Manufacture of Wet-Aminated TATB at the Holston Army Ammunition Plant

2013 Insensitive Munitions & Energetic Material Technology Symposium

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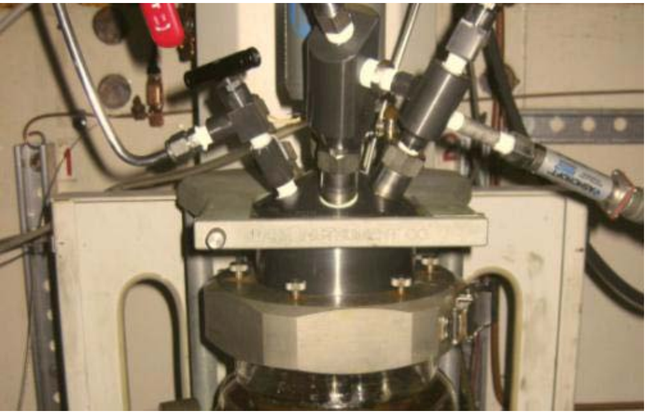
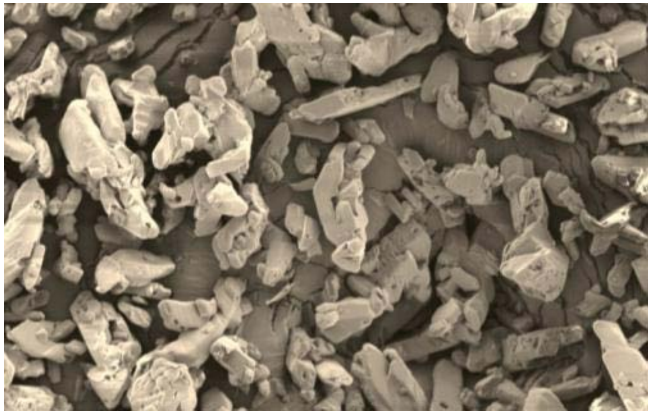




Program goals

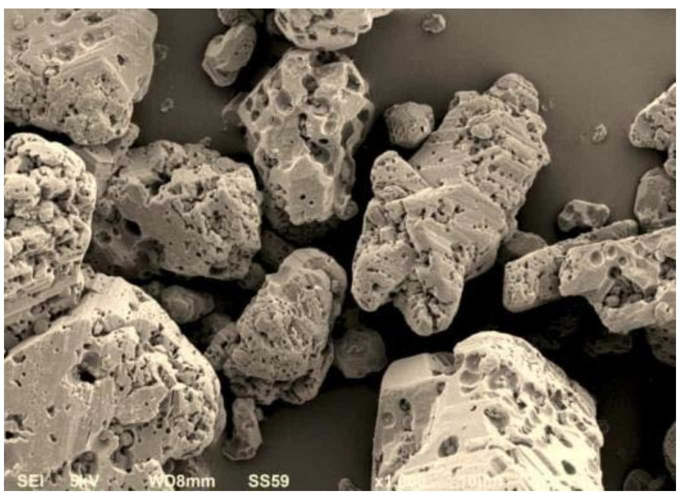
- Reestablish wet-aminated (WA) TATB manufacturing capability in the United States
  - Like Dry-aminated (DA) TATB, manufacture of WA TATB has not been practiced in recent times and stockpile beginning to be depleted.
  - Manufacture of DA TATB at HSAAP is currently in qualification phase
  - Manufacture of WA TATB is ~2 years behind DA TATB effort
- Three part collaborative effort between LLNL and BAE Systems
  - Begin at lab scale to establish a “drop-in” process for the manufacturing facility at HSAAP
  - Assess the process on the pilot scale (100 gallon) for TATB quality and limited performance testing in formulations
  - Qualify TATB and formulations at full scale (1000 gallon)

