Bradley Sleadd

Synthesis and Scale-up of *Sym*-Triaminotrinitrobenzene at Holston Army Ammunition Plant

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BAE Systems
Holston Army Ammunition Plant

Acknowledgments

- Ed LeClaire - Agile Plant Mgr. & Process Development
- G-10 Staff – Flawless Manufacturing Scale-Up
- Lisa Hale – Process & Analytical Support
- Jim Owens – Analytical Method Development & Support

Holston TATB Goals

- Low Cost/High Volume Supplier
- Equivalent Quality
- Inclusion in Many New IM Formulations
- Good Fit for Existing Holston Infrastructure
- Minimal Initial Capitalization
- Short Time to Production Quantities

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Available Technologies

- Traditional Trichlorobenzene (TCB) Route
  - Harsh conditions; waste streams
  - TCB not domestically available
- Phloroglucinol Route
  - Not a good fit for Holston infrastructure
  - Highly sensitive process intermediate
- Vicarious Nucleophilic Substitution Route
  - Not a good fit for Holston infrastructure
  - Starting materials not readily available

Holston TATB Synthesis Method

- Based on Chemistry Developed by Benziger and Ott
- New Process/Synthesis Route Developed by OSI Scientists
- Readily Scalable on the Holston Infrastructure
- Good Fit for Agile Manufacturing Plant (G-10)
- Multiple Sources Identified for Raw Materials
  - Including CONUS

Holston TATB

- Chemistry Demonstrated on Laboratory Scale
  - Two step process
  - Process optimization on-going
  - Several lab batches ranging from 0.1 mole to 15 mole scale
    - ≈ 3 lbs. TATB product from largest lab batch
  - Typical yields around 85 – 90%
  - Purity comparable to reference (Bridgwater)
  - Particle size typically 5-10 microns

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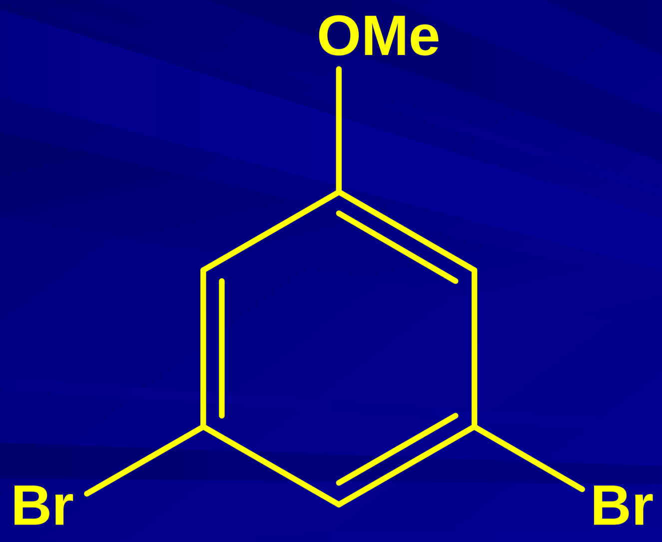
Holston Starting Material

- 3,5-Dibromoanisole
- Solid material at Room Temperature
- Melting Point 34℃
- High Purity Material Available from Multiple Sources



