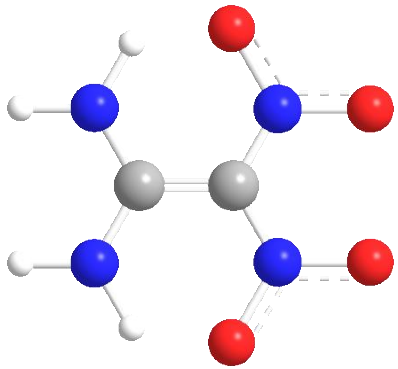
National Defense Industrial Association Insensitive Munitions Energetic Materials Technology Symposium

24 April 2018



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Funding provided by
Joint Insensitive Munitions Technology Program (JIMTP)

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❖ Develop a Continental United States (CONUS) manufacturing capability for FOX-7

❖ Demonstrate the capability to produce all 4 classes of FOX-7 currently available from EURENCO Bofors with equivalent purity/quality

EURENCO offers 4 different classes of DADNE (FOX-7) with different crystal sizes:

o Class 1: 20 – 40 µm

o Class 2: 50 – 100 µm

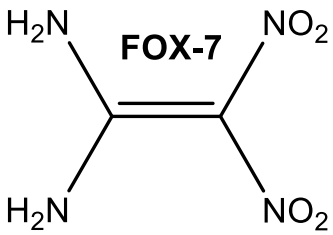
o Class 3: 100 – 200 µm

o Class 4: 250 – 300 µm

EURENCO Bofors FOX-7

- 1,1-Diamino-2,2-dinitroethene (FOX-7) is an energetic material developed by FOI Sweden in the late 1990s as an insensitive RDX replacement

- Technology was then transferred to NEXPLO Bofors AB (now EURENCO Bofors AB) for pilot/production scale manufacture



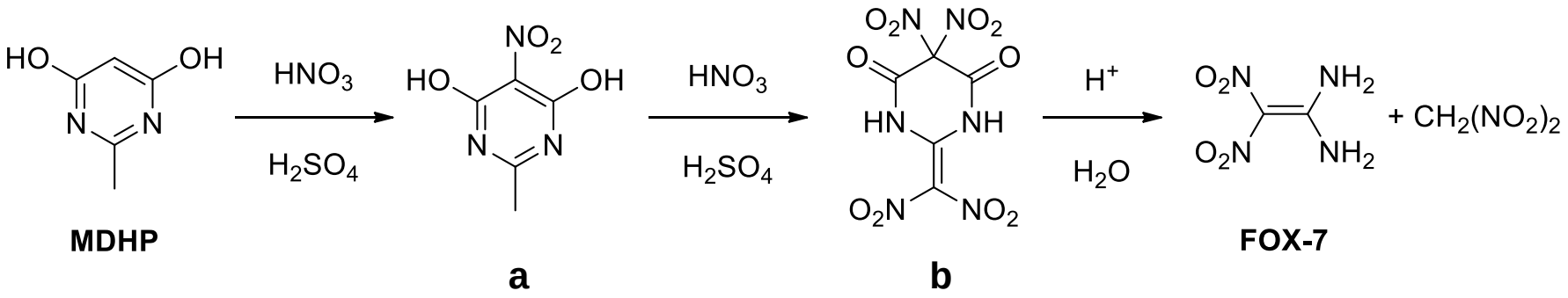
2,2-dinitroethene-1,1-diamine

Chemical Formula: $C_2H_4N_4O_4$

Exact Mass: 148.02

Appearance	Yellow crystals
Drop weight sensitivity	20-40 J (RDX 4-5J)
Friction sensitivity	> 350 N (RDX 120 N)
Small Scale Gap Test at 1.63 g/ml	6.22 mm (RDX 9.33 mm, HMX 10.3 mm, TNT 6.4 mm)
ESD	> 8 J (HMX 0.2 J)
Detonation velocity	8800 m/s
Density	1.885 (crystal)
Purity HPLC	> 99%
Vacuum stability	0.1 – 0.4 ml/g,h at 120^0C
Measured detonation pressure	34 GPa (RDX 35 GPa).
Appearance	Yellow crystals

Synthesis



MDHP **a** **b** **FOX-7**

Mixed acid nitration conducted at 10-30°C

- **"b" is insoluble in mixed acid**

Resultant slurry was poured into ice water

Delayed foaming (dinitromethane decomposition) and NOx generation

For larger scales, slurry will be dose-quenched into warm/hot water

Scale Up Protocol

Round-bottomed flask or MT EasyMax

- 5 gram theoretical yield
  - Small scale safety data
    - Impact, friction, ESD, DSC
  - Reproducibility & yield

- 20 gram theoretical yield
  - Small scale safety data
    - Impact, friction, ESD, DSC
  - Reproducibility & yield
  - Recrystallization
    - SEM & PSD

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Differential Scanning Calorimetry

