Environmentally Acceptable Alternatives To Existing Primary Explosives

Replacements for lead azide, lead styphnate and tetrazene

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Technical Portions of this Presentation ITAR Approved 30Sept09 Ref. 09-S-2870

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.

Green Energetics – Background

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, ClCP, 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

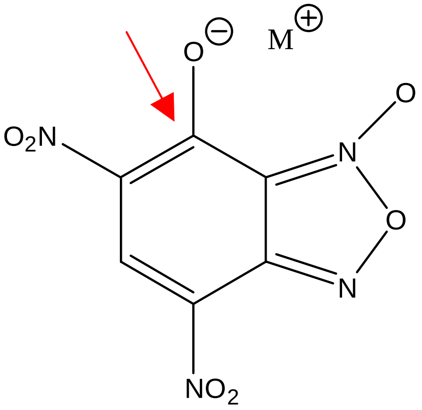
Extremely impact and friction sensitive.

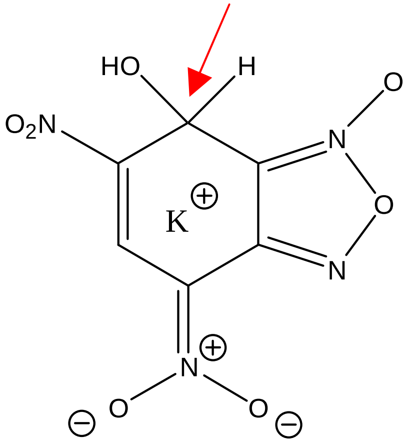
PSEMC is currently involved, under contract with ONR, in a project to find a high stability replacement

Iso-DTET has sensitivity equivalent to tetrazene with high thermal and water stabilities

Green Energetics – KDNP

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.





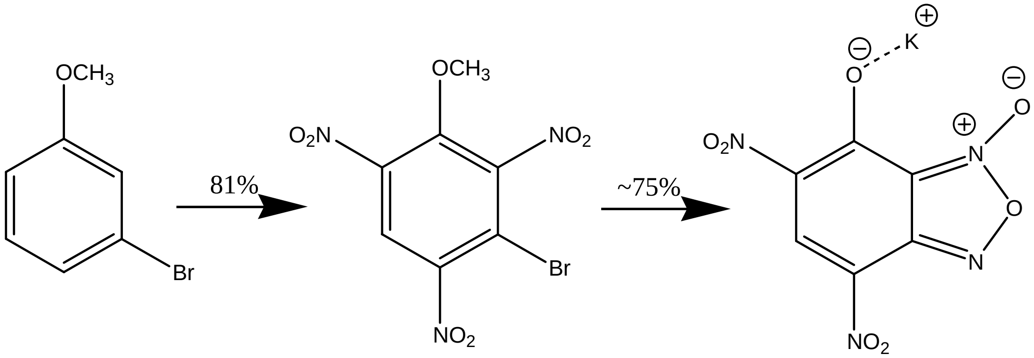
4,6-Dinitro-7-hydroxybenzofuroxan, salt
MDNP
Safe Journal, Vol 35, #1, 14 (2007)

DSC exo 271°C

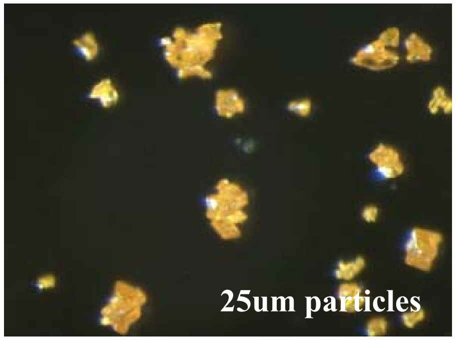
Potassium dinitrohydroxy hydrobenzofuroxan
KDNBF
Jackson-Meisenheimer adduct
Well known material introduced 1950's

DSC exo 217°C

Green Energetics – KDNP



KDNP



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 PSEMC and NSWC-IH

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

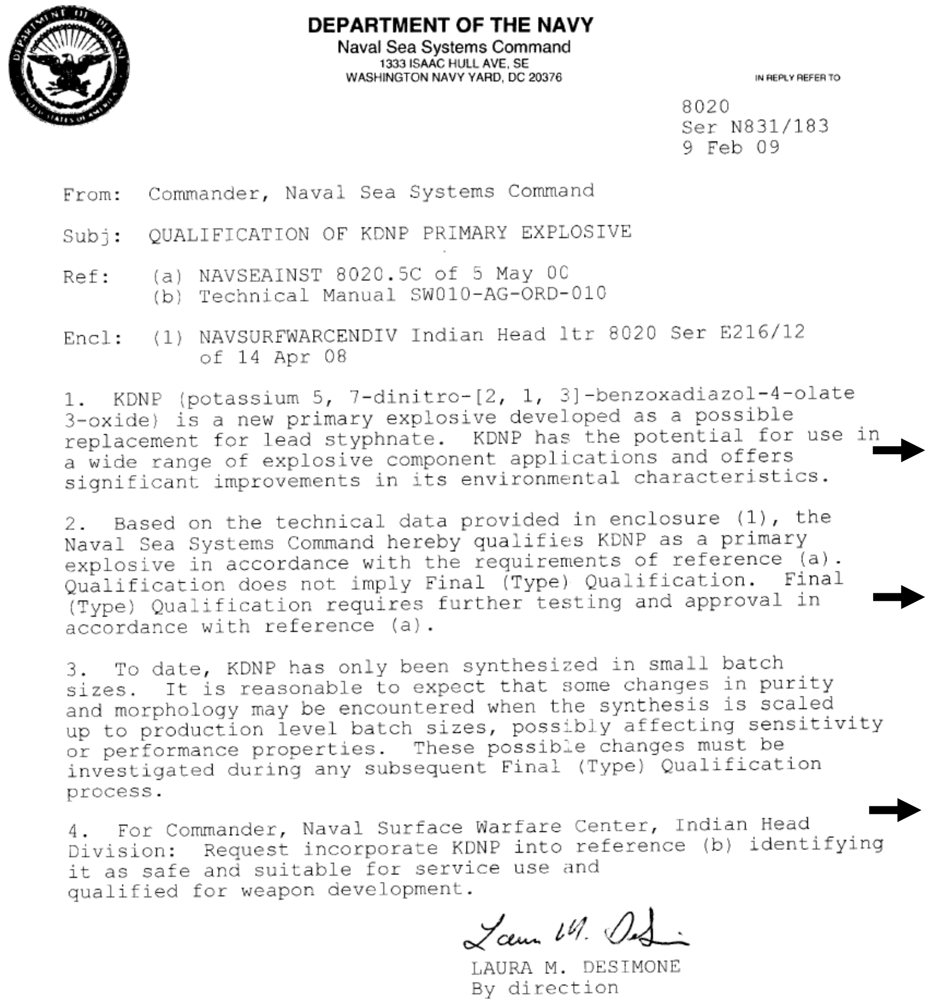
KDNP has been evaluated vs. LS successfully in a variety of applications including

- 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, BKNO$_3$, Red Dot, HiTemp, etc)

PSEMC completed Compound Qualification Testing on KDNP per NAVSEAINST 8020.5C in 2008

PSEMC and NSWC-IH are currently working alternate syntheses/MANTECH scale-up projects KDNP

Green Energetics – KDNP



DEPARTMENT OF THE NAVY
Naval Sea Systems Command
1333 ISAAC HULL AVE, SE
WASHINGTON NAVY YARD, DC 20376

IN REPLY REFER TO
8020
Ser N831/183
9 Feb 09

From: Commander, Naval Sea Systems Command

Subj: QUALIFICATION OF KDNP PRIMARY EXPLOSIVE

Ref: (a) NAVSEAINST 8020.5C of 5 May 00
(b) Technical Manual SW010-AG-ORD-010

Encl: (1) NAVSURFWARCENDIV 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

PATENTS PENDING

→ "KDNP is a green replacement for lead styphnate"

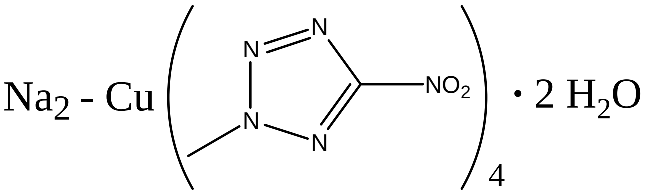
→ "Naval Sea Systems Command hereby qualifies KDNP as a primary explosive in accordance with the requirements of NAVSEAINST 8020.5C"

→ "Request incorporate KDNP into SWO10 identifying it as safe and suitable for service use and qualified for weapons development."

Green Energetics – DBX-1

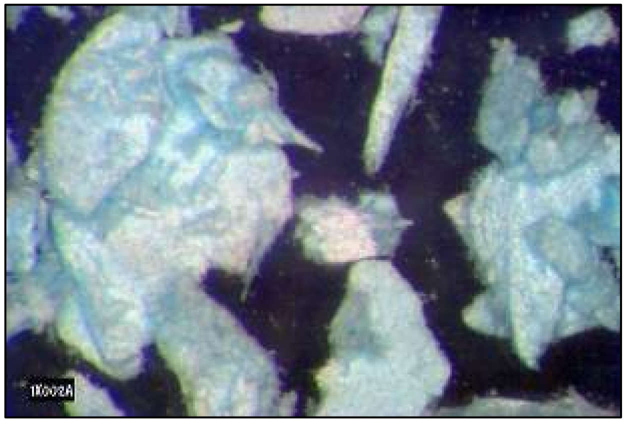
DBX-1 Background

Composition:



$Na_2 - Cu(\text{nitrotetrazole})_4 \cdot 2\,H_2O$

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**

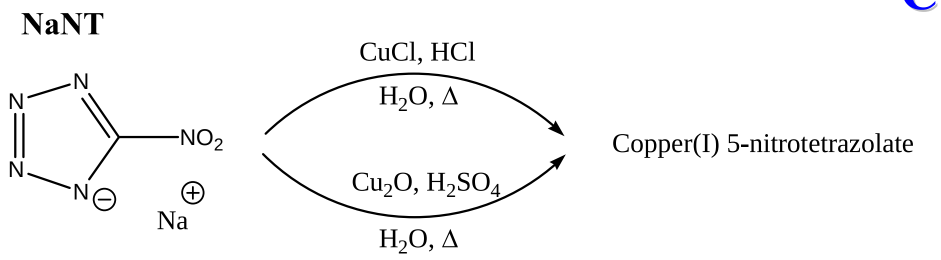
Attempts to reduce Cu(II) to Cu(I) with hydrazine gave crude DBX-1 (Sept 05')
Attempt substitute water with coordinating ligand (carbohydrazide) (Nov 05')
(Dr. Al Stern – NSWC-IH)

Modifications of these studies led to discovery of DBX-1

LANL-*Proceedings of the National Academy of Sciences* DOI: 10.1073/pnas.0600827103

Green Energetics – DBX-1

Copper(I) Complex of 5-Nitrotetrazole



Use of conventional laboratory techniques & equipment…

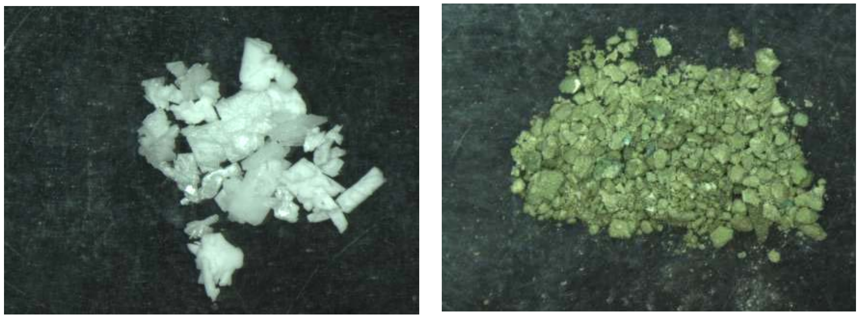
Starting materials added at front end

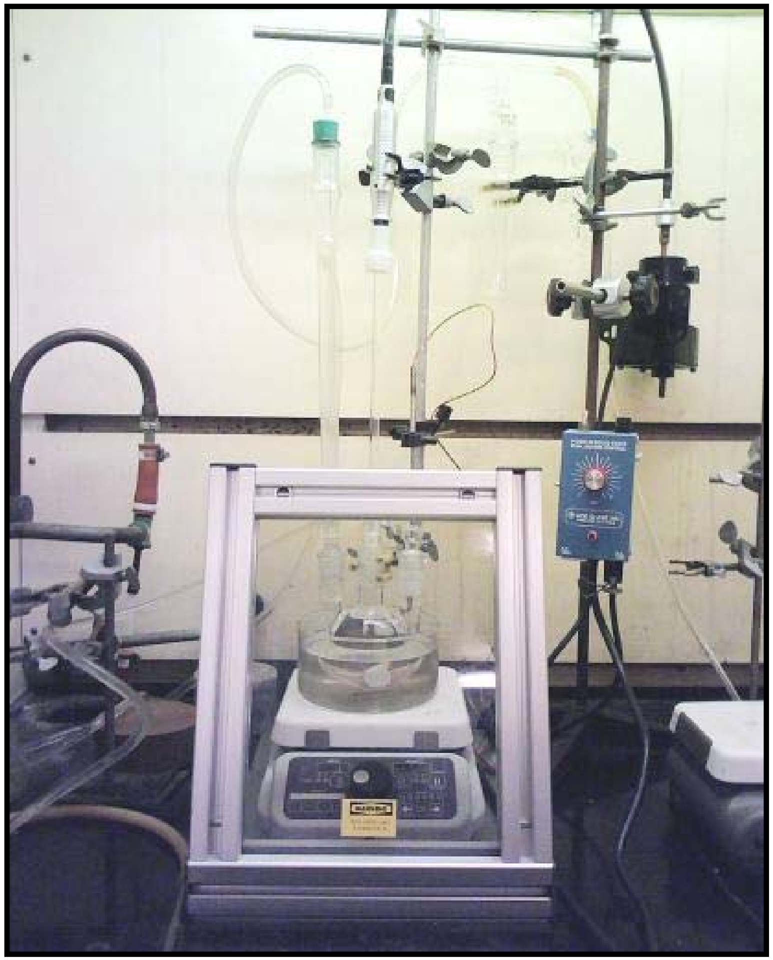
Unusual reaction – brown slurry to crystals

variable crystallization induction periods

DBX-1 isolated ~1 hour

Have evaluated variations – ratios, heating, acid etc.