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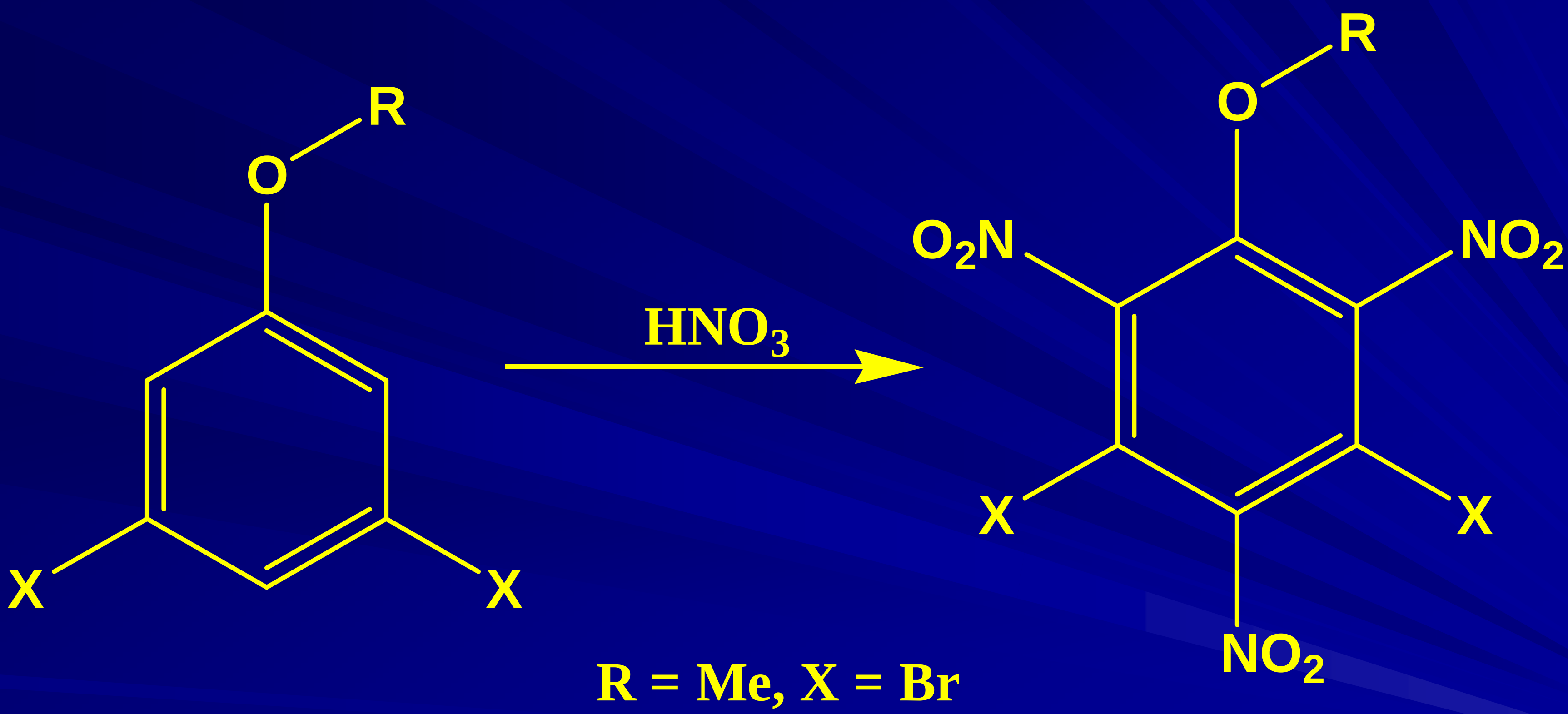
Nitration of 3,5-Dibromoanisole



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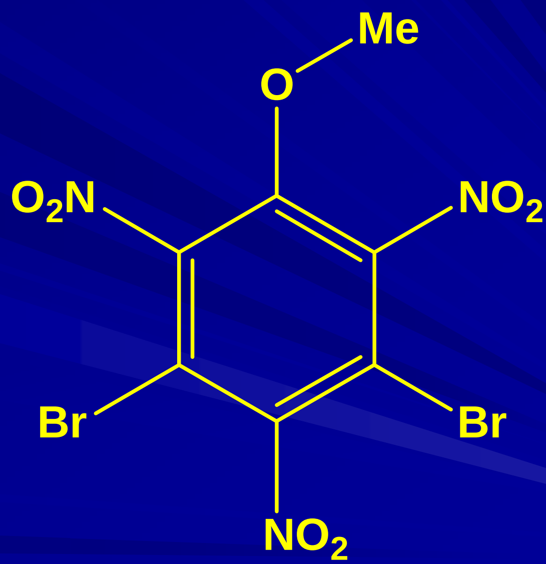
Laboratory Nitration of 3,5-Dibromoanisole (DBA)

