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

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*Dr. David Price, Dr. Jacob Morris, Dr. Neil Tucker
Dr. Tri Tran, Dr. Mark Hoffman

BAE Systems Ordnance Systems / HSAAP
Lawrence Livermore National Laboratory
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
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

1-2 pounds of WA TATB synthesized and sent to LLNL for evaluation
## Analysis of early lab scale WA TATB

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

- **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

- 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

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

*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 scaleamination 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
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

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  • Ed LeClaire, Dr. Jeremy Headrick, Kelly Guntrum, Robyn Wilmoth, Chris Long, Jim Haynes, Todd Dye, Matt Hathaway, Denise Painter
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