



R&D of Energetic Ionic Liquids

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

Partners in Environmental
Technology

Washington D.C. VA

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AFRL/RZSP



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14. ABSTRACT 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. Vaghjani, 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. Vaghjani, J. Phys. Chem. A, 2008, 112, 7816-7824.					
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RESEARCH AND DEVELOPMENT OF ENERGETIC IONIC LIQUIDS

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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).

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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

<u>System</u>	<u>Mission</u>
FtSatCom	Communications
STARDUST	Deep Space Probe
INTELSAT	Communications
HEAO-B	X-Ray Astronomy

- Hundreds of Satellites Use Hydrazine for RCS & ACS





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



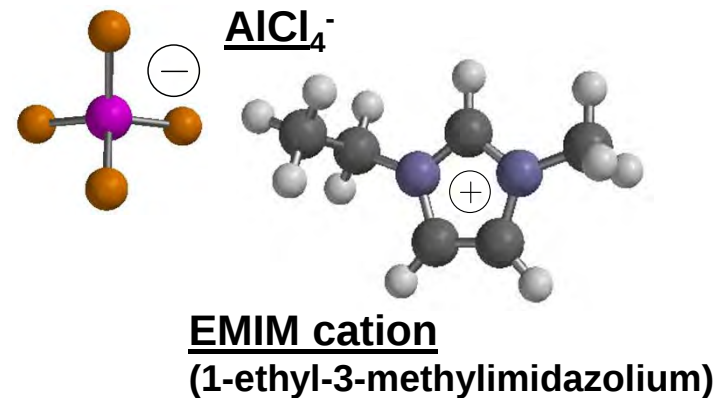
Energetic Ionic Liquids

Avenues to Lower Toxicity & Higher Performance



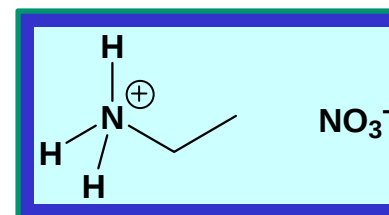
• History

- 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



Liquid propellants:
Spacecraft thrusters
DACs/ACS
Booster engines





'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

Constituents	Weight %
ADN	60-65
Methanol	15-20
Ammonia	3-6
H ₂ O	balance

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

Properties	LMP-103S	AF-M315E	Hydrazine
Isp _{vac} , lbf sec/lbm (e = 50:1 Pc = 300 psi)	252 (theor.) 235 (del)	266 (theor.) ~ 250 (del)	242 (theor.)
Density , g/cc	1.24	1.465	1.01
Vapor Pressure (torr)	Ammonia Methanol H ₂ O	<0.1 (w/o H ₂ O)	14.3

* Hawkins et.al., Proc. 4th International Association for the Advancement of Space Safety, Huntsville AL, 19 May 2010; Hawkins et.al., Proc. Fourth International Conference on Green Propellants for Space Propulsion, Noordwijk, The Netherlands, 20-22 June 2001.



