DBX-1, A Potential Drop-In Replacement for Lead Azide

and an Extremely Brief Update on MTX-1, an Alternative to Tetrazene

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Green Energetics – Background

Lead Styphnate:

Major ingredient in stab and percussion primers, used as ignition element in hot-wire devices

KDNP (4,6-Dinitro-7-hydroxybenzofuroxan, salt) appears suitable as a drop-in replacement & offers high performance

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

Lead Azide:

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

DBX-1, under suitable conditions, may be an appropriate substitute for DLA

8020.5C Qualification Testing was completed in 2010 and approval is expected in 2012

Tetrazene:

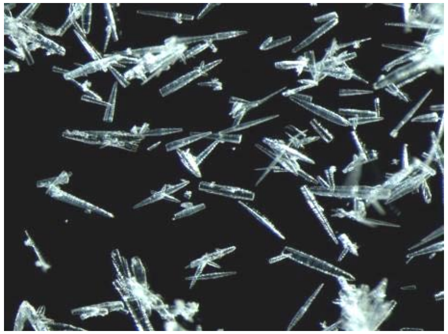
Explosive high nitrogen material used for sensitization of a variety of priming compositions (mil/com ammunition)

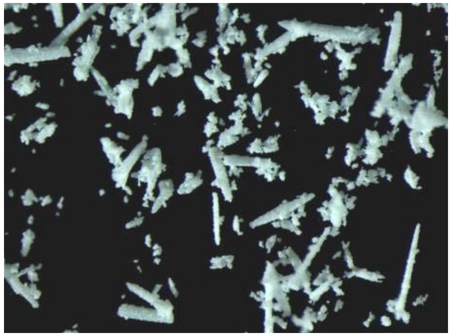
Tetrazene is a material containing no heavy metals but has low hydrolytic and thermal stability

Extremely impact and friction sensitive

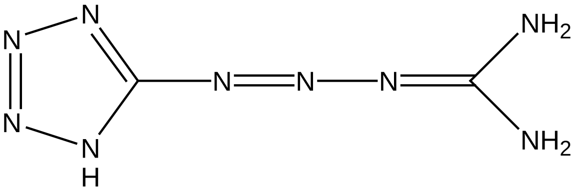
PSEMC is currently involved, with ONR, in a project to find a high stability replacement

MTX-1 has sensitivity nearly equivalent to tetrazene with much higher thermal and water stabilities





100X

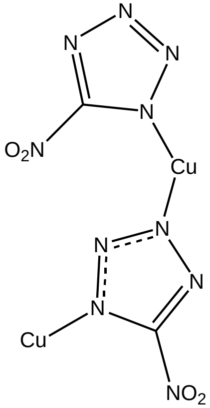


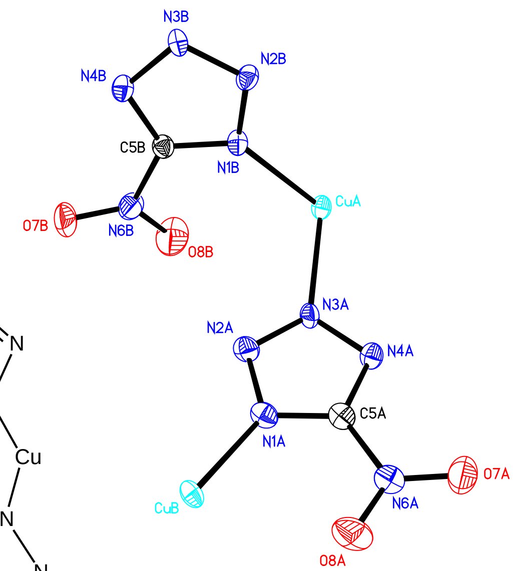
MTX-1

DBX-1

Physical Properties

Physical State: red, rust solid
Particle size: 10-140 μm
Molecular weight: 355.20 ($C_2Cu_2N_{10}O_4$)
Density: X-ray: 2.58 g/cc
He pycnometry: 2.59 g/cc
Tap density: 1.01 g/cc
Oxygen balance: 0% (to Cu), -9.01 (to Cu_2O), -18.02% (to CuO)
Hot Stage Ign Temp: 1 sec – 356.2 °C, 5 sec – 350.7 °C, 10 sec – 345.2 °C
Heat of Explosion: 3816.6 J g^{-1} (argon)
Heat of Formation: 280.9 J g^{-1}
Critical Temp: 256-281 C; 0.64cm dia. Cyl @ 80% TMD
E_A=193.3 kJ mol^{-1}
Thermal Conductivity: 0.03 W m^{-1} K^{-1} powder
Vacuum Stability: 0.47 mL gm^{-1} $48hr^{-1}$ (0.2g, 100 C) (<2)
VISAR (NASA-JSC): DBX-1 2.3km/sec; RD1333 2.1km/sec



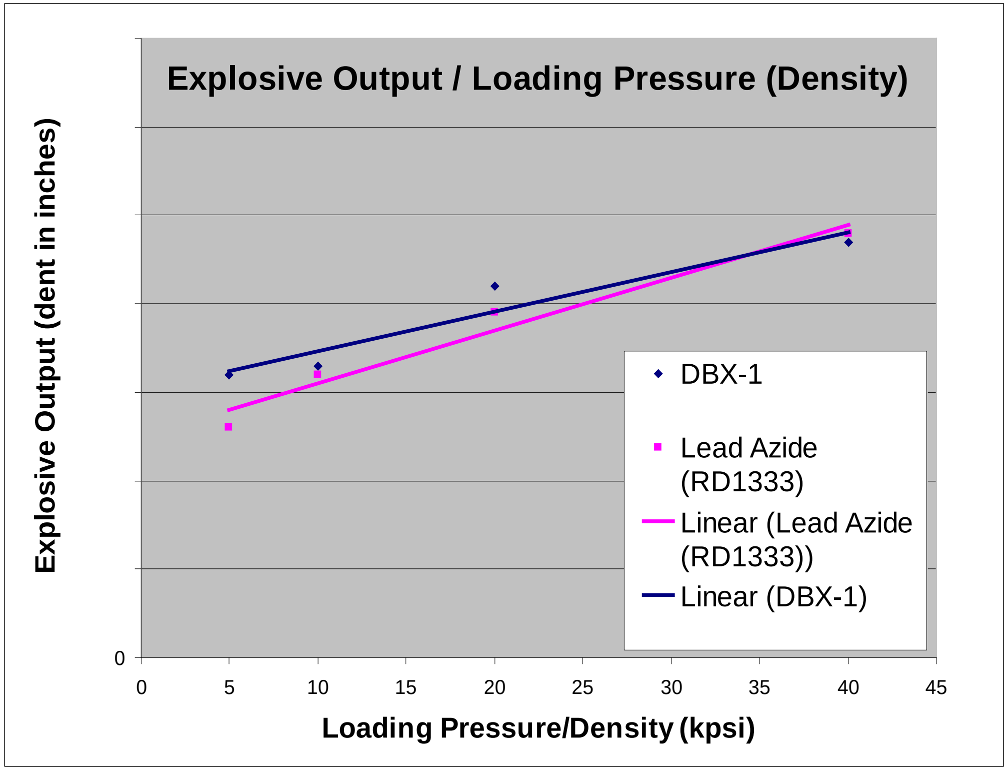


X-ray: Dr. D. Parrish at NRL

Hygroscopicity

Hygroscopicity at **25ºC**	Large Particle (EL3C106A) ~100-120 um	Small Particle (EL3O009B) ~10-30 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



Safety & Performance Properties

VLPSC:
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 kpsi.
The units were loaded into fixtures and fired (4uf cap, 300V) onto 1" aluminum blocks.
*** = considering redesign**

Safety:
DSC: TA Instruments MDSC Q2000
Impact: Ball drop instrument/ Bruceton analysis
Friction: Julius-Peters Small BAM
Density: Micromeritics He Pyncnometry
TGA: TA Instruments TGA Q5000
ESD: Low Energy Electrostatic Analyzer

SAMPLE	DSC (20°C/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	329°C	337°C	0.040±0.010	0g	10g	2.59 (Cu)	260 °C	12μJ
LA (RD1333)	332°C	341°C	0.050±0.004	0g	10g	4.80 (Pb)	166 °C	6.75μJ

