Emerging Applications for Ionic and Electric Energetic Materials

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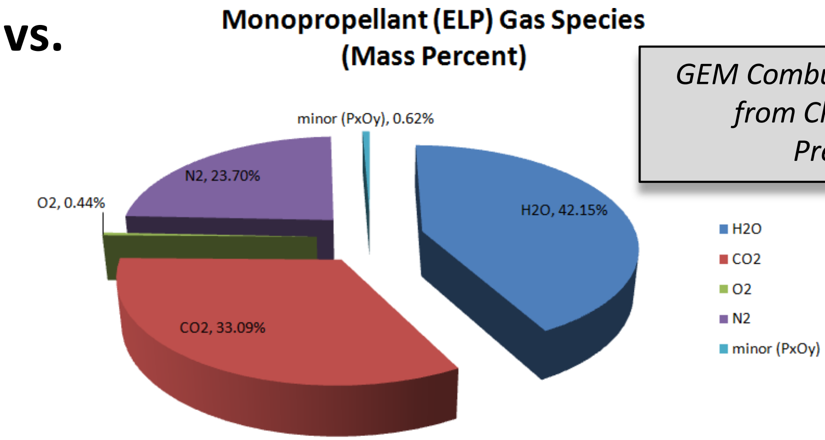
Ionic Energetics Are Arguably "Safer and Greener"

Ionic Liquid Propellant Toxicity vs. Hydrazine

- ***Not*** a carcinogen
- ***No*** vapor pressure
- ***Not*** a mutagen
- ***Nontoxic*** combustion
- ***Nontoxic*** thermal decomposition products: international studies

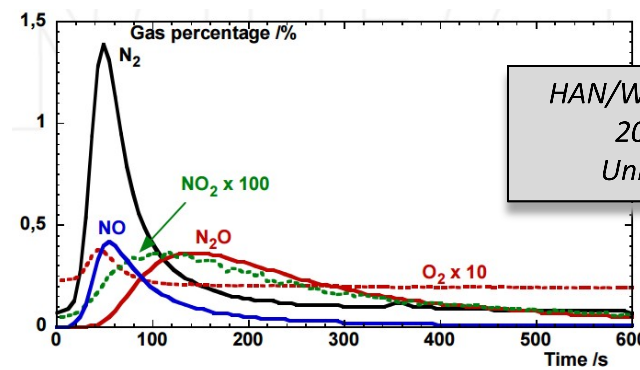
Ionic Propellant Toxicity vs. Conventional

- ***NO*** perchlorates, nitroglycerine, or other legacy bad actors
- ***NO*** groundwater or disposal issues



GEM Combustion at 300 psia, from Cheetah (LLNL) Predictions

Characteristically "Green" Exhaust Species



HAN/Water Decomposition at 200 °C (Measured), Univ. of Poitiers, 2011

Fahrat Kamal, Batonneau Yann, Brahmi Rachid and Kappenstein Charles (2011). Application of Ionic Liquids to Space Propulsion, Applications of Ionic Liquids in Science and Technology, Prof. Scott Handy (Ed.), ISBN: 978-953-307-605-8, InTech, Available from: http://www.intechopen.com/books/applications-of-ionic-liquids-inscience-and-technology/application-of-ionic-liquids-to-space-propulsion

HAN Brief History

Liquid Gun Propellant –
- Picatinny, XM-46, LGP-1846, 70's to 2002
- NOS-365 (Navy)
- Crusader, 155mm Artillery

HAN/LGP1846 production,
- Picatinny, ATK Elkton, SACHEM, Olin, and Arch
- commodity studies

Emulsion Technology – Aerojet
- "A3L", refocused IR&D, Aerojet & AFRL EAFB 90's

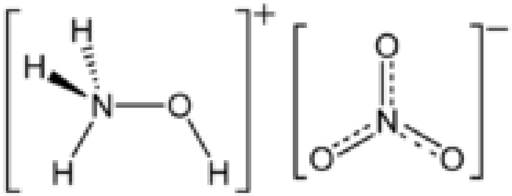
AF-M315E– AFRL Edwards 90's onwards

First ELECTRIC propellants- 1995-2005
- Aerojet alumni Art Katzakian and Charlie Grix
- *First ELECTRIC propellants*

