Pilot plant synthesis of triaminotrinitrobenzene (TATB) from a novel process

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Outline

● Novel TATB process
  ● Driving force behind development
  ● Process overview

● Process results
  ● Nitration
  ● Alkylation
  ● Ammonolysis

● Conclusions
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Why TATB Synthesis?

- Current production method produces undesirable waste (trichlorobenzene route)
- Future supplies of TCB uncertain – could become a major cost driver for future TATB production
- Development of an alternate route to ensure uninterrupted supply of TATB for needed applications
  - environmentally acceptable waste streams
  - cost-competitive product (vs. current TATB)
  - uncomplicated and robust process to be credibly transitioned to production
TATB Advantages

- TATB could be utilized as a valuable material for achieving IM compliance
  - High density - 1.93 g/cm³
  - High thermal stability
  - Low shock sensitivity

<table>
<thead>
<tr>
<th>Compound</th>
<th>Impact sensitivity (N m)</th>
<th>Confined detonation velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroglycerine</td>
<td>0.2</td>
<td>7600</td>
</tr>
<tr>
<td>RDX</td>
<td>7.5</td>
<td>8750</td>
</tr>
<tr>
<td>TNT</td>
<td>15</td>
<td>6900</td>
</tr>
<tr>
<td>TATB</td>
<td>50</td>
<td>7350</td>
</tr>
</tbody>
</table>


- TATB is already qualified in a number of systems
Three-step process was proposed starting from phloroglucinol

- phloroglucinol found in naturally-occurring glycoside derivatives
- worldwide, approximately 140-200 metric tons of phloroglucinol are produced each year
- numerous synthetic industrial routes (including demil of TNT)

Proposed process first reported in UK by Bellamy, Golding and Ward

Considerable route development performed at ATK Thiokol

- necessary for scale-up consideration
**TATB Transition to Scale-Up**

- **Lab scale**
  - 1 g to <1000 g
  - multiple laboratory fume hoods
  - 5, 10, 22-L reactors (kilo bays)

- **Kilogram scale**
  - multiple kilograms
  - dedicated facility including remote operation capability
  - 50-L, 5 gallon reactors for batch processes
  - loop reactor and continuous reactor set-up for continuous operation

- **Pilot facility**
  - 100’s lbs.
  - 20, 50, 200, 500-gallon reactors
  - remote operations
  - dedicated operators
Nitration

- Reaction exotherm easy to control
- Over 1,000 lbs. (450 kg) of TNPG produced
- Reaction yields have been greatly improved (from ~ 75% to >92%)
  - excellent scalability and reproducibility

Small scale safety data

<table>
<thead>
<tr>
<th>Safety Test</th>
<th>TNPG</th>
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</thead>
<tbody>
<tr>
<td>ABL impact (cm)</td>
<td>1.8</td>
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<tr>
<td>ABL friction (lbs)</td>
<td>800 @ 8 ft/s</td>
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<tr>
<td>Electrostatic discharge</td>
<td>1.86 J (mass ignition @ 8 J)</td>
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</tbody>
</table>
Alkylation

- Efficient, straightforward process
- High reactor loading levels
- Isolated yields >90%
- Triethylorthoformate used for cost considerations
- TETNB relatively insensitive and easy to handle

Small scale safety data

<table>
<thead>
<tr>
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<th>TETNB</th>
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</thead>
<tbody>
<tr>
<td>ABL impact (cm)</td>
<td>64</td>
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<tr>
<td>ABL friction (lbs)</td>
<td>800 @ 8 ft/s</td>
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<tr>
<td>Electrostatic discharge</td>
<td>&gt;8 J</td>
</tr>
</tbody>
</table>
Ammonolysis

- Simple process that can yield complicated results
  - particle size & shape, purity
- Target particle size 40-60 micron (to match current TATB spec)
- Yield generally >98%

Small scale safety data

<table>
<thead>
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<th>Safety Test</th>
<th>TATB</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABL impact (cm)</td>
<td>80</td>
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<tr>
<td>ABL friction (lbs)</td>
<td>800 @ 8 ft/s</td>
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<tr>
<td>Electrostatic discharge</td>
<td>2.7 J (no mass ignition)</td>
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<tr>
<td>Lot number</td>
<td>Particle size (µm) (10, 50, 90%)</td>
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<tr>
<td>--------------</td>
<td>----------------------------------</td>
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<tr>
<td>346-04-001</td>
<td>18.9, <strong>21.9</strong>, 25.6</td>
</tr>
<tr>
<td>346-04-005</td>
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<td>590-04-0158</td>
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<td>37.1, <strong>54.1</strong>, 105.0</td>
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<tr>
<td>346-04-012</td>
<td>60.5, <strong>82.6</strong>, 142.9</td>
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</table>
Purity determination was a concern due to TATB insolubility

HPLC/MS used to identify impurities

- ammonium diaminopicrate and 1-ethoxy-3,5-diamino-2,4,6-trinitrobenzene are process impurities
- quantification of impurities by HPLC an approximation due to similar absorbance spectra
- TATB produced generally 95-99% pure
TATB Thermal Behavior

- TATB possesses excellent thermal stability

Decomposition onset at 370°C
Conclusions

- A novel process for producing TATB from phloroglucinol has been successfully transitioned from the lab to the pilot plant level.

- The three step process reduces the environmental impact of TATB production when compared to the traditional trichlorobenzene route.

- TATB particle size control possible via the current route.

- The TATB produced under this effort will undergo extensive testing and evaluation at the completion of the program.