

1. 200mg RDX, pressed at 10kpsi in a 5052 aluminum cup (0.295” OD, 0.262” ID, 2.985” length)
2. 0.01g to 0.10g RD-1333 or DBX-1 samples, weight determined by Bruceton
3. plastic spacer to hold fuze, seal can – positioned at top of can
4. 1020 Steel plate dent block, 1” OD, 0.5” think
5. PMMA holder 1.25” long, 1” OD

A charge of between 0.10g and 0.010g of primary (either RD1333 or DBX-1) was weighed out and poured into the can (loose loaded) on top of the RDX charge. Safety fuze lit with electric match.

In both the RD1333 (MIL-L-46225, LN40148) and DBX-1 tests it was determined that a loose charge of 0.010g was insufficient to cause detonation of the RDX charge. Larger loads (0.025 or 0.040g) gave go/no-go results.

<table>
<thead>
<tr>
<th>CANDIDATE</th>
<th>Priming Ability Test (Bruceton Analysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Level 50₀ (gms)</td>
</tr>
<tr>
<td>DBX-1, T= 0 months</td>
<td>0.0263</td>
</tr>
<tr>
<td>DBX-1, T= 6 months</td>
<td>0.0279</td>
</tr>
<tr>
<td>DBX-1, T= 12 months</td>
<td>0.0256</td>
</tr>
<tr>
<td>DBX-1, T= 12 months (un-aged)</td>
<td>0.0250</td>
</tr>
<tr>
<td>RD1333</td>
<td>0.0288</td>
</tr>
</tbody>
</table>
DBX-1 has demonstrated compatibility with:

Secondary explosives:
- RDX
- HMX
- NOL-130
- CL-20
- HNS
- PYX
- ZPP

No incompatibility with any materials tested

Metals:
- Bridge materials:
  - Tophet A, Tophet C, EvenOhm

Coupon Tests:
- Al, Brass, SST, Guilding metal, copper in-process

LA is not compatible with some of the above metals and various secondaries.
DSC Incompatibility of RD1333/HMX.
**Green Energetics – DBX-1**

**DBX-1 104477-202 Detonator ATP Results**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature</th>
<th>I (amp)</th>
<th>Function Time (DLA)</th>
<th>Function Time (DBX-1)</th>
<th>Dent (DLA)</th>
<th>Dent (DBX-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-10</td>
<td>Ambient</td>
<td>3.9</td>
<td>3.71 0.58</td>
<td>3.68 0.33</td>
<td>0.0141</td>
<td>0.0149</td>
</tr>
<tr>
<td>11-20</td>
<td>200°C</td>
<td>4.0</td>
<td>3.24 0.32</td>
<td>3.17 0.15</td>
<td>0.0134</td>
<td>0.0138</td>
</tr>
<tr>
<td>21-30</td>
<td>-65°C</td>
<td>3.8</td>
<td>4.44 0.59</td>
<td>4.14 0.51</td>
<td>0.0136</td>
<td>0.0140</td>
</tr>
</tbody>
</table>

ALL UNITS FUNCTIONED NORMALLY
DBX-1 = HIGHER OUTPUT
PSEMC In-House Study to Evaluate Temperature Capabilities and Compatibility for DBX-1 Containing Components

F-18 Directed Tests – Cookoff Testing

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>DBX-1/HNS-I (°F/Dent – mils)</th>
<th>RD1333/HNS-1 (°F/Dent – mils)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (MIL-1-23659)</td>
<td>500/fired 475/no-fire (31 mils)</td>
<td>525/fired 500/no fire (20,2 mils)</td>
</tr>
<tr>
<td>12 (MIL-1-23659)</td>
<td>450/fired 400/no-fire (31 mils)</td>
<td>450/fired 400/no-fire (22 mils)</td>
</tr>
<tr>
<td>50</td>
<td>340/no-fire (30 mils)</td>
<td>340/no-fire (24 mils)</td>
</tr>
<tr>
<td>Untreated</td>
<td>29 mils</td>
<td>27 mils</td>
</tr>
</tbody>
</table>

F-18 Requirement: 300°F for 50 hours (MIL-DTL-32122, 2005)

Had issues with RD1333/HNS at 340°F for 50 hrs so the requirement was reduced to 300°F.

During 50hr. high temp exposure (340°F/50hr), DBX-1 domes far less and has a greater dent compared to RD1333. No Compatibility Issues between DBX-1 and common secondary explosives were discovered during thermal conditioning DBX-1 is very stable alone, or as the primary explosive with secondary explosives at extremely high temperatures.

DBX-1/HNS combination exceeds the 50 hour 300°F requirement of the F-18 FIREX cartridge.