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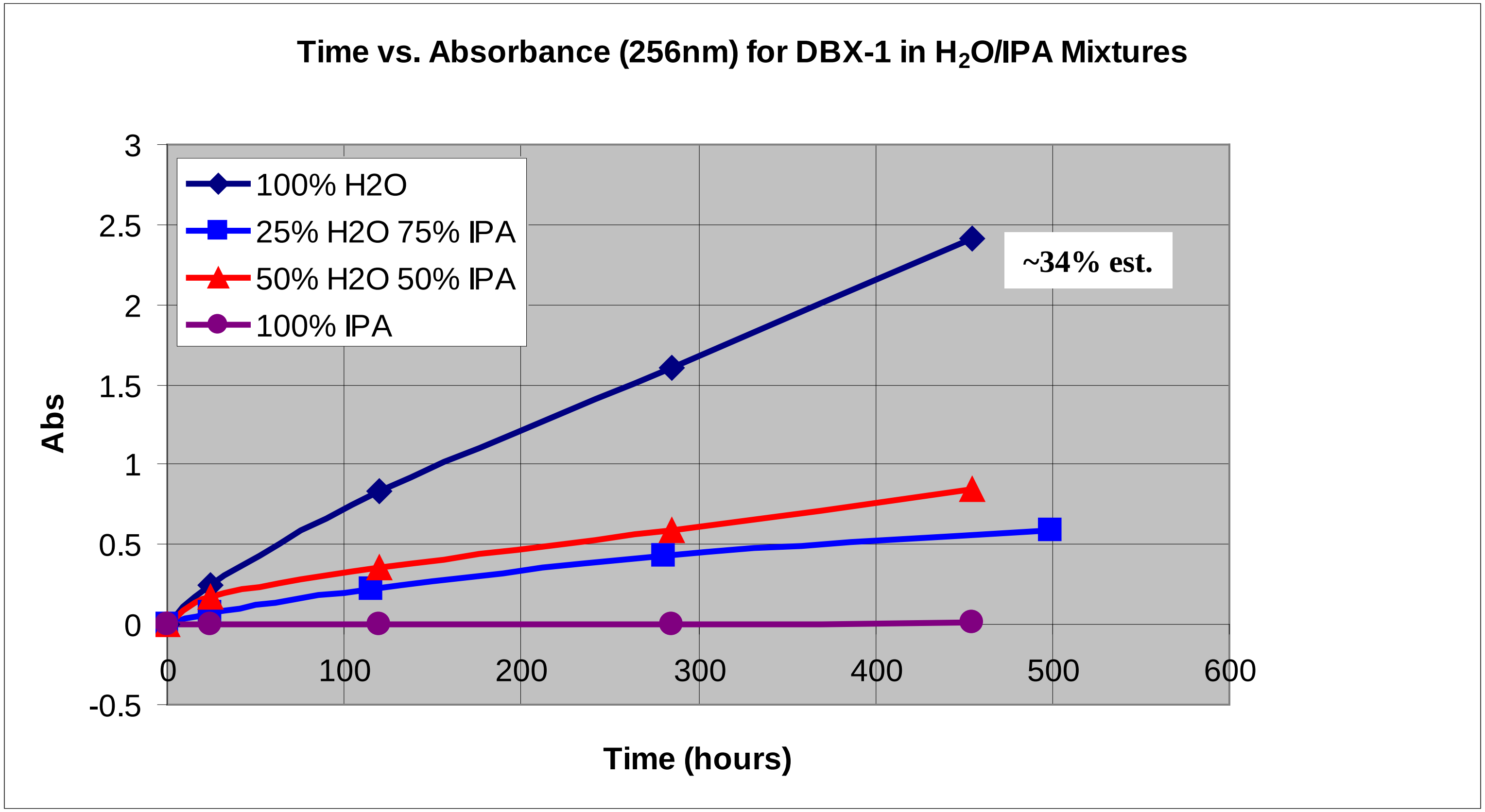
DBX-1 Stability/Solubility in IPA/Water

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.

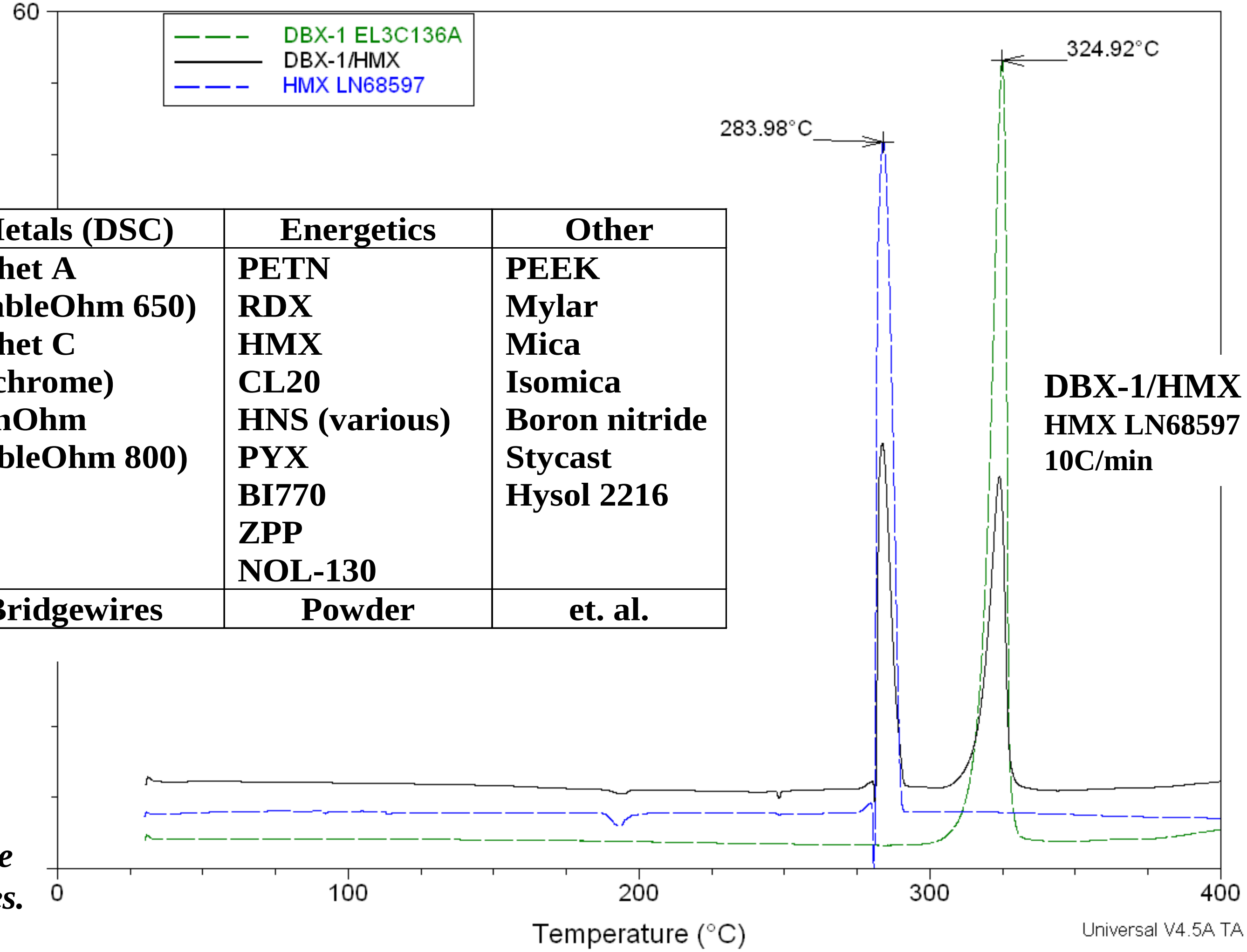


Increased 2-propanol content suppresses the decomposition of DBX-1 with neat 2-propanol having **no reactive effect.**
Currently revisiting with long duration testing & alternate solvents – IPA: 2 months, no change

DBX-1 Compatibility

DBX-1 has demonstrated compatibility with:

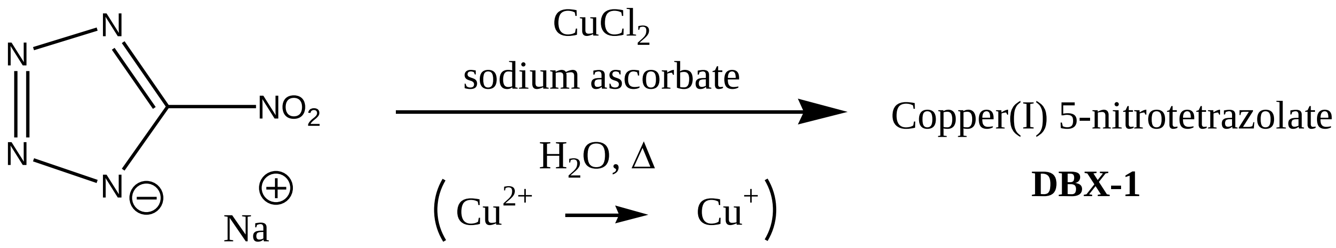
Metals (coupon test)	Metals (DSC)	Energetics	Other
1100 aluminum 6061-T6 aluminum 2029-T3 aluminum 304 stainless steel Brass MK107 gilding metal (95% Cu, 5% Zn)	Tophet A (StableOhm 650) Tophet C (Nichrome) EvenOhm (StableOhm 800)	PETN RDX HMX CL20 HNS (various) PYX BI770 ZPP NOL-130	PEEK Mylar Mica Isomica Boron nitride Stycast Hysol 2216
Housings	Bridgewires	Powder	et. al.