Toxicity Assessment of AF-M315E



Toxicity Testing Results



- Time consuming
- Expensive

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



- Low hazard
- Low cost

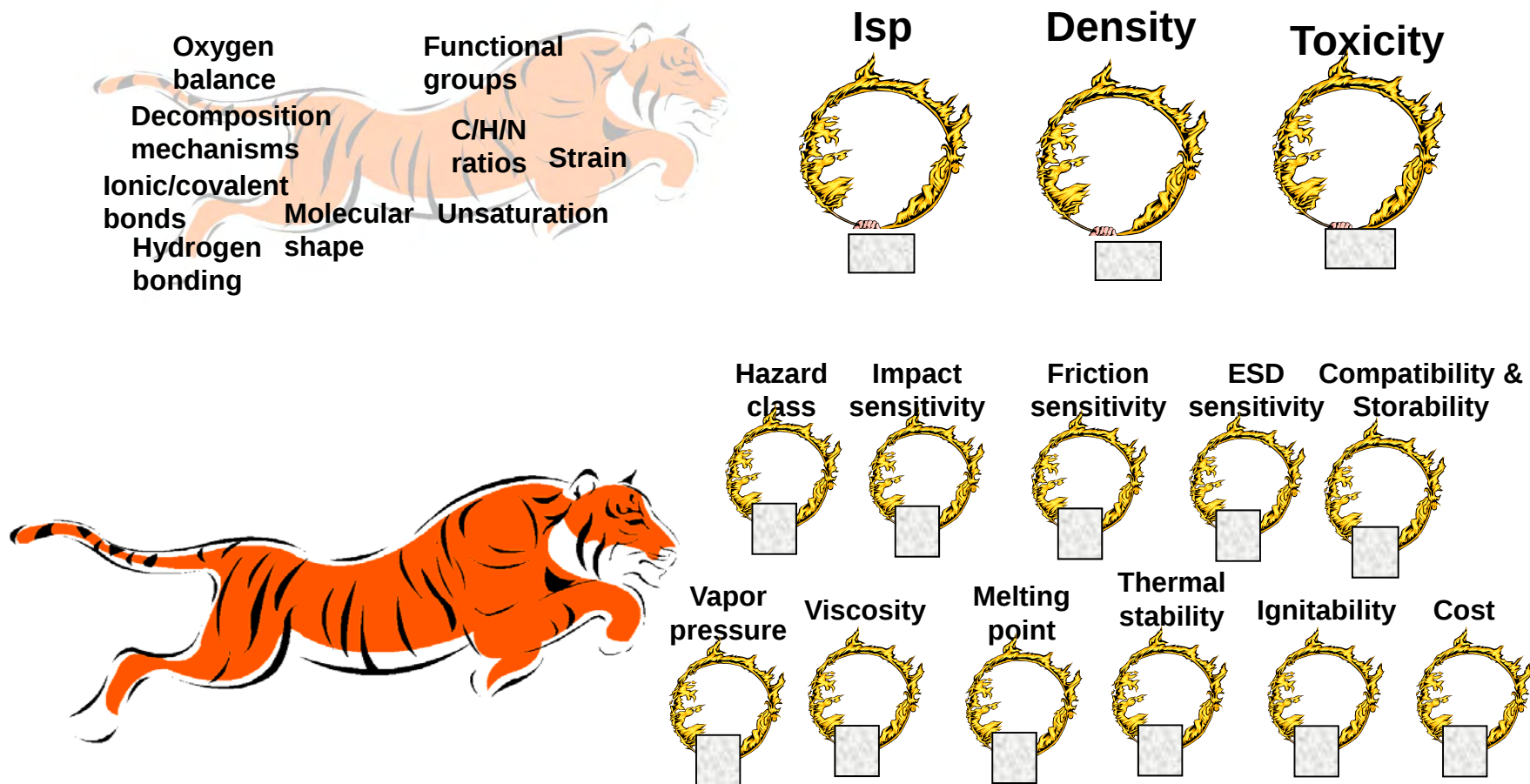
Toxic Vapor Components Testing

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)



Propellant *Development*

There is more to it than performance & toxicity





Much Effort Required in Small-Scale Safety/Hazard Evaluations



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

•Hawkins et.al., 4th International Association for the Advancement of Space Safety, Huntsville AL, 19 May 2010; Hawkins et.al., Proc. Fourth International Conference on Green Propellants for Space Propulsion, Noordwijk, The Netherlands, 20-22 June 2001.

**M. Nagamachi et.al., J.Aero.Technology and Management, V. 1, n. 2, Jul. - Dec. 2009; K. Anflo et.al., AIAA 2006-5212 42nd AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, 9 - 12 July 2006, Sacramento, CA.



Even More Effort Required for Large-Scale Safety/Hazard Properties



Transition of AF-M315E to Aerospace Industry Requires a Final Hazard Classification (FHC)

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 ¼ 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



Mild burning reaction!

Unconfined Package Test



**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)**



Liquid Engine Alternative Propulsion Development Program (LEAP-DP)