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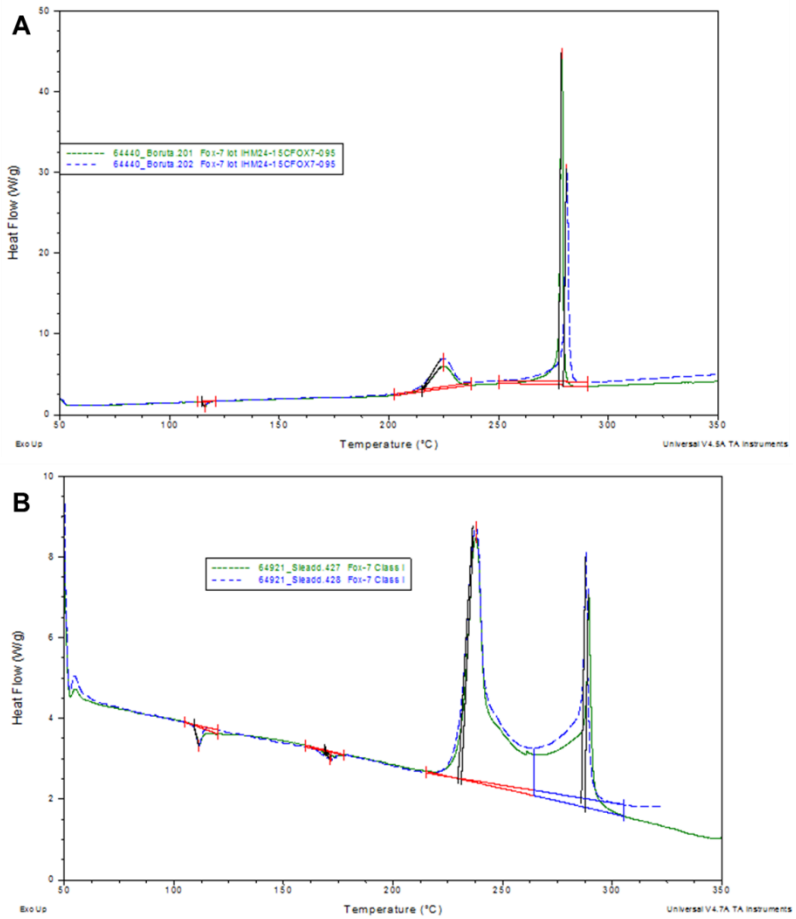
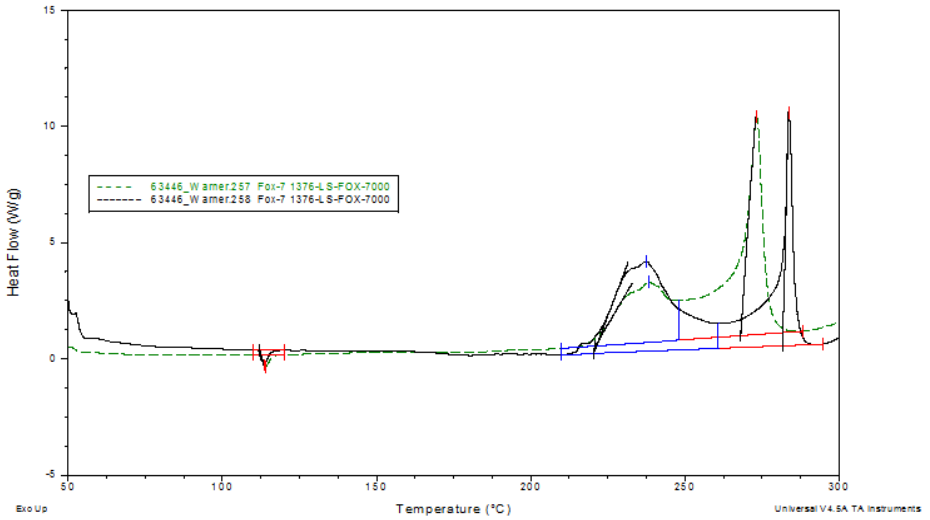


