Innovative Nitrogen-Doped Boron Propellants

Presented by:

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Paul H. Matter, LLC**
OUTLINE

- The Problem
- Status/Testing
  - Experimental Section
    - Propellant Processing
    - Closed Bomb Test
    - Propellant Wear and Erosion Test
- Prior Art and Advantages Over Prior Art
- Status/Testing
  - Results and Discussion
    - Nano-Boron Nitride
  - Burn Rates
  - XPS/SEM/TEM
- Conclusions / Future Work
Army needs more powerful and balanced propellants

Barrel wear and erosion is a problem

BN is interesting because:
- Hexagonal BN is lubricating
- Boron doping of steel improves its hardness
- Boron has low molecular weight
- Resistant to chemical attack
Currently fielded 155mm artillery propelling charge, M232/M232A1, has exhibited spiral wear and erosion problems.

- Wear reducing liner
Many Low Vulnerability (LOVA) Propellant Formulations contain RDX.
- RDX is highly chemically erosive

New, experimental low-erosivity LOVA propellants have been produced by
- Reducing RDX content
- Introducing nitrogen-rich energetic binder or filler compounds.
- Compromises between performance, sensitive and erosivity must be reached in these cases
- Ceramic additives to the propellant can theoretically reduce barrel deterioration by coating the inside of the barrels[3]
  - Challenges with dispersing the particles in the propellant, and due to abrasion from incomplete sublimation, propellant and ceramic composites that produce regenerative wear-resistant coatings have not been demonstrated
- Ceramic Barrel Liners have been identified as a promising technology for some time.
  - Very good wear characteristics and thermal resistance
  - Susceptibility of ceramics to fracture, driven by stress, induced by the different thermal expansion properties of steel and ceramics
**Approach:**

1. **Additive + Propellant**
2. **Mix and extrude**
3. **Propellant Composite**
4. **Propellant Fired**
5. **Coated and hardened barrel**

(Dramatized image of BN$_x$O$_y$ coating B-doped Fe)
# Particles Size / Surface Area Control

<table>
<thead>
<tr>
<th>Synthesis Condition</th>
<th>Surface Area (m²/g)</th>
<th>Calculated Particle Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Conc. A</td>
<td>20.0</td>
<td>143</td>
</tr>
<tr>
<td>High Conc. B</td>
<td>23.0</td>
<td>124</td>
</tr>
<tr>
<td>Intermediate Conc. A</td>
<td>37.8</td>
<td>76</td>
</tr>
<tr>
<td>Intermediate Conc. B</td>
<td>51.2</td>
<td>56</td>
</tr>
<tr>
<td>Low Conc.</td>
<td>77.4</td>
<td>37</td>
</tr>
</tbody>
</table>
SEM Imaging

BN NANO-PARTICLE SPHERES

- Particle agglomerate upon drying
- Individual particles are spheres
- Spheres with diameters in the nanometer range.
TEM Imaging

TEM images showing nano-spheres of boron nitride used for propellant additive testing (US Patent Pending).
EELS Analysis, showing the material has a 1:1 B:N ratio (US Patent Pending).
XPS Analysis showing (a) the N 1s region, and (b) the B 1s region for the BN nano-particle propellant additive compared to a commercial hexagonal boron nitride sample.
# IMR-4198 Composition

<table>
<thead>
<tr>
<th>Propellant Name</th>
<th>Nitrocellulose Composition (wt%)</th>
<th>Dinitrotoluene Composition (wt%)</th>
<th>Other Components (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M1</strong></td>
<td>86%</td>
<td>9.9%</td>
<td>3% Dibutylphthlate 1% Diphenylamine</td>
</tr>
<tr>
<td><strong>M14</strong></td>
<td>90%</td>
<td>8%</td>
<td>2% Dibutylphthlate 1% Diphenylamine 0.7% Residual solvent 0.6% Moisture 0.2% Graphite</td>
</tr>
<tr>
<td><strong>IMR 4198 (Hodgdon)</strong></td>
<td>&gt;85%</td>
<td>&lt;10%</td>
<td>&lt;10% Non-hazardous additives</td>
</tr>
</tbody>
</table>
Propellant Testing