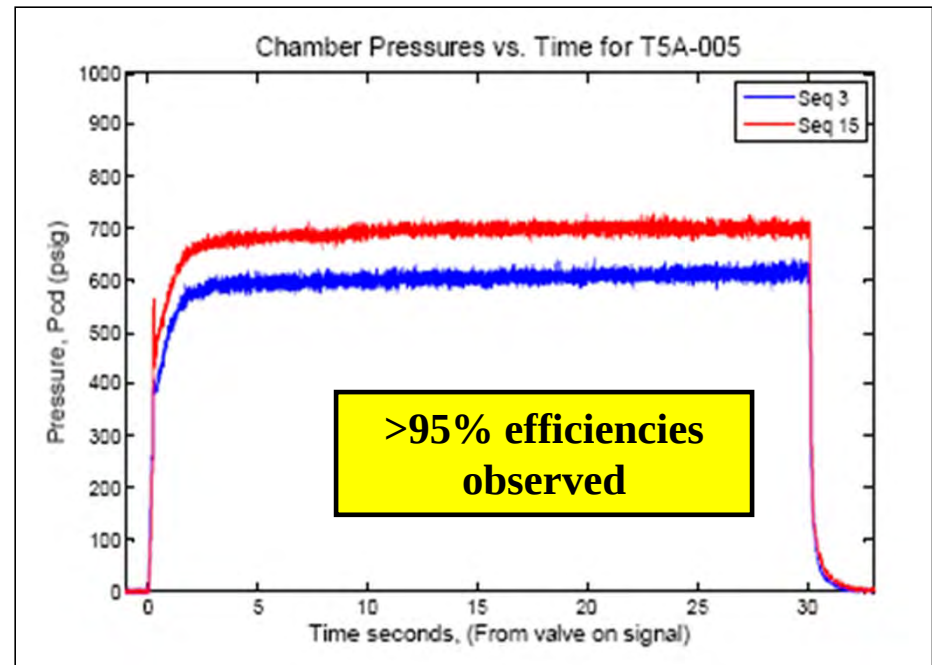
Technology Development

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

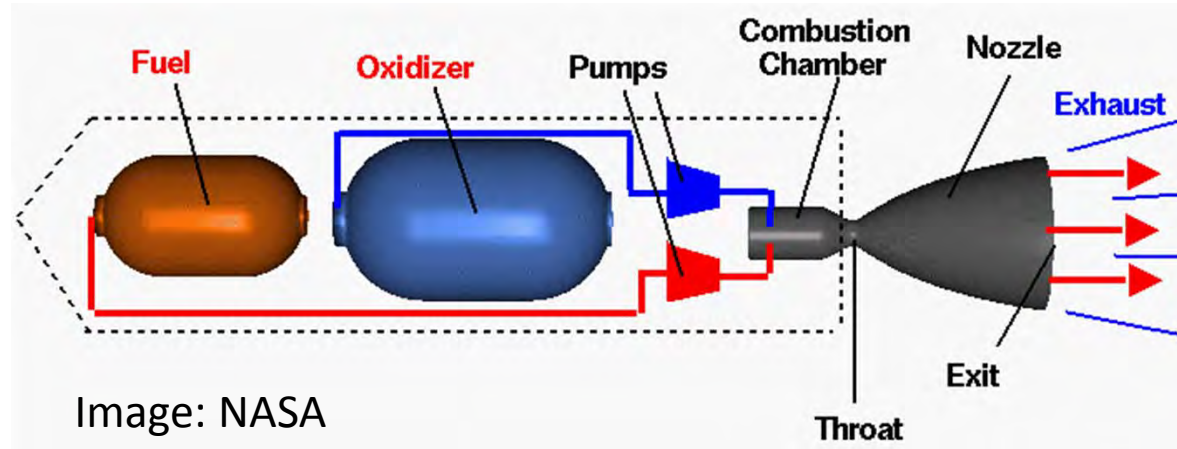
4.5 lbf Brassboard Thruster Pulses



Future work to concentrate on conversion from heavy weight to flight weight hardware



Ionic Liquids as Bipropellant Fuels



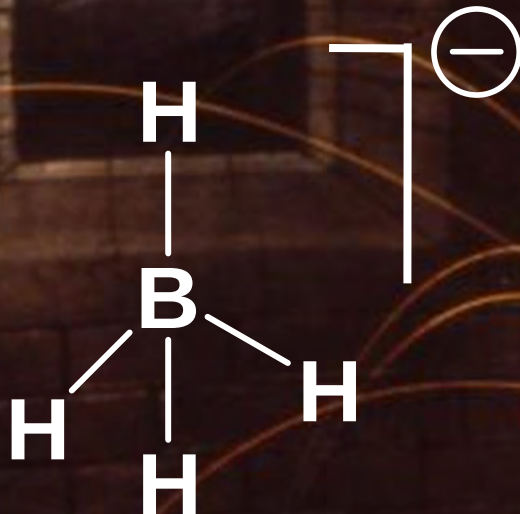
- ☐ **Ignites**
- ☐ **Ignites Fast (10ms)**
- ☐ **Ignites Fast & Green(er)**



High Performance Ionic Liquid Fuels: Harnessing Metal Hydride Anions



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 LiBH₄ in organic solvents are hypergolic with H₂O₂.