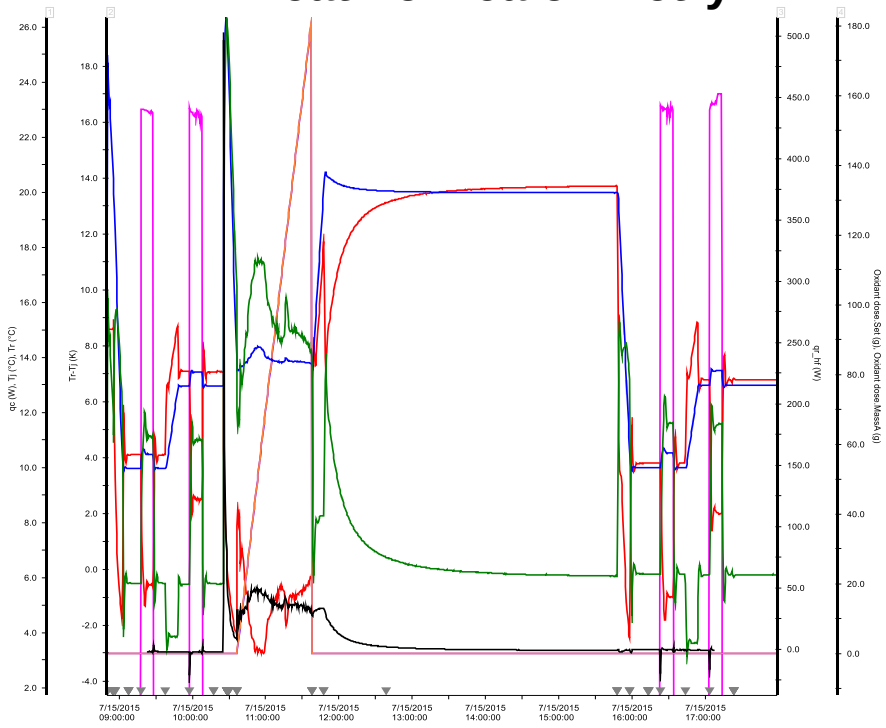
Selected DSC traces of NSWC IHEODTD FOX-7: 5g recrystallized batches. A) FOX-7 recrystallized from hot water at IHEODTD. B) FOX-7 recrystallized from NMP/water at IHEODTD



DSC trace of EURENCO Bofors FOX-7

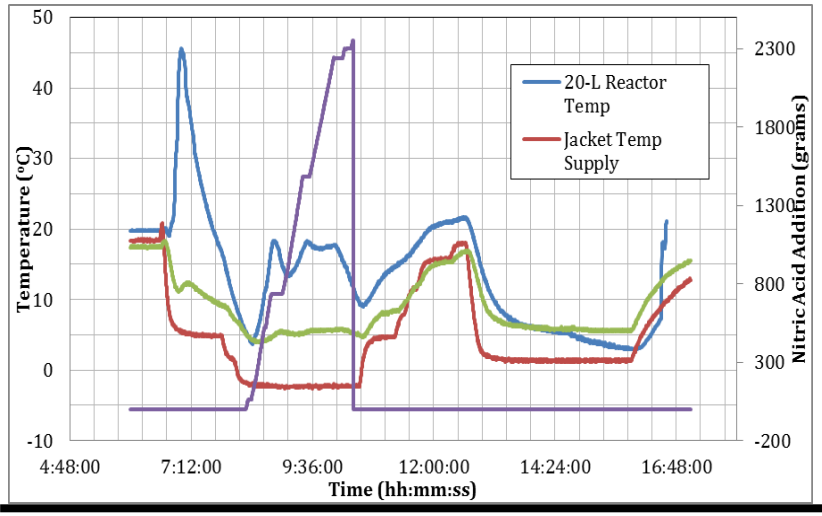
Mettler Toledo RC1e Reaction Calorimeter

- 100 gram theoretical yield
  - Small scale safety data
    - Impact, friction, ESD, DSC
  - Reproducibility & yield
  - Recrystallization
    - SEM & PSD
  - **Heat flow calorimetry**

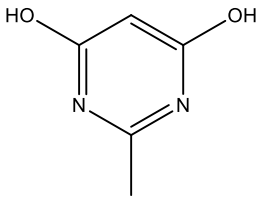


Scale Up: Nitration

1 kg theoretical yield



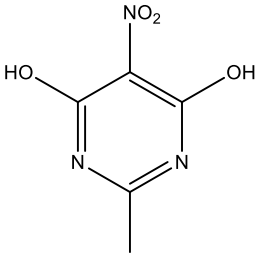
Chemical Formula: $C_5H_6N_2O_2$
Exact Mass: 126.04



1

HNO_3
H_2SO_4

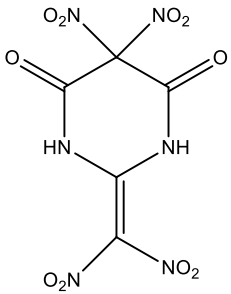
Chemical Formula: $C_5H_5N_3O_4$
Exact Mass: 171.03