No incompatibility
with any materials tested

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

Preparation of DBX-1 from Cu(II)



NaNT

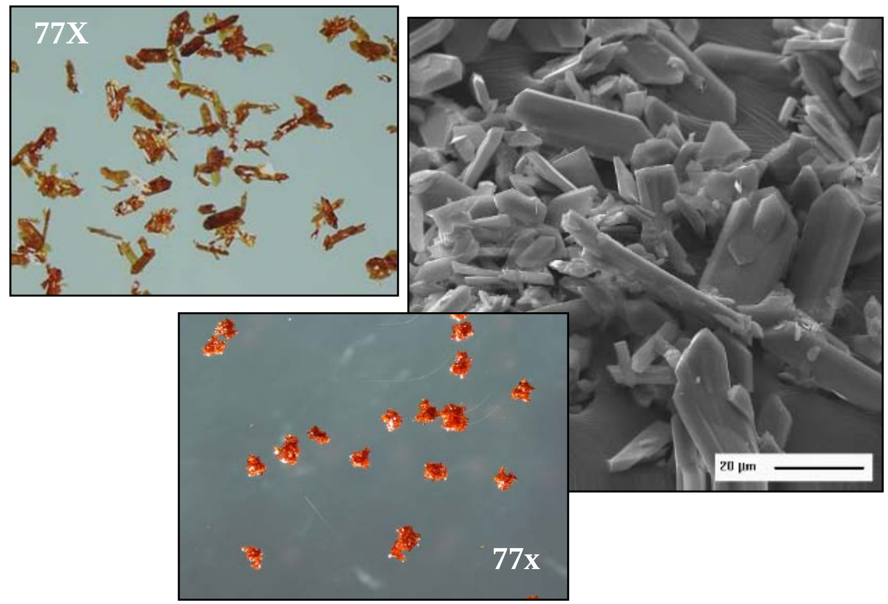
Initial process from Cu(I):
~ 1 hour process with induction period

New process:
Low induction period for crystallization
Reaction time 10-15 minutes
Yield: 80-90%
Prep > 100 X

This process *is* suitable for scale-up and is used in the current ManTech Program

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

Particle size tends to be *slightly* smaller



Full Paper
DBX-1 – A Lead Free Replacement for Lead Azide
Propellants Explos. Pyrotech., 2011, *36*, 541-550.

Process Development & Scale-Up of DBX-1

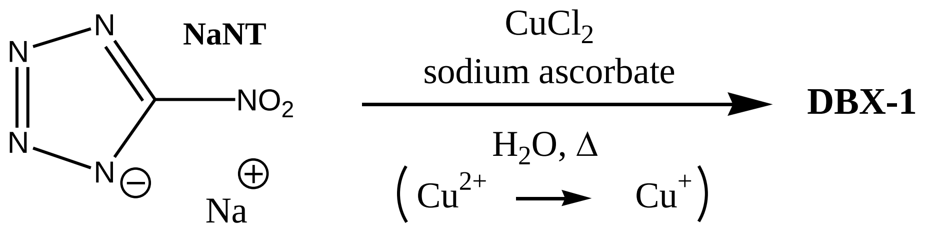
Goals & Objectives	Initiative Information
The goal of this initiative is to develop an optimized and reproducible method for production of the lead azide replacement material DBX-1. Particular attention will be given to DBX-1 particle size and morphology to insure that the final product is suitable for handling and loading in existing tooling. An objective is to scale production of this optimized DBX-1 to the 100 gram level and provide this material for testing in military hardware and devices.	Initiative Lead: Michael Williams - PSEMC Team Members: John Fronabarger Jonathon Bragg Stan Hartman Lisa Dagostini – all of PSEMC Nalas Engineering Services Period of Performance: 3Nov2010-29Nov2012

Milestones & Technical Achievements	Implementation & Payoff
Nov10: Kickoff Meeting - C Jul11: Chemical Process Optimization - C Aug11: NaNT (reactant) Evaluation - C DBX-1 lot Characterization - C Sept11: 100gm DBX-1 Process Validation - C Apr12: DBX-1 Disposal Study - C Oct12: 100gm DBX-1 Process Review - S IP - in process, C- completed, S - scheduled	Schedule: 31 October 2012. Status: On track The initiatives successful completion will afford a reproducible scale-up process for DBX-1 (copper(I) 5-nitrotetrazolate). DBX-1 is a lead-free (green) replacement for the lead azide component of a variety of DoD devices.

