Early Development of Melt-Pour Explosives: Desensitizing Ionic Liquid Formulations

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Overview

• Introduction: Ionic liquids
• Concept: Desensitizing ionic liquids for melt-pour formulations
• Approach
  • Ionic liquid compounds synthesized/investigated
  • Compatibilities with explosives
• Performance testing to date
• IM testing to date
• Future directions
Introduction: Ionic Liquids

- Ionic liquids are defined as organic salts with melting points <100°C
  - Low vapor pressures, high densities
- Energetic ionic liquids have been extensively investigated as a concept
  - Azide or nitro groups covalently bonded to nitrogen-based heterocycles (Katritzky, Shreeve)
  - Energetic anions such as nitrate, perchlorate, or tetraniitroaluminate, often in combination with nitrogen-based heterocycles (Drake, Shreeve, Hawkins, Galvez-Ruiz, Christie, Klapotke)
Insensitive Materials Development

- Energetic materials R&D is increasingly driven by IM requirements
- Per US DoD Directive 5000.2-R, all new munitions must be designed to withstand unplanned stimuli
- Approaches to IM:
  - Design of new energetic molecules and materials
    - Potentially very rewarding, but development of material/process is extremely time consuming with no guarantees
  - Formulate existing explosives with less sensitive materials
    - Dilution of explosive performance must be minimized
• ATK Launch Systems has developed this concept under direction of US Army ARDEC

• Concept: utilize dense, inert ionic liquids to desensitize energetic formulations
  
  • Ionic liquid with melting point between 80 and 100 °C targeted in order to enable use of existing TNT melt-pour facilities/equipment
  
  • Legacy explosive(s) added to molten ionic liquid and poured into article
    
    • Ionic liquid incorporated as continuous phase of the formulation
    
    • Allows for variable article geometries
    
    • Theoretically allows for unlimited working time with the material (in contrast to cast-cure)
• Strategy used in selecting desensitizing ionic liquid candidates:
  • Minimize saturated carbon (fuel) content of compounds since they require addition of oxidizer for efficient detonation
  • Incorporate groups that maximize density (halocarbons, ketones, carboxylates, planar structures)
  • Tendency toward low MW gaseous detonation products (H₂, N₂, HF)
  • Non-corrosive anions (no perchlorates or halide anions if possible)

• Program goals:
  • Demonstrate significant IM enhancement in melt-pour IL formulation with performance between TNT and Comp-B (or higher)
Dozens of new IL’s have been synthesized and characterized at ATK Launch systems on this program.

Synthesis of most of these IL’s have proceeded by one of two generic routes to guanidinium and aminoguanidinium-based materials.

Essentially quantitative in yield, with water and CO₂ as sole byproducts (“green” chemistry; no purification necessary).
Other types of candidates explored

• Hydroxylammonium and hydrazinium salts also explored
• Azole-based anions and cations (e.g. - 5-aminotetrazolate)
• Most of the salts had melting points within 50 degrees C of desired range
• Several display melting points extremely close to desired range
  • Aminoguanidinium glycolate (peak mp = 108 °C)
  • Aminoguanidinium 5-aminotetrazolate (peak mp = 94 °C)
  • 60:40 AG:G Oxalate (peak mp = 77 °C)
  • 60:40 AG:G Malonate (peak mp = 107 °C)
  • Aminoguanidinium trifluoroacetate (peak mp = 67 °C)
## Compatibilities of Ionic Liquids with Explosives

<table>
<thead>
<tr>
<th></th>
<th>AG·TFA</th>
<th>60:40 AG:G Oxalate</th>
<th>60:40 AG:G Malonate</th>
<th>AG Glycolate</th>
<th>AG 5-AT</th>
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<tbody>
<tr>
<td>RDX</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>HMX</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
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<tr>
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<td>Yes</td>
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<td>CL-20</td>
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<tr>
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<td>No</td>
<td>No</td>
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</table>

- Not all of the ionic liquids are compatible with all explosives
- Chemical origin of these incompatibilities are not yet understood
- Only aminoguanidinium trifluoroacetate (AG·TFA) compatible with all explosives tested
AG·TFA Formulations: Sensitivity Testing

AG·TFA = Aminoguanidinium trifluoroacetate

- Initial formulation plan - (50% AG·TFA / 25% Ground RDX / 25% Unground RDX)
  - ABL Impact – 80cm
  - ABL Friction – 800lb @ 8ft/s
  - ABL ESD – 0.077J
  - SBAT Onset – 275 °F
  - Russian DDT – No Go @ 500PSI (6.9gm, slight report)
**AG·TFA: Dent-Rate Testing**

<table>
<thead>
<tr>
<th>Formulation</th>
<th>AGTFA (%)</th>
<th>Energetic material</th>
<th>% Unground</th>
<th>% Ground</th>
<th>Total Nitramine (%)</th>
<th>Detonation Velocity (km/s)</th>
<th>Dent Depth (in)</th>
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<tr>
<td>1</td>
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<td>3.23</td>
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<td>0</td>
<td>2.53</td>
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</table>

- Dent/rate articles with neat AG·TFA (non-energetic) material appear to burn but not detonate
- Positive detonation velocity, but no dent on plate
### AG·TFA Formulations: Dent-Rate Testing

<table>
<thead>
<tr>
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<th>Energetic material</th>
<th>% Unground</th>
<th>% Ground</th>
<th>Total Nitramine (%)</th>
<th>Detonation Velocity (km/s)</th>
<th>Dent Depth (in)</th>
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<tr>
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<td>63</td>
<td>7.56</td>
<td>0.43</td>
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</table>

- Performance at 50% RDX loading is between TNT and Comp B
Setup for Cook-Off Testing

81mm Mortar Slow Cook-Off setup
AG·TFA w/ 50% RDX: Slow Cook-Off Results

- Slow cook-off: (heated at 6 °F/min); max oven temp 550 °F
- No visible reaction; “type 5 like” behavior

SCO: 3.3 °C /min to 288 °C max
81mm Slow Cook-off AGTFA (50%) RDX Mix 2079-79-1
Reaction Temperature = 306 deg F (17.22 hr. from start of ramp)
AG·TFA w/ 50% RDX: “Fast Cook-Off” Results

- Faster cook-off: (heated at ~50 °F/min); max oven temp 550 °F
- Contents charred, no violent reaction; “type 5 like” behavior

“FCO”: 28 °C /min to 288 °C max
Test Configuration:

- Passed 50 cal bullet impact
- No detonation; mortar body shattered by bullet
- No reaction of fill; “type 6 like” behavior
Test Configuration:

- 25 mm SCJ
- 1/2-Inch Steel Witness Plate
- 81 mm Mortar
- 1/4-Inch Aluminum Witness Plate

Results:

- No Damage to Plate
- Unreacted Fill
- Body Fragments

- Passed 25mm SCJ test
- No detonation; mortar body shattered by jet
- Much of the fill did not even burn (white residue on plate); “type 5” behavior
Conclusions

• Concept of “desensitizing ionic liquids” appears to be promising

• Aminoguanidinium trifluoroacetate used as pathfinder material
  • Promising with regard to performance
    • At 50% loading performance between TNT and Comp B (measured by dent-rate)
  • Promising with regard to IM
    • Passed Slow Cook Off, “Faster” Cook Off, 50mm Bullet Impact and 25mm SCJ

• Future work: new candidate under investigation which is closely related to AG·TFA but exhibits essentially ideal melting behavior
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