TATB source timeline

- 1993 - CONUS production of TATB ceased
- 1999 - DOD began OCONUS TATB procurement from UK
- 2005 - Last qualified TATB source ceased production (and closed in 2006)
- 2007 - DOD / DOE Joint Working Group established
- 2008 - NNSA / DOE TATB Study Group established
- 2010 - Lab and pilot demonstrations of Benziger TATB synthesis at HSAAP
- 2012 - TATB manufacturing facility construction begins at BAE Systems HSAAP
- 2012 - Lab scale wet-aminated TATB demonstrations at HSAAP
- 2013 - Dry-aminated TATB qualification runs at HSAAP
- 2013 - Wet-aminated TATB pilot demonstrations begin (December 2013)
- 2014 - Wet-aminated TATB qualification runs at HSAAP (4th quarter 2014)

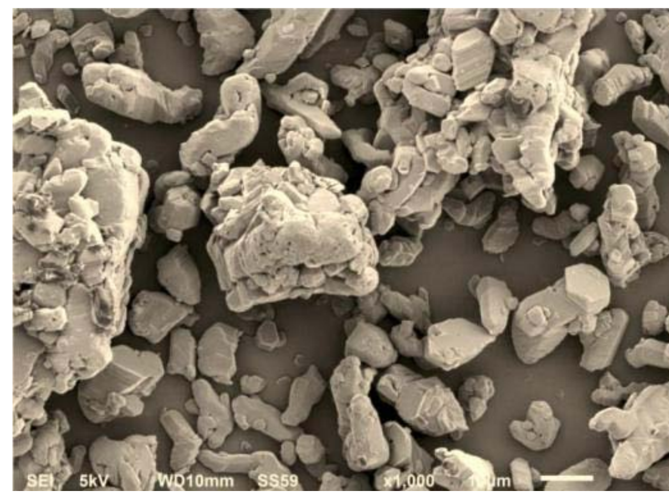
Wet and dry-aminated TATB differences

- Synthesis of WA TATB requires water in the amination step
- Morphology of WA TATB is free of worm holes
- Average particle size of WA TATB is smaller compared to DA TATB
- Total chlorine content of WA TATB is below 0.2% compared with 0.5% in DA TATB
- Otherwise, both DA and WA TATB are very similar



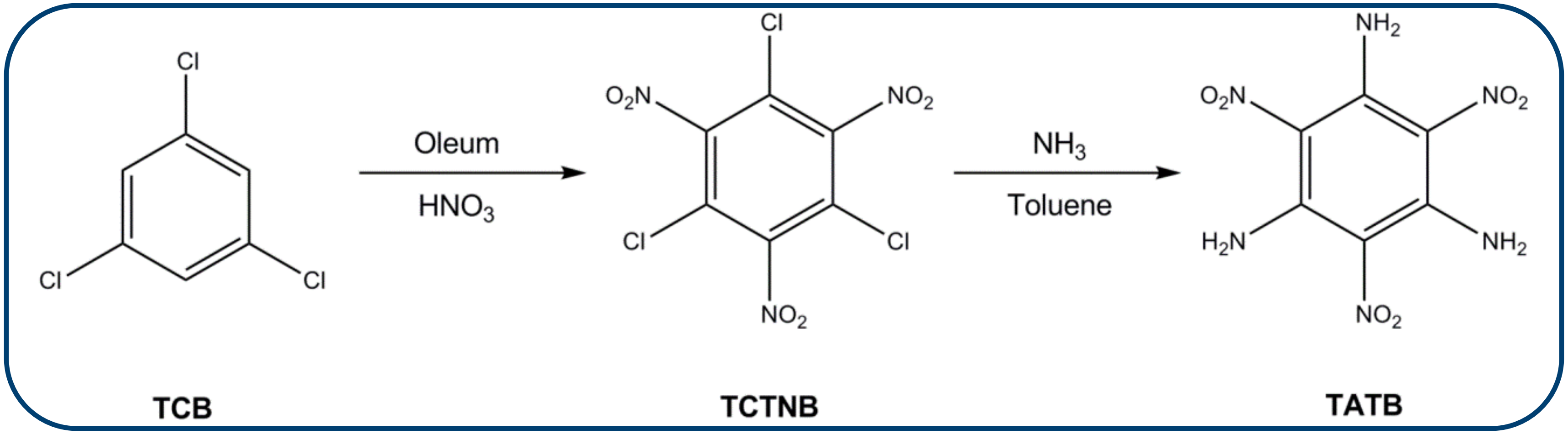
Wet-aminated TATB

Dry-aminated TATB



Synthesis method

Two Step "Benziger" Synthesis Route



- TCB is first nitrated to TCTNB in an oleum / nitric acid solution
- TCTNB is then aminated with ammonia gas to yield TATB
- The type of TATB depends on amination conditions (i.e. whether water and / or an emulsifier is present in the reaction)