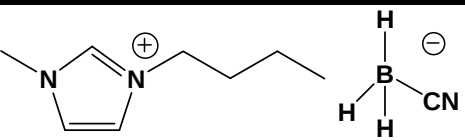
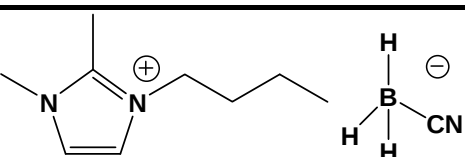
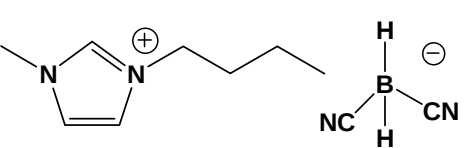
- a) T.L. Pourpoint, J.J. Rusek, *5th International Hydrogen Peroxide Propulsion Conference*, Purdue University, West Lafayette, IN, September 2002.
b) J.J. Rusek, *Proceedings of the 2nd International Conference on Green Propellants for Space Propulsion* (ESA SP-557), Sardinia, Italy June 2004;



"The GREEN Flame" Initial Borohydride-Based ILs



**Demonstrated hypergolic
with nitric acid-
*But not with N₂O₄ or H₂O₂***

Cyanoborohydride Ionic Liquid Fuels	Ignition delay[m]	Decomp. Onset [°C]
* 	 11	146
	 600	249
** 	 28	307



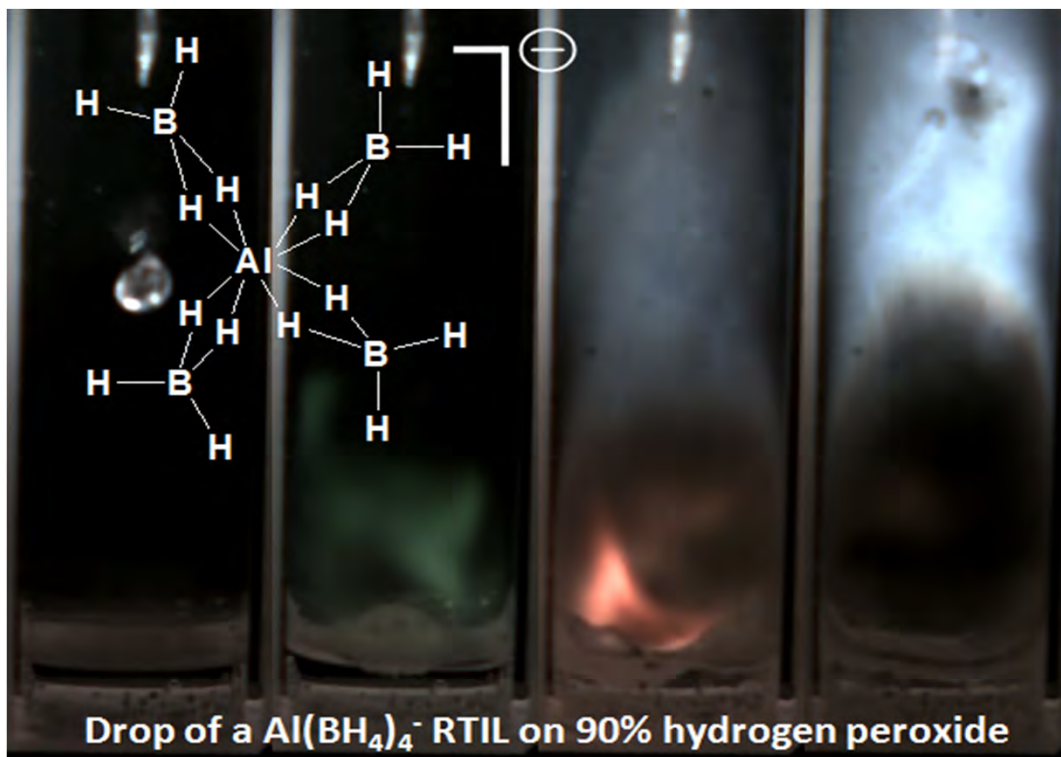
□ Remarkable impact of cation (and anion) structure on reactivity/stability

* T. Hawkins, S. Schneider, L. Hudgens, M. Rosander Invention Disclosure, "Environmentally enhanced hypergolic ionic liquids", Feb 4, 2010; Provisional Patent Application, June 17, 2010.

