Synthesis and Scale-Up of TATB
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May 2009
TATB Program Goals

Low Cost/High Volume Supplier
• Inclusion in Many New IM Formulations
• Good Fit for Existing Holston Infrastructure
• Minimal Initial Capitalization
• Short Time to Production Quantities
• Equivalent Quality to Traditional TATB
  • Similar Shock Sensitivity in PBXN-7 needed…
Technical Issues of Earlier TATB Efforts

- In PBXN-7, OSI TATB (5 micron) performed well in all examined aspects except:
  - Shock sensitivity:

<table>
<thead>
<tr>
<th>Material Tested</th>
<th>Average Pellet Density, g/cm³</th>
<th>NOL LSGT, cards/kbars</th>
<th>Detonation Velocity, m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBXN-7 manufactured by NSWCIIH Yorktown Det with ATK TATB</td>
<td>1.781</td>
<td>50% kbar increase</td>
<td>7464</td>
</tr>
<tr>
<td>PBXN-7 with OSI TATB (supplied by OSI)</td>
<td>1.789</td>
<td>70% kbar increase</td>
<td>7572</td>
</tr>
<tr>
<td>Historical data</td>
<td>1.78</td>
<td></td>
<td>7660</td>
</tr>
</tbody>
</table>

- Reduction in sensitivity thought to be caused by small particle size and/or crystal morphology of TATB (as compared to traditional TATB (50 micron)
Available Technologies

• Traditional Trichlorobenzene (TCB) Route- “Benziger Route”
  • Harsh conditions; waste streams
  • TCB not domestically available
Holston TATB Synthesis Method

New 2-Step Process/Synthesis Route Developed by OSI Scientists

- Scalable on the Holston Infrastructure
- Good Fit for Agile Manufacturing Plant (G-10)
- Multiple Sources Identified for Raw Materials-Including CONUS

- Purity comparable to reference (Bridgwater)
- Particle size typically 40 microns
- Produced ~20 lbs TATB to date
Laboratory Nitration of DCPB

- DCPB is fed as a liquid into nitric acid
- Initial reaction is mildly exothermic
- Reaction performed several times in 5 gal reactor (10 lb batch size)
- Yields $\geq 95\%$
- Purity typically $> 99\%$
DCTNPB
(3,5-Dichloro-2,4,6-trinitropropoxybenzene)

- Insensitive Intermediate
- Melting Point = 121°C
- Exotherm Onset = 220°C (as determined by DSC)
- Impact Sensitivity > 80 cm (Holston Method)

Chemical Formula: C₉H₇Cl₂N₃O₇
Molecular Weight: 340.07
Laboratory Amination of DCTNPB

- DCTNPB is aminated in toluene with gaseous ammonia at high temperature and under pressure (similar to Benziger route)
- Reaction Scaled to 1 mole (2 gal Parr)
- Yields are ~ 75%
- **Known Impurities:**
  - Ammonium diaminopicrate (ADAP)
  - 3,5-Diamino-2,4,6-trinitropropoxybenzene (PDAP-seen in early development, not detected in current process)
  - Mp = 214 C
Formation and Elimination of Ammonium Diaminopicrate (ADAP)

Affords ADAP

\[ \text{H}_2\text{N}\text{O}_2\text{N}^-\text{NH}_4^+ \]

Affords TATB

\[ \text{O}_2\text{N}^-\text{NH}_4^+ \]

\[ \text{O}_2\text{N}^-\text{NH}_3 \]

\[ \text{O}_2\text{N}^-\text{NH}_2 \]

Average % ADAP Pre-Wash

<table>
<thead>
<tr>
<th>Lot</th>
<th>% ADAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lot 1</td>
<td>0.15%</td>
</tr>
<tr>
<td>Lot 2</td>
<td>0.15%</td>
</tr>
<tr>
<td>Lot 3</td>
<td>0.58%</td>
</tr>
</tbody>
</table>

Average % ADAP Post-Wash

<table>
<thead>
<tr>
<th>Lot</th>
<th>% ADAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lot 1</td>
<td>0.04%</td>
</tr>
<tr>
<td>Lot 2</td>
<td>0.02%</td>
</tr>
<tr>
<td>Lot 3</td>
<td>0.02%</td>
</tr>
</tbody>
</table>

• Washing with hot water until wash water becomes light yellow lowers ADAP contamination considerably
# TATB Analytical Summary

## Batch 1

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>DSC</td>
<td>354°C</td>
</tr>
<tr>
<td>TGA</td>
<td>250°C (0.78%), 325°C (18.4%), 400°C (78.7%)</td>
</tr>
<tr>
<td>Mean particle size</td>
<td>40.7 μm</td>
</tr>
<tr>
<td>% ADAP</td>
<td>0.03%</td>
</tr>
<tr>
<td>VTS (100°C, 48 hrs)(mL/g)</td>
<td>0.1167</td>
</tr>
<tr>
<td>% Chloride</td>
<td>0.12%</td>
</tr>
</tbody>
</table>

## Batch 2

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC</td>
<td>354°C</td>
</tr>
<tr>
<td>TGA</td>
<td>250°C (0.42%), 325°C (16.6%), 400°C (77.1%)</td>
</tr>
<tr>
<td>Mean particle size</td>
<td>34.4 μm</td>
</tr>
<tr>
<td>% ADAP</td>
<td>0.02%</td>
</tr>
<tr>
<td>VTS</td>
<td>N/A</td>
</tr>
<tr>
<td>% Chloride</td>
<td>0.10%</td>
</tr>
</tbody>
</table>
Particle Size Analysis

![Graph showing particle size distribution with values d(0.1): 22.889 um, d(0.5): 52.310 um, d(0.9): 104.338 um.]