Laboratory synthesis of wet-aminated TATB

- Goal to establish a “drop-in” process for the manufacturing facility at HSAAP
  - Understand parameters which effect TATB yield, purity, particle size, particle quality and develop an optimized process.
  - TCTNB used in the development was manufactured on the pilot scale (100 gallon Pfaudler)
  - Aminations were performed using a 1 liter Parr 5100 reactor
    - Glass and zirconium wetted parts
    - Ammonia gas metered into reactor with TCTNB, toluene, and water
  - Purifications performed in a 3 liter Holston still

1L Parr reactor

3L Holston still

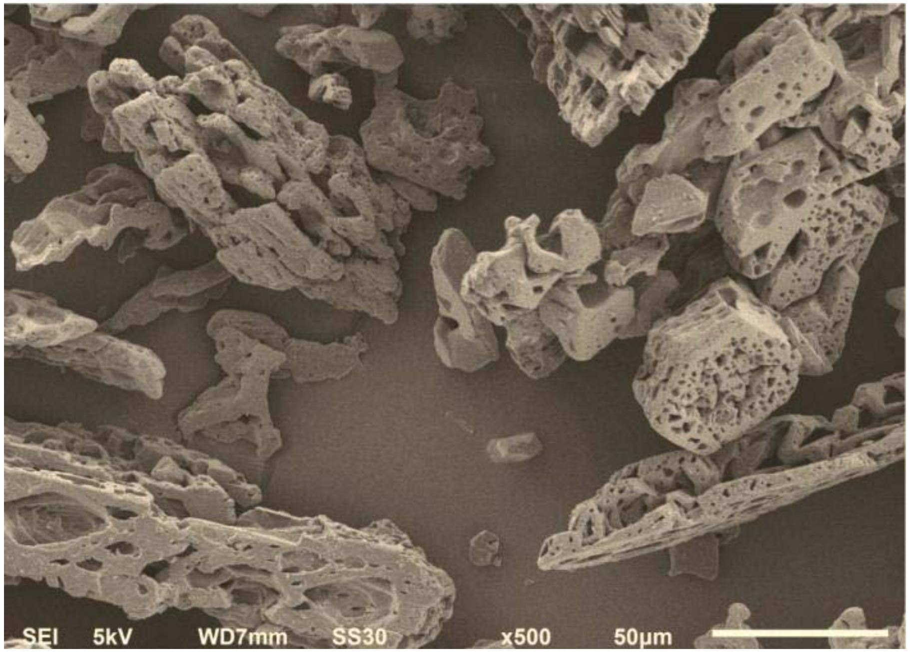
1-2 pounds of WA TATB synthesized and sent to LLNL for evaluation

