R&D of Energetic Ionic Liquids

Next Generation Energetic Materials – Striking a Balance between Performance, Insensitivity, and Environmental Sustainability

Partners in Environmental Technology
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Tom Hawkins
AFRL/RZSP
R&D of Energetic Ionic Liquids

Current research programs are aiming to develop ionic liquids (ILs) as energetic materials for various applications. Such applications for ILs include both propulsion and explosives. Within the propulsion arena, a focus is to replace hydrazine (a highly toxic compound) as a fuel. The approach to replacing hydrazine is the synthesis and development of ILs with substantially less vapor toxicity and superior energy density. Hypergolic bipropellants are defined as fuel and oxidizer combinations that, upon contact, chemically react and release enough heat to spontaneously ignite, eliminating the need for an additional ignition source. The feasibility that an IL can undergo hypergolic ignition with a common oxidizer like nitric acid was demonstrated for the first time in our laboratory a few years ago (see references 1 and 2, below). Hazardous characteristics, undesirable physical and chemical properties of such ILs must be identified before further development by a potential user. IL-based fuels and their properties will be discussed (including limited safety and sensitivity, and thermophysical properties). 1. S. Schneider, T. Hawkins, M. Rosander, G. Vaghjiani, S. Chambreau and G. Drake, Energy Fuels, 2008, 22, 2871-2872. 2. S.D. Chambreau, S. Schneider, M. Rosander, T. Hawkins, C.J. Gallegos, M.F. Pastewait and G.L. Vaghjiani, J. Phys. Chem. A, 2008, 112, 7816-7824.
RESEARCH AND DEVELOPMENT OF ENERGETIC IONIC LIQUIDS

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Performance/Environmental/Safety Challenge

Hydrazines are SOTA spacecraft fuel:

- **Increased Operations Costs:**
  - Carcinogenic Vapor (Respiratory Route)
  - Dermal Toxicity
  - Strong Reducing Agent
  - Flammable (LEL = 4.7%, UEL = 100%)

- **On-Orbit Propulsion Systems Affected**

<table>
<thead>
<tr>
<th>System</th>
<th>Mission</th>
</tr>
</thead>
<tbody>
<tr>
<td>FltSatCom</td>
<td>Communications</td>
</tr>
<tr>
<td>STARDUST</td>
<td>Deep Space Probe</td>
</tr>
<tr>
<td>INTELSAT</td>
<td>Communications</td>
</tr>
<tr>
<td>HEAO-B</td>
<td>X-Ray Astronomy</td>
</tr>
</tbody>
</table>

- **Hundreds of Satellites Use Hydrazine for RCS & ACS**

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Advanced Chemical Propulsion For Spacecraft

Communication (Iridium)

Spacecraft / Satellite propulsion employ hydrazines in both monopropellants and bipropellants

Global Positioning & Navigation (NAVSTAR GPS)

Weather (NASA TRMM)

Reduced toxicity can give:
- lower handling cost
- lower transport cost
- more rapid response

Higher performance gives:
- longer lifetime
- faster response time
- larger payloads

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Energetic Ionic Liquids
Avenues to Lower Toxicity & Higher Performance

• History
  – An ionic compound that has a melting point at or below 100°C
  – Seminal work at USAFA (Wilkes et.al.)
  – Industrial solvents, green chemistry
    – Low vapor pressure, low vapor toxicity
    – Wide solubility ranges

• ILs as Energetic Materials
  – First energetic ILs: chemical oddities
  – AFRL realizes chemical structure manipulation leads to new classes of highly, energy dense materials (HEDM) for advanced propulsion
‘Greener’ Chemical Propulsion-ILs in Advanced Monopropellants

ADN (M.P. 92°C) is also an Energetic Ionic Liquid

- ADN-based monopropellant (LMP-103S) from ECAPS, Swedish Space Corporation
- High performance ‘green’ propellant (30% Improved Isp*Density vs. hydrazine)
- 1 N Thruster using thermal and catalytic ignition flight qualified and flown (PRISMA)

AF-M315E is US Air Force IL-Based Monopropellant

- Significant physical property and performance advantages (50% improved Isp*Density)
- Ongoing hardware developments

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADN</td>
<td>60-65</td>
</tr>
<tr>
<td>Methanol</td>
<td>15-20</td>
</tr>
<tr>
<td>Ammonia</td>
<td>3-6</td>
</tr>
<tr>
<td>H₂O</td>
<td>balance</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties</th>
<th>LMP-103S</th>
<th>AF-M315E</th>
<th>Hydrazine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isp vac, lbf sec/lbm (e = 50:1 Pc = 300 psi)</td>
<td>252 (theor.)</td>
<td>266 (theor.)</td>
<td>242 (theor.)</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>1.24</td>
<td>1.465</td>
<td>1.01</td>
</tr>
<tr>
<td>Vapor Pressure (torr)</td>
<td>Ammonia Methanol H₂O</td>
<td>&lt;0.1 (w/o H₂O)</td>
<td>14.3</td>
</tr>
</tbody>
</table>