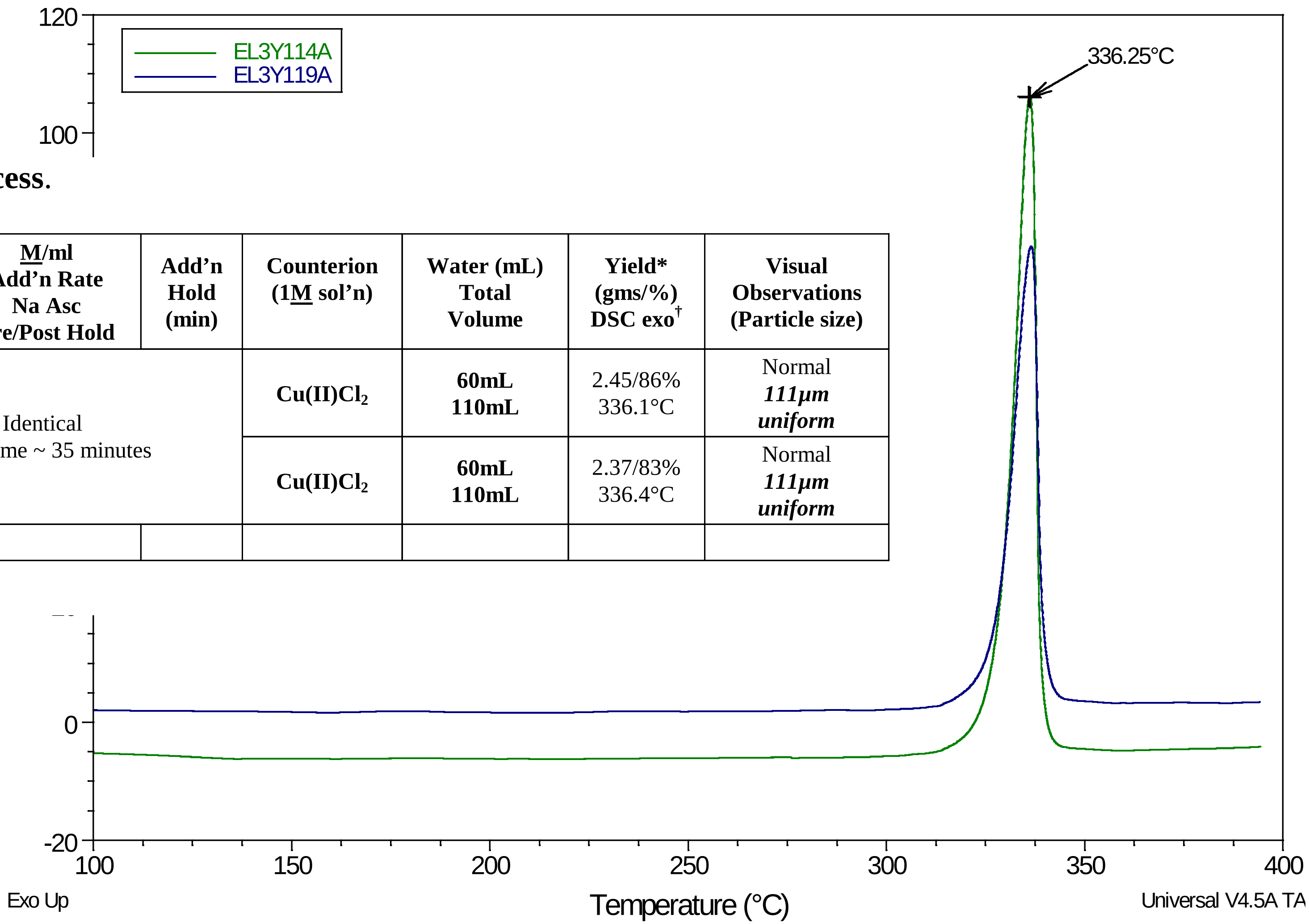
DBX-1 ManTech

Summary of Reaction Variables

variations from "standard"
yield, purity, particle size & distribution



- **pH - pH should not be appreciably above 3.0 and preferably untreated (8, 0.99-5.00)**
- **Concentration - overall reaction concentration has little effect (6, 94-194 mL)**
  high concentrations affords a larger, bimodal product
- **Counter-ion - anions other than chloride result in smaller and multimodal particles (6, various)**
  acetate and nitrate counter-ions afford products with lower DSC exotherms
- **Addition Rates - ascorbate addition rates have little effect (5, 0.25 ml/min-10.0 mL/min)**
  faster addition rates may increase DBX-1 particle size, narrow the particle distribution
  very fast addition provides larger particle/lower DSC
- **NaNT Stoichiometry - lower NaNT/Cu(II) should be avoided – stoichiometric 5% (5, 0.84 eq. -1.12 eq.)**
- **Ascorbate Stoichiometry - initial 2 electron reduction occurs quickly while an additional 2 electron reduction of the didehydroascorbic acid (initial) oxidation product occurs more slowly and provides additional DBX-1. Changing stoi./rxn time gives larger size distribution**
- **Alternate Reducing Agent – replacement of ascorbate with α-D-glucose does not reduce Cu(II) to Cu(I)**



Modified DBX-1 Process.

Lot #	mL/eq. Lot# NaNT	M/ml Add'n Rate Na Asc Pre/Post Hold	Add'n Hold (min)	Counterion (1M sol'n)	Water (mL) Total Volume	Yield* (gms/%) DSC exo[†]	Visual Observations (Particle size)
3Y114A	Identical Total time ~ 35 minutes			**Cu(II)Cl_2**	**60mL 110mL**	2.45/86% 336.1°C	Normal ***111μm uniform***
3Y119A				**Cu(II)Cl_2**	**60mL 110mL**	2.37/83% 336.4°C	Normal ***111μm uniform***

Final Lab Scale Process

DBX-1 ManTech

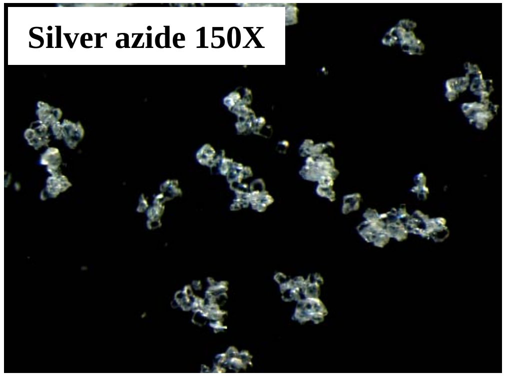
PSEMC/Franklin Engineering Scale-up Reactor

Currently used for large scale synthesis of:

DBX-1 – to 100+g lots
Silver azide – to 100g lots

Remote Control Operation

- **Reactors – 1, 3, 20L capability**
- **Reaction –**
  - **Addition and Reaction**
  - **Filtration and Washing**
  - **Dispensing and Weighing**
- **Computer controlled**
- **Heating and Cooling**
- **Remotely monitored**



Silver azide 150X

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Preparation of DBX-1 – Initial Scale-up (Reactor)

Lot #	Total Volume	Yield (gms/%) DSC exo	Particle Size
3U085 (10g)	808mL	7.5gms/66% 337°C	95 um
3U087 (12g)	1212mL	11gms/65% 336°C	113 um
3U089 (25g)	1555mL	20gms/70% 336°C	104 um
3U113 (10g)	795mL	5.4gms/60% 336°C	97um
3U121 (25g)	1808mL	25gms/81% 336°C	95um

>1 eq. NaNT, various concentration

ascorbate addition rates varied

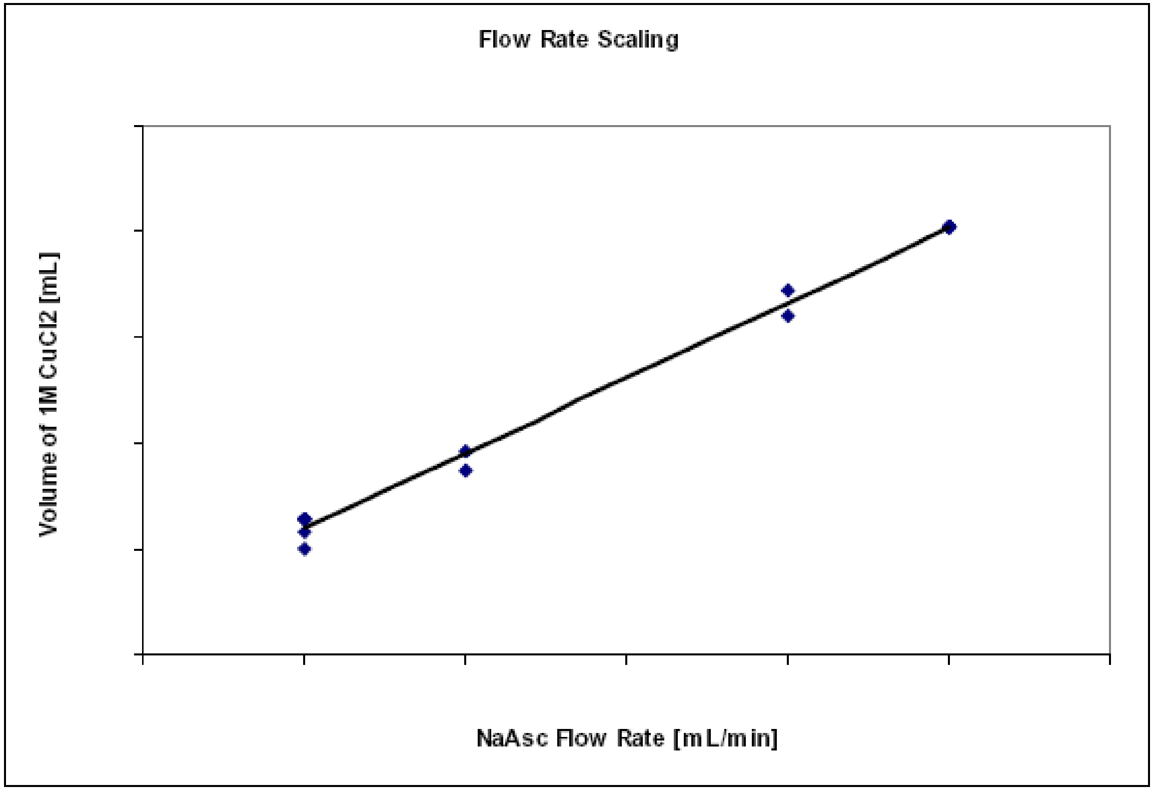
550-600 RPM

granulation times: 9-17min.

92 C

MicroTrac S3500 light scattering analyzer

Sodium Ascorbate Addition Rate @ Scale-up



Adding larger quantities of the reducing agent at the rate (or time) used in the lab scale is clearly untenable.
During 25 gm scale-up experiments determined rate should be based on the amount of copper present in the reaction.
Curve shows the rates for a variety of scales, extrapolation provided suitable addition rates at the 25/100 gm scale.

Preparation of DBX-1 – 25gm Scale-up

Lot #	Water (mL) Total Volume (mL)	Yield* (gms/%) DSC exo†	Particle Size (mean)
4C061	1132 mL 1742 mL	27.2/76% 336°C	140 µm
4C063*	1132 mL 1700 mL	26.9/75% 336°C	110 µm
4C065*	1132 mL 1700 mL	27.3/76% 336°C	117 µm
4C067	1382 mL 1950 mL	23.3/65% 337°C	93 µm
4C069	1132 mL 1700 mL	23.0/64% 337°C	116 µm
4C071	1382 mL 1950 mL	26.3/74% 336°C	109 µm
4C073†	1286 mL 1700 mL	18.5/71% 337°C	99 µm
4C075†	1286 mL 1700 mL	16.5/63% 336°C	130 µm

~1 eq. NaNT, various concentration

ascorbate addition rates varied

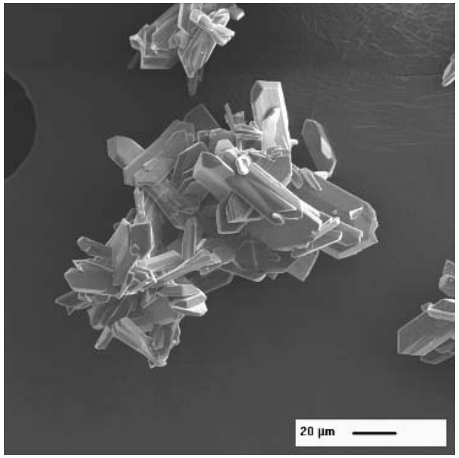
400-640 RPM

granulation times: 12-18 min.