DSC Testing

<table>
<thead>
<tr>
<th>Propellant Material Tested</th>
<th>Heating Rate (°C/min)</th>
<th>Sample Amount (mg)</th>
<th>Exotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Onset (°C)</td>
</tr>
<tr>
<td>IMR4198 w/o BN</td>
<td>10</td>
<td>0.36</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.15</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.58</td>
<td>159</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>161</td>
</tr>
<tr>
<td>IMR4198 w/ BN</td>
<td>10</td>
<td>0.22</td>
<td>163</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.40</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.45</td>
<td>161</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>161</td>
</tr>
</tbody>
</table>
## Heat of Combustion

<table>
<thead>
<tr>
<th>Material Tested</th>
<th>Heat of Combustion; ASTM D240 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMR-4198 w/o BN</td>
<td>10038</td>
</tr>
<tr>
<td>IMR-4198 w/ BN</td>
<td>10036</td>
</tr>
</tbody>
</table>
Propellant Testing

Closed Bomb Testing

200 CC CLOSED BOMB
## Propellant Testing

### Closed Bomb Testing

<table>
<thead>
<tr>
<th>Material Tested</th>
<th>Amount (gram)</th>
<th>Closed Bomb Chamber pressure (psig)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMR-4198 w/o BN</td>
<td>5.0</td>
<td>10k</td>
<td>Oxidation (rust color)</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>15k</td>
<td>Deep oxidation (rust)</td>
</tr>
<tr>
<td>Mix 50/50 of pure and composite (WITH A% BN)</td>
<td>5.0</td>
<td>10,250</td>
<td>Black residue on the surface, no visible oxidation</td>
</tr>
<tr>
<td>IMR-4198 w/ BN</td>
<td>5.0</td>
<td>10k</td>
<td>Black residue on the surface, no visible oxidation</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>15k</td>
<td>Possible slight oxidation (green color)</td>
</tr>
<tr>
<td>IMR 4198 as received</td>
<td>5.0</td>
<td>9,170</td>
<td>Reference sample, used high speed DAQ system.</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>15,470</td>
<td>Reference sample, used high speed DAQ system.</td>
</tr>
</tbody>
</table>
Characterization

Closed Bomb Inserts

(a) No BN, 10K psi
(b) A% BN, 10K psi
(c) B% BN, 10K psi
Characterization

Closed Bomb Inserts

(d) No BN, 15K psi

(e) With BN, 15K psi
Characterization

XPS Analysis

More oxidized appearance

Surface Composition (mole %)

Sample

5 g w/ BN

7.5 g w/ BN

5 g w/o BN

7.5 g w/o BN

B
Fe
K
F
SEM – Fresh Insert
Characterization

SEM – Insert Fired w/o BN
Characterization

SEM – Insert Fired w/o BN

SE 03-Jul-13
WD 9.7mm 15.0kV x10k 5um
SEM – Insert Fired with BN
Figure 1: RPD380 w/o BN - Single Perf grain used in erosion testing

Figure 2: RPD-380 w/BN Single Perf grains used in erosion testing
**Figure 10**: Wear and Erosion Test Results for hard and unhardened sleeves (US Patent Pending).
Note: Sleeves 1 and 2 were hardened to approximately Rockwell Hc 41. Sleeves 3 and 4 were approximately Rockwell Hc 12. See ICP

The effect of the BN propellant additive (US Patent Pending) suggests an apparently significant reduction in the mass loss for both hardened and unhardened insert sleeves relative to baseline RPD-380 propellant. The results look compelling at 2.8 and 1.8 times life increase for hard and unhardened insert sleeves, respectively.
WEAR AND EROSION CHARACTERIZATION

- **SEM:**
  - Hardened and cleaned – both with and without BN
  - Unhardened and un-cleaned – imaged cleaned areas of both with and without BN (un-cleaned areas were too resistive).