** Y. Zhang, J. M. Shreeve, *Angew. Chem.* 2011, 123, 965-967; *Angew. Chem. Int. Ed.* 2011, 50, 935-937.

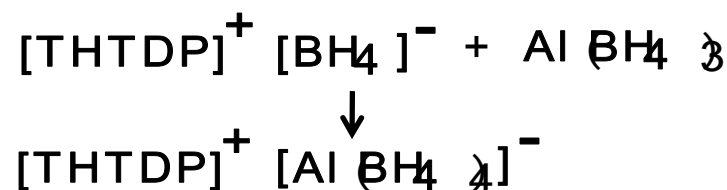


A Stable, Room Temperature IL Fuel Based on Borohydride Anion: $[Al(BH_4)_4]^-$



- trihexyl-tetradecyl-phosphonium (THTDP) cation known to be stable with bases and reducing agents*
- THTDP known to reduce melt point and promote liquidus
- $[Al(BH_4)_4]^-$ also promotes liquidus

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

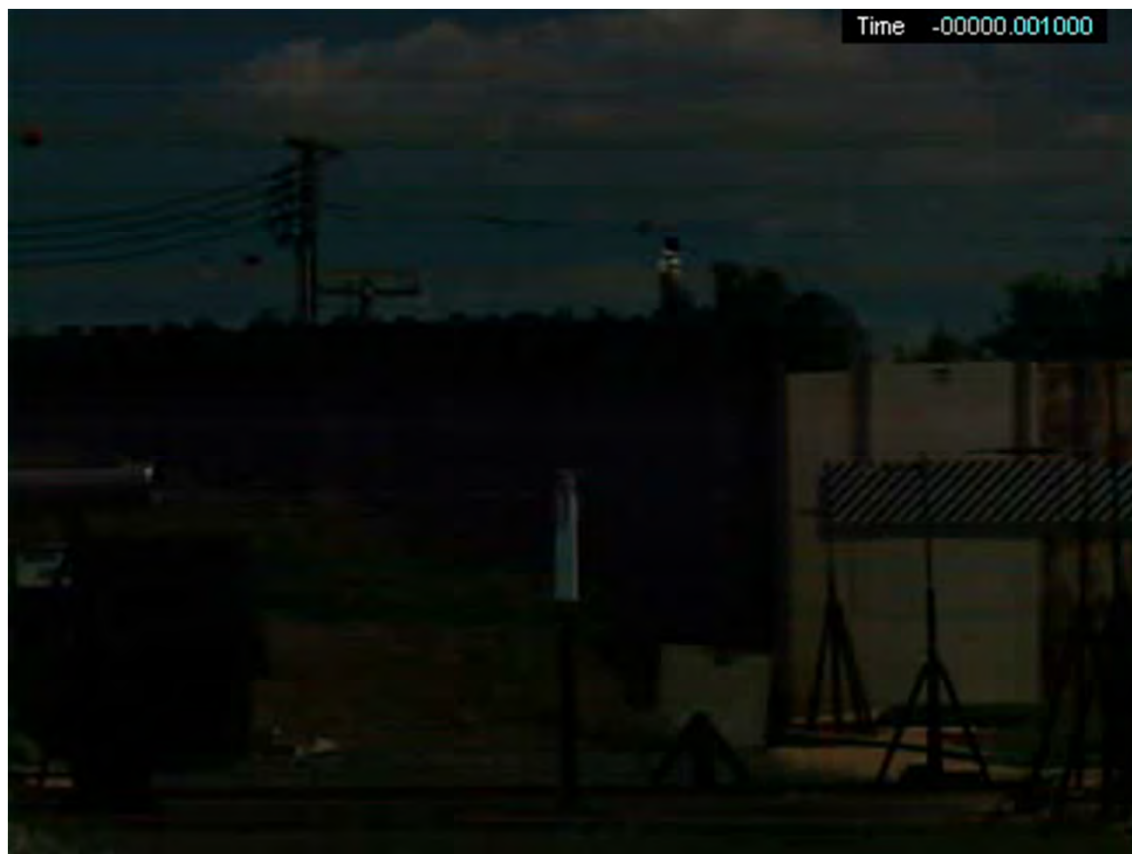


Fuel\Oxidizer	90% H_2O_2	98% H_2O_2	N_2O_4	WFNA
$R_4P^+ Al(BH_4)_4^-$	Ignition	Ignition	Ignition	Explosive Rxn
Ignition Delay	< 30ms	< 30ms	Vapor ignition	-