DBX-1/HNS combination will exceed 50 hour 339°F. DBX-1 will allow use of original 340°F for 50 hr requirement……
New Preparation of DBX-1

\[
\begin{align*}
\text{CuCl}_2 & \quad \text{reducing agent} \\
\text{H}_2\text{O}, \Delta &
\end{align*}
\]

\[\text{Copper(I) 5-nitrotetrazolate}\]

No induction period for crystallization
Reaction time 10-15 minutes
Yield: 80%
Particle size may be modified (larger)

This process is suitable for scale-up

Normal analysis for DBX1 indicates this material made by this method is as good or better than previous lots
Green Energetics – DBX-1

New Preparation of DBX-1

Sample: EL3R172A
Size: 0.1910 mg
Method: Standard 20C-min to 400C
Comment: Ar@50ml/min

File: \Data\DSC\Mike V\EL3R1EL3R172A.001
Operator: Williams
Run Date: 23-Mar-10 15:46
Instrument: DSC Q2000 V24.2 Build 107
Green Energetics – DBX-1

New Preparation of DBX-1

![Graph showing weight percentage vs temperature for different DBX samples.

Key points:
- 250.05°C
- 256.97°C
- 267.05°C

Samples:
- DBX-1 EL3R172A HR
- DBX-1 EL3S038a HR
- DBX-1 EL3S036a HR
- DBX-1 EL3C080a HR TEST
- DBX-1 EL3C080a HR

Universal V4.5A TA Instruments

Joint Armaments Conference – Dallas, TX  20May2010
Green Energetics – DBX-1

DBX-1 Scale-Up

Remote Control
• Reactors – 1, 3, 20L
• Reaction –
  Addition and Reaction
  Filtration and Washing
  Dispensing and Weighing

Progress
• ~10g
• ~25g

Designed and Fabricated by Franklin Engineering
A silicon/glass based system which avoids use of (batch) copper(II) salts used to stabilize diazonium intermediate (only small amounts present)

A continuous flow system which:
- Dramatically increase safety – smaller quantities = reduced risk
- Increase quality – faster heat and mass transfer, no lot variability
- Improve efficiency – computer monitored, incorporation of analytical tools

Kinetics analysis of both diazotization/substitution are finalized

Temperature, pH, ionic strength, etc. assessed for maximum yield

Safe production of 4.5 gm/hr NaNT achieved in single reactor system (83%)

Production System: 40-50gm/hr
Green Energetics – DBX-1

Completion of 8020.5C Program

• 8020.5C program completed Oct 2009, submitted for qualification
Initially Prepared in 1910 by Roth and Hoffman

Has found use as primer sensitizer as it is “non-toxic” (mercury fulminate) and non-corrosive

Current primer mixes (NOL-130) generally contain 40% LS, 20% LA, 20% BaNO₃ and 15% Sb₂S₃

Tetrazene is used as a sensitizer due to low impact and friction sensitivity levels

Tetrazene has **low thermal and hydrolytic stabilities**
- decomposes completely at 90°C in 6 days
- decomposes completely in boiling water

\[
\begin{align*}
\text{NN} & \text{NH}_2 \\
\text{NH} & \text{NH} \\
\text{H}_2\text{O} & 90^\circ\text{C} \quad 6\text{ days} \\
\text{NN} & \text{NH}_2 \\
\end{align*}
\]

via guanyl azide intermediate

**PSEMC Project – Improve thermal stability used in normal or high temperature applications**

Generate new materials cheaply and without utilizing toxic reactants or effluents

“Thermal Decomposition of Tetrazene at 90°C”, Bird, R. and Power, A.J.,

“The Kinetics and Thermochemistry of the Thermal Decomposition of the Initiating Explosive, Tetrazene,…”,
Preparation of Iso-DTET

Structure is undetermined at this time – structure elucidation in progress
- Iso-DTET dissolves in 1N NaOH and is regenerated on treatment with concentrated HCl (weakly acidic?)
- Iso-DTET exhibits partial solubility in concentrated hydrochloric acid
- Iso-DTET is unaffected by the extended exposure to neat acetic anhydride or neat acetyl chloride at ambient
- Refluxing of Iso-DTET with acetic anhydride for 4 hours degrades it providing a non-energetic material melting at 210°C.

Does Iso-DTET have an amino group shown in the Iso-DTET structure?

Equivalent weight based on KOH titration data is estimated at 160-175 (181)

X-ray structure: varying results with salts of Cu(II), Fe(II), Fe(III), Mn(II) and Cs – gives only starting material or hydrates
working tetramethylammonium and tetraphenylphosphonium salts

NMR: material very insoluble in common deuterated solvents, salts may offer better properties
### Sensitivity of Iso-DTET

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>DSC (20°C/minute)</th>
<th>IMPACT (J)</th>
<th>FRICTION (grams)</th>
<th>ESD (mJ)</th>
<th>TGA % Wt Loss @ 167 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset</td>
<td>Peak</td>
<td>No Fire</td>
<td>Low Fire</td>
<td>No Fire</td>
</tr>
<tr>
<td>Tetrazene</td>
<td>138°C</td>
<td>144°C</td>
<td>0.021</td>
<td>1100</td>
<td>1200</td>
</tr>
<tr>
<td>Iso-DTET</td>
<td>208°C</td>
<td>214°C</td>
<td>0.016</td>
<td>800</td>
<td>900</td>
</tr>
</tbody>
</table>

**Similar crystal morphology**

- Tetrazene
  - 100X Optical
  - 1000X SEM
- Iso-DTET
  - 100X Optical
  - 1000X SEM
Tetrazene Replacement Project