Analysis of early lab scale WA TATB

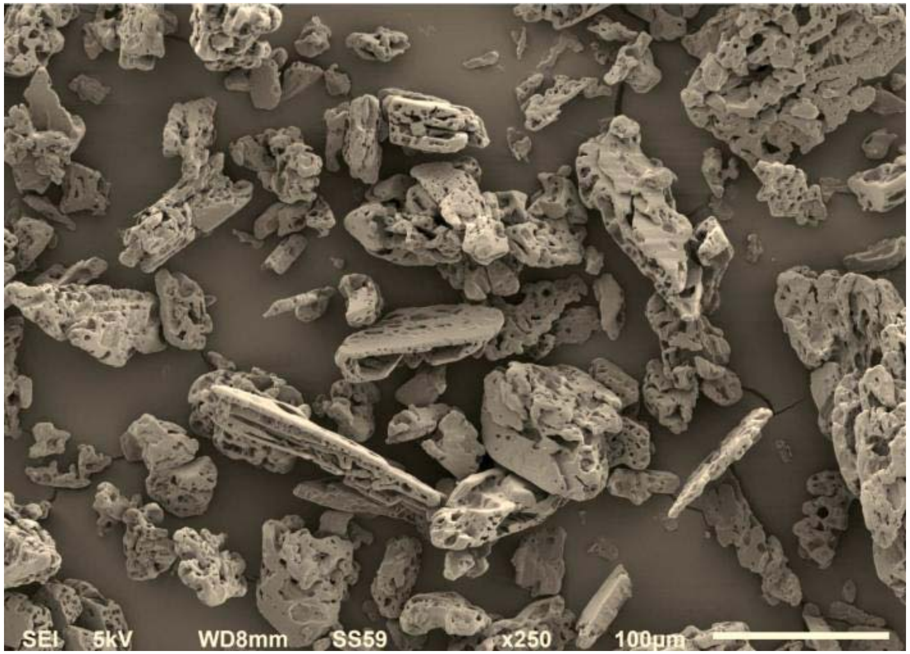
Experiment	Actual Yield (%)	DSC Onset (°C)	DSC Peak (°C)	Particle Size	Total Chlorine (%)
1	99%	381.2	386.7	Fail	0.55
2	101%	381.2	385.0	Fail	0.63
3	99%	381.2	386.6	Fail	0.45
4	95%	381.4	386.6	Fail	0.64
5	91%	379.9	384.1	Fail	0.66
6	60%	378.6	384.4	Fail	1.64
7	68%	381.9	386.5	Fail	0.82
8	96%	381.0	385.3	Fail	0.80
9	49%	376.6	383.4	Fail	1.18
10	58%	382.6	385.6	Fail	0.64
11	96%	376.4	380.9	Fail	0.46
12	96%	383.3	385.7	Fail	0.26
13	97%	384.0	387.0	Fail	0.18
14	81%	381.0	384.5	Pass	0.41
15	97%	381.5	387.4	Fail	0.19
16	98%	381.9	386.4	Fail	0.35
17	98%	379.4	384.7	Fail	0.43
18	97%	382.9	386.9	Fail	0.25
19	98%	382.9	385.9	Fail	0.19
20	98%	381.6	385.4	Fail	0.31
21	98%	383.2	385.4	Fail	0.18
22	97%	381.6	385.4	Fail	0.24
23	96%	382.7	385.6	Fail	0.19

- Experiments focused on optimizing:
  1) Ammonia feed rate
  2) Stirring rate
  3) Concentrations
  4) Temperature
- Most experiments have good yields (95-100%, final purified) and high DSC decomposition temperatures 380-386°C
- Nearly all fail particle size and total chlorine (pass is <0.2%)

