Improved Energetic Materials as Fuze Ingredients:

TATB

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May 2010
TATB Applications

- Besides the two biggest users of PBXN-7 (FMU-139 and FMU-152 bomb fuze programs) there are also other users of PBXN-7 which include FMU-143 (BLU-116, BLU-109), FMU-148A/B (Tomahawk), FMU-155/B (SLAM ER), MK436 fuze (MK146 warhead 2.75), M734A1, M934, and JSOW
- PBXW-14
- LX-17
- PBX-9502
- And many others
A Brief History of TATB

- 1888: TATB first described (no mention of use as explosive)
- 1950s: TATB evaluated as high-temperature resistant explosive for space applications
- 1960s:
  - TATB evaluated for use in nuclear weapons
  - Benziger process initially developed
  - Initial formulations developed with TATB and polymeric binders
  - Process affords 5 micron TATB
  - Process affords 30-40 micron TATB (very similar to Benziger TATB)
TATB Program Goals

We are proposing a new nomenclature system for TATB to avoid confusion and offer standardization when discussing and using TATB:

- **(Holston) Type 1**: Traditional Benziger TATB
- **(Holston) Type 2**: Small particle size (5 micron) TATB made from alkylated phenols
- **(Holston) Type 3**: Large particle size (30-50 micron) TATB made from alkylated phenols
Benziger TATB: Type 1

- Benziger TATB starts with trichlorobenzene, an environmentally-unfriendly compound which is also not available from a US supplier.
- The nitration conditions are rather severe, requiring mixed acids and high temperatures.
- The nitration to obtain the desired TCTNB is also complicated by the generation of significant amounts of impurities (T3 and T4).
  - TCTNB purity is typically only 87-90%.
  - T3 and T4 are impurities that will be present in the final TATB and must be reduced to very low levels.
Benziger TATB: Type 1

- TCTNB is then aminated in toluene at high temperatures to form Benziger (Type 1) TATB.
- Conversion of TCTNB to TATB is nearly quantitative
Holston Type 2 TATB Synthesis Method

- Based on Chemistry Developed by Benziger and Ott
- New Process/Synthesis Route Developed by OSI Scientists
- Readily Scalable (and scaled) on the Holston Infrastructure
- Good Fit for Agile Manufacturing Plant (G-10)
- Multiple Sources Identified for Raw Materials
  - Including CONUS
- Affords 5 micron (nominal) TATB
Type 2 TATB Production at Agile Manufacturing Plant

- **Nitration**
  - 3,5-Dibromoanisole (2500 lbs) is Melted and Fed as a Liquid into 98% Nitric Acid at or Below 50°C in a 2000 gal. glass-lined reactor
  - Initial Reaction is Mildly Exothermic
  - Reaction is Complete in 4-5 hrs. at Reflux, or 24 hrs. at Ambient Temperature
  - Yield is Essentially Quantitative (~3600 lbs. DBTNA after quench and wash)
  - Product (DBTNA):
    - Insensitive Intermediate
    - Melting Point = 140°C
    - Exotherm Onset = 288°C
    - Impact Sensitivity > 80 cm (Holston Method)
    - DBTNA not isolated; Slurried and pumped directly to amination vessel
Type 2 TATB Production at 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 Occurs Over 36 hours at 25 C
- Main By-Product is NH$_4$Br
- Known Impurities
  - Ammonium diaminopicrate (ADAP)
  - Starting material - DBTNA
- Yields are ~ 90%
Type 2 TATB Production at 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

Nutsches of Type 2 TATB
Technical Issues of Early Type 2 TATB Efforts

• In PBXN-7, OSI Type 2 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 with OSI TATB (supplied by OSI)</td>
<td>1.789</td>
<td>70% kbar increase</td>
<td>7572</td>
</tr>
<tr>
<td>Historical data a</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 (lack of voids) of TATB (as compared to traditional TATB (50 micron)…
SEM Analysis

Holston Type 2 TATB

Traditional Type 1 TATB

500x mag

2500x mag
Holston Type 3 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 Type 1 TATB
- Particle size typically 30-40 microns
- Produced ~20 lbs TATB to date
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)
- DCTNPB (product):
  - Yields > 95%
  - Purity typically >99%
  - Insensitive Intermediate
  - Melting Point = 121 °C
  - Exotherm Onset = 220 °C
    (as determined by DSC)
  - Impact Sensitivity > 80 cm (Holston Method)
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)
    - Mp = 214°C
  - Accounts for most of missing mass
Formation and Elimination of Ammonium Diaminopicrate (ADAP)