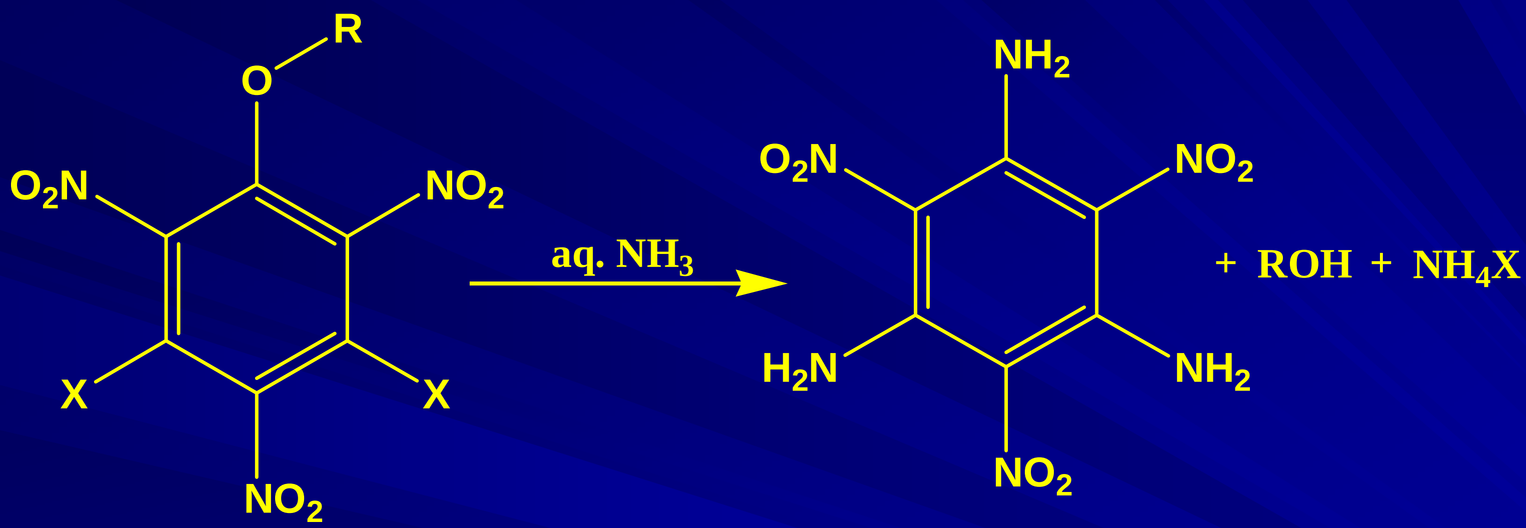
- 3,5-Dibromoanisole is Melted and Fed as a Liquid into 98% Nitric Acid at or Below 50℃
- Initial Reaction is Mildly Exothermic
- Reaction is Complete in 4-5 hrs. at Reflux, or 24 hrs. at Ambient Temperature
- Yield is Essentially Quantitative
- This Step has been Scaled to 5 Gallon Reactor Yielding ~5 – 6 kg of Product

3,5-Dibromo-2,4,6-trinitroanisole (DBTNA)

- Insensitive Intermediate
- Melting Point = 140°C
- Exotherm Onset = 288°C
- Impact Sensitivity > 80 cm (Holston Method)



Conversion of DBTNA to TATB



R = Me; X = Br

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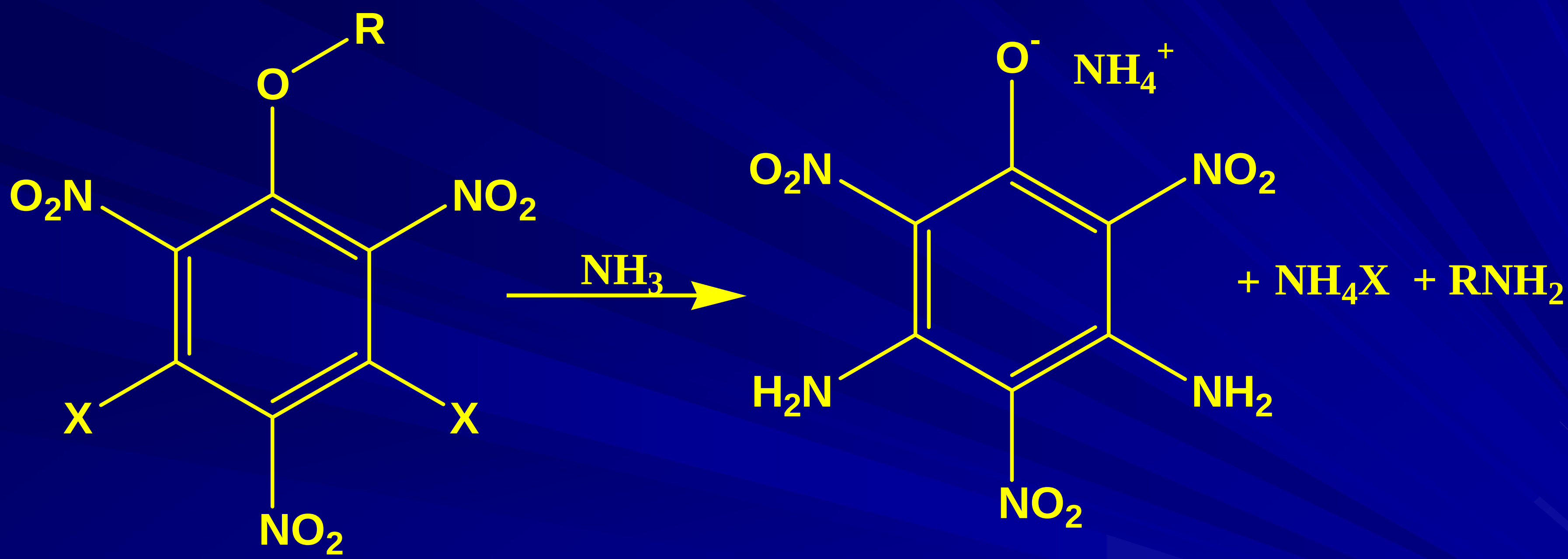
Laboratory Ammonolysis of DBTNA