2

HNO_3
H_2SO_4

Chemical Formula: $C_5H_2N_6O_{10}$
Exact Mass: 305.98

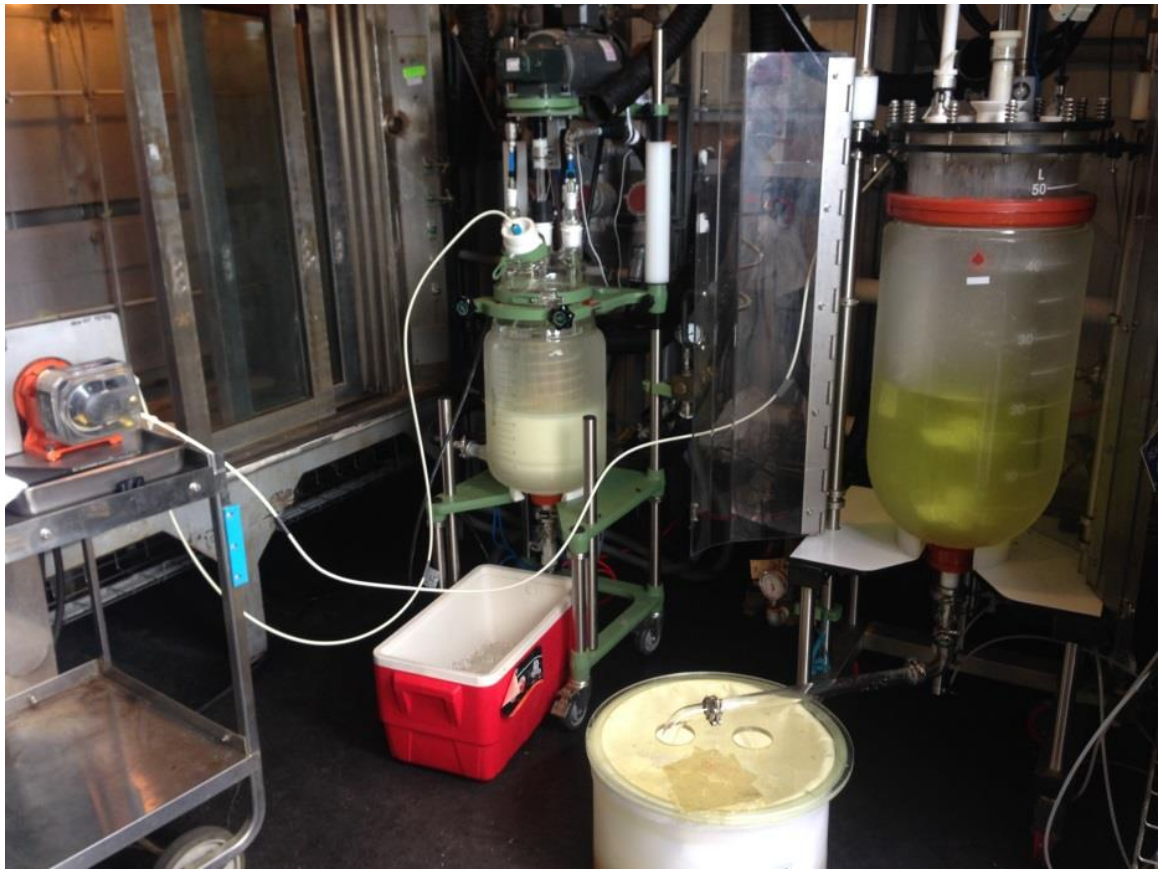


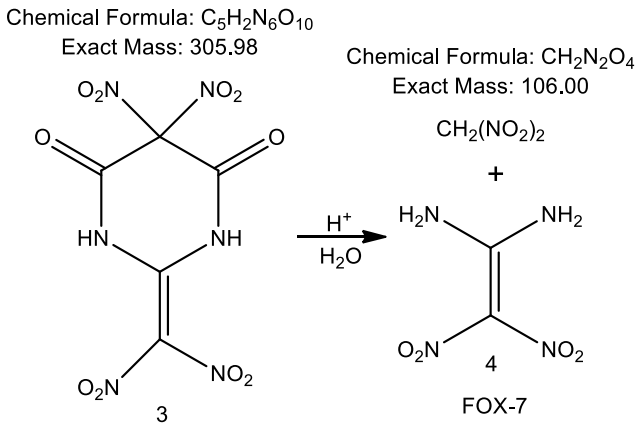
3

Solids mass increase x 2.4

Scale Up: Nitration & Quench

Solids mass decrease x 2.9





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Scale Up: Quench

Nitration mixture is pumped into warm water

Yields typically ~70%

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Scale Up: Nitration

2 kg theoretical yield

Solids mass increase x 2.4!