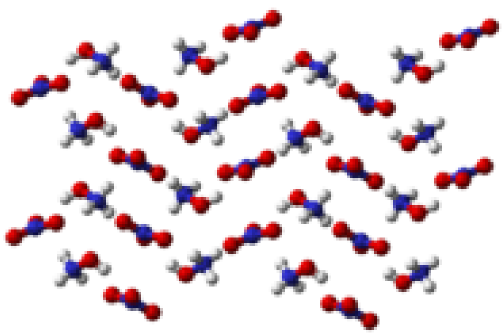
ESP and GEM- DSSP 2005 onwards
- IQT, Moog and Shell GameChanger funding
- SBIRs: Navy, Air Force, MDA, NASA, DARPA, and Army

http://www.army-technology.com/projects/crusader/crusader5.html

Electrical Propellant Ionic Liquid Oxidizer



Hydroxylammonium Nitrate



HAN Liquid Semicrystalline Behavior

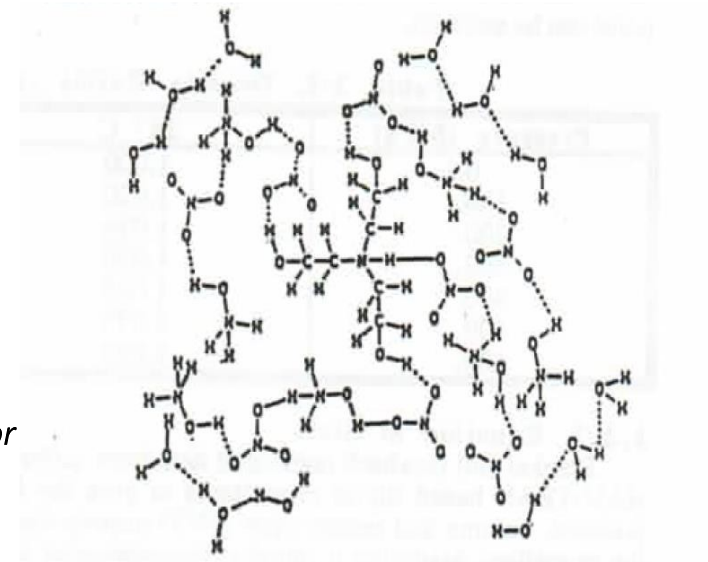
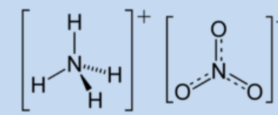
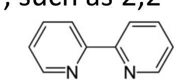


Fig. 2-1. A Sample LP XM46 Structure Showing the HAN-TEAN Cluster Surrounded by Water



Ammonium Nitrate (Co-oxidizer)

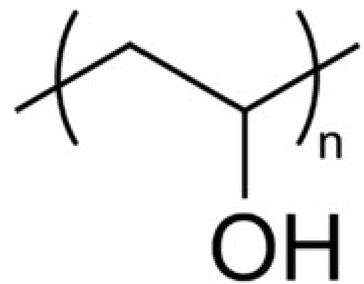
Stabilizers: phosphates
Buffers: (hydroxyl) amines, borates
Sequestrants: chelating agents for transition metals such as Fe^{++}, Fe^{+++}, such as 2,2'-dipyridyl

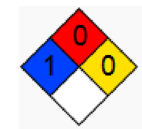


Note also that significant USAF development efforts are ongoing with the HAN-based monopropellant, AF-M315E (Hawkins et al., 2010).

Plastisol Binder (Fuel)

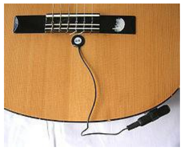
- (Poly)vinyl alcohol, PVA
  - High molecular weight
  - High degree of crystallinity
  - Purity, particle size, PSD, important

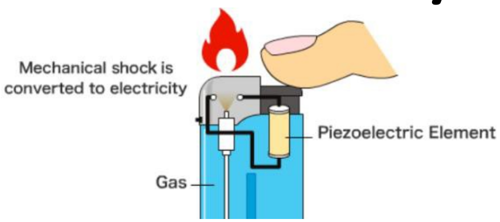




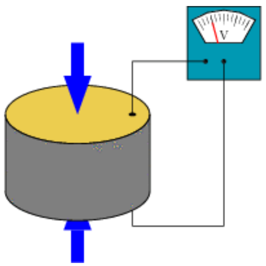
- "Cure" – plastisol based, no isocyanate chemistry
  - Similar to double-base propellant manufacturing
- Conventional characteristics: cast/pour, "cure"
- "Out-of-the-box" characteristics
  - **Pyroelectric phenomenon**: response to electrical input signals as function of temperature and pressure
  - **Electrically ignitable and throttleable**