- DBTNA is Slurried in Aqueous Ammonia
- Reaction Occurs Over 36 hours at 25℃
- Main By-Product is NH_4Br
- Known Impurities
  - Ammonium diaminopicrate (ADAP)
  - Starting material - DBTNA
- Reaction Scaled to 3 moles
- Yields are ~ 90%

Formation of Ammonium Diaminopicrate (ADAP)



R = Me; X = Br

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Selected Analytical Results

Sample ID	purity (%)	total X% (as Cl)	C% (27.92)	H% (2.34)	N% (32.55)	ADAP (%)	DBTNA (%)
Method	a	c	d	d	d	b	b
1037-101-3	99.1	0.38	27.78	2.43	31.59	0.74	0.19
1037-101-4	99.5	0.67	27.81	2.37	31.51	0.50	0.19
1037-101-5	99.9	0.57	27.73	2.42	31.54	0.44	0.26
1037-101-6	98.6	0.53	27.74	2.45	31.53	0.99	0.26
1037-101-7	99.0	0.50	27.70	2.42	31.55	0.47	0.25
1037-101-8	99.2	0.47	27.71	2.46	31.48	0.50	0.22
AE603	99.1	0.02	29.18	2.43	31.18	0.60	0.00
Bridgwater	99.9	0.19	28.14	2.31	31.98	0.00	0.00

Particle Size and Thermal Data

Sample ID	purity (%)	DSC (10°C/min.) onset/peak	mean particle size (μm)
1037-101-3	99.1	356.3/366.5	
1037-101-4	99.5	358.3/364.3	
1037-101-5	99.9	357.4/368.0	5.24
1037-101-6	98.6	355.8/366.9	
1037-101-7	99.0	358.0/366.4	
1037-101-8	99.2	358.1/367.9	
AE603	99.1	357.9/368.7	5.91
Bridgwater	99.9	381.6/388.7	52.91
1037-83RC	99.9	379.6/385.5	47.83
1037-25RC	99.9	375.1/380.9	42.39
1037-45	96.1	357.7/366.5	5.03
1037-110	91.7	356.3/366.6	
1037-111	94.1	359.4/364.6	