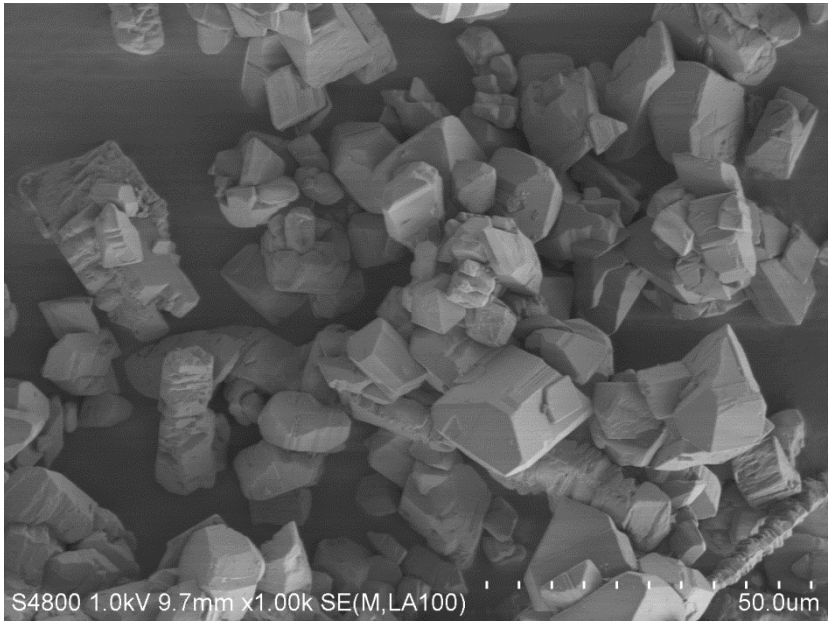
Scale Up: Nitration

Subsequent batches were limited to 1.5 kg
Second “upper” impeller was installed on agitator shaft

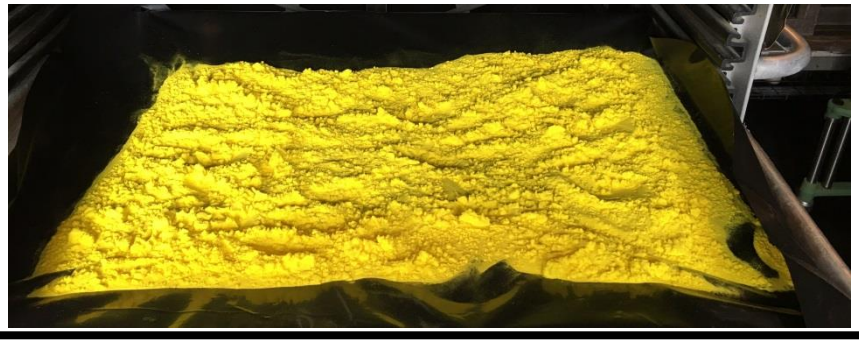
Recrystallization

2 L Scale; RC1

All four classes were obtained
At the 2 L scale



Recrystallization



2 kg scale

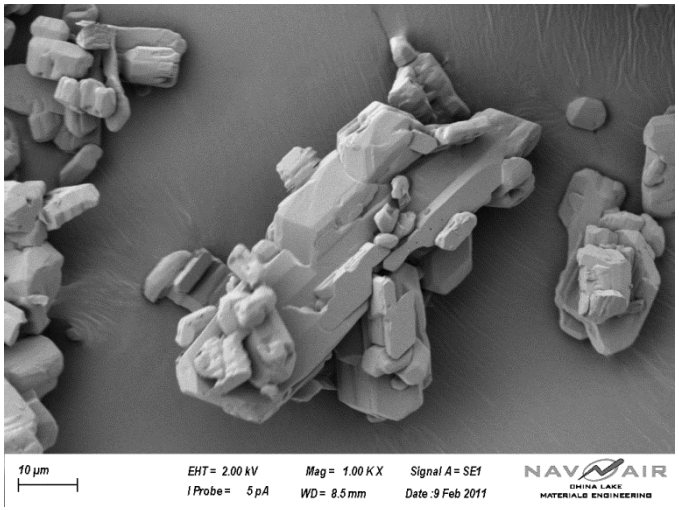
Recovery typically >80%

Recrystallization

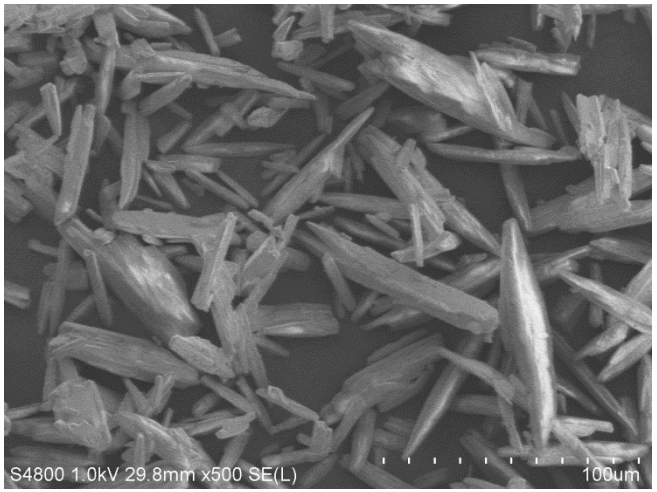
Recrystallization parameters did not scale!
Conditions that worked at the 2 L scale
Did not work at the 50 L scale (not surprising)