Pyroelectric Behavior

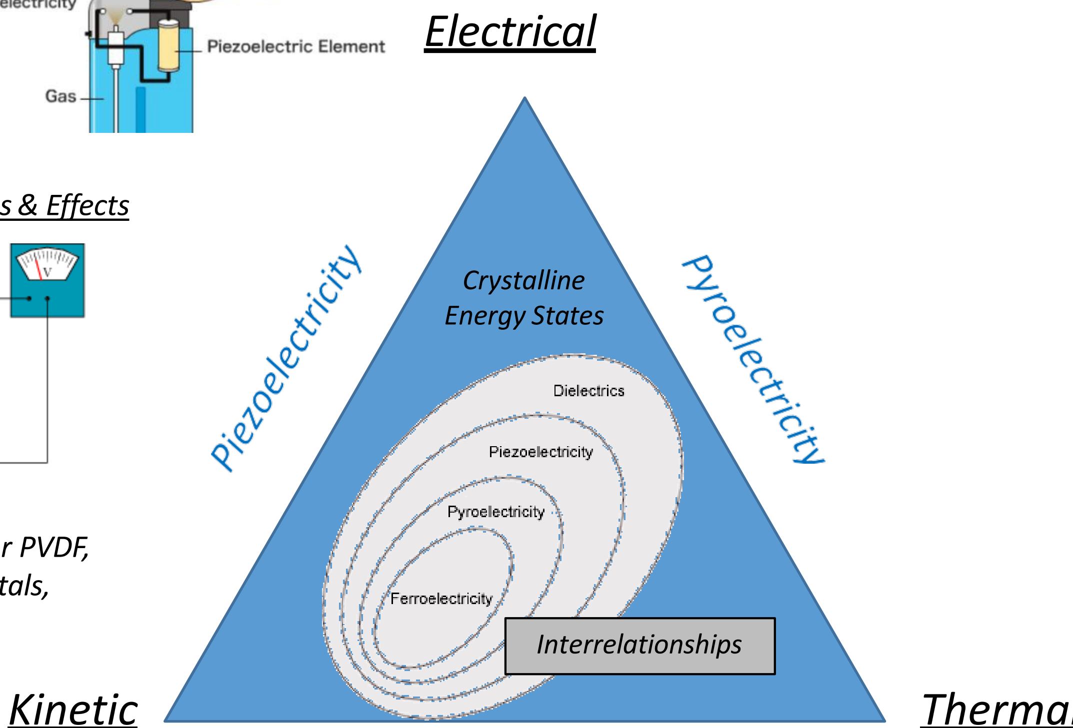


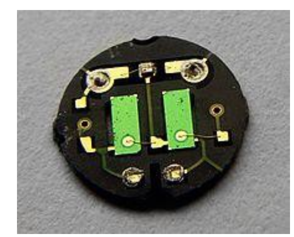


Piezoelectrics & Effects



Examples: Kynar, or PVDF, also quartz crystals, ceramics

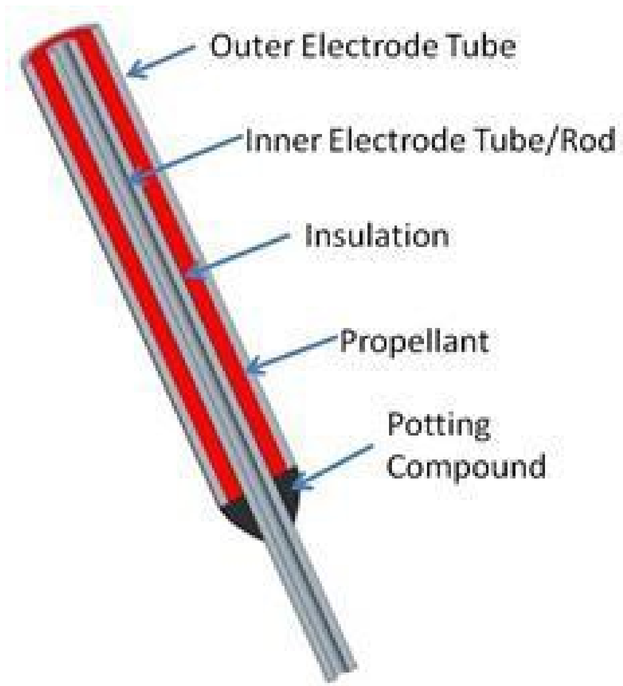


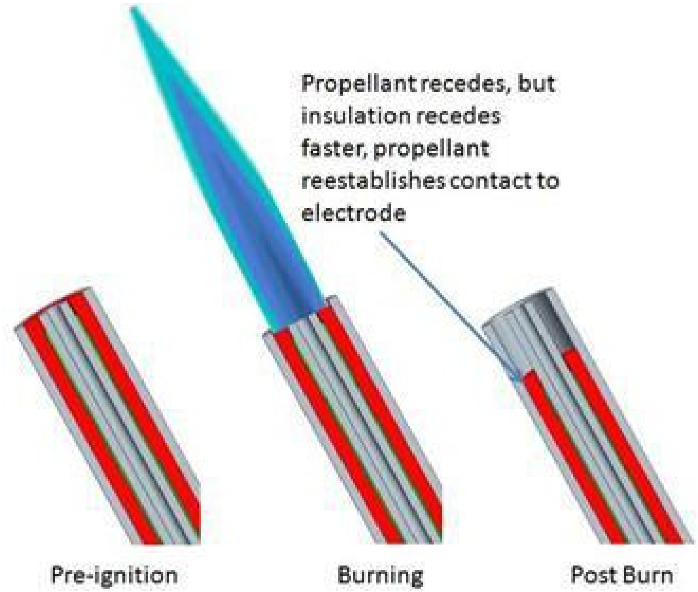


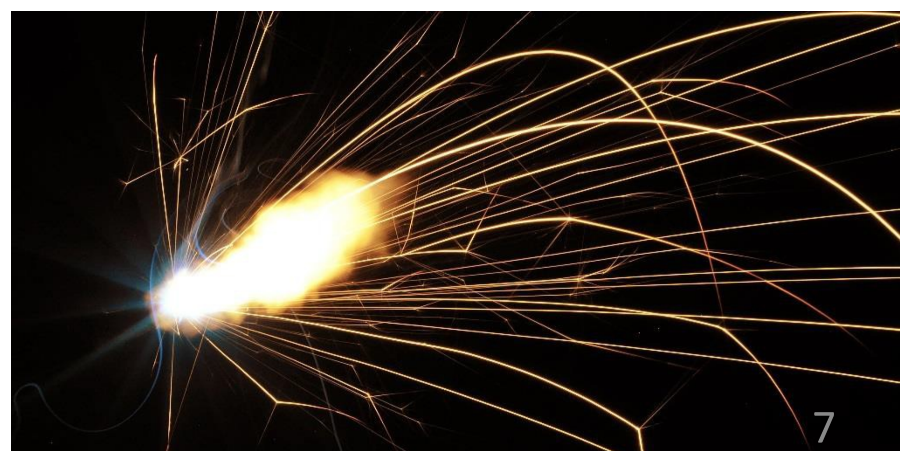
Pyroelectric sensors

The side between electrical and thermal corners represents the pyroelectric effect and