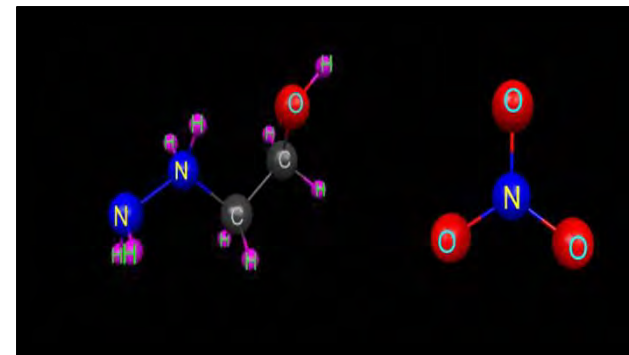
* Stefan Schneider, Tom Hawkins, Yonis Ahmed, Michael Rosander, Jeff Mills and Leslie Hudgens , *Angew. Chem. Int. Ed.* 12 May 2011, DOI: 10.1002/anie.201101752



Ionic Liquids as Explosives



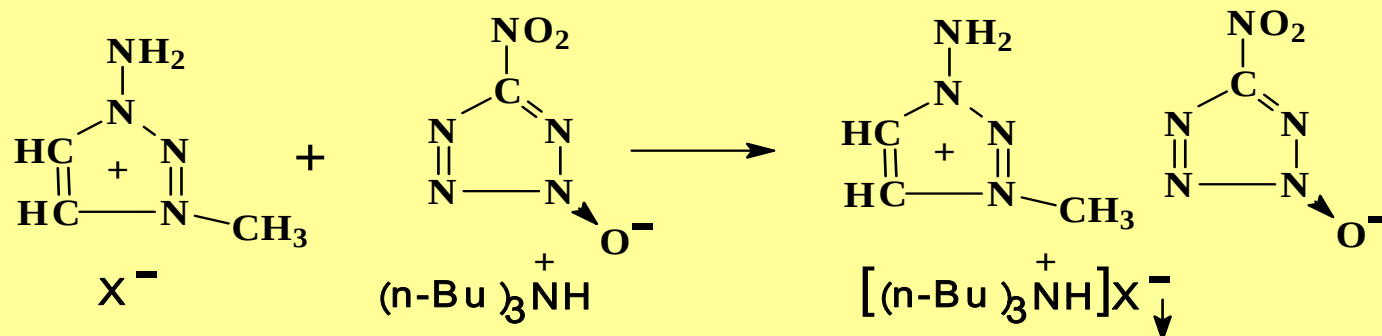
HEHN-Based Explosive Detonability Test (2-kg)



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



IL-Based Explosive Properties



-AMT-ONT from
metathesis rxn
-Performance > TNT

*J. C. Bottaro, M. A. Petrie, P. E. Penwell, NANO/HEDM Technology: Late Stage Exploratory Effort, Contract Number: F49620-02-C-0030, Final Report October 2003 (Public Release).

Ingredients	Heat of Formation (Kcal/mol)	Density (g/cc)	Total Detonation Energy (KJ/cc)	Shock Velocity (mm/ms)	C-J Pressure (GPa)
AMT-ONT	+140 (est)	1.58	8.30	7.91	23.9
1-AMTN*	+17 (est)	1.63	7.92	8.12	23.6
TNT	-15 (exp) ⁵	1.65	6.94	7.06	19.7

* T. Hawkins, G. Drake and A. Brand, US Patent 7,645,883, Jan 12, 2010.