* Sjoberg et.al., Insensitive Munitions & Energetic Materials Technology Symp. Proc., Tucson, USA, May 11-14, 2009


Toxicity Assessment of AF-M315E

Toxicity Testing Results

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>AF-M315E</th>
<th>HYDRAZINE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD50 (rat), mg/kg</td>
<td>550</td>
<td>60</td>
</tr>
<tr>
<td>Dermal Irritation (rabbit)</td>
<td>None - Slight</td>
<td>Corrosive</td>
</tr>
<tr>
<td>Dermal Sensitization (guinea pig)</td>
<td>Non Sensitizer</td>
<td>-</td>
</tr>
<tr>
<td>Genotoxicity (Ames)</td>
<td>3 Negative/2 Positive</td>
<td>Positive</td>
</tr>
</tbody>
</table>

Toxic Vapor Components Testing

NASA White Sands Test Facility – No chemical species detected in the propellant headspace that are identified as carcinogens or have regulated vapor concentration limits (detection limit 2-3 ppb)

- Time consuming
- Expensive

- Low hazard
- Low cost

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Propellant Development

There is more to it than performance & toxicity

Oxygen balance
Decomposition mechanisms
Ionic/covalent bonds
Hydrogen bonding

Molecular shape

Functional groups
C/H/N ratios
Strain
 unsaturation

Isp
Density
Toxicity

Hazard class
Impact sensitivity
Friction sensitivity
ESD sensitivity
Compatibility & Storability

Vapor pressure
Viscosity
Melting point
Thermal stability
Ignitability
Cost

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Much Effort Required in Small-Scale Safety/Hazard Evaluations

<table>
<thead>
<tr>
<th>Propellant</th>
<th>AF-M315E*</th>
<th>LMP-103S**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unconfined Burn</td>
<td>Test 1 and 3: No reaction Test 2: burn</td>
<td>Negative (burn)</td>
</tr>
<tr>
<td>Drop Weight Impact Sensitivity (JANNAF Test Method)</td>
<td>126 Kg-cm ($E_{50}$) Lot 32 Reference material: N-Propyl Nitrate (21 kg-cm)</td>
<td>Under US Evaluation</td>
</tr>
<tr>
<td>Sliding Friction (Julius Peters –BAM)</td>
<td>352 N (5 consecutive “no go” ) Lot 32</td>
<td>Under US Evaluation</td>
</tr>
<tr>
<td>TGA (75°C/48 hours)</td>
<td>0.86 Wt % Excluding Volatiles</td>
<td>Under US Evaluation</td>
</tr>
<tr>
<td>Critical Diameter</td>
<td>4 in&lt; $D_c$&lt;7 in , Confined</td>
<td>~ 0.4 in (10 mm) , Confined</td>
</tr>
<tr>
<td>Electrostatic Discharge</td>
<td>&gt;1J</td>
<td>Under US Evaluation</td>
</tr>
</tbody>
</table>


Approved FHC Test Plan

- **External Fire Test**
  - Six 5-gallon composite pails

- **Sympathetic Detonation**
  - 5-gallon container in 20 gallon overpacks
  - Initiation method consisted of a \( \frac{1}{4} \) lb C-4 booster on the container

External Fire Test
External Fire and Stack Test Results

External Fire Test

• Propellant pails popped their lids and then individually burned mildly 6-8 minutes into the test
• All propellant and inner poly bottles were consumed
• No fragments thrown
• Thermocouples measured the flame temperature up to 1428°F

Unconfined Package Test

Mild burning reaction!

No detonation/No burn-Passes test!

US DOT Granted Allowance For Two Package Configurations of AF-M315E

U.N. PROPER SHIPPING NAME AND NUMBER:
Propellant, liquid, UN0495
➢ 5 gallon composite container- 55 lbs of propellant in a 20 gallon drum over-pack (EX2010060551)
Technology Development

- Demonstrate a survivable thruster to meet IHPRPT Phase II spacecraft monopropellant goal: 
  50% increase in $I_{sp} \rho$ over hydrazine

- AFRL sponsored program performed by Gencorp Aerojet, Redmond WA, USA

Achievements

- High temperature catalysts and chamber materials capable of withstanding combustion temperature

- Good ignition response times

- Stable combustion - good chamber pressure roughness

4.5 lbf Brassboard Thruster Pulses

Future work to concentrate on conversion from heavy weight to flight weight hardware
Ionic Liquids as Bipropellant Fuels

- Ignites
- Ignites Fast (10ms)
- Ignites Fast & Green(er)

Image: NASA

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Do Stable, Room Temperature Borohydride-Based ILs Exist that are Hypergolic to all Known Liquid Oxidizers (including the ‘Greenest’ Oxidizer Hydrogen Peroxide)?