Class I: 20-40 µm

EURENCO Bofors Class I

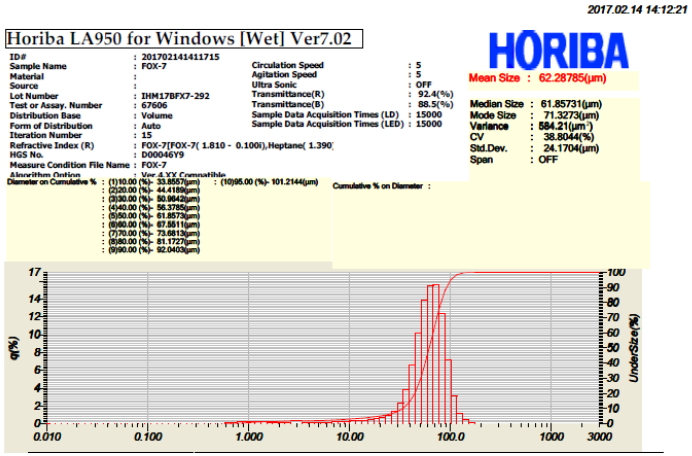


CONUS Class I (bad solvent)

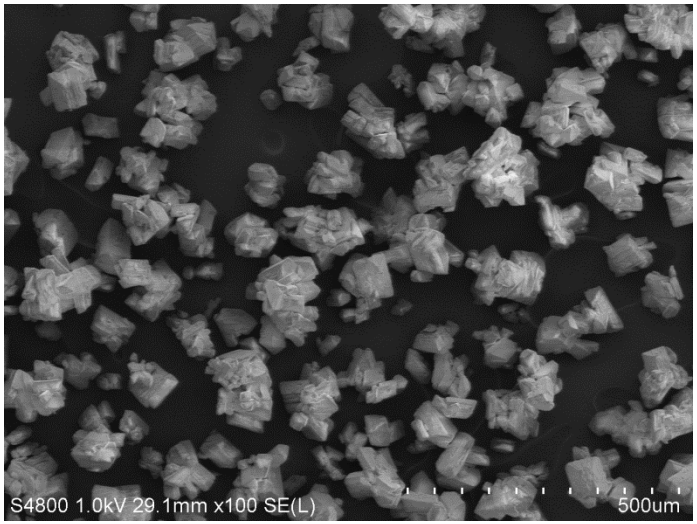


Recrystallization
CONUS FOX-7

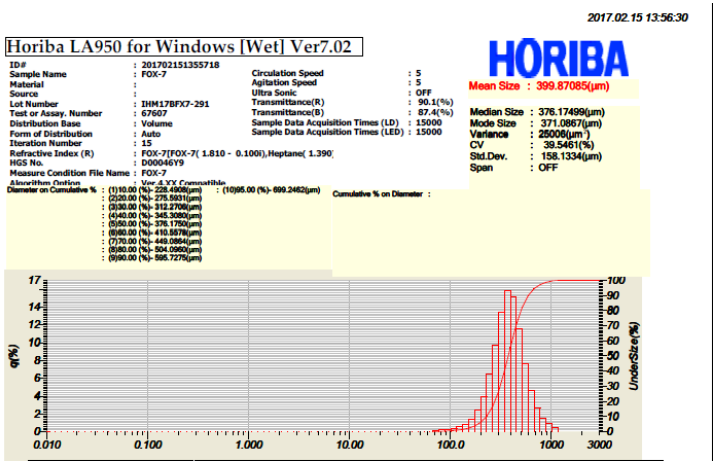
Class I; too large!



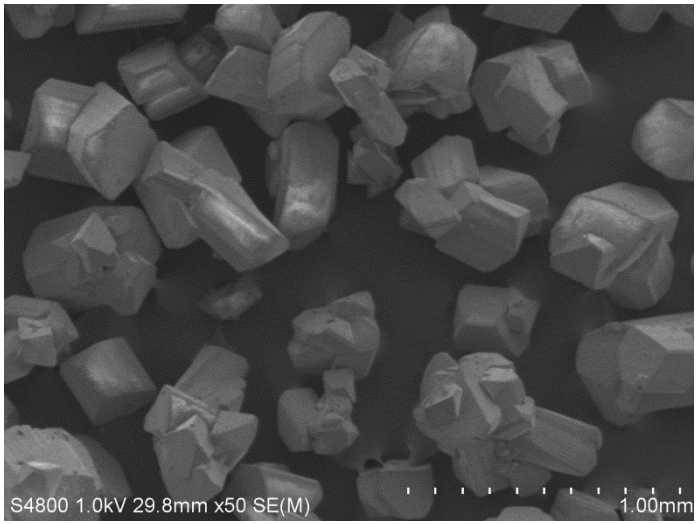
62 µm



Class IV; too large!