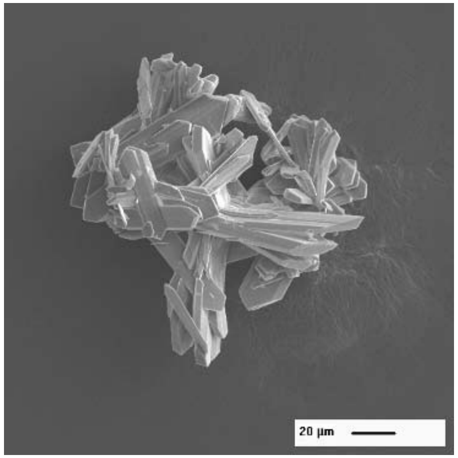
4C063 and 4C065 were run under identical conditions to confirm process reproducibility.

SEM & Photomicrographs of 25gm Batches

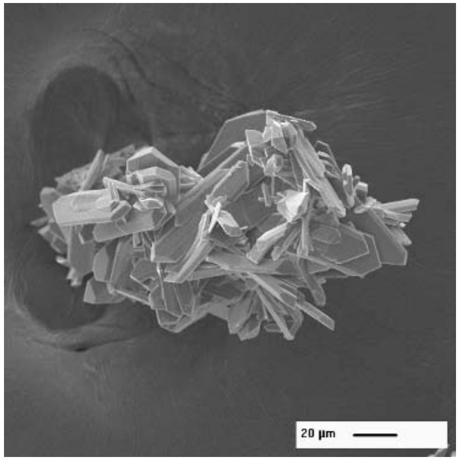
500x



EL4C067 – 94 µm



EL4C069 – 112 µm

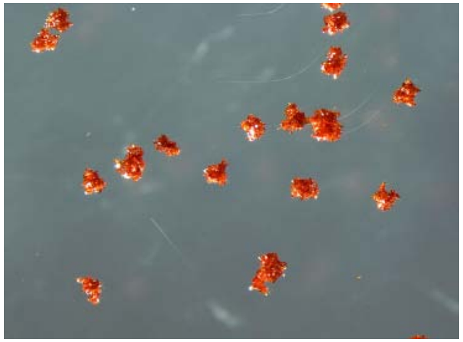


EL4C071 – 109 µm

77x

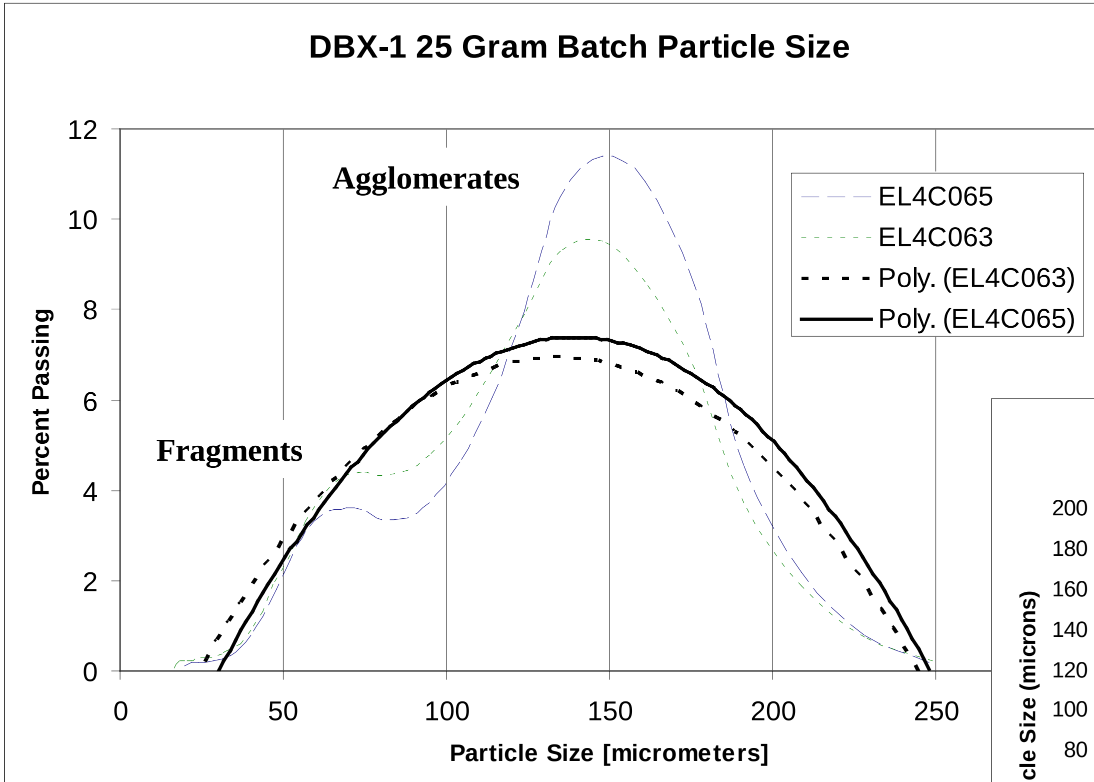
EL4C067 – 94 µm

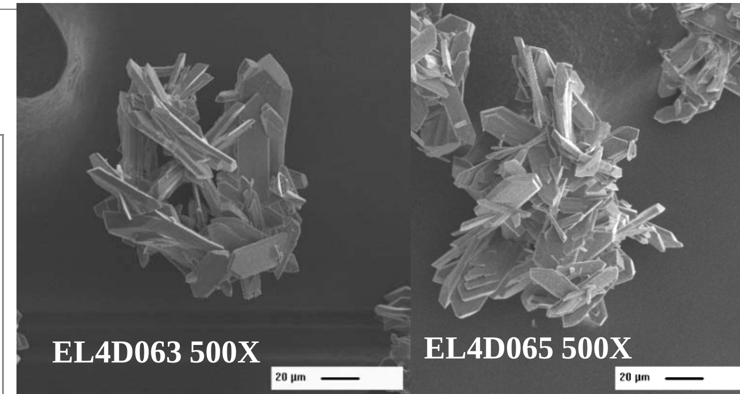
EL4C069 – 112 µm

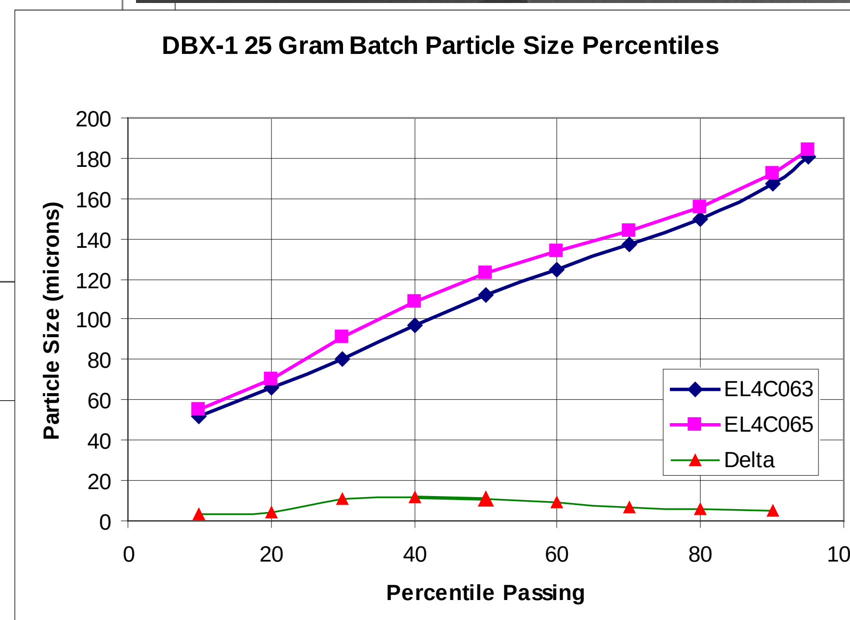


EL4C071 – 109 µm

Consistent Preparations of DBX-1 Lots at 25gm Level







Characteristic Bimodal Distribution

DSC (Peaks) – 336 C
Based on reproducibility, continue at 100g scale

Preparation of DBX-1 – 100gm Scale-up (20L)

