

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

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- 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





- 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 tetranitroaluminate, often in combination with nitrogen-based heterocycles (Drake, Shreeve, Hawkins, Galvez-Ruiz, Christe, 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



Concept: Desensitizing Ionic Liquids



- 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/Criteria/Goals for IL Candidates



- 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)



Routes to Ionic Liquids



- 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 aminoguandinium-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

	AG-TFA	60:40 AG:G Oxalate	60:40 AG:G Malonate	AG Glycolate	AG 5-AT
RDX	Yes	Yes	No	No	No
HMX	Yes	Yes	No	Yes	No
TNT	Yes	No	No	Yes	No
CL-20	Yes	No	No	No	No
NTO	n/a	Yes	No	No	No

- 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





- 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)





Formulation	AGTFA (%)	Energetic material	% Unground	% Ground	Total Nitramine (%)	Detonation Velocity (km/s)	Dent Depth (in)
1	100	-	-	-	-	3.23	0
2	100	-	-	-	-	1.5	0
3	100	-	0	0	0	2.53	0

- 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



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Formulation	AGTFA (%)	Energetic material	% Unground	% Ground	Total Nitramine (%)	Detonation Velocity (km/s)	Dent Depth (in)
4	80	RDX	0	20	20	2.94	0
5	60	RDX	0	40	40	6.09	0.24
6	60	RDX	20	20	40	6.25	0.259
7	50	RDX	25	25	50	6.75	0.363
8	40	RDX	30	30	60	7.22	0.368
9	30	RDX	35	35	70	7.31	0.337
10	60	HMX	20	20	40	6.56	0.263
11	50	HMX	25	25	50	7.29	0.315
12	34	HMX	66	0	66	8.04	0.375
13	25	CL-20	45	30	75	8.38	0.404
14	0	Comp B			63	7.56	0.43

• Performance at 50% RDX loading is between TNT and Comp B



Setup for Cook-Off Testing



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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



Time/Temperature Profile: Slow Cook-Off





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



50mm Bullet Impact Test: AG-TFA / RDX 50:50



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Test Configuration:



- Passed 50 cal bullet impact
- No detonation; mortar body shattered by bullet
- No reaction of fill; "type 6 like" behavior



AG-TFA w/ 50% RDX: 25mm SCJ



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Test Configuration:



- No detonation; mortar body shattered by jet
- Much of the fill did not even burn (white residue on plate); "type 5" behavior





- 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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