produces no kinetic energy. The side between kinetic and electrical corners represents the piezoelectric effect and produces no heat.

Basic Electric Solid Propellant On-Off Design







Pyroelectric Materials Respond to Voltage

- *240 V*

  Flame emerges from surface
- *300 V*

  Smooth burning flame

  *Threshold**
- *320 V*

  Arc discharge

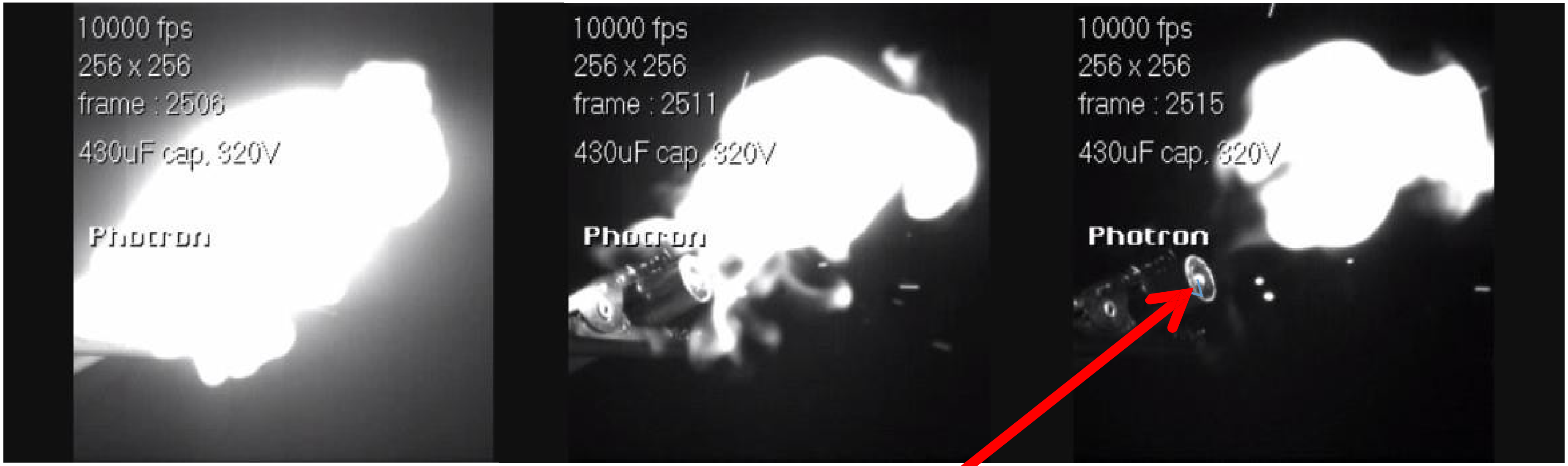
High Temperature

Plasma Combustion….