Early lab scale WA TATB, crystal morphology



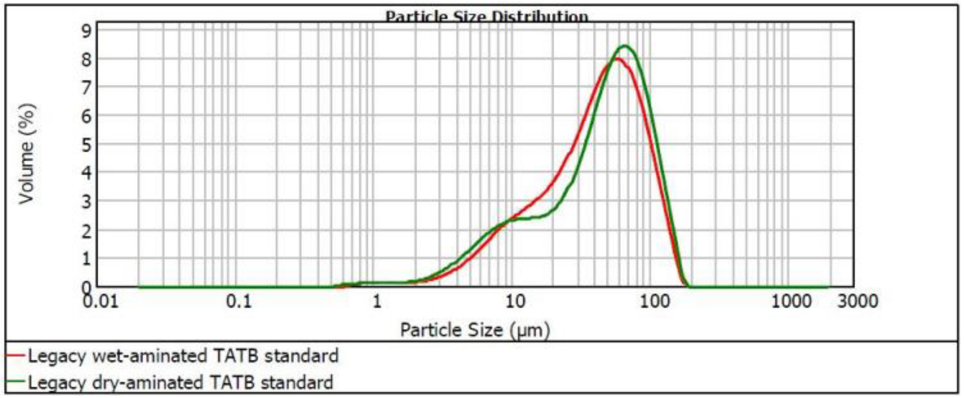
SEM image 500x magnification



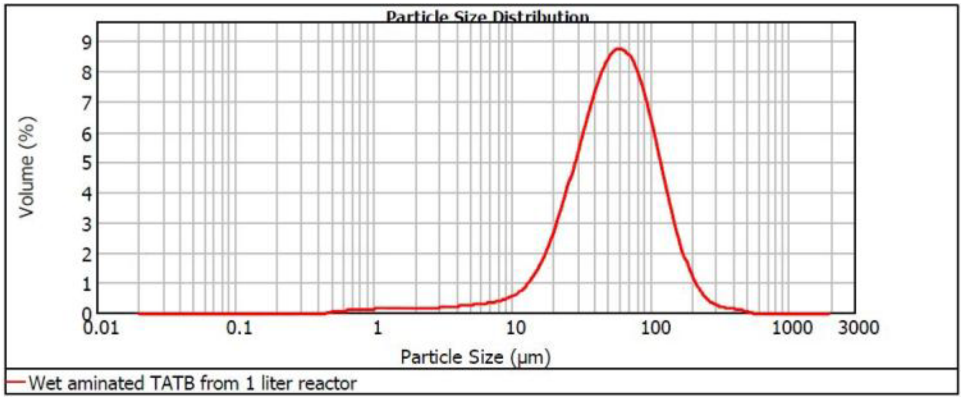
SEM image, 250x magnification

- Stark differences between legacy and lab scale synthesized WA TATB
  - Porous surfaces with elongated crystals, loss of defined crystal shape/face, high chlorine content
- Inefficient stirring in 1 liter reactor most likely cause
  - TATB clumped in reactor at agitation rates used
  - Heterogeneous reaction requires interaction between water and growing TATB crystal

Particle size distribution in TATB; lab scale vs. legacy



•Legacy WA and DA TATB show pseudo bimodal distribution



•1L Reactor generates single mode distribution of particles

- •Possibly due to a lack of turbidity (pseudo baffle does not adequately disrupt flow)