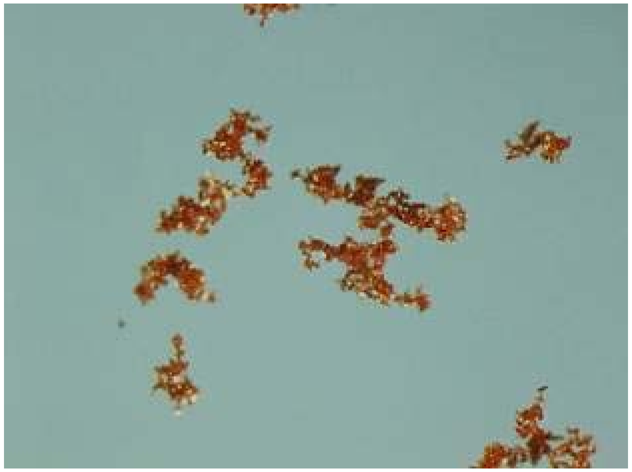


Green Energetics – DBX-1

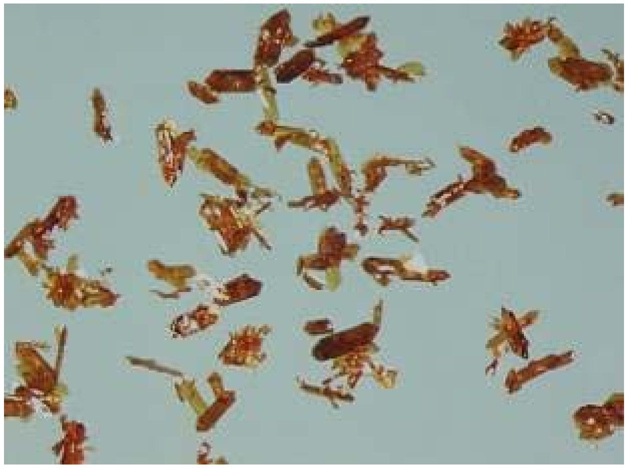
EL3C098A

EL3C106A

Optical



77x



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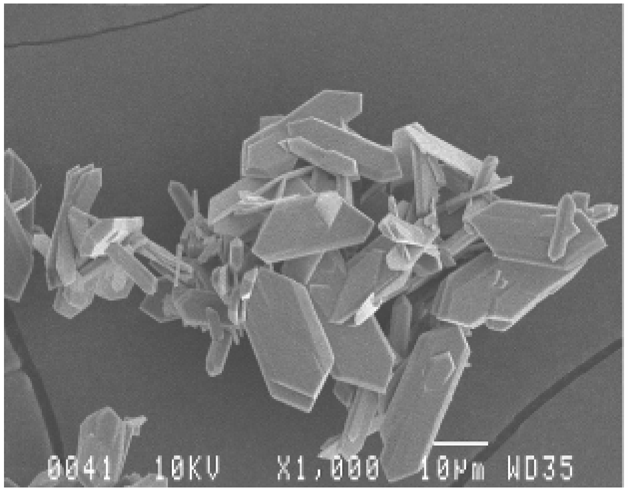
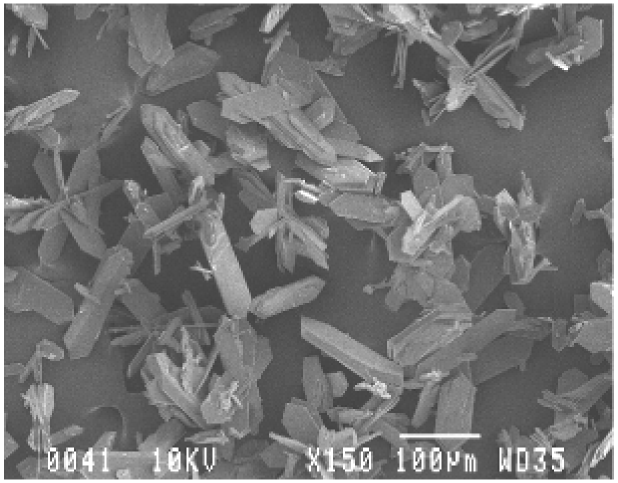
SEM



1000x



150x

Copper(I) Complex of 5-Nitrotetrazole (DBX-1)

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_2O) 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%

X-Ray confirmed 1:1 of 5-NT and Cu

- Density: (He pycnometry) 2.59g/cm^3, (X-ray) 2.58g/cm^3

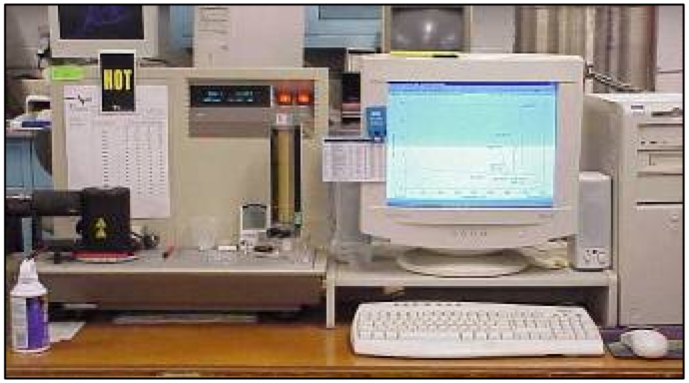
Green Energetics – DBX-1

DBX-1 Sensitivity Testing

Essentially Equivalent to Lead Azide

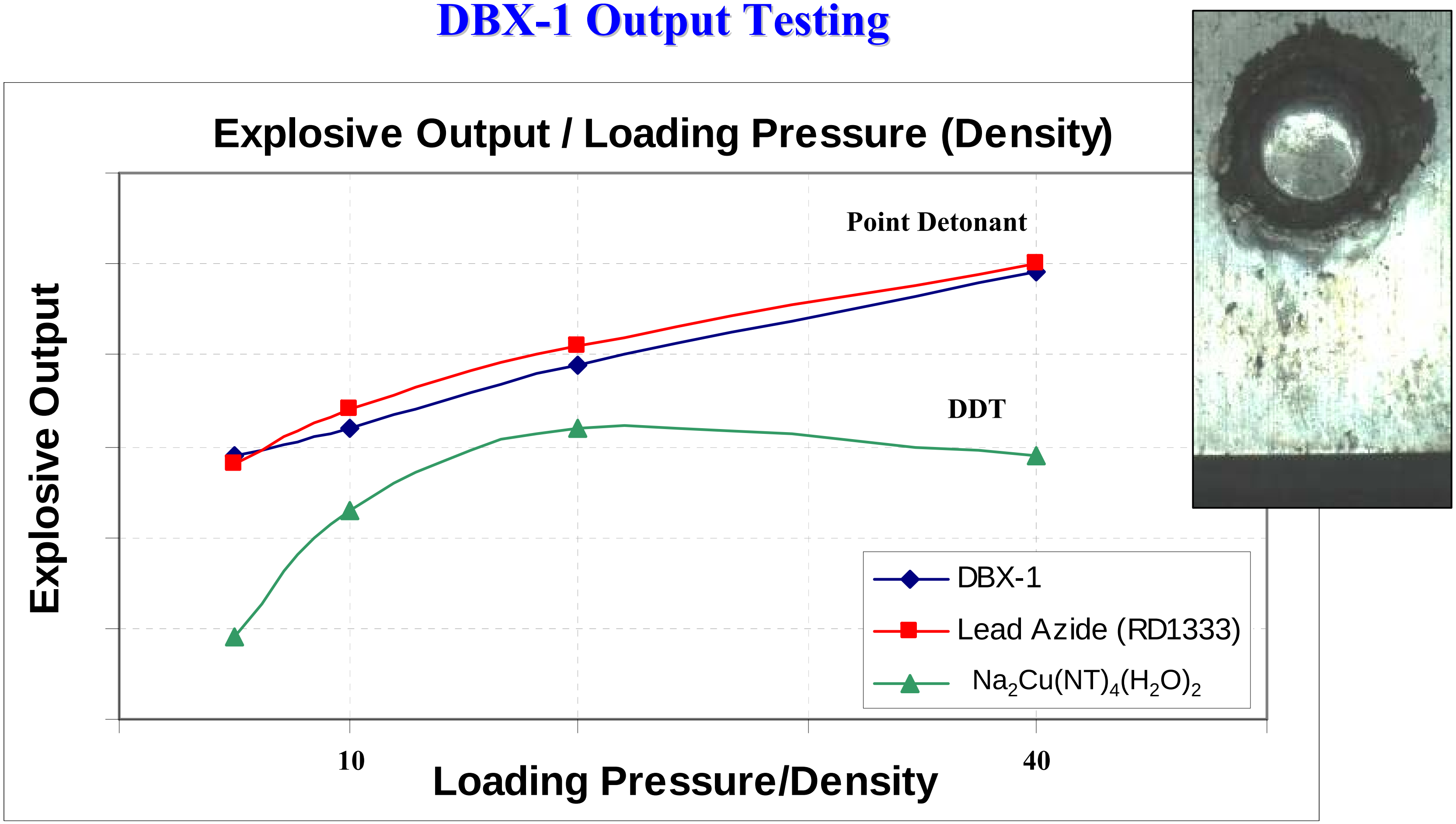
SAMPLE	DSC (20ºC/minute)		IMPACT (J) (Ball Drop)	FRICTION (Small BAM)		DENSITY (g/cc) TMD	High Res TGA Onset of Wt. Loss	ESD (LEESA)
	Onset	Peak		No Fire	Low Fire			
DBX-1	329ºC	337ºC	0.040±0.010	0g	10g	2.59 (Cu)	260 ºC	12µJ
LA (RD1333)	332ºC	341ºC	0.050±0.004	0g	10g	4.80 (Pb)	166 ºC	6.75µJ

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



Green Energetics – DBX-1

DBX-1 Output Testing

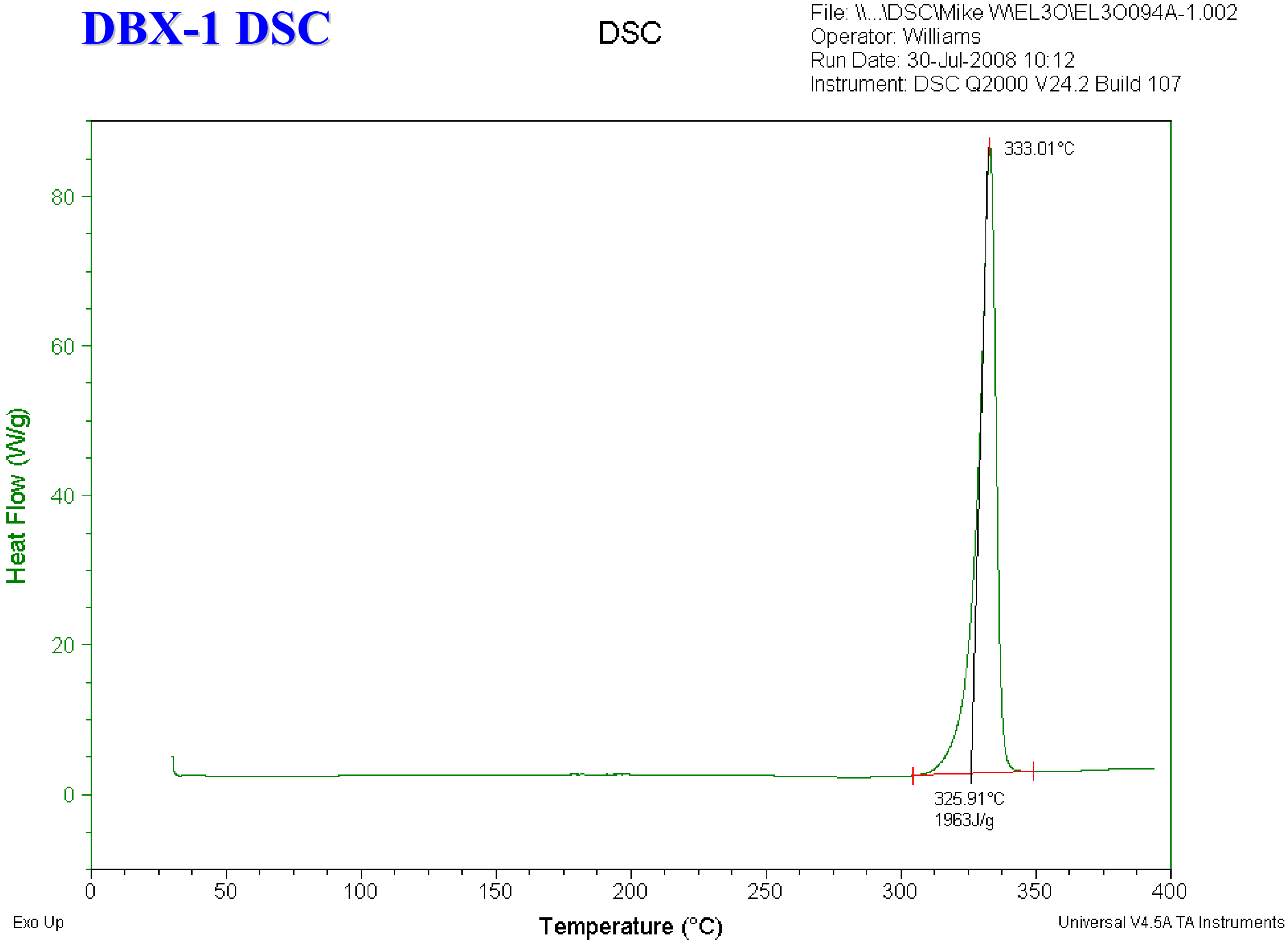


ZPP (24mg) was pressed into a header having a 1 ohm 0.0022” stablohm bridgewire at 10 kpsi.
Materials were loaded into stainless steel cans having a 7 mil wall thickness and pressed 5,10,20,40.
The units were loaded into fixtures and fired (4uf cap, 300V) onto 1” aluminum blocks