Lot #	Water (mL) Total Volume (mL)	Yield gms/% DSC exo	Particle Size (mean) Sur. Area (M^2/g)
4C077 100 gm	8901 mL 11571 mL	95.5/58% 336°C	98 µm
4C079 100 gm	9325 mL 11690 mL	113/74% 336°C	101 µm 0.39
4C081 100 gm	9324 mL 11691 mL	118/77% 336°C	70 µm 0.36
4C083 100 gm	8594 mL 11690 mL	147/78% 336°C	104 µm 0.35
4C085 100 gm	8480 mL 11639 mL	129/68% 336°C	87 µm

Sept-Oct 2011

~1 eq. NaNT, various concentration

ascorbate addition rates varied

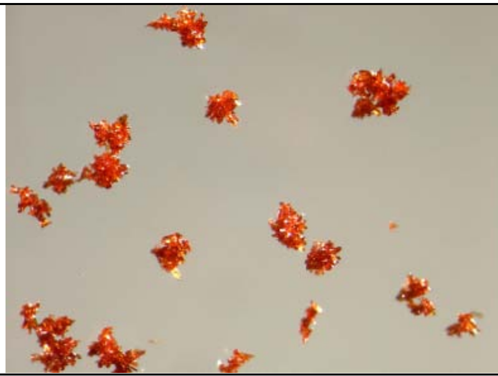
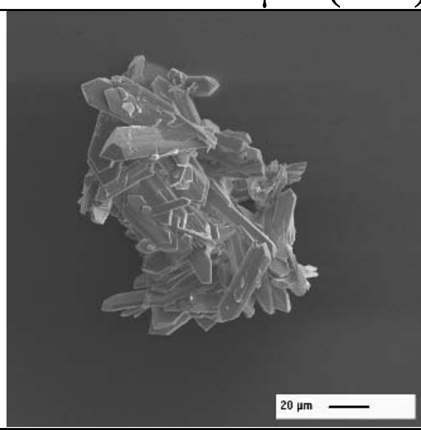
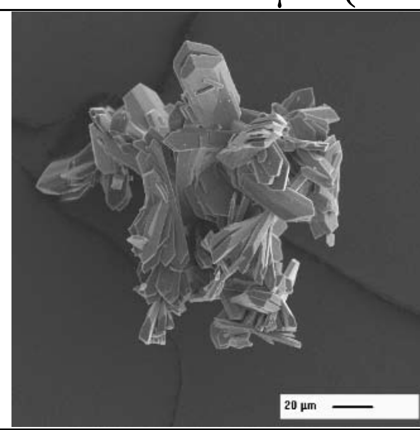
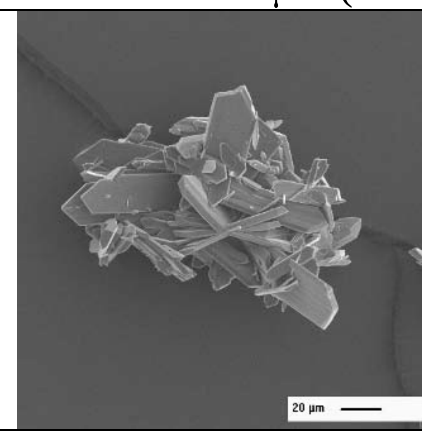
340-640 RPM

granulation times: 24-35 min.

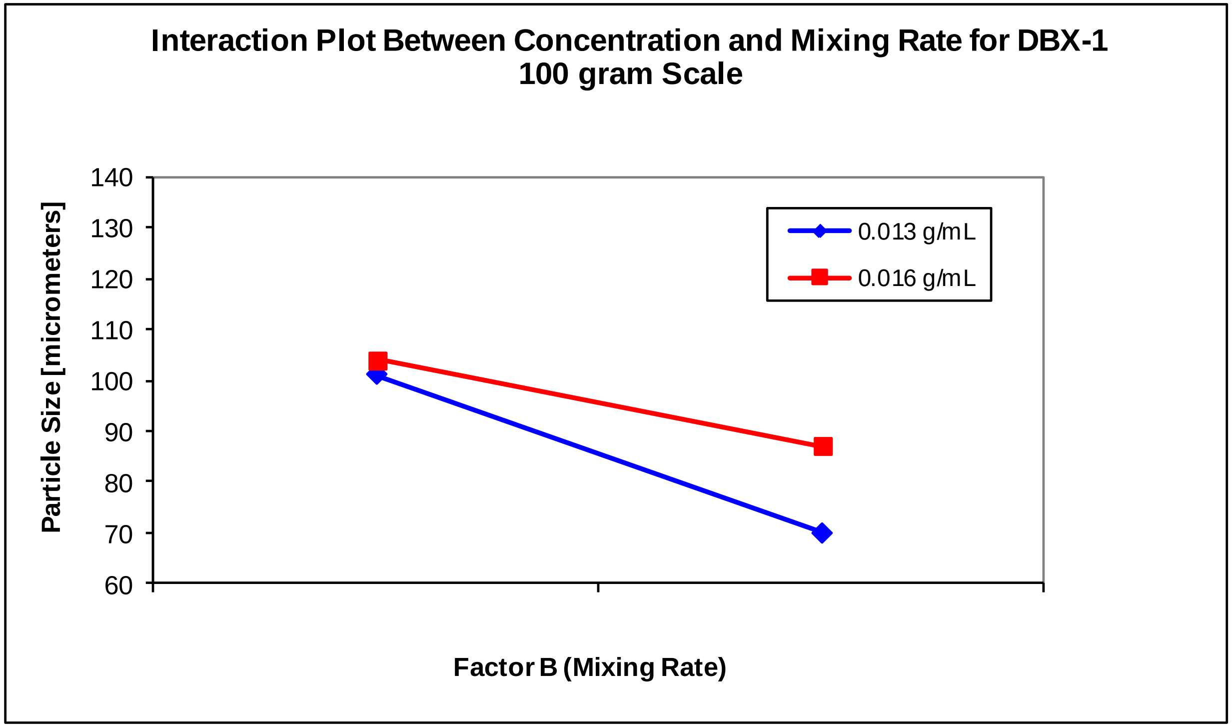
stirring rate, NaNT concentration, total volume modified to assess the effect on particle size with results as shown

100 gm scale takes longer than 25 gm scale due to the additional heating time required to get the mixture to 90 C.
Initial EL4C077 had an extended time to granulation minutes in un-seasoned reactor, subsequent reactions were seeded & had normal time to granulation of ~25 minutes.
Overall reaction time (or amount of time to run the DBX-1 synthesis once the reactants are at temperature) is less than 1 hour start to filter, even at the 100 gm scale

SEM & Photomicrographs of 100gm Batches

		
EL4C077 – 98 µm (77X)	EL4C079 – 101 µm (77X)	EL4C081 – 70 µm (77X)
		
EL4C077 – 98 µm (500X)	EL4C079 – 101 µm (500X)	EL4C081 – 70 µm (500X)