![Graph showing particle size distribution with values d(0.1): 22.216 um, d(0.5): 53.906 um, d(0.9): 100.625 um.]

TATB Bridgewater Averaged Result, Thursday, October 27, 2005 2:28:44 PM

TATB 1070-119 - Average, Monday, August 11, 2008 3:28:52 PM
SEM Analysis

New OSI TATB

Traditional TATB

1000x mag

5000x mag
DSC phenomenon

- DSC of new TATB found to be significantly different than traditional TATB

- DSC* not affected by:
  - Glass vs SS reactor
  - Wet or dry amination
  - Amination temp.
  - Purity
  - Digestion in DMSO
  - Amination under N2

*All DSCs performed at 5C/min unless otherwise noted
TATB DSC (5°C/min)

- G10-3 is production run using previous dibromoanisole aqueous route.
- 1073-97 is from DCTNPB route, recrystallized from DMSO.
- 1073-103 is RT aqueous amination of DCTNPB (90% yield).
ADAP spiking of aminations - TATB DSC (5°C/min)

- Aminated TCTNB w/ varying levels of ADAP present in reaction medium
- TCNTB does not afford ADAP.
- ADAP levels in TATB from spiked reactions are consistently low.
Effect of varying length of alkyl chain on yield and DSC (5°C/min)

- Amination of DCTNA (methyl group) gives low yields.
- Ethyl, propyl, and butyl groups show no effect on DSC.
- Yields modestly increase as length of alkyl chain increases.
Formulations: PBXN-7

- Several lab batches
- Consistent process and product

<table>
<thead>
<tr>
<th>Screens (%Pass)</th>
<th>batch 1</th>
<th>batch 2</th>
<th>batch 3</th>
<th>composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>#6</td>
<td>met spec</td>
<td>met spec</td>
<td>met spec</td>
<td>met spec</td>
</tr>
<tr>
<td>#14</td>
<td>met spec</td>
<td>met spec</td>
<td>met spec</td>
<td>met spec</td>
</tr>
<tr>
<td>#18</td>
<td>met spec</td>
<td>slightly out</td>
<td>met spec</td>
<td>met spec</td>
</tr>
<tr>
<td>#100</td>
<td>met spec</td>
<td>met spec</td>
<td>met spec</td>
<td>met spec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bulk Density (g/cm³) (Naval)</th>
<th>met spec</th>
<th>met spec</th>
<th>met spec</th>
<th>met spec</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Composition</th>
<th>met spec</th>
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<th>met spec</th>
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</thead>
</table>

<table>
<thead>
<tr>
<th>Moisture</th>
<th>N/A</th>
<th>N/A</th>
<th>N/A</th>
<th>met spec</th>
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<table>
<thead>
<tr>
<th>Impact Sensitivity (ERL, cm)</th>
<th>N/A</th>
<th>N/A</th>
<th>N/A</th>
<th>met spec</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>VTS by PT Method (100°C, 48h)(mL/g)</th>
<th>N/A</th>
<th>N/A</th>
<th>N/A</th>
<th>met spec</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Press Density (g/cm³)</th>
<th>N/A</th>
<th>N/A</th>
<th>N/A</th>
<th>slightly out (low)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Comments</th>
<th>Blend of 1, 2, and 3</th>
</tr>
</thead>
</table>
Formulations: PBXW-14

- One batch made in lab
- Successful integration of TATB made from the new OSI method into the existing W-14 formulation procedure.
- No performance data at this time.
Conclusions

- Two-step TATB manufacturing process developed at HSAAP
- Process is robust and safe
- Quality equivalent to traditional sources of DOD “grade” material (Bridgwater)
- Competitive cost to traditional TATB
- Process and cost optimization ongoing
- Difference in thermal properties (DSC) appear to be caused by ADAP impurity in process
- TATB currently appears to be a “drop-in” replacement in DOD formulations (waiting for performance testing)
Acknowledgments

• BAE Systems:
  • Neil Tucker and Jim Haynes - Nitrations and Aminations (lots of them!)
  • Ed LeClaire - Agile Plant Mgr. & Process Development
  • Lisa Hale and Kelly Guntrum – Analytical Support
  • Jim Owens – Analytical Method Development & Support
  • Brian Alexander - PBXN-7 formulation

• Navy:
  • Al Stern, Brad Sleadd, Tim Mahoney
    - Useful discussions, suggestions, and direction
  • ONR Mantech Program-Funding
  • Chuck Painter-Mantech director