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

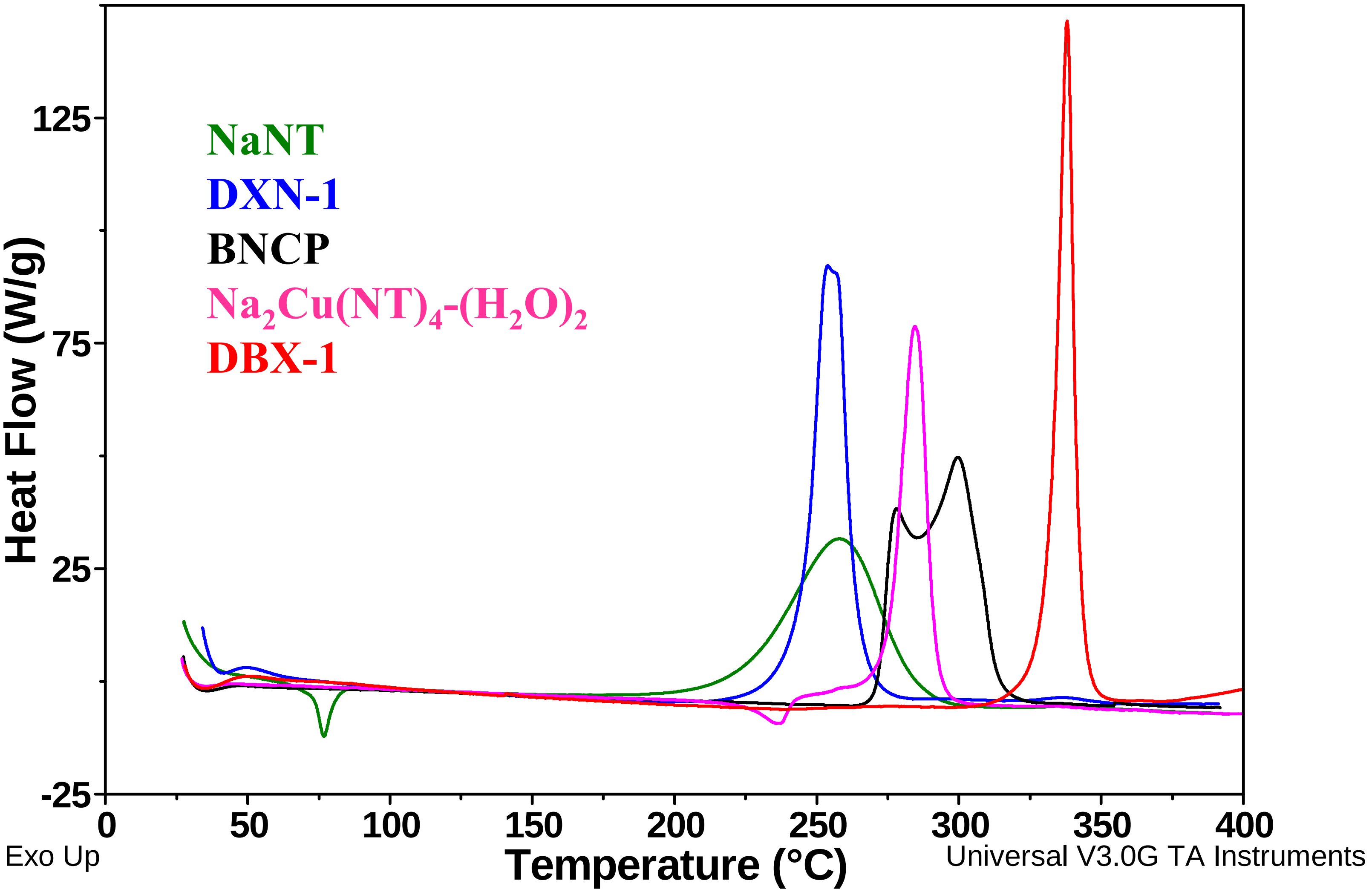


DSC

File: \\...\DSC\Mike W\EL3O\EL3O094A-1.002
Operator: Williams
Run Date: 30-Jul-2008 10:12
Instrument: DSC Q2000 V24.2 Build 107

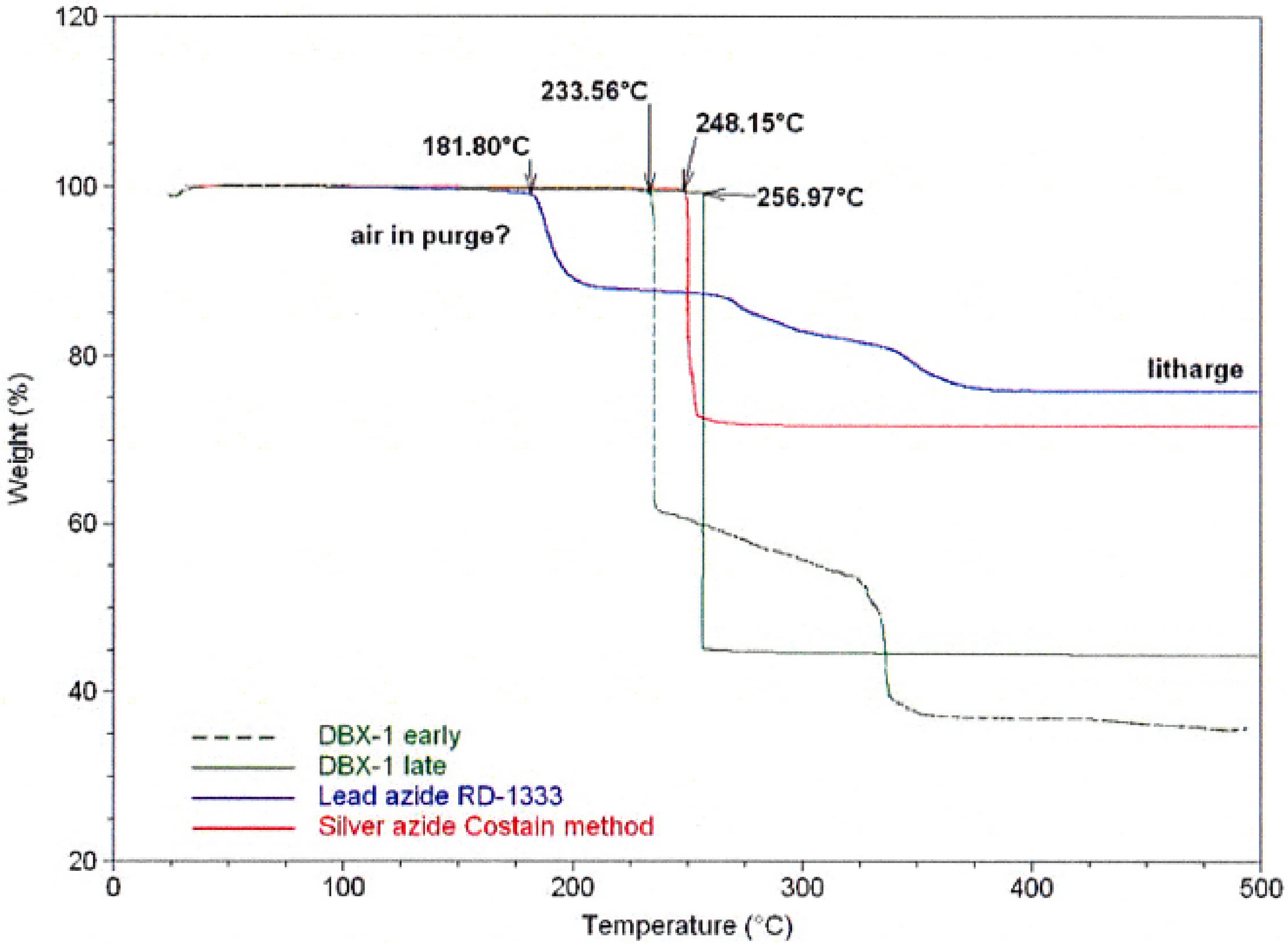
Green Energetics – DBX-1

DBX-1 DSC Comparison



Green Energetics – DBX-1

High Resolution TGA



Green Energetics – DBX-1

RD1333/DBX-1 Stability Comparison

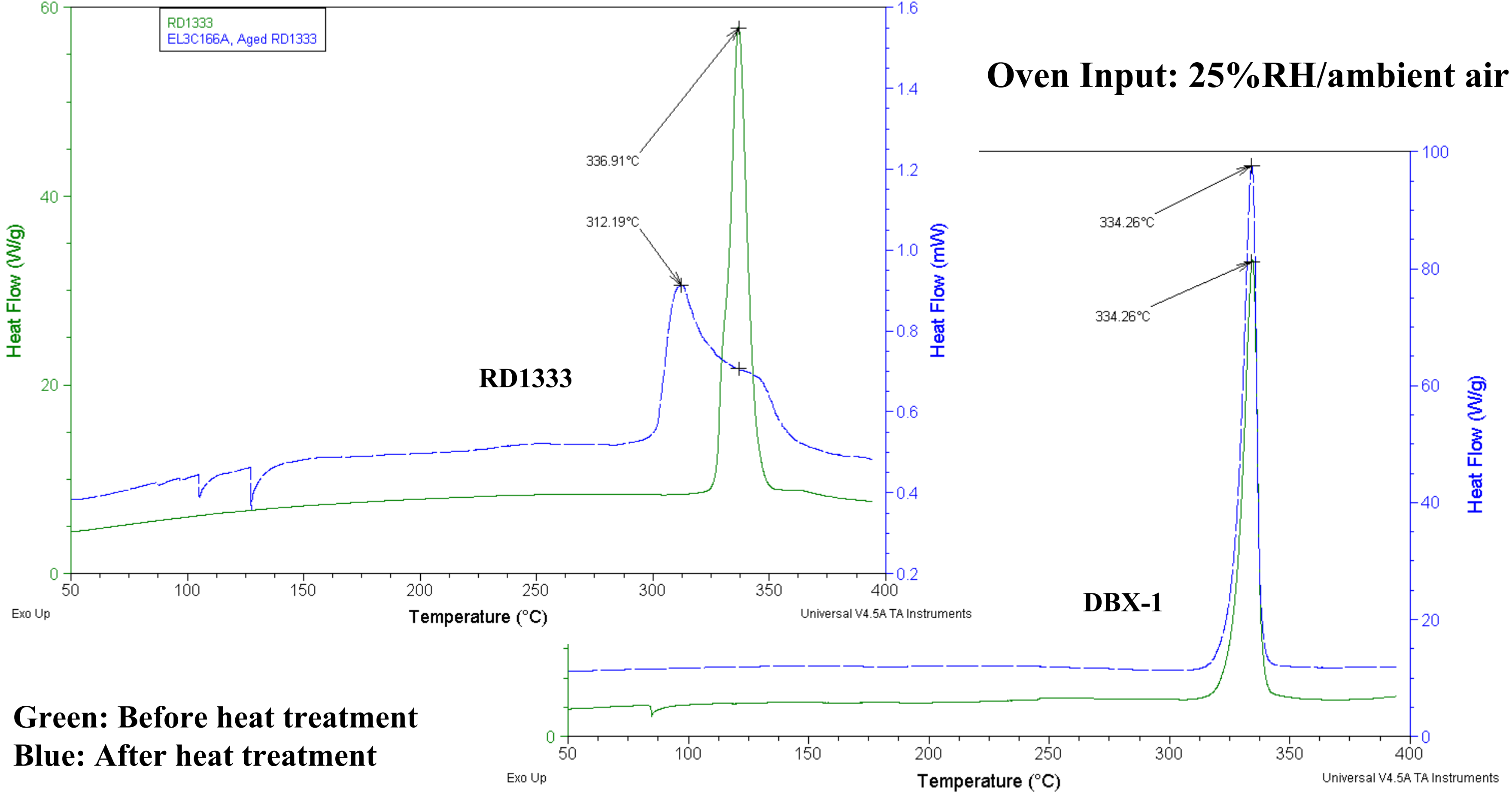
(High Temperature)

Weight loss after 24hr @ 181ºC (358ºF):

RD1333: 14.57%

DBX-1: 0%

Oven Input: 25%RH/ambient air



Green: Before heat treatment
Blue: After heat treatment

Green Energetics – DBX-1

Compound Qualification 8020.5C Project

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

NSWC-IH Contracts:
N00714-06-C-0079
N00178-04-D-4149

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/metals/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

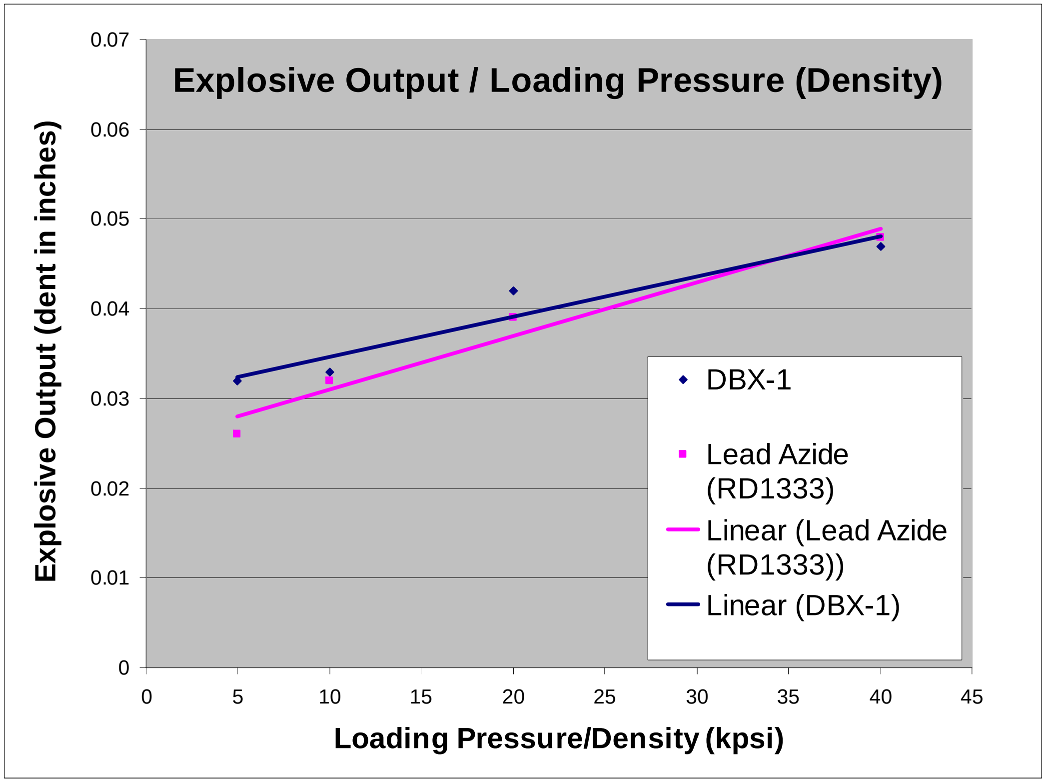
Green Energetics – DBX-1

DBX-1 8020.5C Study

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.