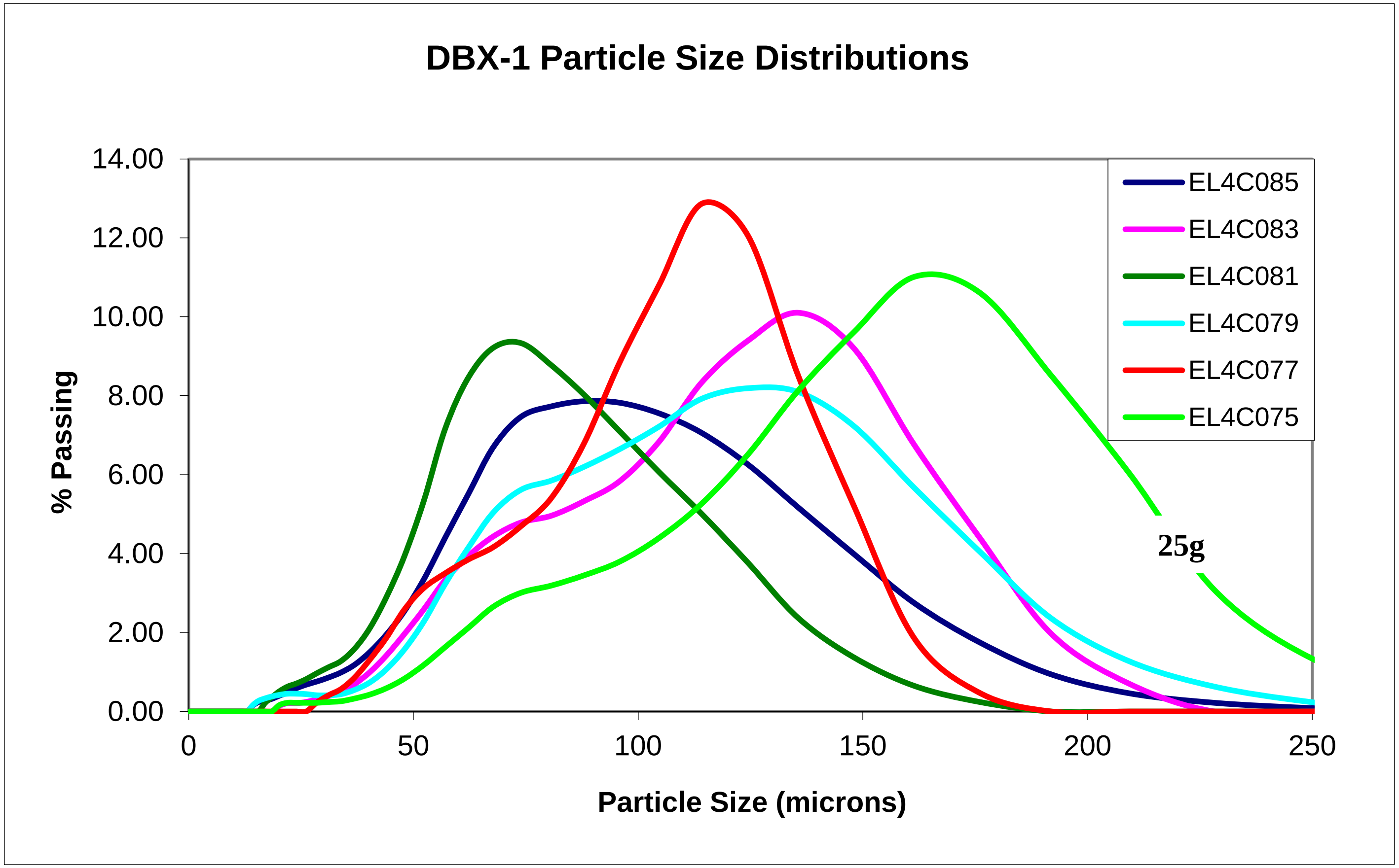
Particle Size Control – 100gm Scale-up (20L)



Particle size range of interest (60-140µm) versus stirring speed.
Line color shows effect of overall NaNT concentration on particle size.

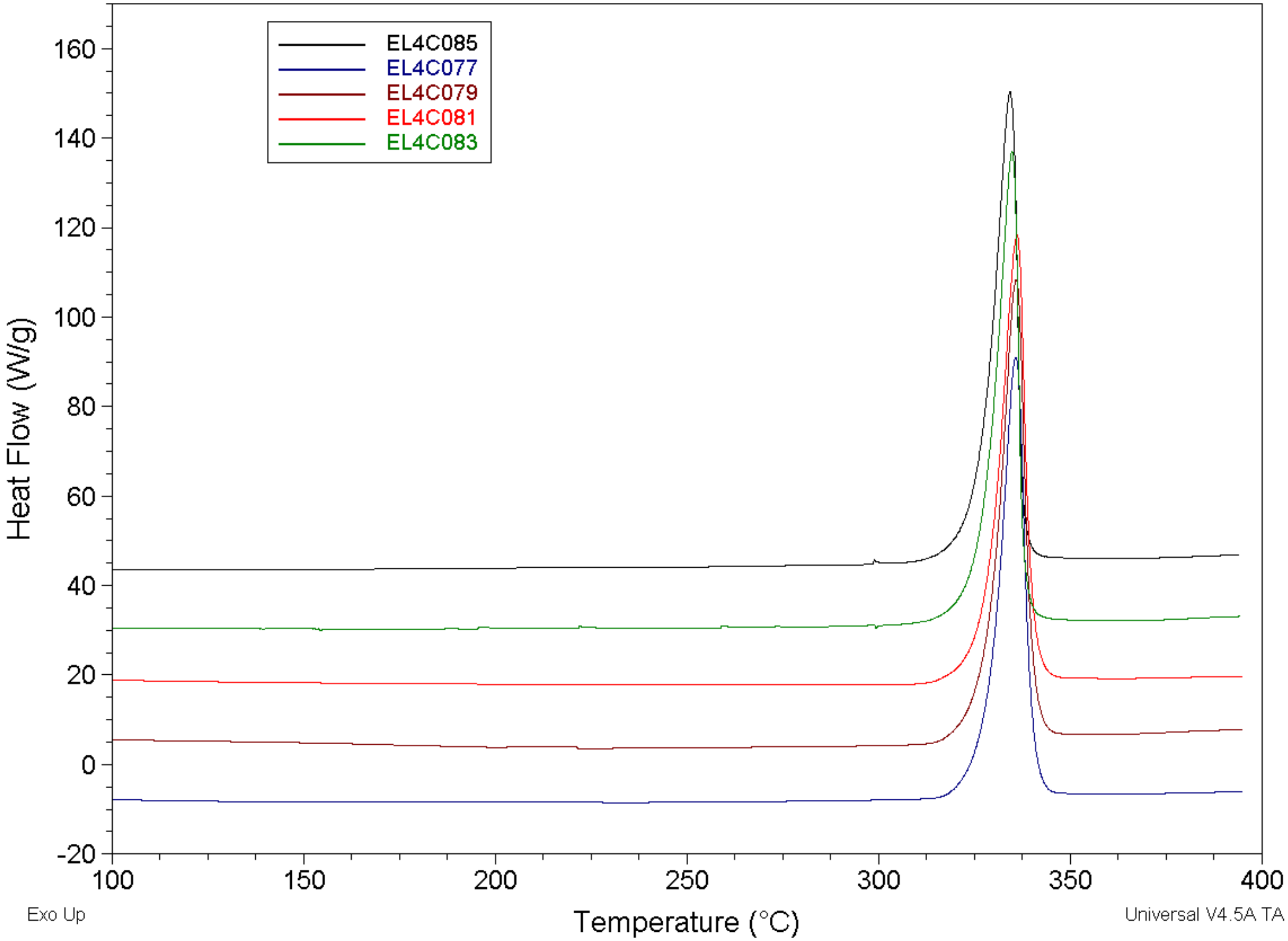
Either of these variables alone or in conjunction will afford control over particle size of the DBX-1 produced.

Particle Size/Distribution of 100gm Batches

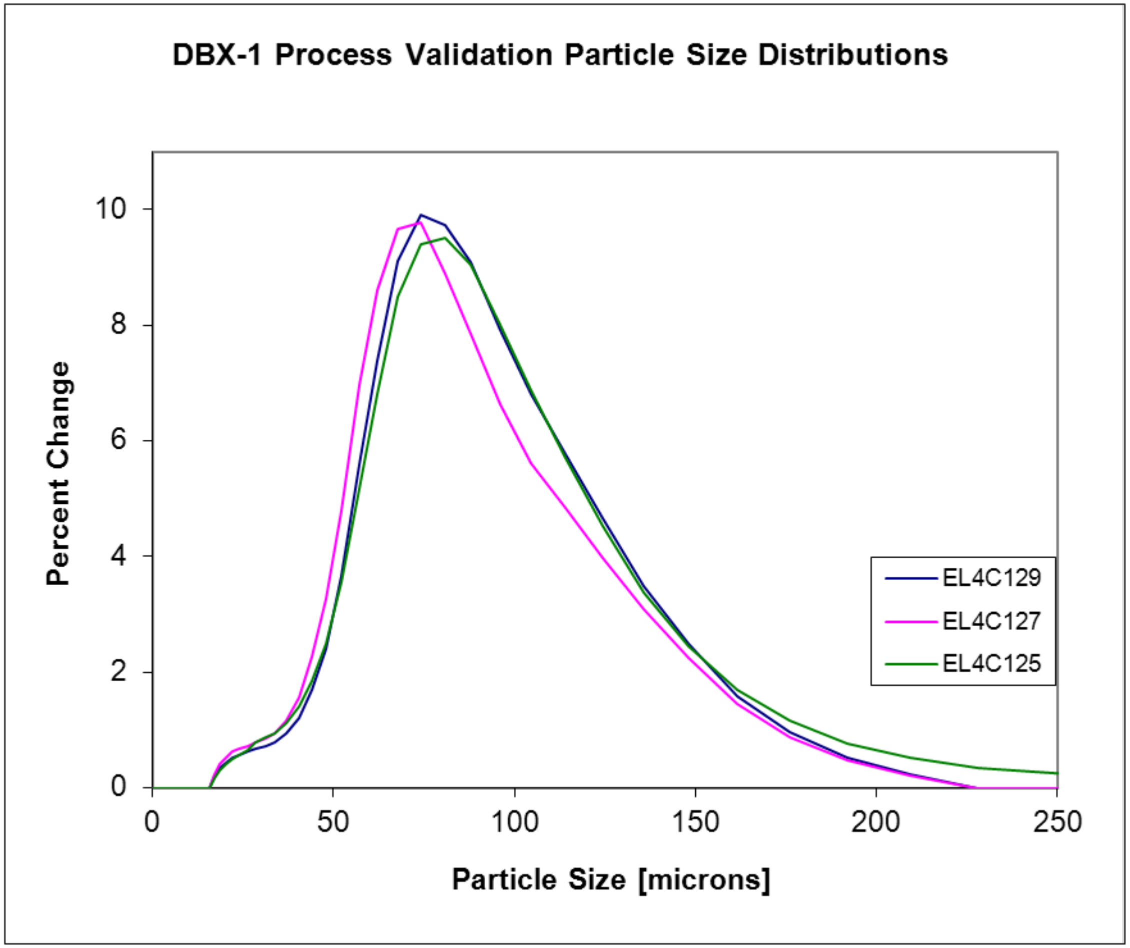


Moving from a bimodal distribution (light blue & light green) to a "normal" distribution. This gives lower *average* particle size