* Voltage threshold depends on geometry and size

Electric Energetics

Electric: Ignition, Extinguishment, and Re-ignition



Complete extinguishment with no smolder

Solid state, no moving parts required for re-ignition

Solid and Liquid Ionic Energetics

Solid propellant/explosives: composed of HAN-based liquid oxidizer combined with dissolvable energetics, stabilizers, ballistic modifiers, etc., in a PVA polymer matrix.

Liquid monopropellant: family is a blend of HAN-based oxidizer with water and dissolved fuels, stabilizers, or additives for performance and safety.

- **Solids**
  - **HIPEP**
    - Non-metallized, min.-smoke propellant
  - **HOT**
    - High operating temperature (thermite-like)
  - **BADB**
    - Boron reduced-smoke propellant
  - **HIPEX**
    - Aluminized explosive
- **Liquids**
  - **AF-M315e** (Air Force/Edwards)
  - **GEM**

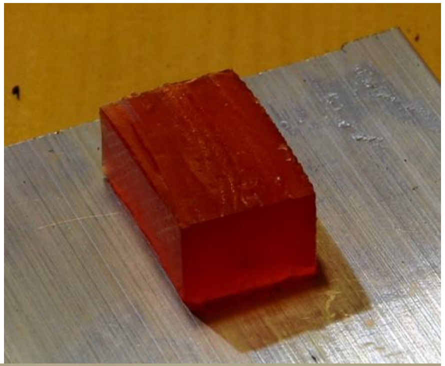
Left to Right: HIPEP, BADB, ANAV or HIPEX, GEM

Ingredient	*Purpose*	*Weight %*
Hydroxylammonium Nitrate	Oxidizer	65-75%
Polyvinylalcohol polymer	Binder	15-25%
Ammonium Nitrate	Co-Oxidizer	3-5%
Ammonium Dihydrogen Phosphate	Buffer, Stabilizer	0.50%
2,2'-Bipyridyl	Stabilizer, Sequestrant	0.50%
Proprietary Soluble Stabilizers	Stabilizer, Gas Generant	0.50%
Water	Desensitizer	0.5-2.5%

Generic *HIPEP* MSP Formulation

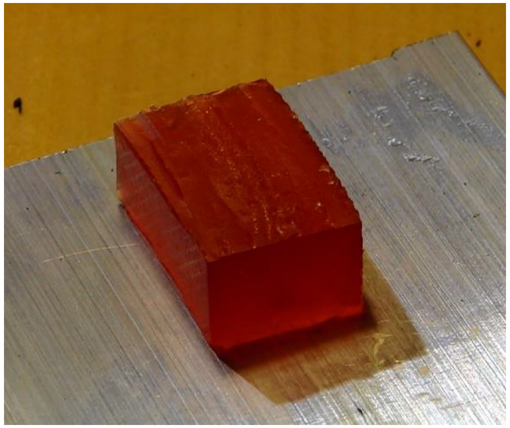
High-Performance Electric Propellant

- **General Characteristics: HIPEP**
  - Typical onset temperature by DSC is 175-180 °C (347-356 °F)
  - Propulsion performance:
    - 230-245 s Isp Chemical
    - 1000 s Isp Arcjet
  - Flame temp.: ~2650 K (2377 °C/4310 °F)
  - Baseline HIPEP extremely flame insensitive at 1 atm.
    - It chars during flame impingement; with flame removal, it extinguishes.
  - Sustained combustion occurs at around 2-300 psi
  - High electrical conductivity
  - Response to electrical power
    - On/off control with electrical power input
  - Low hazards/low toxicity
  - Throttles
    - Burning rate adjustable via power input