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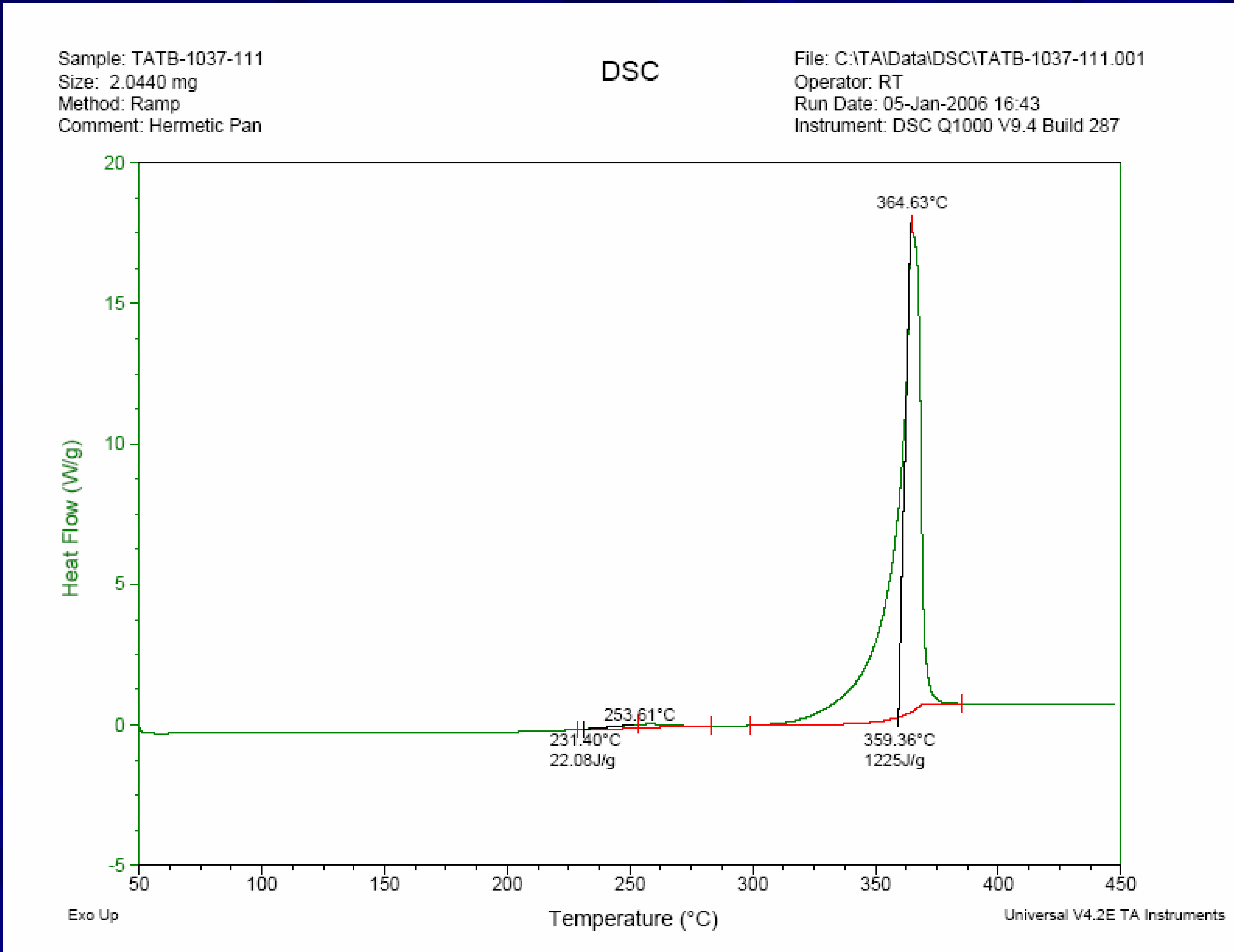
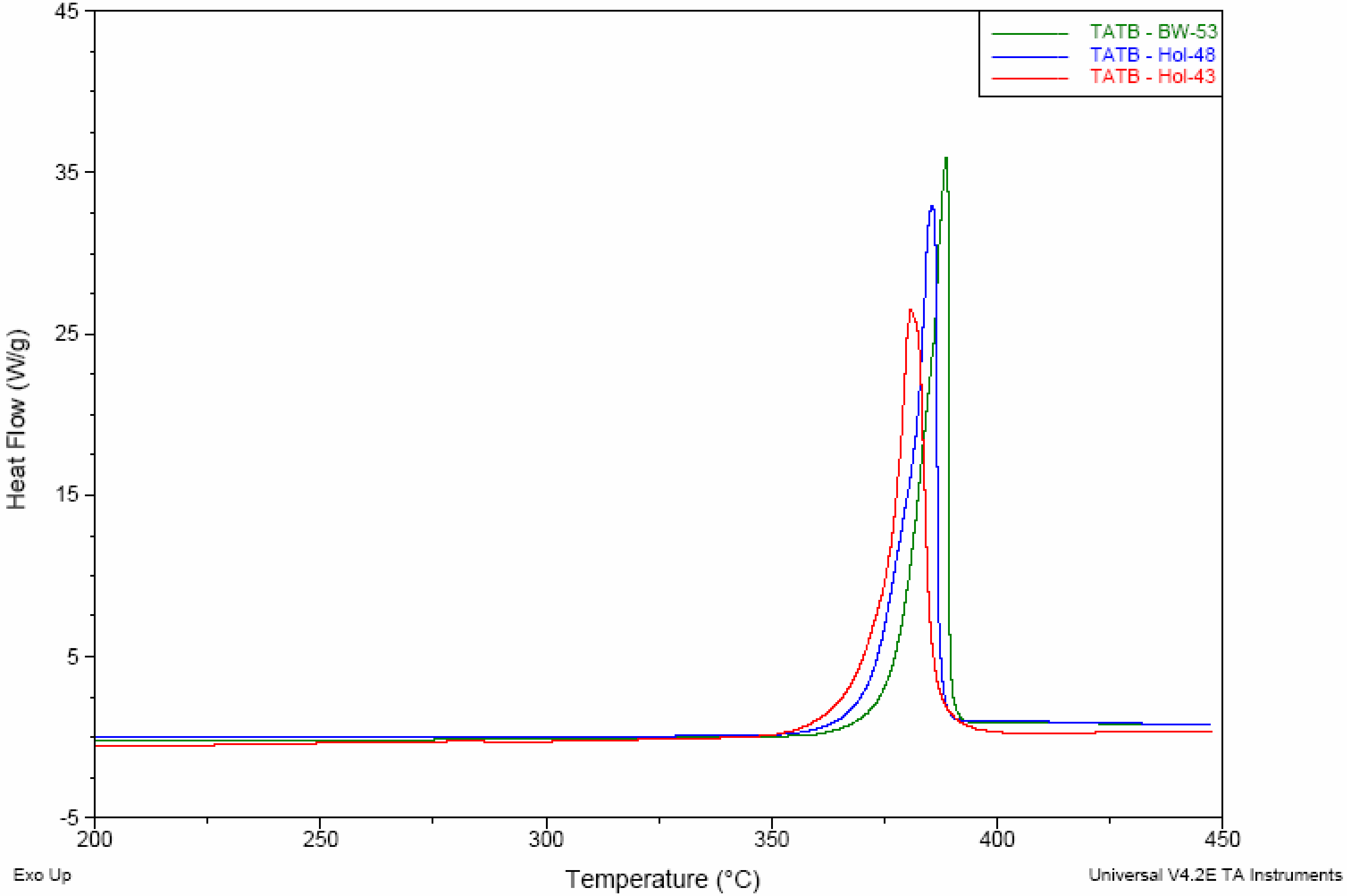