Synthesis parameters adjusted to meet WA TATB requirements

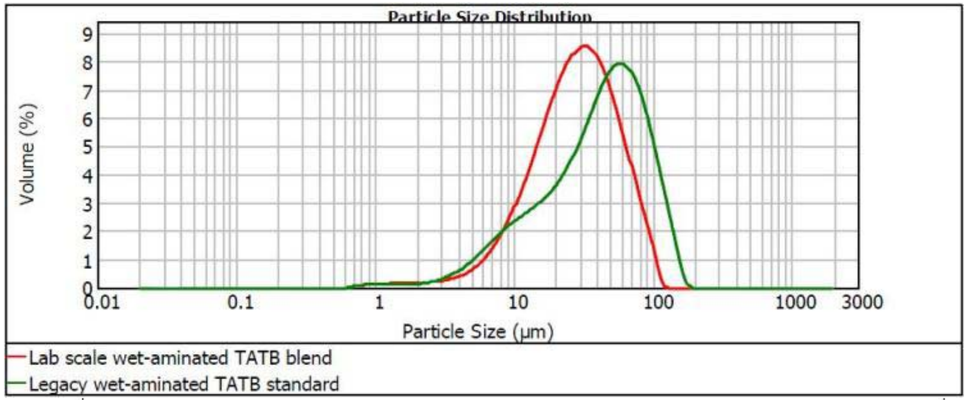
Final lab scale WA TATB batches

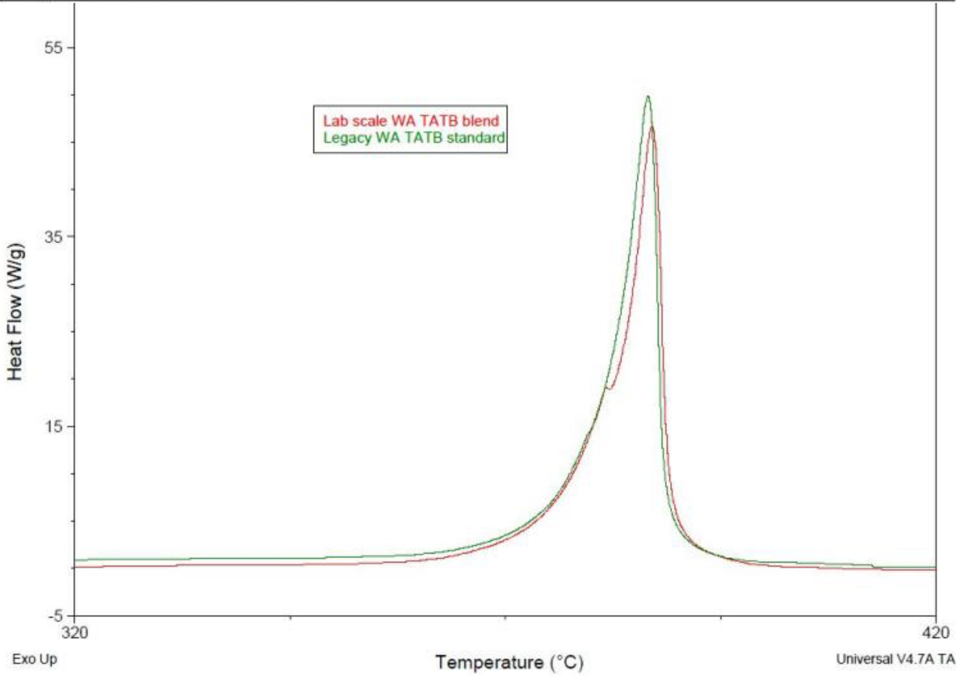
- Parameters adjusted from early experiments to meet WA TATB specification
- Following a short prove out of the chosen parameters, 1.6 pounds were synthesized over 15 batches
  - The batches were blended wet and tested to a specification vs. legacy WA TATB
  - With exception of particle size, all analysis passes specification
  - Shape of particle size distribution is not representative of production TATB and is expected to improve on the pilot scale prove out
- The WA TATB blend was shipped to LLNL
  - Currently undergoing evaluation on the lab scale

Analysis of lab scale and legacy WA TATB

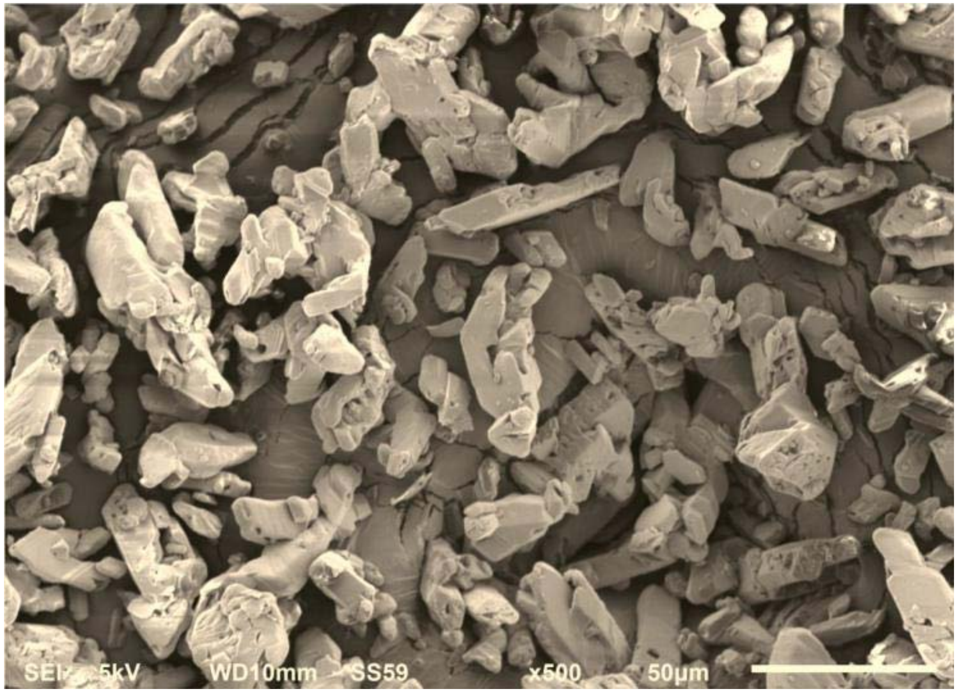
Sample	Lab scale blend	Legacy standard
Particle size (μm, mean)	28.3	42.5
Crystal Morphology (SEM)	Pass	Pass
Total Chlorine (%)	0.11	0.07
Organic impurities	Pass	Pass
Ash content	0.0	-*
DSC (°C, onset)	382.0	380.8
DSC (°C, Peak)	387.0	386.6
IR	Pass	Pass
Impact (cm)	>200	>200
Friction (N)	>360	>360
VTS (mL/g)	0.1	-*