~10-40um, 100X

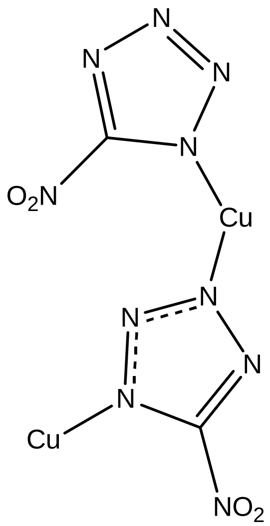
Repeated strong confinement to *confirm* crossblend's output properties

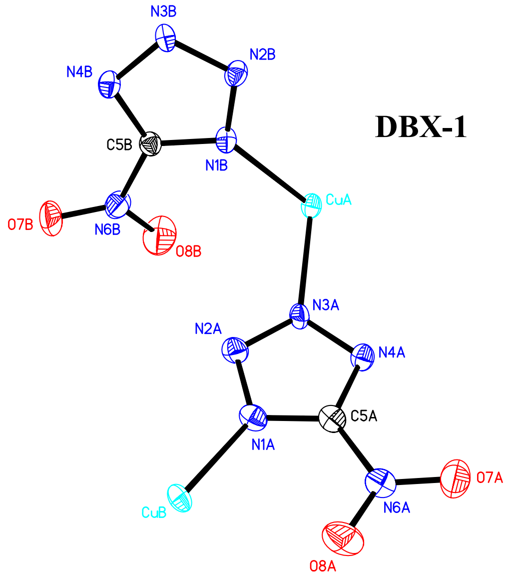


Green Energetics – DBX-1

Properties of 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 µm
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 100°C 48hrs: 0.470 mL/gram
Thermal Conductivity: free powder 29.5°C: 0.03 W/mK
Hygroscopity:



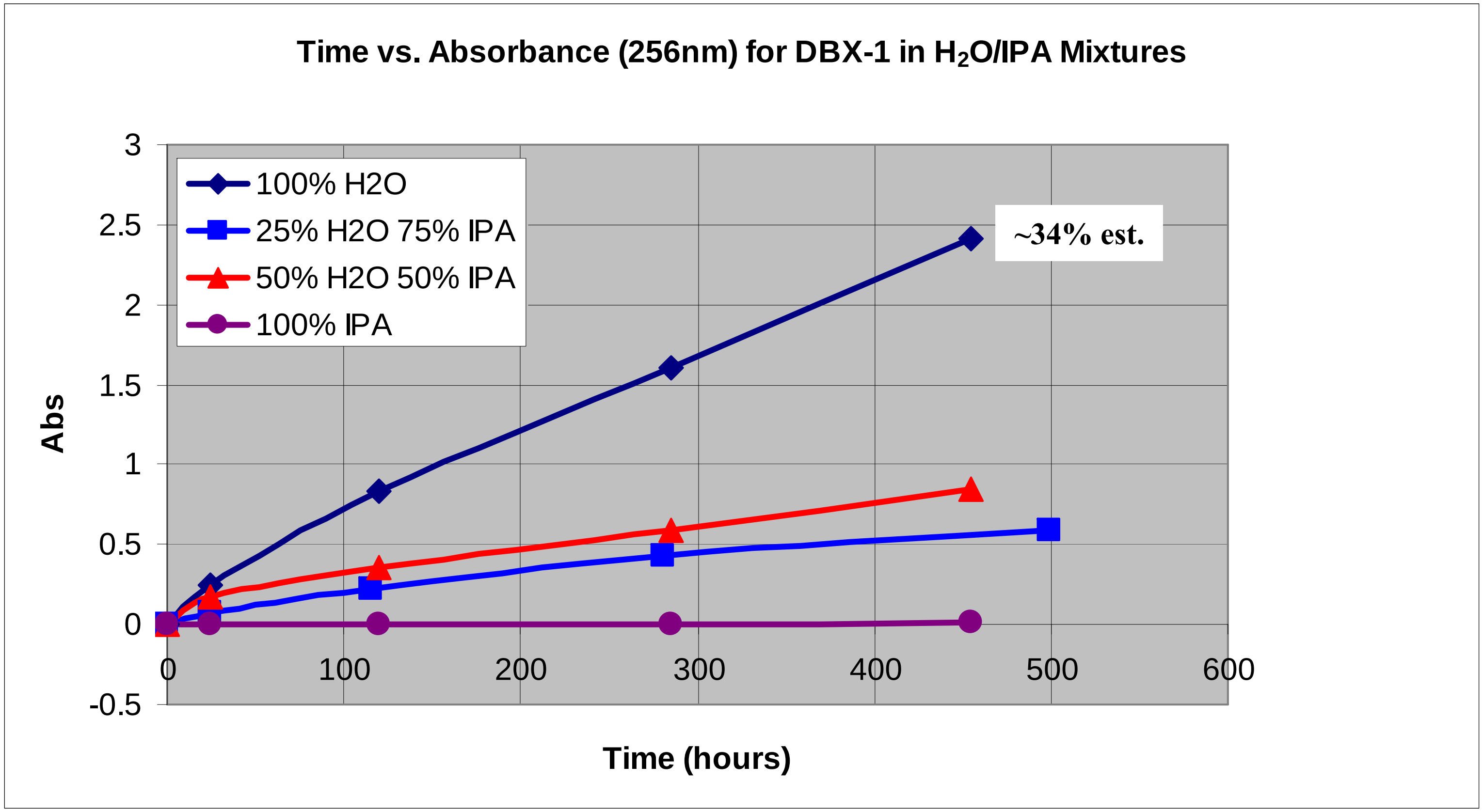


Damon Parrish, NRL

Hygroscopicity at 25ºC	Large Particle (EL3C106A) ~110um	Small Particle (EL3O009B)~20 um
24 hrs @ 31% RH	0.01%	0.02%
72 hrs @ 31% RH	0.05%	0.07%
7 days @ 31% RH	0.07%	0.07%
24 hrs @ 74% RH	0.03%	0.03%
72 hrs @ 74% RH	0.03%	0.05%
7 days @ 74% RH	0.03%	0.06%

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.**

Green Energetics – DBX-1

Friction Testing – Julius Peters small BAM

CANDIDATE	NO-FIRELEVEL (gms)	MIN. FIRE LEVEL (gms)
DBX-1, T=0	**0**	**10**
DBX-1, T=6 months	**0**	**10**
DBX-1, T=12 months	**0**	**10**
DBX-1, T=12 months (un-aged)	**0**	**10**
DBX-1, previous contract	**0**	**10**
RD1333	**0**	**10**

Impact Testing – Ball Drop Instrument

CANDIDATE	IMPACT (J)
DBX-1, T=0 months	**0.036±0.012**
DBX-1, T=6 months	**0.042±0.003**
DBX-1, T=12 months	**0.038±0.013**
DBX-1, T=12 months, (un-aged)	**0.037±0.004**
DBX-1, previous contract	**0.040±0.010**
RD1333	**0.089±0.054**

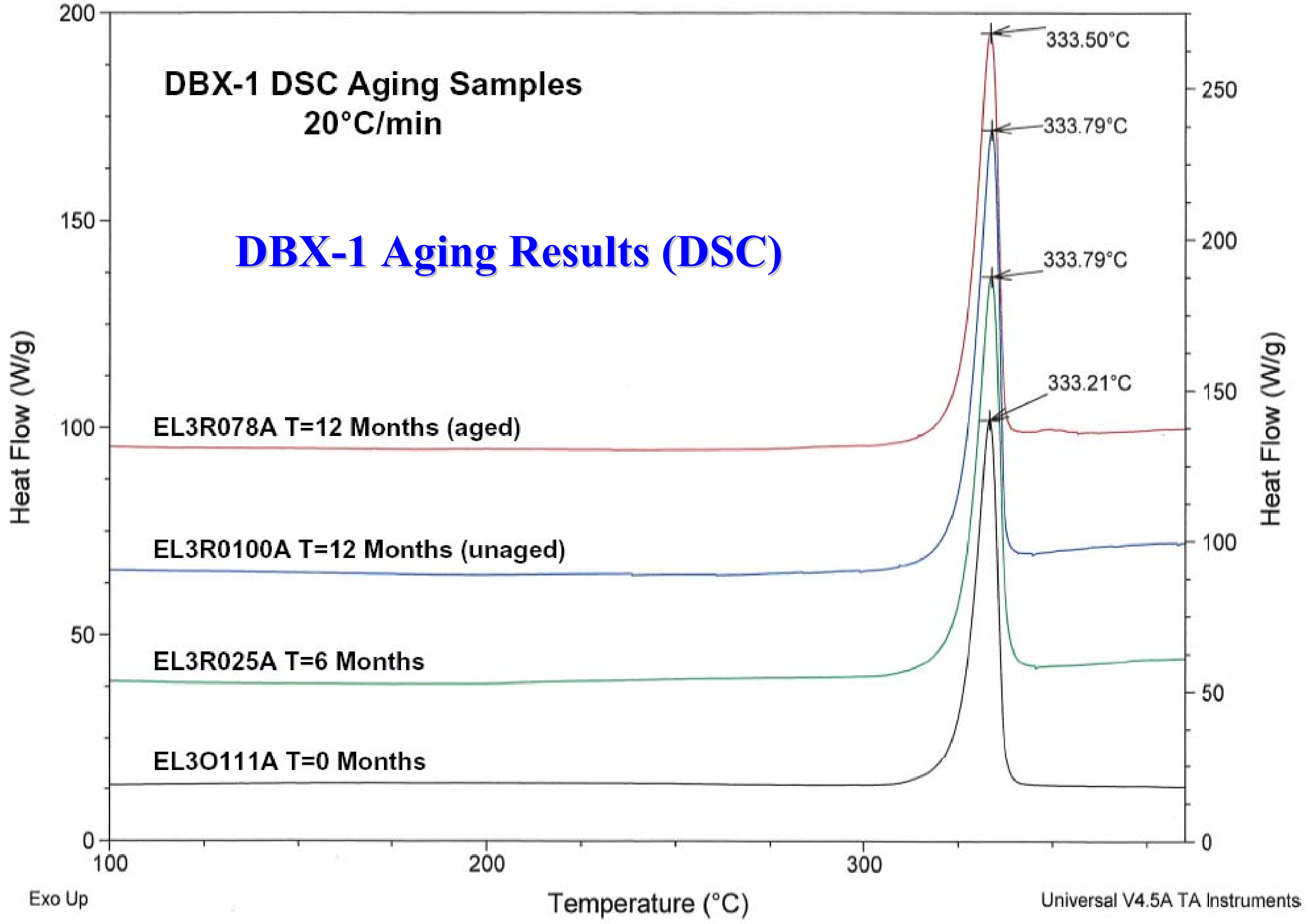
ESD Testing - LEESA

CANDIDATE	MINIMUM FIRE LEVEL (μJ)
DBX-1, T=0 months	**12**
DBX-1, T=6 months	**12**
DBX-1, T=12 months	**12**
DBX-1, T=12 months, (un-aged)	**12**
DBX-1, previous contract	**12**
RD1333	**6.75**

DBX-1 8020.5C Results

Green Energetics – DBX-1

DBX-1 Aging Results (DSC)



Green Energetics – DBX-1

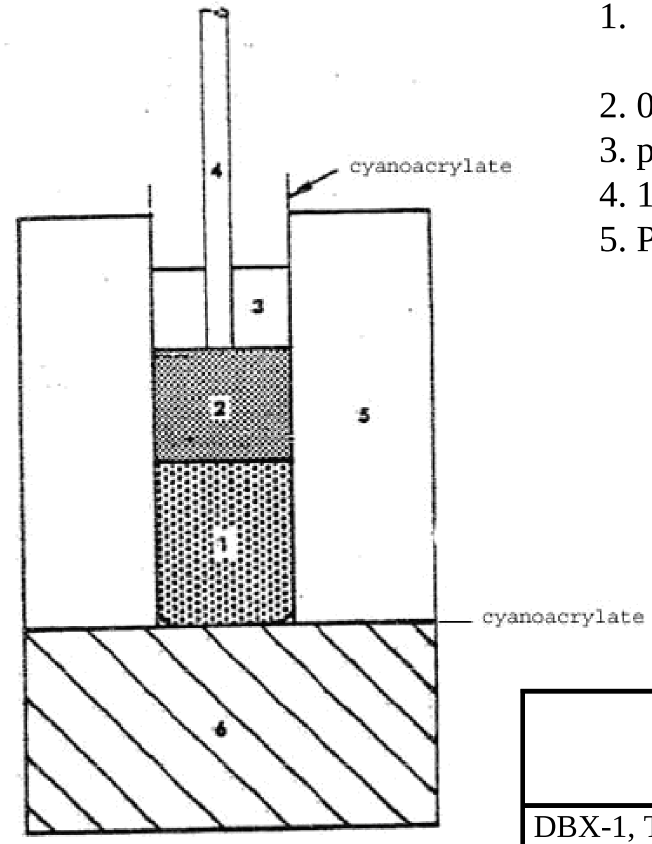
Hot Wire Initiation Test on DBX-1 per 8020.5C

Material	Aging	Bridge	Constant Current			Cap. Discharge	
		Tophet C	Mean (amps)	AF 99.9% (amps)	NF 0.1% (amps)	Mean (volts, mf)	Stored Energy (mJ)
RD1333		0.001	0.299±0.009	0.326	0.272	79.99±3.44, 1.0	3.20
		0.0005	0.132±0.008	0.157	0.108	143.55±35.84, 0.1	1.03
DBX-1	T=0	0.001	0.252±0.017	0.304	0.201	77.62±0, 1.0	3.01
		0.0005	0.106±0.005	0.121	0.092	122.89±6.42, 0.1	0.76
DBX-1	T=6 m	0.001	0.244±0.010	0.276	0.212	79.62±10.94, 1.0	3.17
		0.0005	0.105±0.005	0.120	0.090	126.77±7.82, 0.1	0.80
DBX-1	T=12 m	0.001	0.228±0.014	0.272	0.183	80.74±1.08, 1.0	3.26
		0.0005	0.106±0.007	0.127	0.086	138.23±1.10, 0.1	0.96
DBX-1	Controlled	0.001	0.246±0.028	0.332	0.160	85.31±1.01, 1.0	3.64
		0.0005	0.110±0.007	0.131	0.090	130.32±1.09, 0.1	0.85

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

Green Energetics – DBX-1

Priming Ability Test on DBX-1 per 8020.5C



1. 200mg RDX, pressed at 10kpsi in an 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.