Another Challenge: Predictive Toxicology



- **Background**

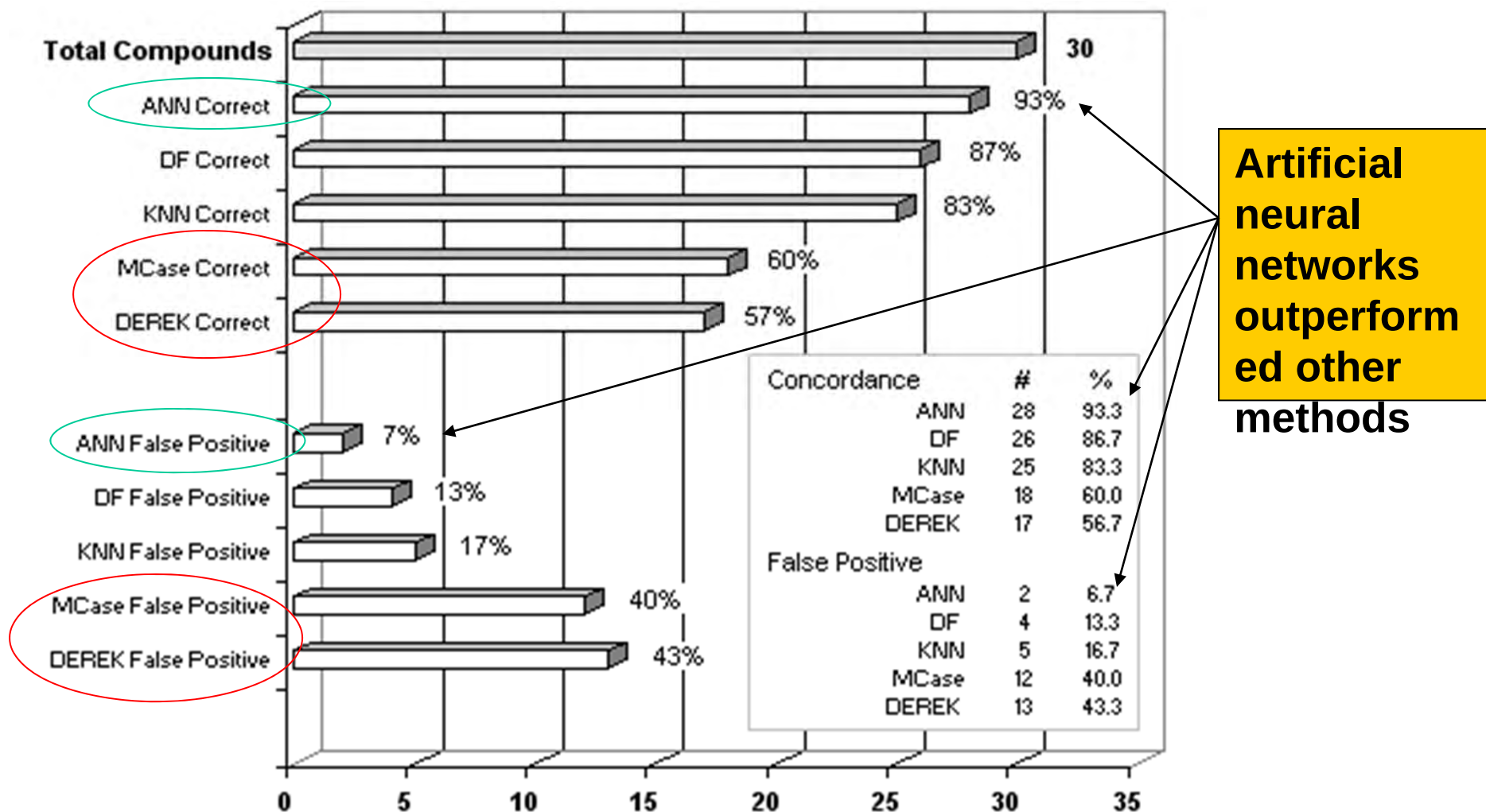
- Next generation propellants & explosives are emerging with many programs championed by US Army, Navy and USAF involvement
 - Environmentally benign impact initiated devices (DOE)
 - Lead-free electrical & percussion primers (Navy/Army)
 - Chlorine-free pyrotechnics (Navy)
 - Chlorine-free (AP-free) 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



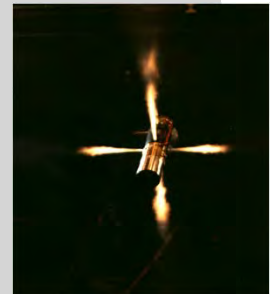
(Golbraikh, A. & Tropsha A., *J. Mol. Graphics Mod.* 2002, 20, 269-276.)



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

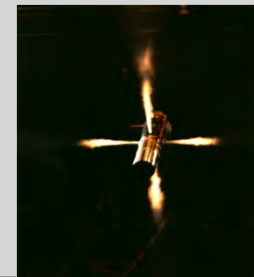




Summary



- 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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- Cliff Bedford, ONR, Energetic ILs for Melt Castable Explosives**