*Did not test, limited amount of material

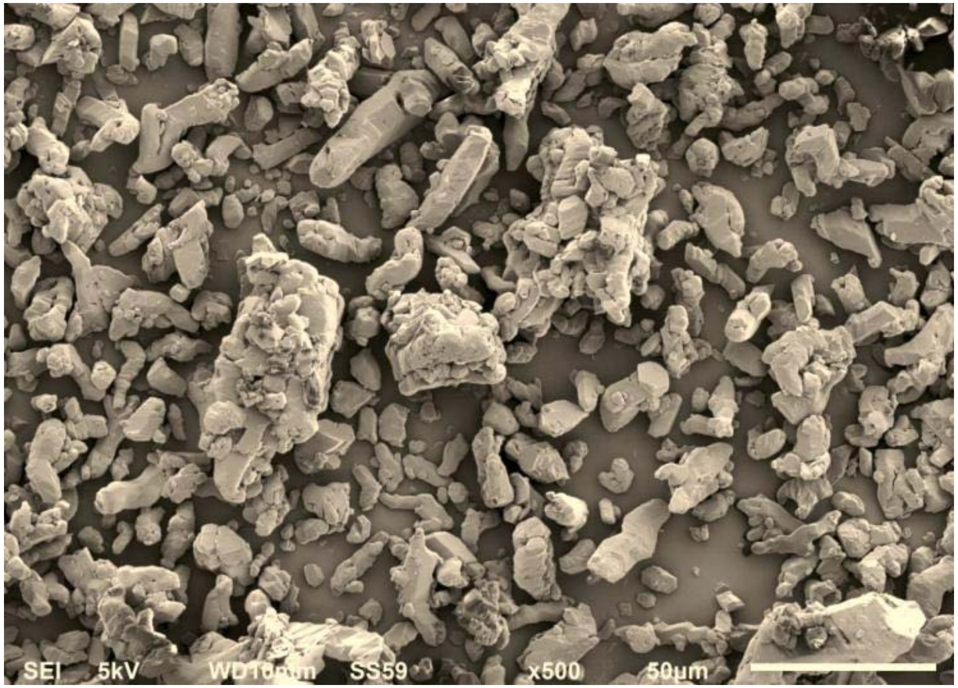




Final WA TATB blend; lab scale vs. legacy



Lab scale blend 500x magnification



Legacy standard 500x magnification

- Adjusted parameters improved crystal quality and lab scale blend now compares well with legacy standard
    - Lab scale still shows some worm holes in select crystals