We know that solutions of LiAl hydrides and LiBH$_4$ in organic solvents are hypergolic with H$_2$O$_2$.

a) T.L. Pourpoint, J.J. Rusek, 5th International Hydrogen Peroxide Propulsion Conference, Purdue University, West Lafayette, IN, September 2002.
b) J.J. Rusek, Proceedings of the 2nd International Conference on Green Propellants for Space Propulsion (ESA SP-557), Sardinia, Italy June 2004;

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“The GREEN Flame”
Initial Borohydride-Based ILs

<table>
<thead>
<tr>
<th>Cyanoborohydride Ionic Liquid Fuels</th>
<th>Ignition delay [m]</th>
<th>Decomp. Onset [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>* <img src="image1" alt="Structure 1" /></td>
<td>11</td>
<td>146</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 2" /></td>
<td>600</td>
<td>249</td>
</tr>
<tr>
<td>** <img src="image3" alt="Structure 3" /></td>
<td>28</td>
<td>307</td>
</tr>
</tbody>
</table>

**Demonstrated hypergolic with nitric acid**

**But not with N$_2$O$_4$ or H$_2$O$_2**

- Remarkable impact of cation (and anion) structure on reactivity/stability


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A Stable, Room Temperature IL Fuel Based on Borohydride Anion: [Al(BH₄)₄]⁻

- trihexyl-tetradecyl-phosphonium (THTDP) cation known to be stable with bases and reducing agents*
- THTDP known to reduce melt point and promote liquidus
- [Al(BH₄)₄]⁻ also promotes liquidus

Combined, the two ions create a low viscosity, hypergolic IL-fuel!

\[
[THTDP]^+ [BH_4^-]^- + Al(BH_4)_4 \rightarrow [THTDP]^+ [Al(BH_4)_4]^- \]

<table>
<thead>
<tr>
<th>Fuel/Oxidizer</th>
<th>90%H₂O₂</th>
<th>98%H₂O₂</th>
<th>N₂O₄</th>
<th>WFNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₄P Al(BH₄)₄</td>
<td>Ignition</td>
<td>Ignition</td>
<td>Ignition Vapor ignition</td>
<td>Explosive Rxn</td>
</tr>
<tr>
<td>Ignition Delay</td>
<td>&lt; 30ms</td>
<td>&lt; 30ms</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


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Ionic Liquids as Explosives

- Initial USAF work on energetic RTILs over 15-years ago
- Recognized potential for advanced explosives
- Navy encouraged R&D on melt cast explosives

HEHN-Based Explosive Detonability Test (2-kg)
## IL-Based Explosive Properties

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Heat of Formation (Kcal/mol)</th>
<th>Density (g/cc)</th>
<th>Total Detonation Energy (KJ/cc)</th>
<th>Shock Velocity (mm/ms)</th>
<th>C-J Pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMT-ONT</td>
<td>+140 (est)</td>
<td>1.58</td>
<td>8.30</td>
<td>7.91</td>
<td>23.9</td>
</tr>
<tr>
<td>1-AMTN*</td>
<td>+17 (est)</td>
<td>1.63</td>
<td>7.92</td>
<td>8.12</td>
<td>23.6</td>
</tr>
<tr>
<td>TNT</td>
<td>-15 (exp)</td>
<td>1.65</td>
<td>6.94</td>
<td>7.06</td>
<td>19.7</td>
</tr>
</tbody>
</table>


**-AMT-ONT from metathesis rxn**

**-Performance > TNT**
Another Challenge: Predictive Toxicology

• Background
  – *Next generation propellants & explosives are emerging* with many programs championed by US Army, Navy and USAF involvement
    • Environmentally benign impact initiated devices (DOE)
    • Lead-free electrical & percussion primers (Navy/Army)
    • Chlorine-free pyrotechnics (Navy)
    • Chlorine-free (AP-free) solid propellant (Army/Navy/AF)
      – USAF AF-M315E
    • Propellant uses ionic liquids to yield low vapor toxicity
      – Sweden/ECAPS LMP-103S
    • Propellant uses ADN-based formulation

New PEP materials are likely to employ advanced energetic molecules

*Issue*: Currently available, predictive toxicology models (e.g. TopKat, EPI Suite, ADMET) do not comprehensively handle EMs, particularly salts
Comparison of prediction methods for general toxicity of 30 drugs in external test set


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Predictive Methods Expected Payoff

• Well-functioning, predictive toxicological methods for EM development can significantly affect life cycle costs for new systems
• DoD will be able to make more informed program decisions
• ESOH risks will be mitigated early in Acquisition/RDT&E process
• DoD will save $$ in clean-up, compliance and restoration costs
Summary

• AFRL continues efforts in energetic ionic liquids research
  – IL-based propellants can convey unique capabilities
  – Energetic ILs have intriguing explosive properties

• IL material properties promise significantly improved performance & reduced toxicity compared to hydrazine fuels
  • Moving to lower testing/operations costs, improved operational responsiveness (as propellant candidates emerge, cost analysis will determine overall system benefits)
  • Leading to next generation systems with increased payload, range, and lifetime

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Acknowledgments

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