<table>
<thead>
<tr>
<th>Lot</th>
<th>Average % ADAP Pre-Wash</th>
<th>Average % ADAP Post-Wash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lot 1</td>
<td>0.15%</td>
<td>0.04%</td>
</tr>
<tr>
<td>Lot 2</td>
<td>0.15%</td>
<td>0.02%</td>
</tr>
<tr>
<td>Lot 3</td>
<td>0.58%</td>
<td>0.02%</td>
</tr>
</tbody>
</table>

• Washing with hot water until wash water becomes light yellow lowers ADAP contamination considerably
Type 3 TATB: Particle Size Analysis
SEM Analysis

Holston Type 3 TATB

Traditional Type 1 TATB
Formulations: PBXN-7

- Several lab batches made with Type 3 TATB
- Consistent process and product

<table>
<thead>
<tr>
<th></th>
<th>batch 1</th>
<th>batch 2</th>
<th>batch 3</th>
<th>composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screens (%Pass)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<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>
<tr>
<td>Bulk Density (g/cm³) (Naval)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>met spec</td>
<td>met spec</td>
<td>met spec</td>
<td>met spec</td>
</tr>
<tr>
<td>Composition</td>
<td>met spec</td>
<td>met spec</td>
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<td>met spec</td>
</tr>
<tr>
<td>Moisture</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>met spec</td>
</tr>
<tr>
<td>Impact Sensitivity (ERL, cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>met spec</td>
</tr>
<tr>
<td>VTS by PT Method (100°C, 48h)(mL/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>met spec</td>
</tr>
<tr>
<td>Press Density (g/cm³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>slightly out (low)</td>
</tr>
<tr>
<td>Comments</td>
<td></td>
<td></td>
<td></td>
<td>Blend of 1,2,and 3</td>
</tr>
</tbody>
</table>
PBXN-7 comparisons

- DSC of new TATB (Type 2 and 3) found to be different than Type 1 TATB
- Phenomenon appears to be caused by presence of ADAP in amination

- DSC* not affected by:
  - Glass vs SS reactor
  - Wet or dry amination
  - Amination temp.
  - Purity
  - Digestion in DMSO
  - Amination under N2
Formulations: PBXW-14

- One batch made in lab with Type 3 TATB.
- Successful integration of TATB made from the new OSI method into the existing W-14 formulation procedure.
- No performance data at this time.
### TATB Safety Data

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>ERL Impact Sensitivity</th>
<th>ABL Friction Sensitivity at 1000 lb</th>
<th>ESD Sensitivity at 0.25 J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 2</td>
<td>OSI</td>
<td>1/18 fires at 200 cm</td>
<td>10/10 no-fires</td>
<td>10/10 no-fires</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2/2 no-fires at 158 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type 2</td>
<td>OSI</td>
<td>4/15 fires at 200 cm</td>
<td>10/10 no-fires</td>
<td>10/10 no-fires</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5/5 no-fires at 158 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type 2</td>
<td>OSI</td>
<td>3/16 fires at 200 cm</td>
<td>10/10 no-fires</td>
<td>10/10 no-fires</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4/4 no-fires at 158 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type 3</td>
<td>OSI</td>
<td>10/10 no-fires at 200 cm</td>
<td>10/10 no-fires</td>
<td>10/10 no-fires</td>
</tr>
<tr>
<td>Type 3</td>
<td>OSI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard-Type 1</td>
<td>DOE</td>
<td>10/10 no-fires at 200 cm</td>
<td>10/10 no-fires</td>
<td>10/10 no-fires</td>
</tr>
<tr>
<td>RDX standard</td>
<td>N/A</td>
<td>17 cm</td>
<td>550 lb_t</td>
<td>10/10 no-fires</td>
</tr>
</tbody>
</table>
## PBXN-7 Qualification
### Small Scale Safety Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Aged “0” months</th>
<th>Aged “2” months</th>
<th>Aged “4” months</th>
<th>Aged “6” months</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact Sensitivity</td>
<td>103.1</td>
<td>110.3</td>
<td>107.2</td>
<td>108.2</td>
<td>cm</td>
</tr>
<tr>
<td>Impact Reference (RDX)</td>
<td>16.6</td>
<td>16.6</td>
<td>16.6</td>
<td>16.6</td>
<td>cm</td>
</tr>
<tr>
<td>Friction</td>
<td>&gt;360</td>
<td>&gt;360</td>
<td>&gt;360</td>
<td>&gt;360</td>
<td>Newt.</td>
</tr>
<tr>
<td>PETN Reference</td>
<td>48</td>
<td>48</td>
<td>48</td>
<td>48</td>
<td>Newt.</td>
</tr>
<tr>
<td>VTS</td>
<td>0.09</td>
<td></td>
<td></td>
<td>0.02</td>
<td>ml/g</td>
</tr>
<tr>
<td>DSC</td>
<td>242.3</td>
<td>242.6</td>
<td>242.3</td>
<td>242.3</td>
<td>° C</td>
</tr>
</tbody>
</table>
# PBXN-7 Qualification
## LSGT Data