CANDIDATE	Priming Ability Test (Bruceton Analysis)	
	Level 50_0 (gms)	**σ_0**
DBX-1, T= 0 months	**0.0263**	**0.0066**
DBX-1, T= 6 months	**0.0279**	**0.0059**
DBX-1, T= 12 months	**0.0256**	**0.0067**
DBX-1, T= 12 months (un-aged)	**0.0250**	**0.0108**
RD1333	**0.0288**	**0.0093**

DBX-1 Compatibility with Various Secondaries

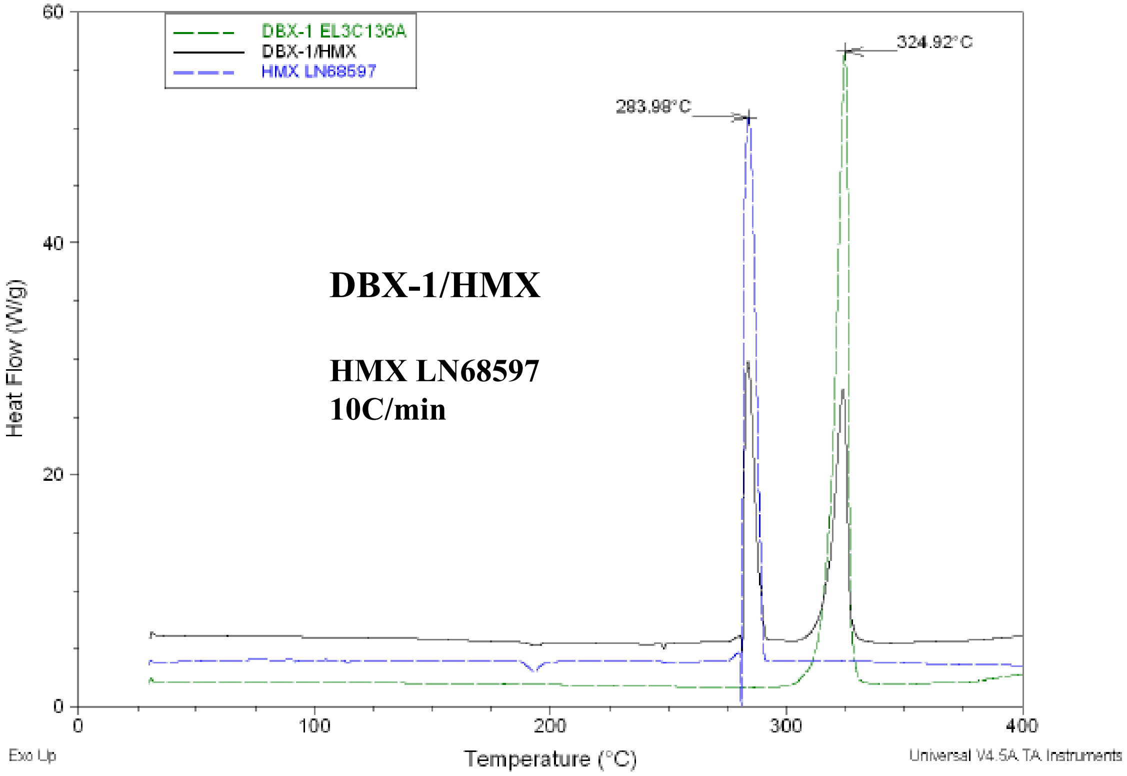
DBX-1 has demonstrated compatibility with:

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

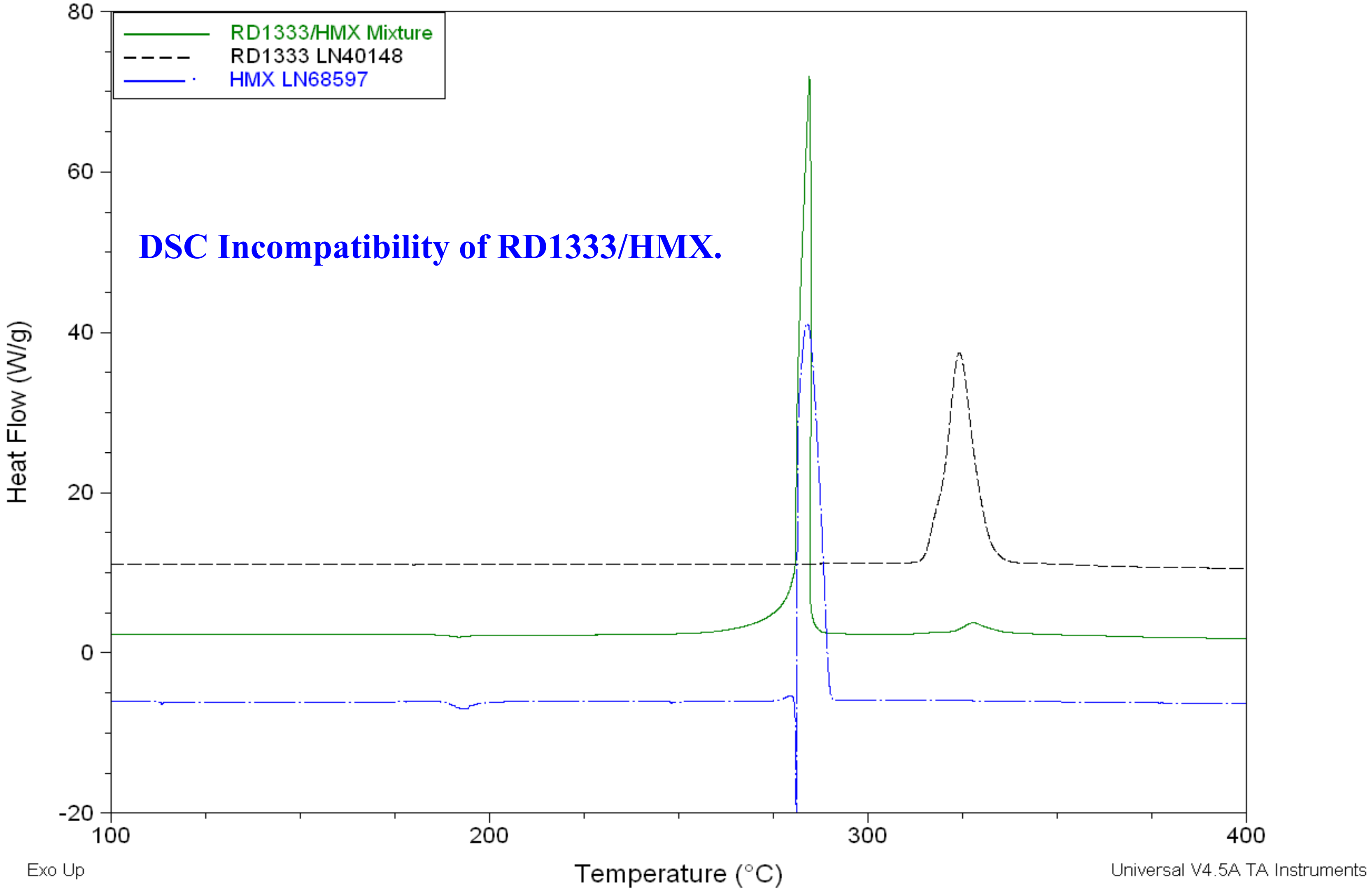
LA is not compatible with some of the above metals and various secondaries.



DBX-1/HMX

HMX LN68597
10C/min

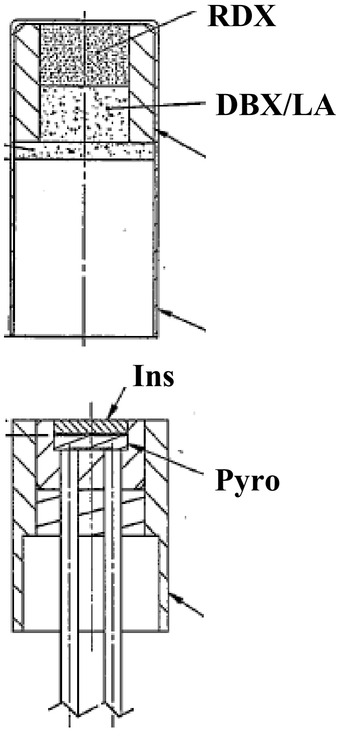
Green Energetics – DBX-1



Green Energetics – DBX-1

DBX-1 104477-202 Detonator ATP Results

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

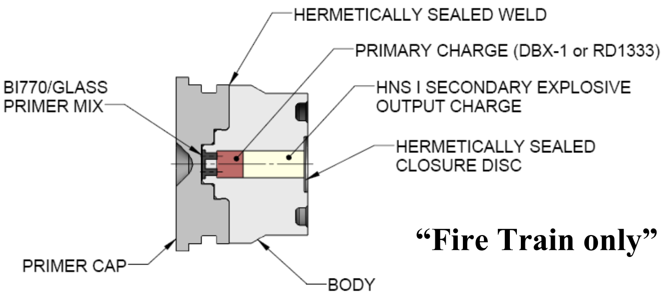


ALL UNITS FUNCTIONED NORMALLY
DBX-1 = HIGHER OUTPUT

PSEMC In-House Study to Evaluate Temperature Capabilities and Compatibility for DBX-1 Containing Components

F-18 Directed Tests – Cookoff Testing

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



"Fire Train only"

PSEMC Oilfield Component

F-18 Requirement: 300°F for 50hours (MIL-DTL-32122, 2005)
Had issues with RD1333/HNS at 340°F for 50 hrs so the requirement was reduced to 300°F.

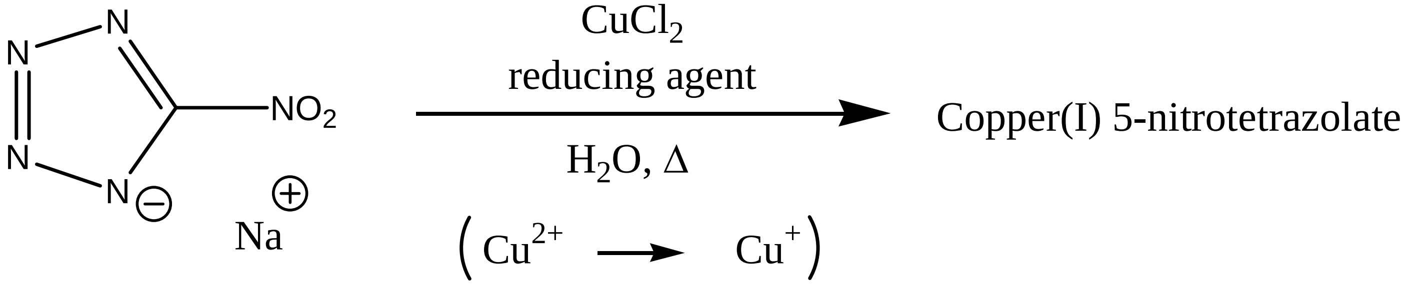
During 50hr. high temp exposure (340°F/50hr), DBX-1 domes far less and has a greater dent compared to RD1333.
***No Compatibility Issues* between DBX-1 and common secondary explosives were discovered during thermal conditioning**
DBX-1 is very stable alone, or as the primary explosive with secondary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