Sample: EL3R118A
Size: 0.1070 mg
Method: Standard 20C-min to 400C
Comment: Ar@50mL/min; T0AI

File: C:TAData\DSC\Mike WA\EL3R\EL3R118A,C
Operator: Williams
Run Date: 05-Nov-2009 10:20
Instrument: DSC Q2000 V24.2 Build 107

DSC of Iso-DTET

Heat Flow (W/g)

Temperature (°C)

214.40°C

208.06°C

1880J/g

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Hydrolytic Stability of Iso-DTET

~0.50g suspended in 250mL of water, ambient conditions, sampled at indicated intervals
Tetrazene – change in conc. over 8 hrs with bathochromic shift to 350nm and increased extinction below 250nm –degrades
Iso-DTET – no shift over time
Residue

Confirms hydrolytic instability of tetrazene while storage of Iso-DTET under aqueous conditions may be possible
Tetrazene Replacement Project

Thermal Stability of Iso-DTET

TGAs of Tetrazene, Iso-DTET
~10mg, isothermal @ 90°C

FTIR analysis of tetrazene residue indicated 5-AT (Bird)

Universal V3.9A TA Instruments
Output Performance of DTET

30 primer cups were loaded with 21±2mg of mixture, pressed at 160lbs (10s dwell) into primer cups

20 shot Neyer analysis was performed with 3.35oz stainless steel ball, pin changed every 10 shots

BLS PN51-8593E LN GY19862 – un-milled, -#100 sieve
Tetrazene, Iso-DTET - -#40 sieve

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mu±σ</th>
<th>0.001 Level</th>
<th>0.999 Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% BLS (EL3Y003)</td>
<td>12.5”±0”</td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>95% BLS/ 5% Tetrazene</td>
<td>4.92”±1.41”</td>
<td>0.56</td>
<td>9.28</td>
</tr>
<tr>
<td>95% BLS/ 5% Iso-DTET</td>
<td>5.91”±0.42”</td>
<td>4.60</td>
<td>7.21</td>
</tr>
</tbody>
</table>

0.048” firing pin, no closure over primer
Preparation of DTET

\[
\begin{align*}
\text{DTET} & \quad \text{DTET} \\
\text{HOAc} & \quad \text{NaNO}_2 \\
\text{H}_2\text{O} & \quad \text{NaOH}
\end{align*}
\]

Structure of DTET

DTET structure confirmed by X-ray analysis of calcium complex (Mike Sitzmann NSWC-IH)

DTET suffers from severe hydration issues (monosodium is ≥monohydrate)
Di- and Tri- sodium salts are insensitive to impact and friction, also heavily hydrated
Salt formation (Rb, Cs, Sr) have been attempted – varying hydration, poor particle morphology
Attempting to prepare free acid, structure confirmation by NMR (material soluble in DMSO-d6)
DTET

Sensitivity of DTET

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<td>138°C</td>
<td>144°C</td>
<td>0.021</td>
<td>1100</td>
<td>1200</td>
</tr>
<tr>
<td>DTET</td>
<td>139°C</td>
<td>156°C</td>
<td>&gt;0.056</td>
<td>&gt;2075</td>
<td>&gt;2075</td>
</tr>
</tbody>
</table>

DTET (monosodium) has little thermal benefit, is lower friction/impact sensitivity compared to tetrazene.
1,5’-Bitetrazole

Preparation of 1,5’-Bitetrazole

Prepared guanidine and triaminoguanidine salts
Still under investigation
Acknowledgments

- Dr. Bill Sanborn - PSEMC
- Dave Grum, Diane Ross, Paul Garber - PSEMC
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- Travis Thom – NSWC-IH
- Dr. Brad Sleadd- NSWC-IH
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- Mike Sitzmann – NSWC-IH (Ret.)
- Gerald Laib - NSWC-IH
- John Hirlinger - Picatinny
- Alex Schuman - NSWC-IH
- Frank Valenta – NSWC-IH
- Dr. Robert Chapman - NAWC-CL
- Dr. Farhad Forohar - NSWC-IH
- Dr. Phil Pagoria – LLNL
- Dr. Damon Parrish – NRL
- Dr. Mike Hiskey
- Dr. Jeff Bottaro

John Fronabarger
Author: Michael Williams  
Contact: 480.763.3063, mwilliams@psemc.com  

Bio Summary: Mike Williams is a Senior Chemist at Pacific Scientific Energetic Materials Company (PSEMC) in Chandler, AZ and is currently the manager of Green Energetic Materials development. Prior to joining PSEMC in 2002, Mike was manager of the Nuclear Magnetic Resonance Lab at Arizona State University specializing in multinuclear solid state and 1 and 2D liquids experiments for determination of molecular structure. From 1995 to 1997 he was an Assistant Research Professor at the Cancer Research Institute at ASU and was involved with the isolation/structure elucidation and synthesis of natural products with antineoplastic properties. Mike has a Ph.D. in Synthetic Organic Chemistry from Rensselaer Polytechnic Institute (Troy, NY) and a BS in Chemistry from St. Michaels College (Colchester, VT).