Sample: TATB-1037-111
Size: 2.0440 mg
Method: Ramp
Comment: Hermetic Pan
DSC
File: C:\TA\Data\DSC\TATB-1037-111.001
Operator: RT
Run Date: 05-Jan-2006 16:43
Instrument: DSC Q1000 V9.4 Build 287
364.63°C
253.61°C
231.40°C
22.08J/g
359.36°C
1225J/g
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.2E TA Instruments

Particle Size vs. Exotherm Onset



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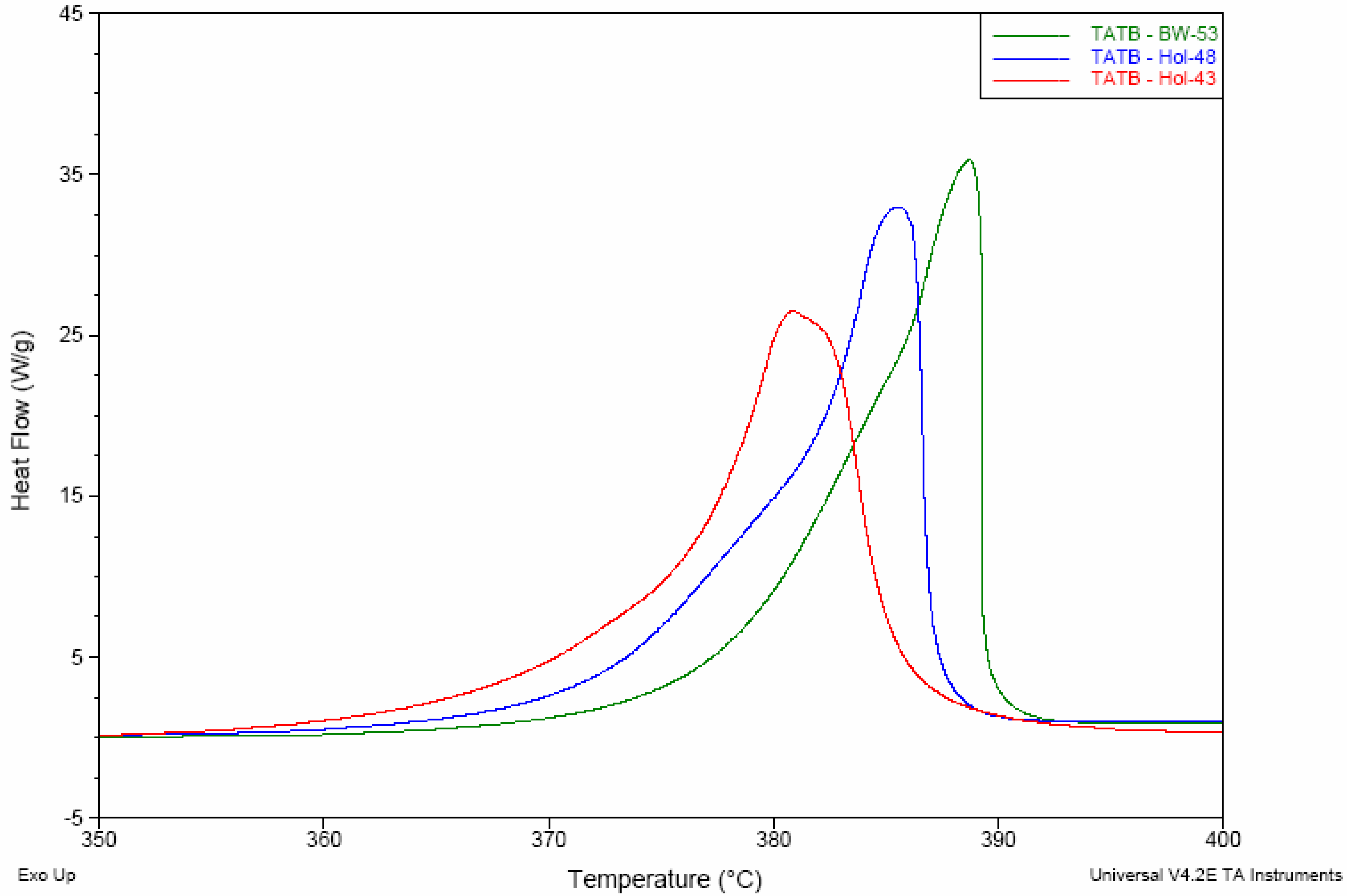
Particle Size vs. Exotherm Onset



TATB Production at the Agile Manufacturing Plant

- Nitration
  - 2500 lbs. of DBA nitrated in 2000 gal. glass-lined reactor
  - Nitration is 1 molar in DBA
  - Yields ca. 3600 lbs. DBTNA after quench and wash
  - DBTNA not isolated
  - Slurried and pumped directly to amination vessel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HYDROLYS

TATB Production at the Agile Manufacturing Plant

- Amination
  - DBTNA slurry is pumped to 6000 gal. still
  - Slurry is dewatered with wand filter
  - 29% aqueous ammonia is pumped in; agitation started
  - Reaction is conducted at 20-25°C for 36 hrs.

TATB Production at the Agile Manufacturing Plant

- Collection in Filter Press
  - TATB slurry is pumped to filter press
  - Blown down and collected; nominal yields ca. 2150 lbs.
  - NH_3 is stripped from reaction filtrate using eductor
  - Used to neutralize spent acid from nitration step


CLEAN
RAGS
ONLY

G-10 Production Data

Batch ID	Mean particle size	DSC onset/peak
	(µm)	(10℃/min.)
G-10-01	5.58	359.9/368.2
G-10-02	6.23	360.0/369.0
G-10-03		
G-10-04		
G-10-05		

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The Proud Uncle in the Nursery

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TATB ROM Pricing

- TATB
  - – 5,000 lb @ \$115 / lb
  - – 10,000 lb @ \$ 75 / lb
  - – 20,000 lb @ < \$ 55 / lb
  - – 50, 000 lb @ < \$ 45 / lb

TATB ROM pricing is based upon OSI projections for the manufacturing process being scaled-up as of January 2006; subject to change following completion of first manufacturing campaign which is scheduled to be completed by end April 2006. OSI’s view is that these ROM price estimates are <u>worse-case</u>; we hope and believe our final product pricing will be better than indicated herein.

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Conclusions

- Two-step process developed at HSAAP
- Process is robust and safe!
- Scaled to ton quantities
- Quality equivalent to current sources
- Competitive cost
- Process and cost optimization ongoing


I
LOVE
TATB