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

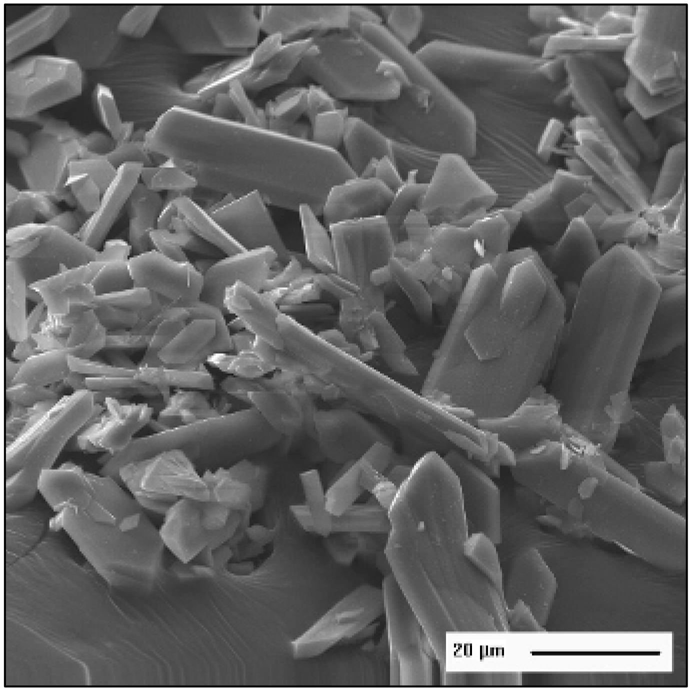
DBX-1/HNS combination will exceed 50 hour 339ºF.
DBX-1 will allow use of original 340ºF for 50 hr requirement……

Green Energetics – DBX-1

New Preparation of DBX-1



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

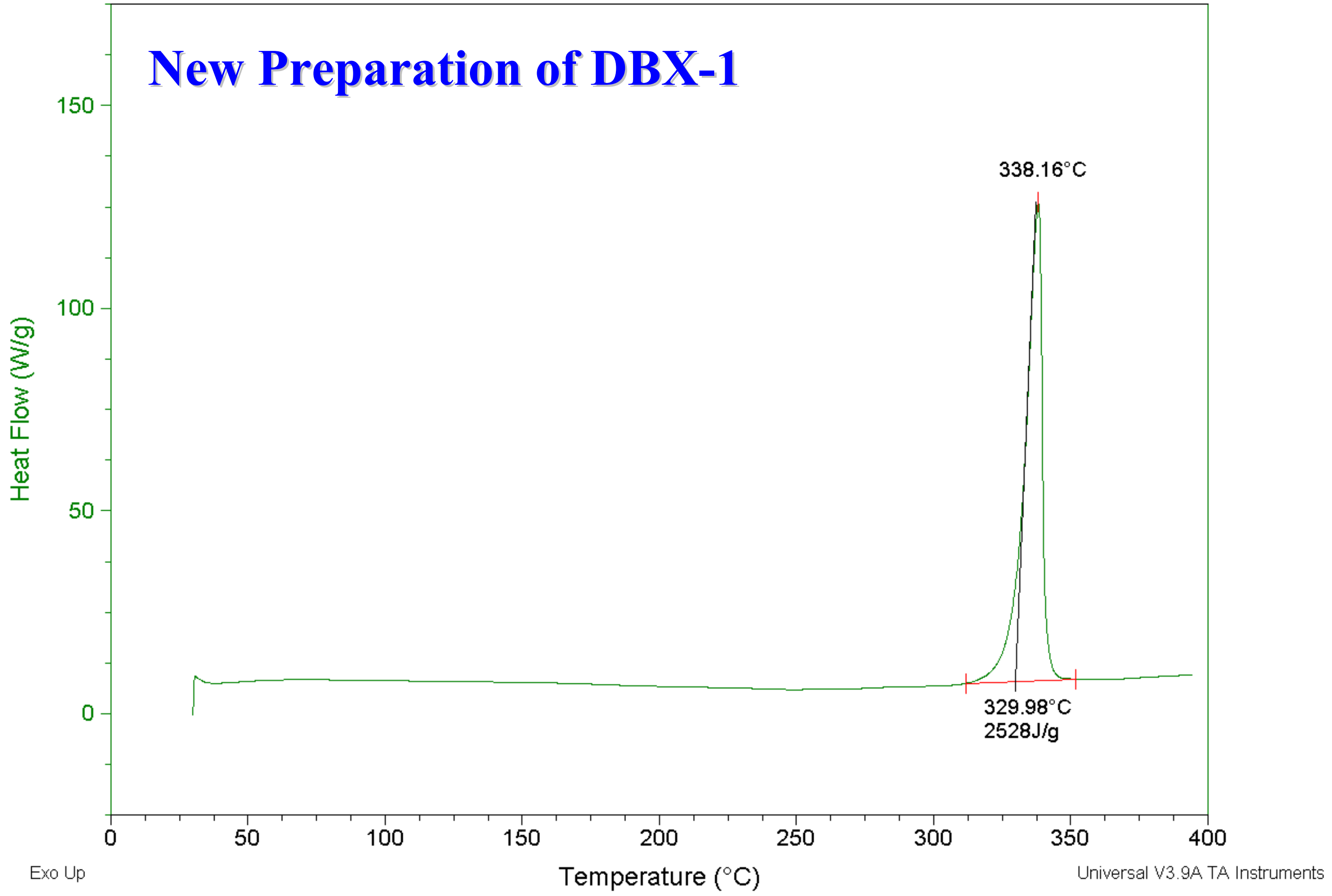
Normal analysis for DBX1 indicates this material made by this method is as good or better than previous lots

Green Energetics – DBX-1

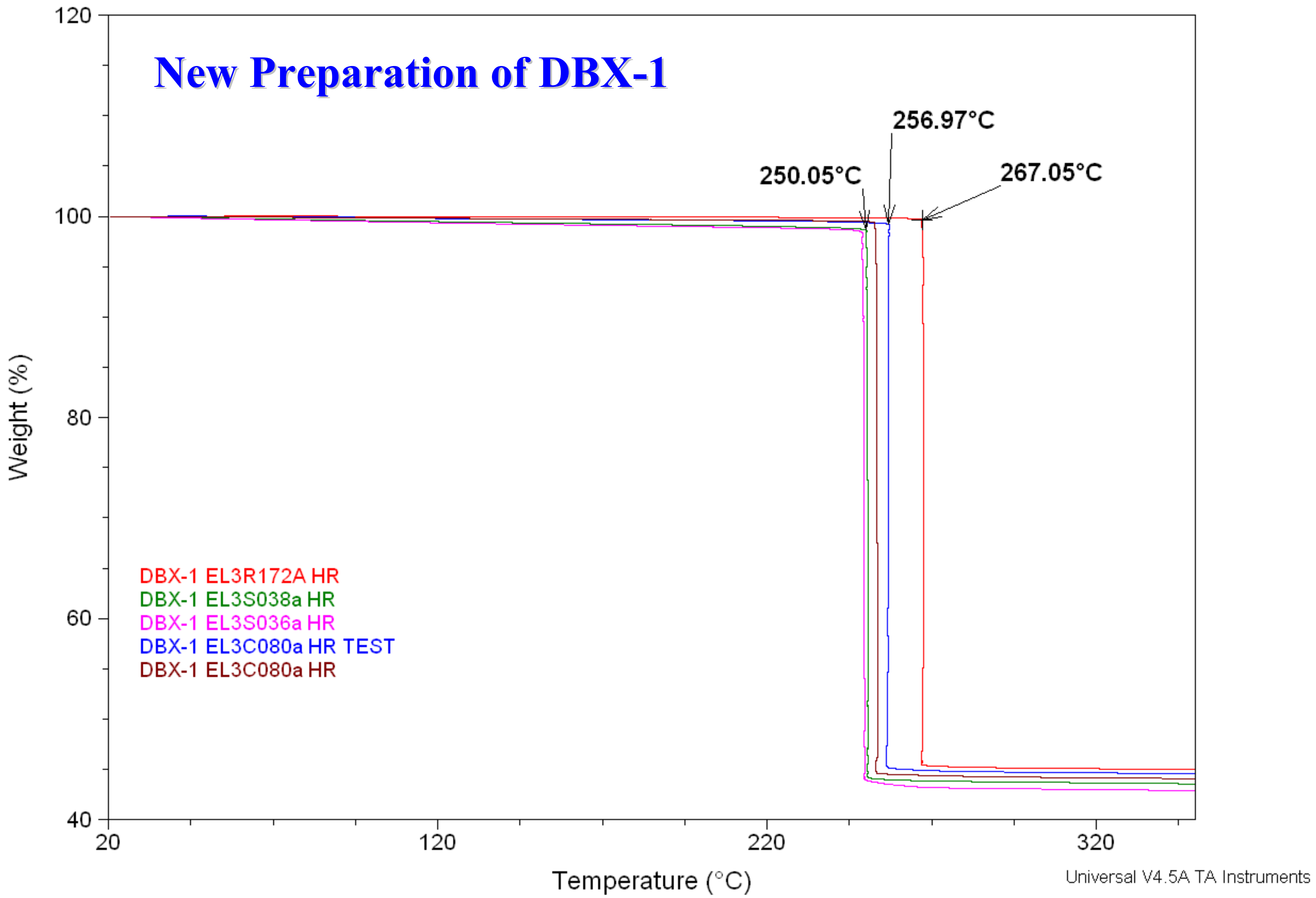
Sample: EL3R172A
Size: 0.1910 mg
Method: Standard 20C-min to 400C
Comment: Ar@50ml/min

DSC

File: \\...\Data\DSC\Mike W\EL3R\EL3R172A.001
Operator: Williams
Run Date: 23-Mar-10 15:46
Instrument: DSC Q2000 V24.2 Build 107

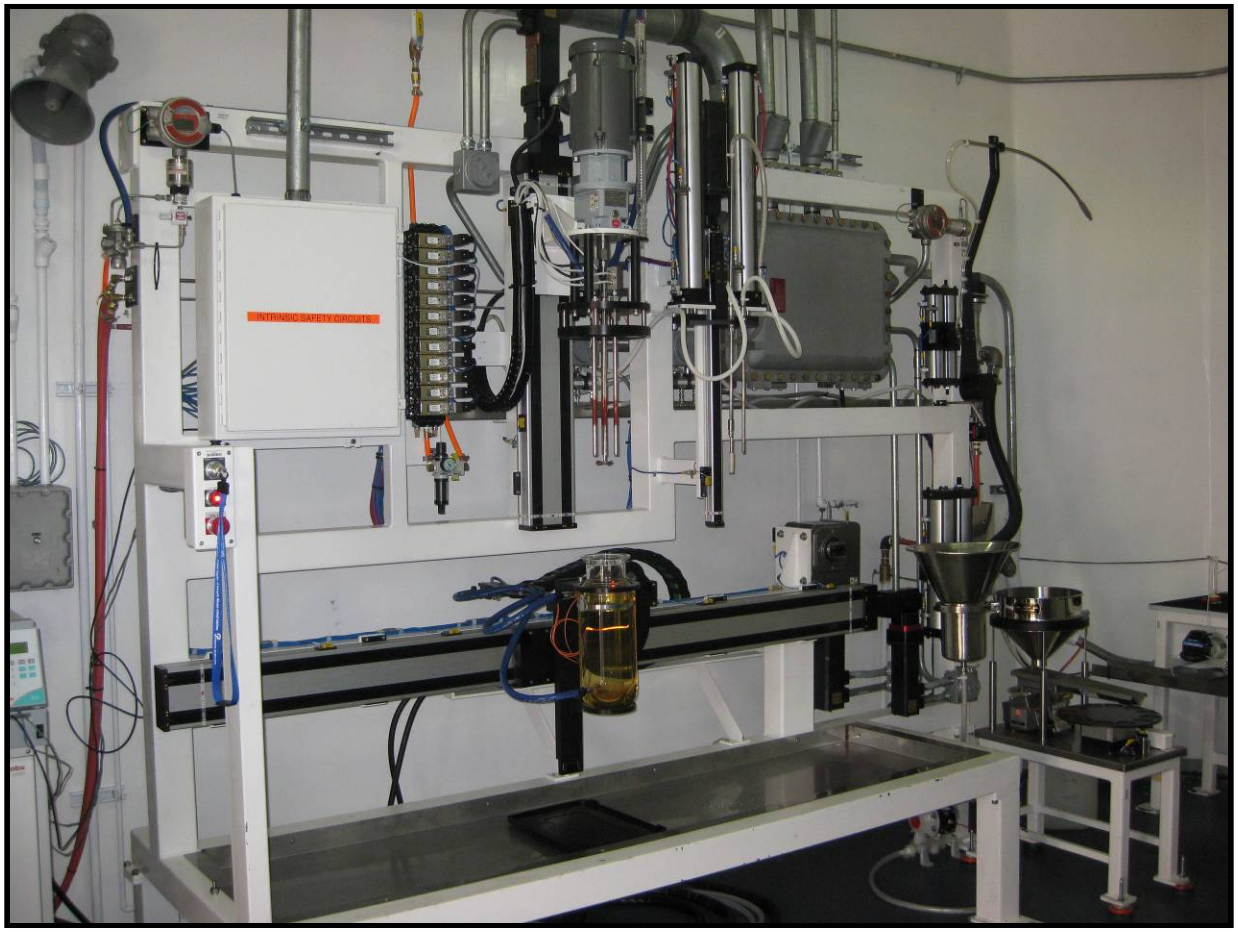

New Preparation of DBX-1

Green Energetics – DBX-1



Green Energetics – DBX-1

DBX-1 Scale-Up

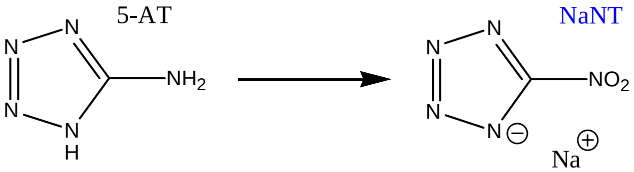


Remote Control
- Reactors – 1, 3, 20L
- Reaction –
  - Addition and Reaction
  - Filtration and Washing
  - Dispensing and Weighing