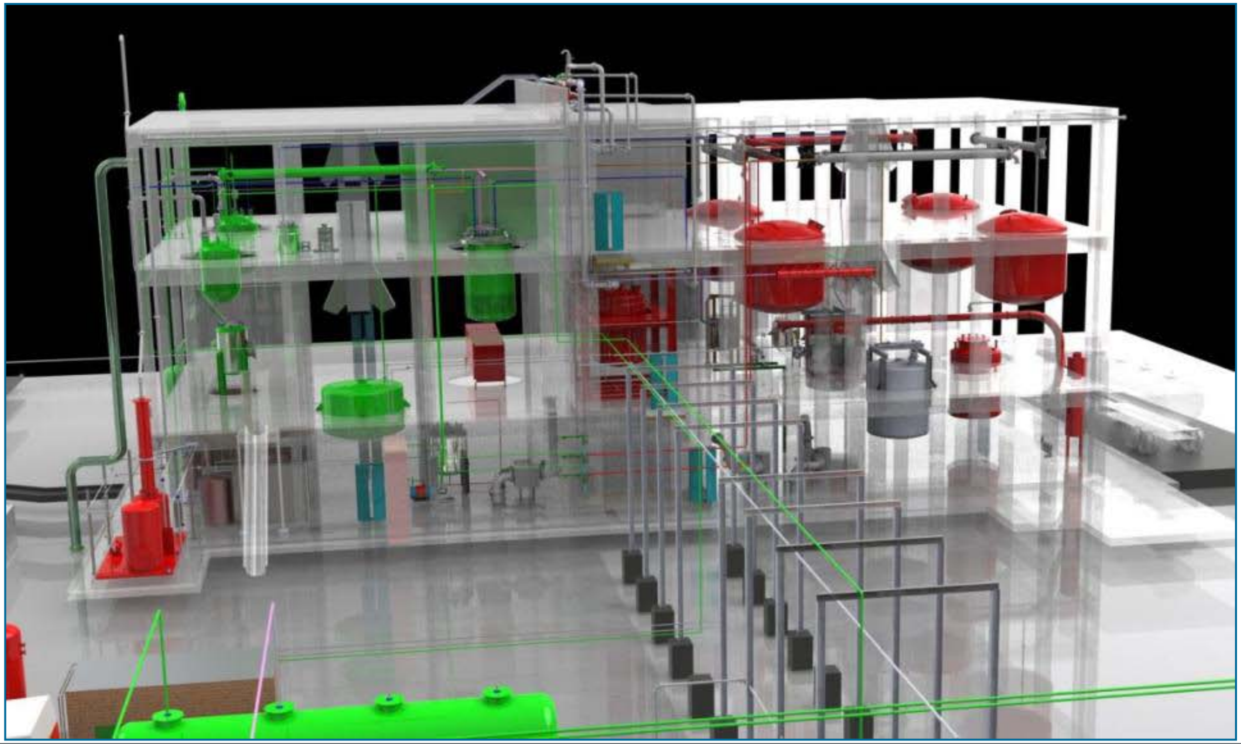
Lab scale WA TATB similar crystal quality to legacy material

Pilot Scale synthesis of WA TATB

- Currently commissioning a Pilot Scale R&D Facility
  - 50, 100, 200 Gallon reactors
  - Commissioning to be completed by Q4 2013
  - Pilot batches to begin Q4 2013
- WA TATB synthesis will be scaled to the 100 gallon reactor
  - Six batch prove out of lab scale amination process (50-60 pound batches)
    - TCTNB will be provided by manufacturing facility at HSAAP
  - Two TATB batches will be shipped to LLNL for testing
  - Limited performance testing of TATB formulations will be completed

Full scale manufacture of WA TATB

- Process from lab and pilot activities will transfer to full scale qualification at TATB manufacturing facility
  - Three to six batches will be synthesized and qualified as WA TATB and formulations
- Qualification expected to begin 4th quarter 2014



Building G-10 Agile Manufacturing Plant for Energetic Materials At Holston AAP

Summary

- LLNL and BAE Systems at HSAAP have embarked on a collaborative effort to reestablish manufacturing capability for WA TATB in the United States
- WA TATB synthesis via traditional Benziger process has been effectively demonstrated on the lab scale at HSAAP
  - Early reactions showed porous surfaces with elongated crystals, loss of defined crystal shape/face and high chlorine content
    - Inefficient stirring during amination most likely cause, possibly due to a lack of turbidity
  - Parameter adjustment improved the crystal quality and lowered the chlorine content of the TATB
  - With exception of particle size, all analysis passes specification
    - Shape of particle size distribution is not representative of production TATB and is expected to improve on the pilot scale prove out
  - Lab scale material currently undergoing evaluation at LLNL
- Pilot scale prove out of the lab scale process is expected to begin December 2013 with full scale qualification runs beginning 4th quarter 2014

Acknowledgements

- BAE Systems / HSAAP
  - Ed LeClaire, Dr. Jeremy Headrick, Kelly Guntrum, Robyn Wilmoth, Chris Long, Jim Haynes, Todd Dye, Matt Hathaway, Denise Painter
- Lawrence Livermore National Laboratory
  - Mark Hoffman, Tri Tran, Phil Pagoria