<table>
<thead>
<tr>
<th>Material Tested</th>
<th>Baseline “0” Months</th>
<th>Aged “6” Months</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBXN-7 Manufactured with Benziger TATB Type 1 Lot # BAE07B382-014</td>
<td>1.79</td>
<td>205 - 210</td>
</tr>
<tr>
<td>PBXN-7 Manufactured with OSI TATB Type 3</td>
<td>1.78</td>
<td>203.8</td>
</tr>
<tr>
<td>PBXN-7 Manufactured with OSI TATB Type 2 Lot # BAE06L382-013</td>
<td>1.79</td>
<td>155.8</td>
</tr>
</tbody>
</table>
### Initiation Validation Test at Cold Temperature

**PBXN-7 LOT # BAE06L382-013 Manufactured with OSI Holston Type 2 TATB**

<table>
<thead>
<tr>
<th>Fuze Configuration</th>
<th>Pellet Density (gm/cc)</th>
<th>Dent Plate Hardness</th>
<th>Dent Depth (inches)</th>
<th>Dent Depth GO Criteria (inches)</th>
<th>GO/NO GO</th>
</tr>
</thead>
<tbody>
<tr>
<td>FMU-139</td>
<td>1.760</td>
<td>90</td>
<td>0.0565</td>
<td>0.0425</td>
<td>GO</td>
</tr>
<tr>
<td>FMU-139</td>
<td>1.760</td>
<td>90</td>
<td>0.0525</td>
<td></td>
<td>GO</td>
</tr>
<tr>
<td>FMU-139</td>
<td>1.800</td>
<td>82</td>
<td>0.0580</td>
<td></td>
<td>GO</td>
</tr>
<tr>
<td>FMU-139</td>
<td>1.800</td>
<td>88</td>
<td>0.0580</td>
<td></td>
<td>GO</td>
</tr>
<tr>
<td>FMU-139</td>
<td>1.800</td>
<td>85</td>
<td>0.0585</td>
<td></td>
<td>GO</td>
</tr>
<tr>
<td>FMU-152</td>
<td>1.760</td>
<td>90</td>
<td>0.0425</td>
<td>0.0346</td>
<td>GO</td>
</tr>
<tr>
<td>FMU-152</td>
<td>1.760</td>
<td>88</td>
<td>No Dent</td>
<td></td>
<td>NO GO</td>
</tr>
<tr>
<td>FMU-152</td>
<td>1.800</td>
<td>84</td>
<td>No Dent</td>
<td></td>
<td>NO GO</td>
</tr>
<tr>
<td>FMU-152</td>
<td>1.800</td>
<td>86</td>
<td>No Dent</td>
<td></td>
<td>NO GO</td>
</tr>
<tr>
<td>FMU-152</td>
<td>1.800</td>
<td>87</td>
<td>No Dent</td>
<td></td>
<td>NO GO</td>
</tr>
</tbody>
</table>
TATB Costs

- Estimates are based on R&D efforts, production efforts, and prior experience and knowledge.
- Costs are normalized to Type 1 cost estimates.
- Type 2 is less than half of the cost of Type 1, due to the simplicity of the process.
Conclusions

- Two TATB manufacturing processes developed at HSAAP (Type 2 and Type 3)
- Processes are robust and safe
- Competitive costs to Type 1 TATB
- Process and cost optimization ongoing
- Quality equivalent to traditional sources of “DOD grade” material
- Difference in thermal properties (DSC) appear to be caused by ADAP impurity in process
- Type 3 TATB currently appears to be a “drop-in” replacement in DOD formulations (waiting for further 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
  • Brian Alexander - PBXN-7 and PBXW-14 formulation

• Navy:
  • Al Stern, Brad Sleadd, Tim Mahoney
    -Useful discussions, suggestions, testing and direction

• ONR Mantech Program-Funding
• Chuck Painter-Mantech director