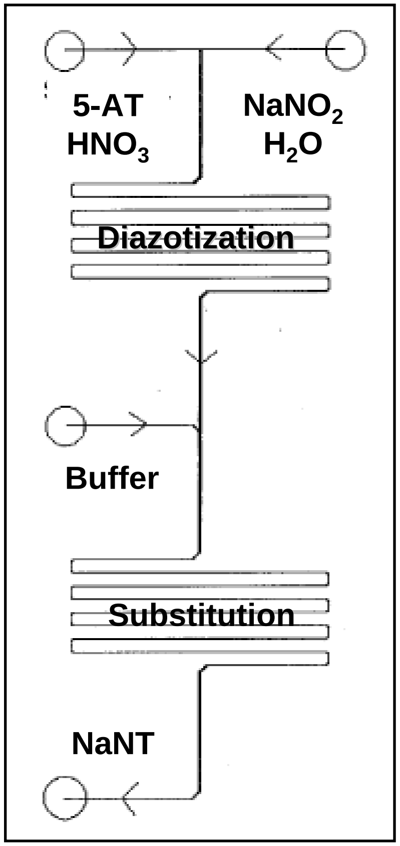
Progress
- ~10g
- ~25g

Designed and Fabricated by Franklin Engineering

Green Energetics – DBX-1



MIT/I2CHEM Reactor System



5-AT
HNO_3

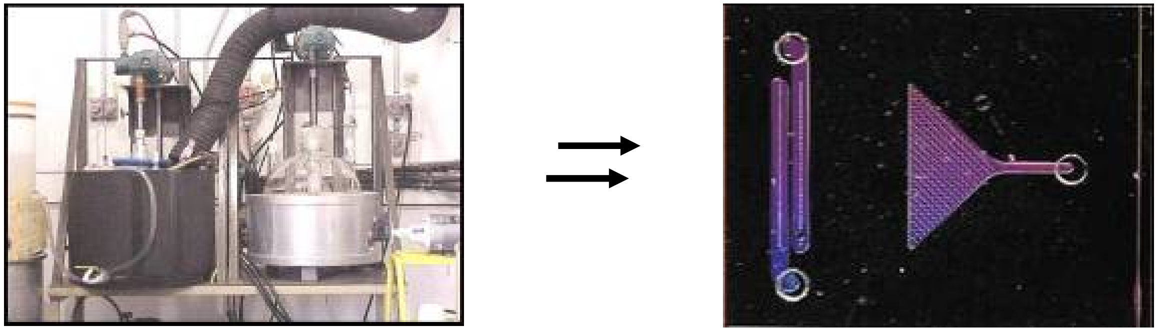
$NaNO_2$
H_2O

Diazotization

Buffer

Substitution

NaNT



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%)

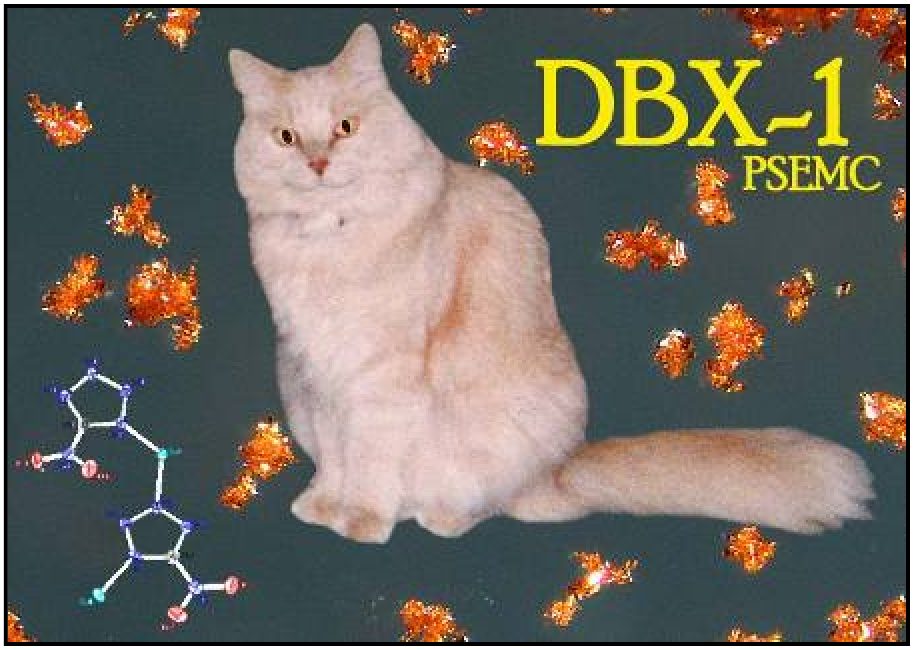
US 7,253,288 August 2007

Production System: 40-50gm/hr

Green Energetics – DBX-1

Completion of 8020.5C Program

- 8020.5C program completed Oct 2009, submitted for qualification

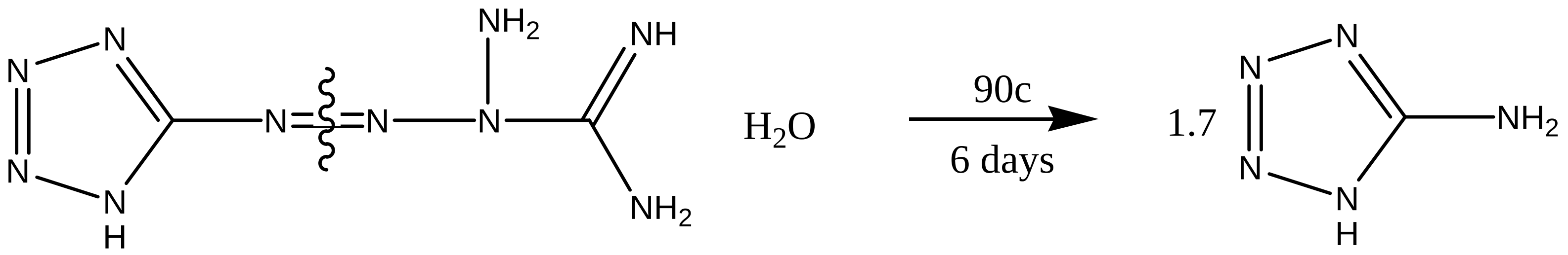


Tetrazene Replacement Project

Tetrazene

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% Sb_2S_3
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



via guanyl azide intermediate

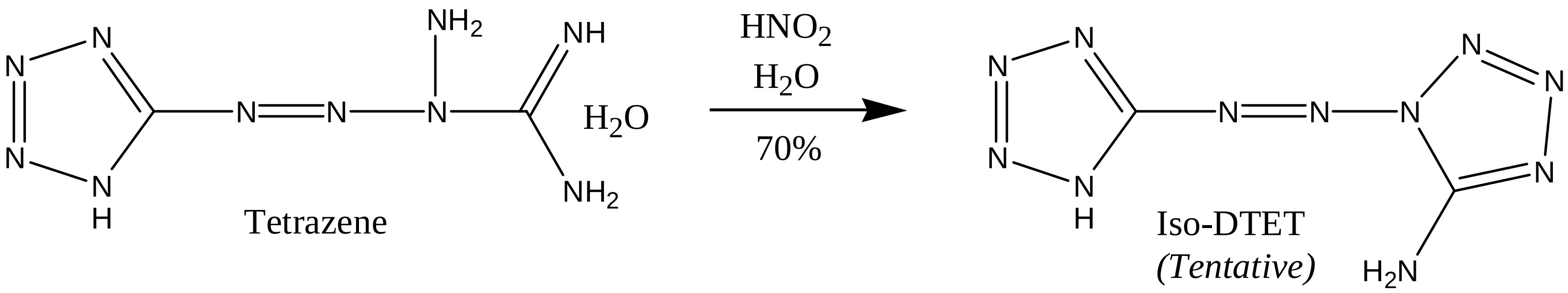
PSEMC Project – Improve thermal stability used in normal or high temperature applications
Generate new materials cheaply and without utilizing toxic reactants or effluents

"Thermal Decomposition of Tetrazene at 90ºC", Bird, R. and Power, A.J., Materials Research Laboratories Report MRL-R-710 (1978).

"The Kinetics and Thermochemistry of the Thermal Decomposition of the Initiating Explosive, Tetrazene,…", Whelan, D.J. and Fitzgerald, M.R., DSTO Aeronautical and Maritime Research Laboratory Report DSTO-TR-0450 (1996).

"Iso-DTET"

Preparation of Iso-DTET



Structure 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

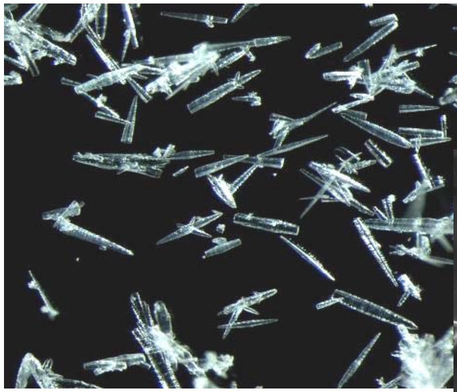
Tetrazene Replacement Project

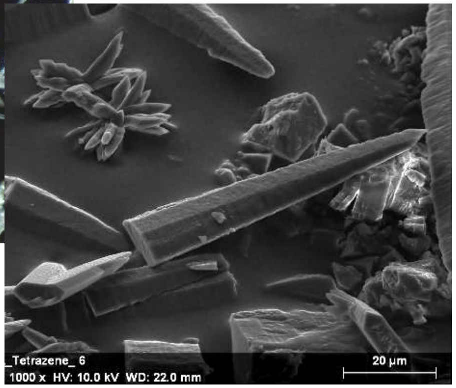
Sensitivity of Iso-DTET

“Iso-DTET”

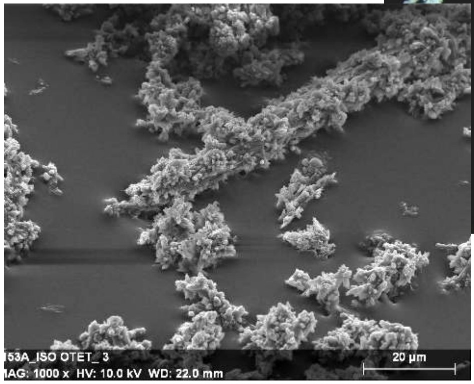
SAMPLE	DSC (20ºC/minute)		IMPACT (J)	FRICTION (grams)		ESD (mJ)		TGA % Wt Loss @ 167 hrs
	Onset	Peak		No Fire	Low Fire	No Fire	Low Fire	
Tetrazene	138ºC	144ºC	0.021	1100	1200	>7.43	NA	36.1%
Iso-DTET	208ºC	214ºC	0.016	800	900	3.30	4.18	3.5%