HIPEP Hazard Properties

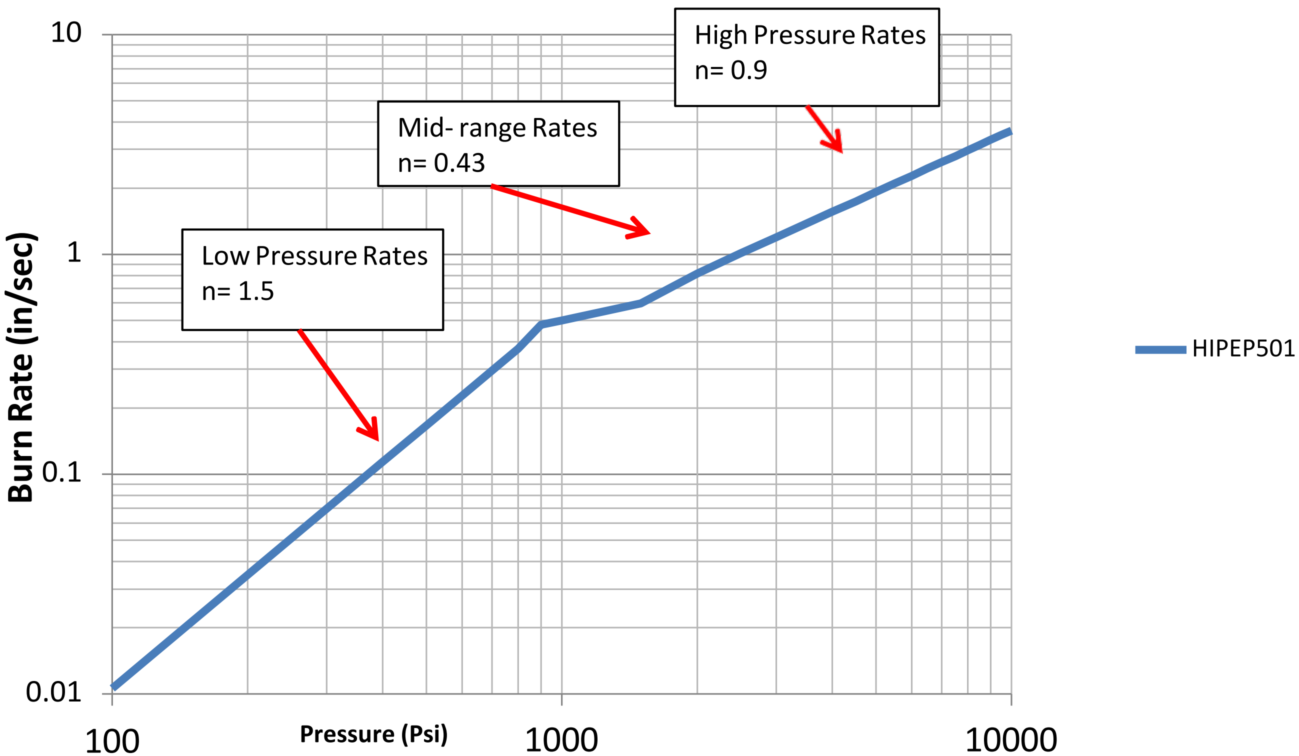
- Flame insensitive, 1 atm
- Electrostatic discharge
  - Negative at highest setting of 0.25 J
- Impact ERL
  - Negative at highest setting of 158.5 cm (RDX is 29.8 cm)
- ABL friction
  - Negative at highest setting of 8000 N (RDX is 1870 N)
- Test at 0 cards
  - Negative
- Bullet impact test (.30 cal)
  - No reaction