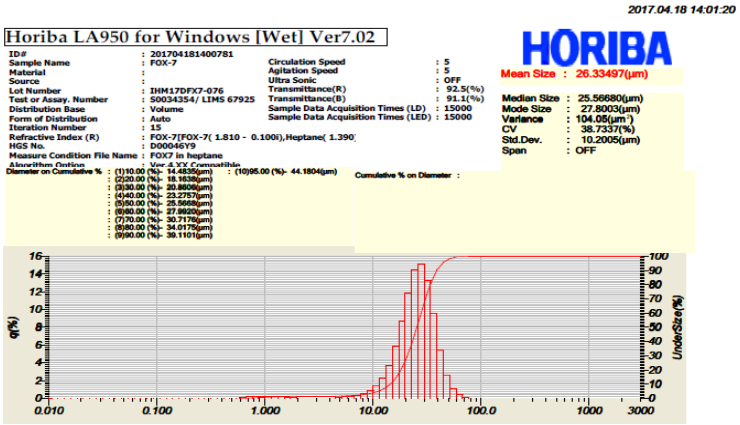


399 µm

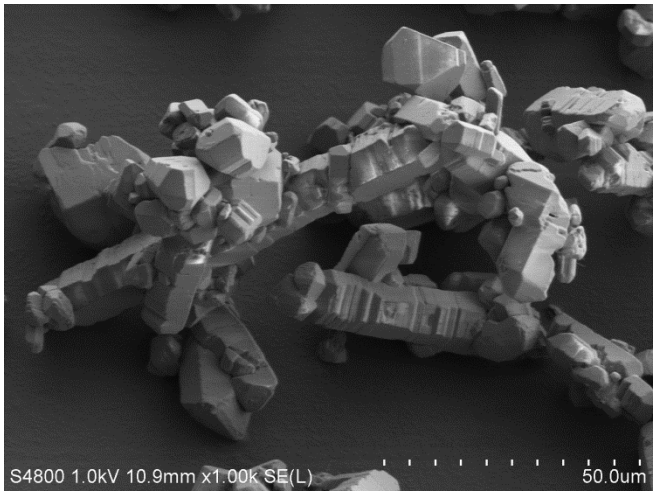


Recrystallization
CONUS FOX-7

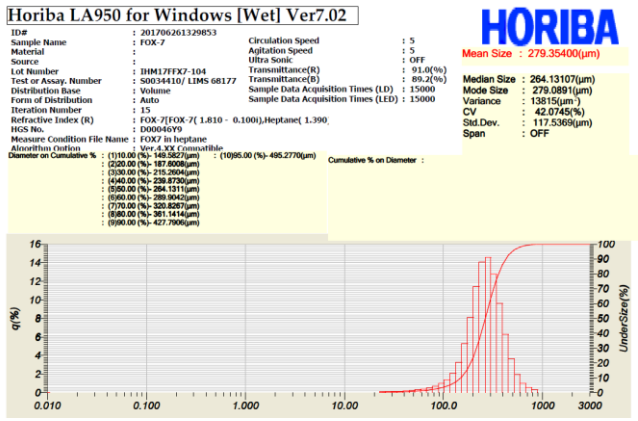
Class I



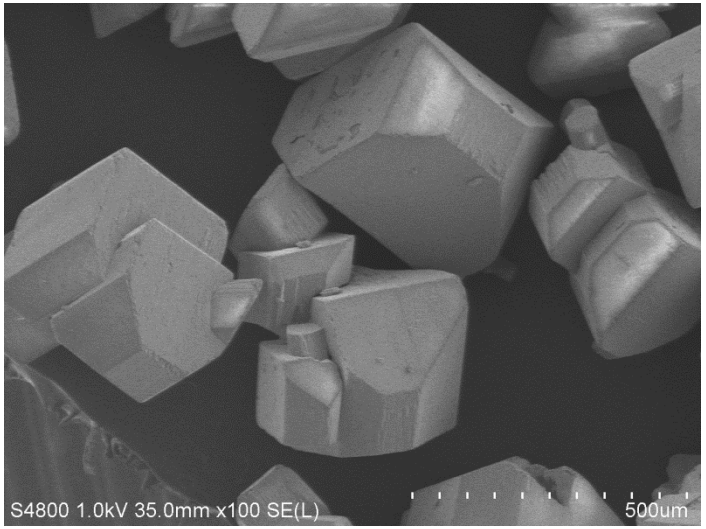
27 µm



Class IV



279 µm



Safety and Thermal Analysis CONUS Round-Robin Testing

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➢ Machine and Method

- **ERL Impact:**
  - ✓ Type 12 Tooling
  - ✓ Mass of drop weight: 2.5kg
  - ✓ Mass of Striker: 520-540gm
  - ✓ 180A Garnet Paper

- **ESD:** SMS Equipment (ARDEC CL), ABL (IH)
  - ✓ Verify Ohm value of in-line resistor
  - ✓ Needle distance-position approximate 0.0020” Hold voltage at 5.785Kv
  - ✓ Run using IH intervals – start at 0.326joules

- **ABL Friction:** SMS Equipment
  - ✓ Wheels and Plates – verify hardness finish use hardened steel ≅ 60microinch
  - ✓ Pressure Gauge Calibration – verify calibration is valid

- **BAM Friction:**
  - ✓ Wheels and Plates – verify hardness finish (new wheels and plates)
  - ✓ Pressure Gauge Calibration – verify calibration is valid

➢ Methods Stipulation:

1. All test masses will be 35mgs ± 2
2. All tests to proceed with ‘lights off’ for observational effect
3. Testing to proceed at 45-55% relative humidity or as close to it as possible - note Hr and T
4. DSC to be run at 5°C/min per ASTM E3537
5. All sites use the older hemetic aluminum pans, closed pan vented

➢ Data Analysis

- ✓ Provide both Bruceton 50% and 20 TIL
- ✓ Provide description of reaction (sparks, pop, fire, consumption, smell) in comments section

Safety and Thermal Analysis CONUS Round-Robin Testing

Site	Sample Lot# Class	Impact (cm)			Friction		ESD (joules)			DSC (°C)
		50%	Low	TiL	ABL (lbf)	BAM (N)	50%	Low	TiL	
Indian Head	IHM170FX7-076 I	*55	51	32	708 (50%)	10/10 NF 216	TBD	0.095	0.037	Doublet 231,282
	IHM17FFX7-104 IV	*46	41	26	20/20 NF 1000	10/10 NF 216	TBD	0.095	0.037	Doublet 228, 282
Picatinny	IHM170FX7-076 I	**79	79	63	20/20 NF @ 1800	10/10 NF 324	TBD	0.095	0.037	Doublet 232, 261
	IHM17FFX7-104 IV	*71	63	32	20/20 NF @ 1800	10/10 NF 360	TBD	0.095	0.037	Doublet 232, 260
China Lake	IHM170FX7-076 I	**71	63	50	20/20 NF @ 1000	10/10 NF 360	8.37	3.80	1.50	Doublet 231, 289
	IHM17FFX7-104 IV	**51	40	32	20/20 NF @ 1000	10/10 NF 360	20/20 NF @ 8.0			Doublet 228, 288

*50% point via Bruceton Method
** 50% point determined by Probit or Modified Bruceton Method

- Analysis:
  - ✓ ERL Impact – IH values tend to trend lower, CL and ARDEC fairly similar
  - ✓ ABL Friction – only IH Class I was observed to be lower than other sites
  - ✓ BAM Friction – IH observations were a couple of logs lower, CL/ARDEC nearly the same
  - ✓ ESD – IH and ARDEC same results, CL significantly different in observations (magnitudes)???
    - ➢ ***ESD differences are likely due to the 'interpretation' of the description of a fire found in AOP-7 edition 2, not the method or machinery. Under NAWC method a fire consists of 'flash, spark, burn, odor, or noise other than instrument noise'***

Safety and Thermal Analysis OCONUS vs. CONUS

Test	Class I		Class IV	
	OCONUS	CONUS	OCONUS	CONUS
ERL Impact (cm) (50%/LF/TiL)	60/40/20	71/63/50	34/32/13	51/40/32
ABL Friction (lbf)	20/20 NF 1000	20/20 NF 1000	20/20 NF 1000	20/20 NF 1000
BAM Friction (N)	10/10 NF 360	10/10 NF 360	288	10/10 NF 360
*ESD (joules) (50%/LF/TiL)	> 8.0/3.80/1.50	8.37/3.80/1.50	> 8.0	> 8.0
DSC (°C)	228, 286	231, 289	228, 286	228, 288

- Analysis:
  - ✓ ERL Impact – Recent CONUS values appear to be slightly higher than the 'as received' OCONUS material but follow the general trend of Class I less sensitive to impact than the larger Class IV material – in general fairly good correlation.
  - ✓ ABL Friction – Both CONUS and OCONUS tested out at the same level with no friction sensitivity up to 1000 pound of applied force.
  - ✓ BAM Friction – All but the OCONUS Class IV tested out to no initiation (fires) up to 360 newtons of force.
  - ✓ ESD – All materials tested to no ignition to spark at 0.25joules of energy

    * The ESD testing used the NAWC method and description called out in AOP-7 edition 2. As noted prior site differences are likely due to the 'interpretation' of the description of a fire per the NAWC method.

Conclusions

A CONUS Manufacturing Capability for FOX-7 has been developed
Need to optimize nitration for larger scales

- Eliminate “yogurt” formation

Recrystallization to match EURENCO classes eventually successful

- Trial and error for conditions when changing scale and equipment

ROM cost estimate at this scale is inadvisable

- Economy of scale not yet realized for MDHP
- Economy of scale not yet realized for nitration/quench
- Economy of scale not yet realized for recrystallization

Acknowledgments

Joint Insensitive Munitions Technology Program (JIMTP)
- Anthony DiStasio, Program Manager
- Jen Duchow, MATG III

JIMTP Task 14-2-68
- Joey Clubb, NAWC WD, Principal Investigator
- Philip Samuels, ARDEC, Co-Investigator

Navy Energetics Manufacturing Technology Center (EMTC)
- Chuck Painter, Director

NSWC IHEODTD Chemicals Development & Manufacturing Branch
- M24; Chemical Scale-up Group;

- Scientists, engineers and analysts at ARDEC, NAWC WD and NSWC IHEODTD for Round Robin testing

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QUESTIONS?