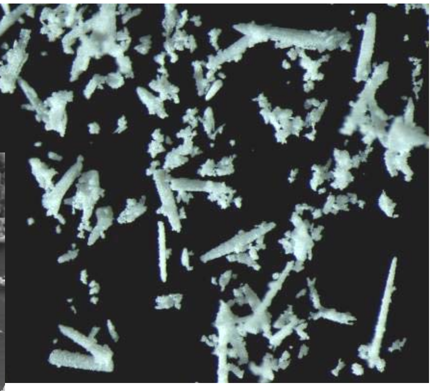
Similar crystal morphology





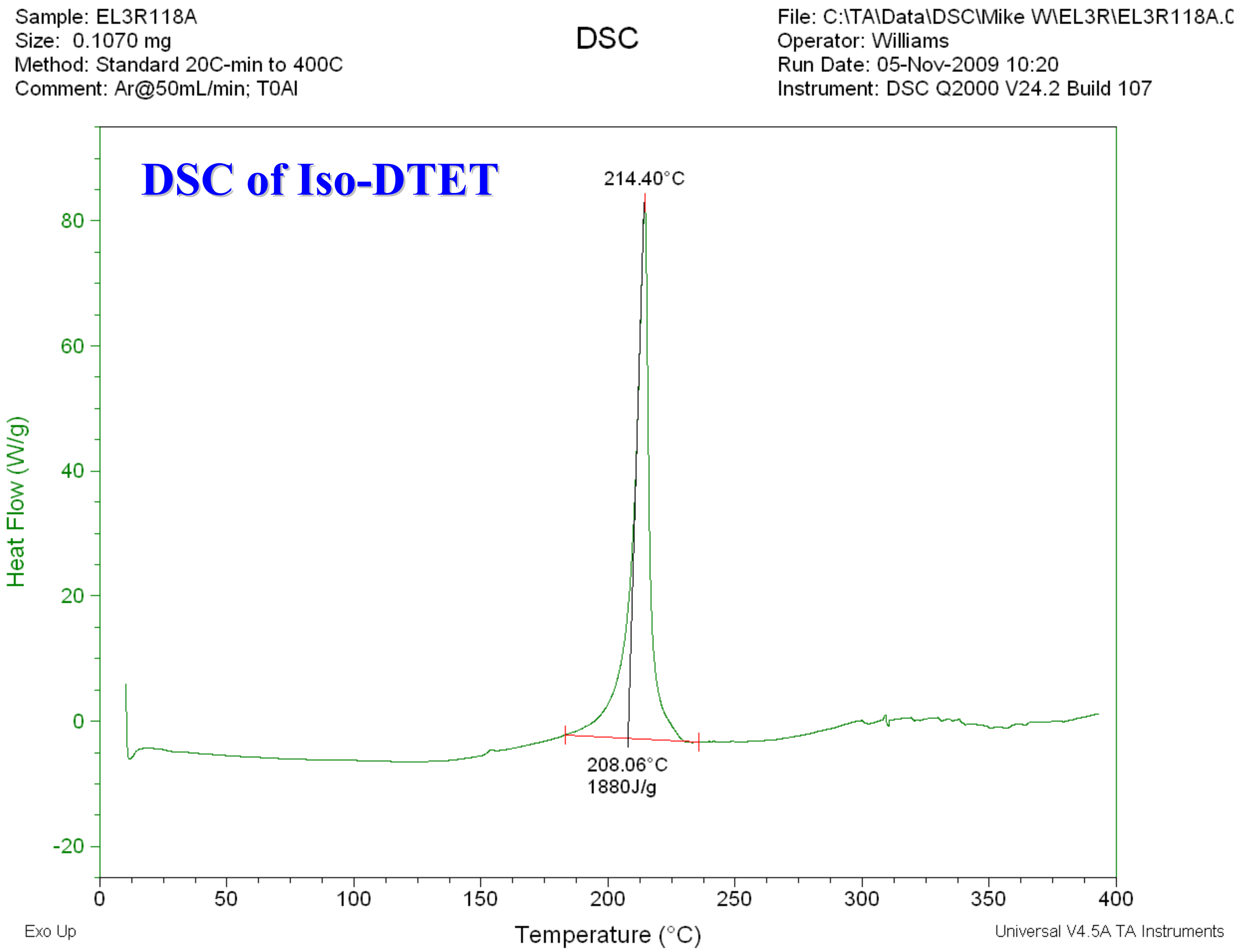
Tetrazene
100X Optical
1000X SEM





Iso-DTET
100X Optical
1000X SEM

DSC of Iso-DTET

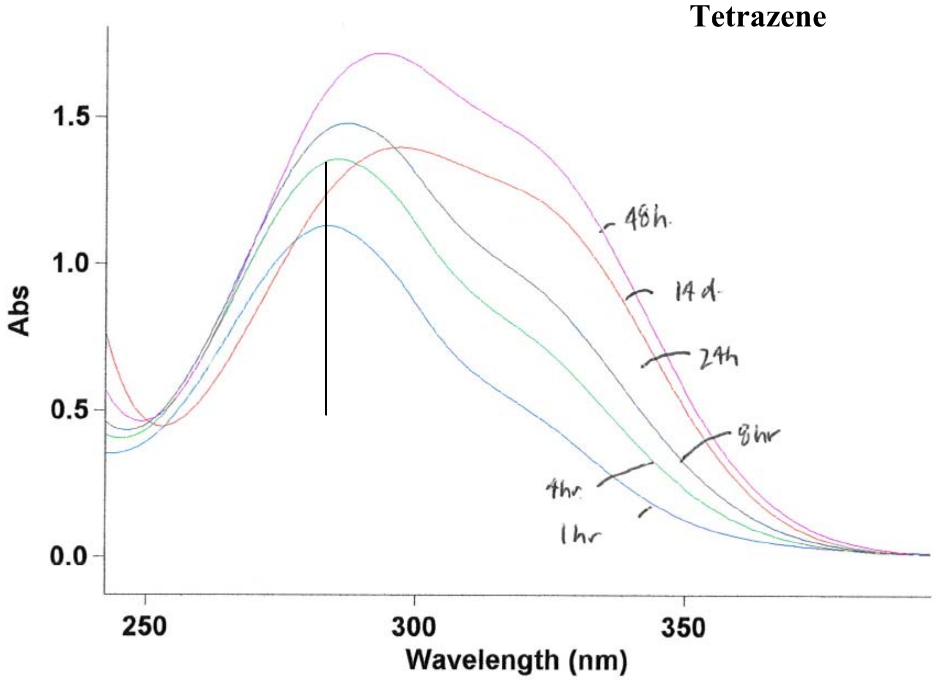


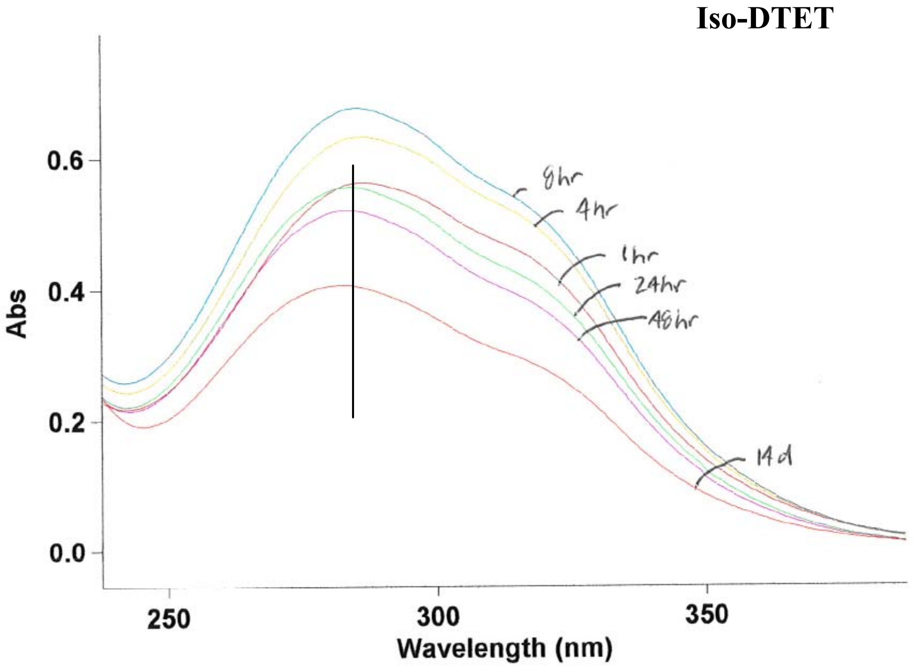
Sample: EL3R118A
Size: 0.1070 mg
Method: Standard 20C-min to 400C
Comment: Ar@50mL/min; T0Al

DSC

File: C:\TA\Data\DSC\Mike W\EL3R\EL3R118A.0
Operator: Williams
Run Date: 05-Nov-2009 10:20
Instrument: DSC Q2000 V24.2 Build 107

Hydrolytic Stability of Iso-DTET



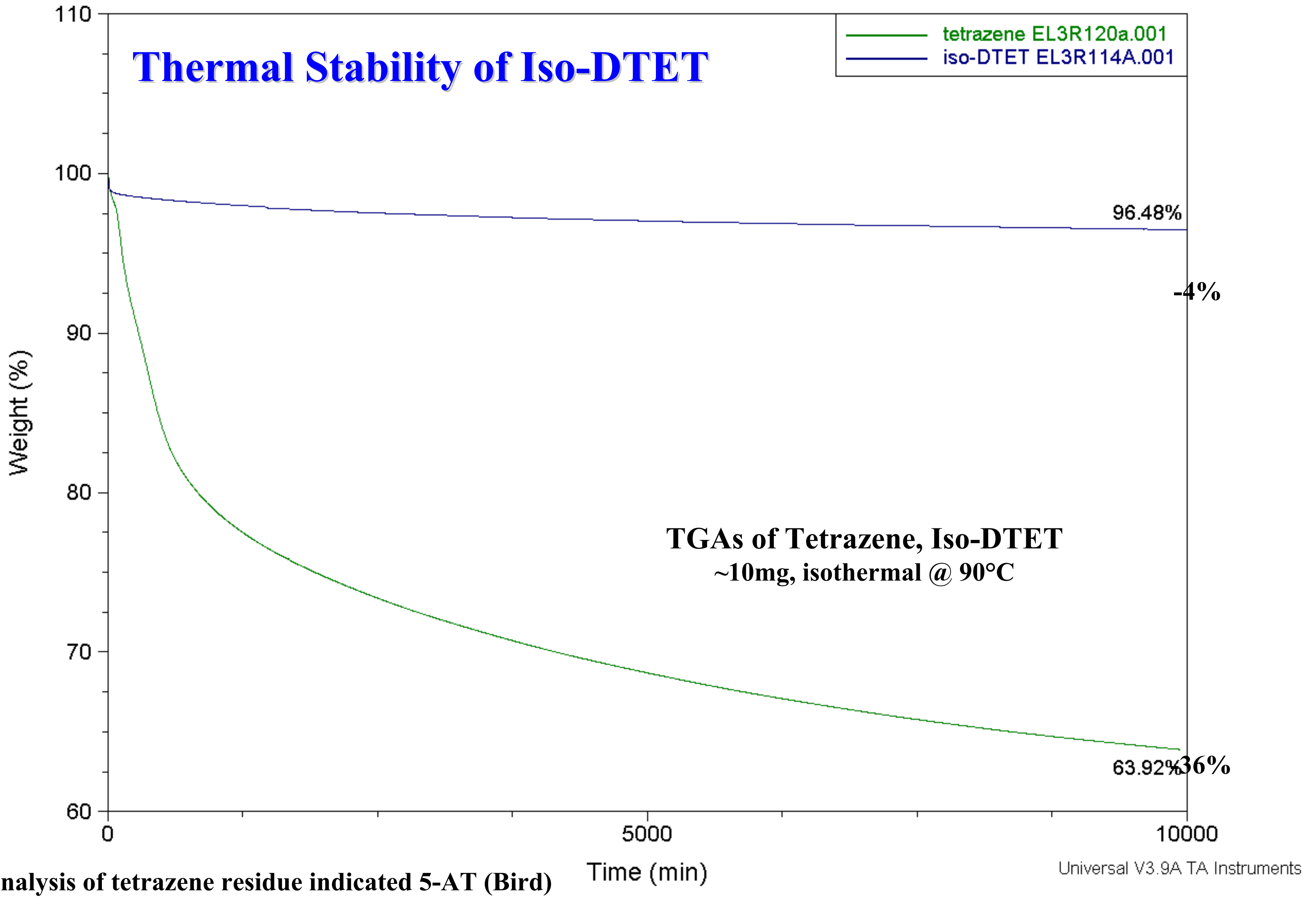


~0.50g suspended in 250mL of water, ambient conditions, sampled at indicated intervals
Tetrazene – change in conc. over 8 hrs with bathochromic shift to 350nm and increased extinction below 250nm -degrades
Iso-DTET – no shift over time
Residue

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

Tetrazene Replacement Project

Thermal Stability of Iso-DTET



-4%

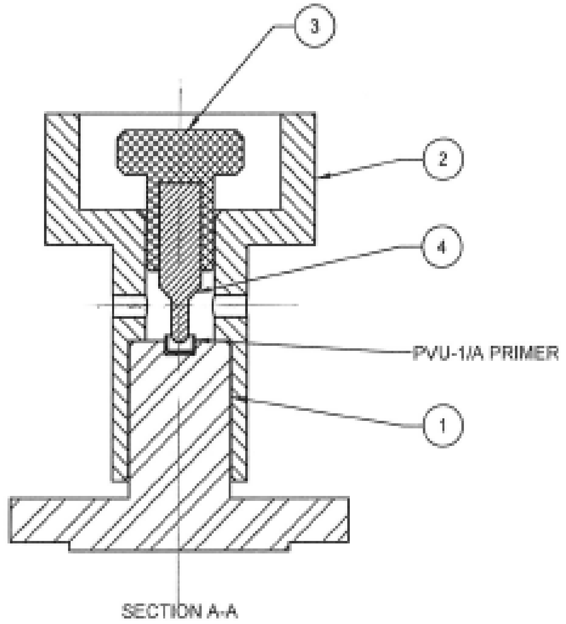
36%

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

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

Output Performance of DTET

0.048" firing pin, no closure over primer



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

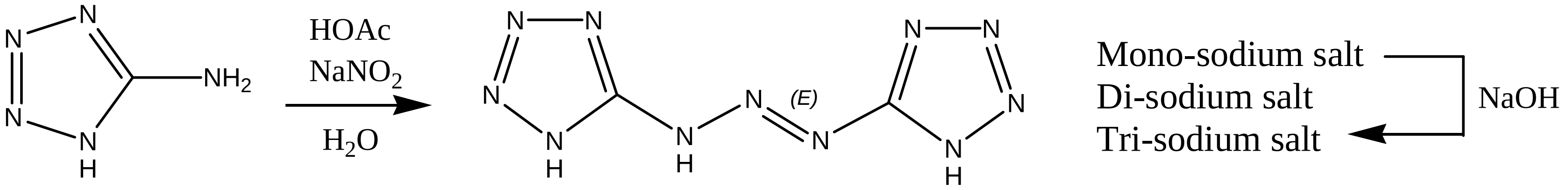
BLS PN51-8593E LN GY19862 – un-milled, -#100 sieve
Tetrazene, Iso-DTET - -#40 sieve

Sample	Mu±σ	0.001 Level	0.999 Level
100% BLS (EL3Y003)	12.5”±0”	12.5	12.5
95% BLS/ 5% Tetrazene	4.92”±1.41”	0.56	9.28
95% BLS/ 5% Iso-DTET	5.91”±0.42”	4.60	7.21

Tetrazene Replacement Project

DTET

Preparation of DTET



DTET

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

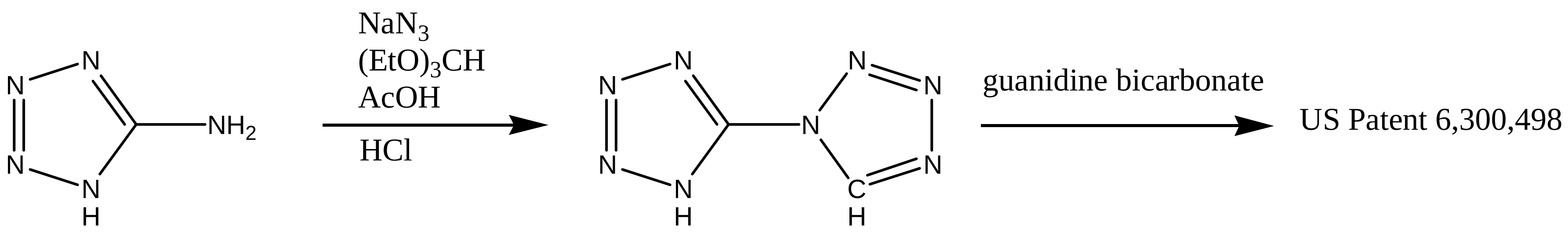
Sensitivity of DTET

SAMPLE	DSC (20ºC/minute)		IMPACT (J)	FRICTION (grams)		ESD (mJ)		TGA % Wt Loss @ 167 hrs
	Onset	Peak		No Fire	Low Fire	No Fire	Low Fire	
Tetrazene	138ºC	144ºC	0.021	1100	1200	>7.43	NA	36.1%
DTET	139ºC	156ºC	>0.056	>2075	>2075	-	-	-

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
- Dr. Alfred Stern – NSWC-IH
- Travis Thom – NSWC-IH
- Dr. Brad Sleadd- NSWC-IH
- Dr. Pete Ostrowski - Energetic Materials Technology
- 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
Company: Pacific Scientific Energetic Materials Co.
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).