Non-Metalized Burn Rates

Baseline HIPEP Propellant

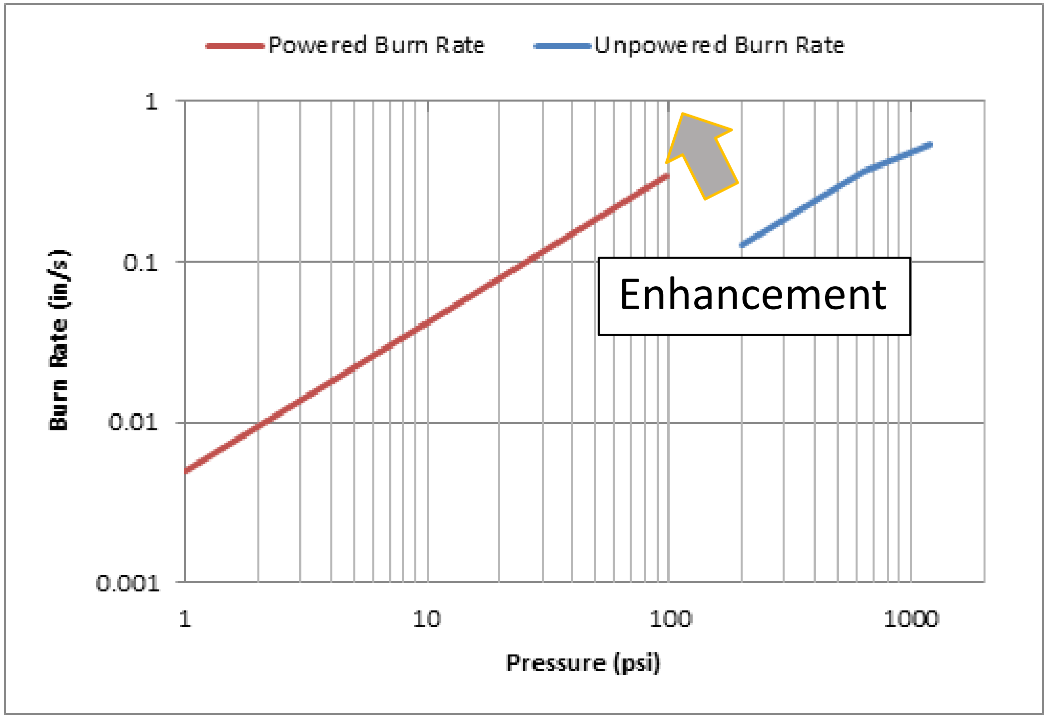
HIPEP501 Burn Rates up to 10,000 psi



- Exponent breaks at 900 psi and around 2000 psi.
- Low-pressure burning characterized by dark zone and flame standoff (partial cause of high exponent).
- Mid-range low slope likely due to no flame standoff and essentially premixed flame.
- High-pressure burning dominated by another mechanism.

Propellant Electrical Properties

- Enhanced burning with electrical power
  - Three “knobs” to affect burn rate: pressure, temperature, and electrical power.
  - Can cause burning to occur at lower pressures and at higher rates.
  - Synergistic effects (burn rates up to 10x normal with electrical burning at high pressures).