DBX-1 Characterization



Consistency of Process at 100g Level



Demonstrates control over particle size and distribution

Demilitarization/Decomposition Studies on DBX-1

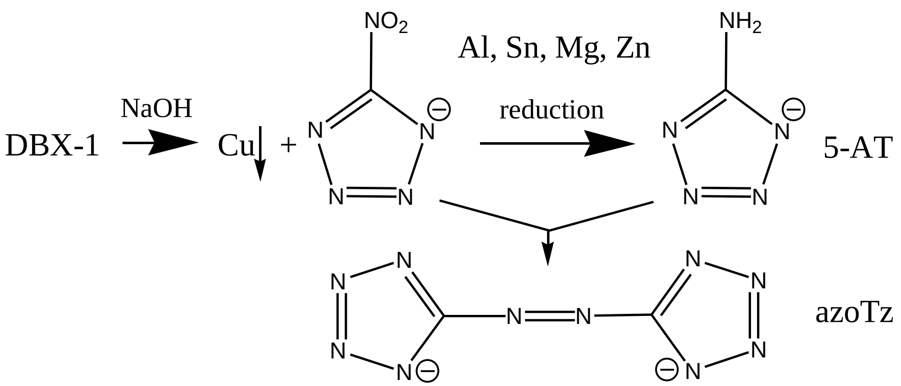
PSEMC has been assessing a variety of methods for disposal of DBX-1 utilizing a number of procedures.

NaNT:
Treatment of DBX-1 with 10% sodium hydroxide decomposes the DBX-1 into an inert copper containing solid (oxide) and the sodium 5-nitrotetrazolate (NaNT) starting material which may be recovered.

Decomposition to inert materials:
Treatment of DBX-1 with 5N HCl and (inexpensive) granular Zn metal further reduces the NaNT to inert 5-aminotetrazole and successfully reduces any of the azotetrazole formed during the process (to 5-AT)

Currently getting > 1:1000 NaNT:5-AT with NO azotetrazole, works under cold & hot conditions

Dissolving DBX-1:
DBX-1 is very insoluble under most conditions.
Treatment with aqueous sodium thiosulfate reacts with the Cu(I) and leaves the NT in solution.
(photographic fixer, binds soft metals)
May suggest a recrystallization method



Primary analysis in solution by Raman spectroscopy
Secondary analyses HPLC, ion chromatography, FTIR and DSC.

DBX-1 ManTech

PSEMC has completed Compound Qualification Testing per NAVSEAINST 8020.5C – (J. Laib input)
DBX-1 data pack forwarded to NSWC-IH for submission to NAVSEA Systems Command for Military qualification

Current Program Complete Nov12

- **Performance testing on 100g level samples**
- **Safety**
- **Output**
  - **Strong confinement**
  - **202 Detonator**
- **Additional compatibility studies**
- **Additional test at NSWC-IH & elsewhere**
- **Final Specification (Preliminary Specification complete)**

Current Studies using DBX-1

Completed Testing:

Prepare PSEMC 104477-202 detonators with LA (DLA) and DBX-1 transfer charges for comparison
successful: DBX-1 functions faster and with a greater output "dent" at -65 F, 200 F and ambient

Prepare NOL-130 primer mix with both DLA and DBX-1 and perform side by side safety tests
Alex Woods, NSWC-IH – successful: replaced RD1333 in Mk125-1 Stab primer in both NOL-130 & output
NOL-130 to DBX-130: > output; RD1333 to DBX (same volume): > output
Sensitivity data for NOL-130 vs. DBX-130 (impact, friction, etc.)

Preliminary Tests with the 2-Piece Stab Detonator
Stu Olson, Stresau – successfully utilized DBX-1 as a "drop-in" replacement for RD-1333
same loading pressure, same height, NOL-130 unchanged – 89 dets from 2 lots, 88 normal

Current Testing:

PSEMC – Chandler - JL42 Firex Cartridge (~120g)
PSEMC – Hollister - ZY56 Drogue Severance Assembly (~60g)
Stresau – 2-Piece Det. then to General Dynamics - Army (~100g)
NSWC-IH – J. Laib for additional qualification tests (~95g)
Action Manufacturing – M100 Detonators – S. Marino
ARDEC – M55 Detonators – N. Mehta, G. Cheng
Army Institute of Public Health – Toxicity – William Eck

Nalas Engineering – synthesis, seeding studies, NaNT
NSWC-IH – synthesis (T. Ricks)
ARDEC – synthesis (N. Mehta, K. Oyler)

NaNT Microreactor

PSEMC/I2Chem/MIT Microreactor

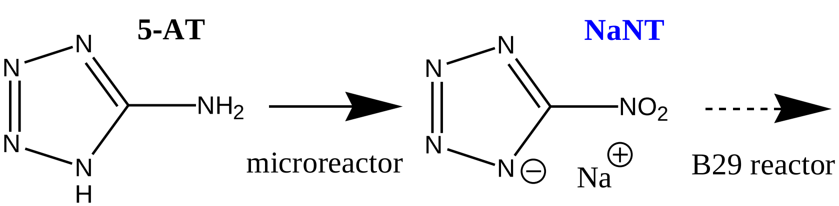
The PSEMC/I2Chem/MIT NaNT microreactor system **continuously converts 5-AT to NaNT** which is the starting material for DBX-1 and BNCP.

Benefits over current batch process:
- **Safety:** minute quantities of unstable intermediates, safe aqueous solvent system
- **Quality:** fast heat and mass transfer rates means no lot variability
- **Efficiency:** computer monitored and autonomous

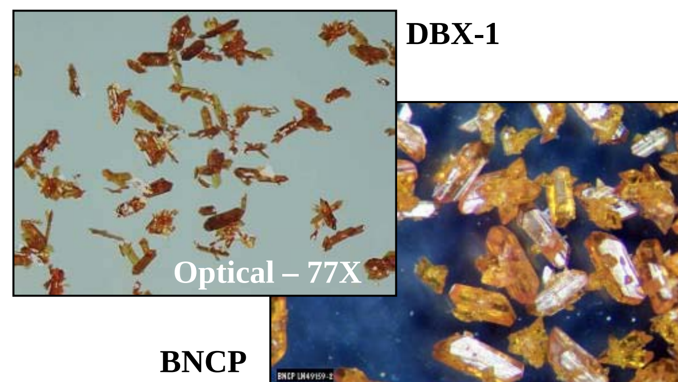
I2Chem delivered 2 systems to PSEMC

Expect production of NaNT from 1 reactor line to be **~20 gms/hr** minimum continuous

Scale-out (add more reactor lines) to increase capability to meet needs



Used in BNCP DBX-1



DBX-1

BNCP

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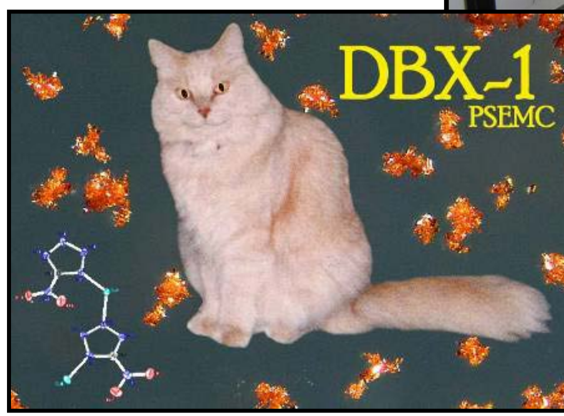

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