- **ICP:**
  - Hardened and cleaned – both with and without BN

- **XPS:**
  - Hardened and cleaned – both with and without BN
  - Unhardened and cleaned –
  - Unhardened and un-cleaned coating
  - Saw material –

- **Moh’s Hardness Testing:**
  - Hardened and cleaned – both with and without BN
  - Unhardened and cleaned – both with and without BN
**Figure 3:** Hardened Steel Sleeves (a) RPD380 P2 flow entrance end, sleeve 1. (b) BN-RPD380 P5 Flow Exit end, sleeve 2 – cleaned after 3 shots
Figure 4: Insert Sleeve 2 – (a) hardened Steel, after firing 3 shots RPD380 Propellant (Cleaned), RPD380 P - Flow Entrance End – cleaned after 3 shots  (b) RPD380 P - Flow Exit End – cleaned after 3 shots
Light Micrographs

Hardened, Cleaned

Without BN                                       With BN
Hardened, cleaned

Without BN

With BN
Hardened, Cleaned

Without BN

With BN
SEM (1,250x)

Unhardened (clear area)

Without BN  With BN
Unhardened (clear area)

Non BN

With BN
Hardened and cleaned surface composition

After firing, the samples were analyzed by XPS to determine surface composition, and ICP analysis to determine the bulk composition.

- Relative surface composition for samples fired in wear and erosion testing.
- ICP analysis showed less than 0.01% B in all samples, and the remaining composition is consistent with the respective steel specification.

<table>
<thead>
<tr>
<th>Element</th>
<th>Hardened (0% BN)</th>
<th>Hardened (B% BN)</th>
<th>Unhardened (B% BN)</th>
<th>Unhardened (B% BN)</th>
<th>Coating from Unhardened B% BN</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>65.2%</td>
<td>19.9%</td>
<td>29.9%</td>
<td>13.1%</td>
<td>64.6%</td>
</tr>
<tr>
<td>B</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.4%</td>
<td>2.3%</td>
</tr>
<tr>
<td>N</td>
<td>2.8%</td>
<td>1.4%</td>
<td>0.0%</td>
<td>0.9%</td>
<td>5.2%</td>
</tr>
<tr>
<td>Fe</td>
<td>32.0%</td>
<td>78.7%</td>
<td>70.1%</td>
<td>85.6%</td>
<td>27.9%</td>
</tr>
</tbody>
</table>
## HARDNESS AND TESTING

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unhardened steel reference</td>
<td>5.5</td>
</tr>
<tr>
<td>Hardened, without BN</td>
<td>7.0</td>
</tr>
<tr>
<td>Hardened, with BN</td>
<td>7.5</td>
</tr>
<tr>
<td>Unhardened, without BN</td>
<td>5.5</td>
</tr>
<tr>
<td>Unhardened, with BN</td>
<td>7.5</td>
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### HARDNESS AND TESTING

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<td>7.5</td>
</tr>
<tr>
<td>Unhardened, without BN</td>
<td>5.5</td>
</tr>
<tr>
<td>Unhardened, with BN</td>
<td>7.5</td>
</tr>
</tbody>
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CONCLUSIONS

- Evidence for reduced erosion observed.
  - The results look compelling at 2.8 and 1.8 times life increase for hard and unhardened insert sleeves, respectively.
- Propellant with BN generates a lower flame temperature.
- Increased hardness was observed in unhardened steel fired with BN additive.
- SEM imaging showed less surface crack density in the samples fired with boron nitride.
- No destabilizing effects on propellant.
- Boron-based coating was observed.
Future Work

- More quantitative hardness testing after extended firing would be useful to verify a hardening mechanism.
- Characterization of the boron, possibly in or on the steel surface, would also be beneficial.
- Further wear and erosion testing of the propellant additive is in progress in a 25mm gun test fixture/projectile test stand that will simulate the conditions of 155 mm artillery.
  - Larger amount of propellant necessary to support a sufficient number of firings to generate supportable statistical conclusions
  - Alternate grain form to allow larger bomb loading density
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