Unpowered: no applied voltage or current
Powered: ~250 V, 0.1 A → 600 V 3A

Pyroelectric Burning vs. Plasma Production

Chemical combustion

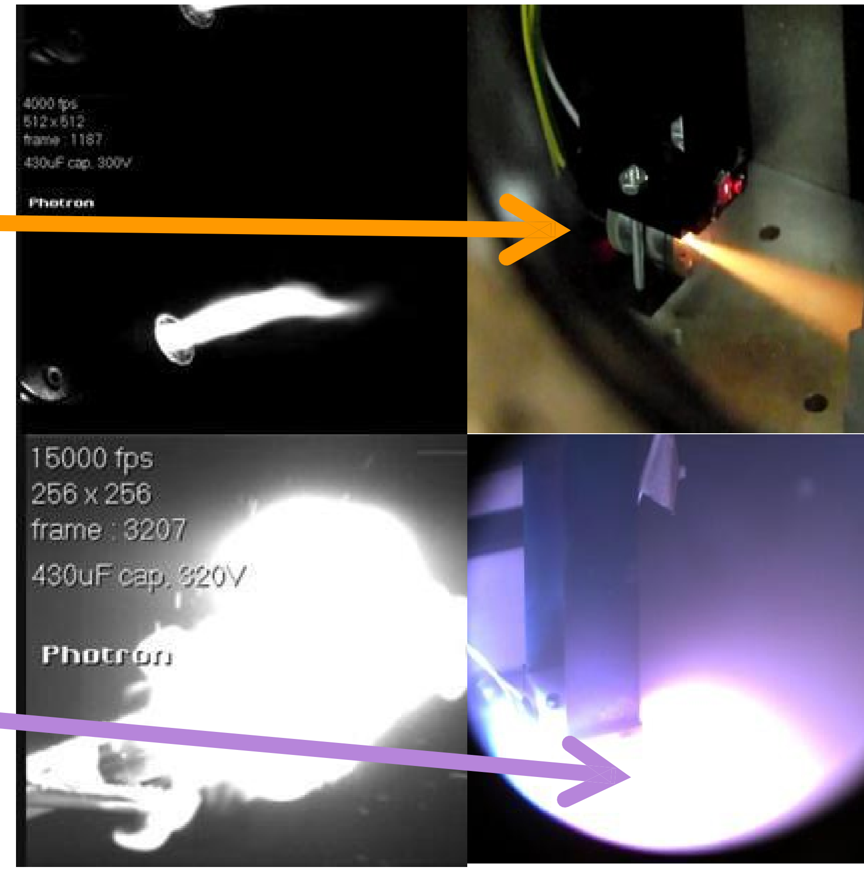
smooth burning

Yellow Flame

Vacuum high temperature

plasma production

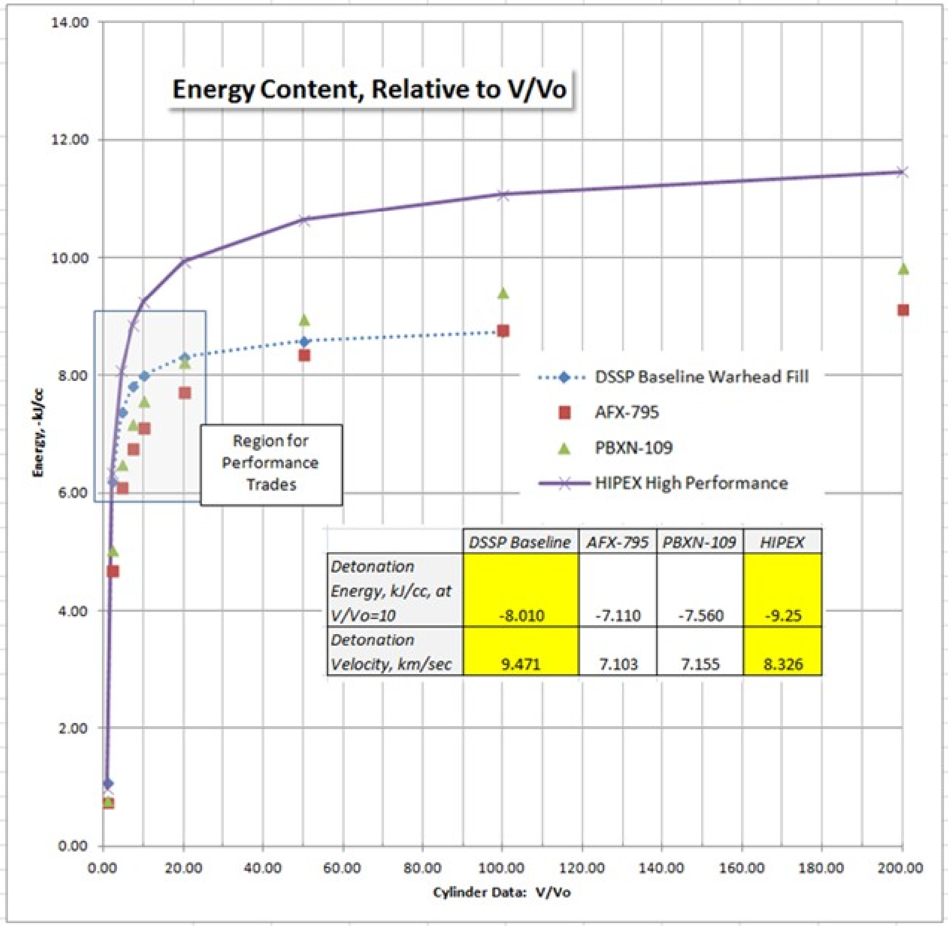
Purple Glow Discharge



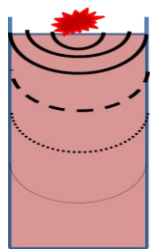
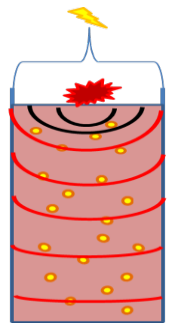
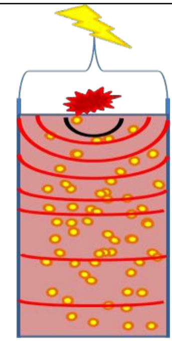
** Voltage threshold depends on geometry and size*

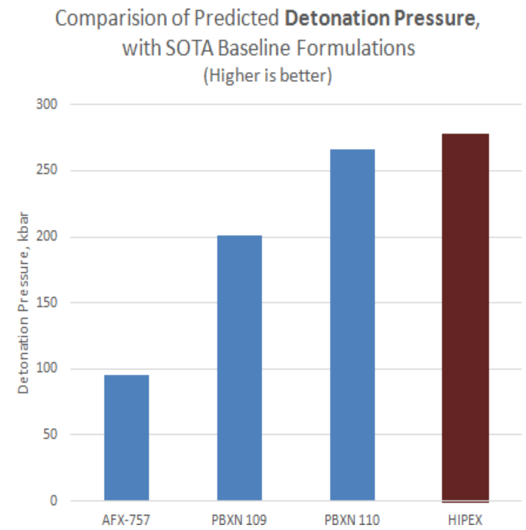
HIPEX:
Electrically Variable Explosive (EVE)

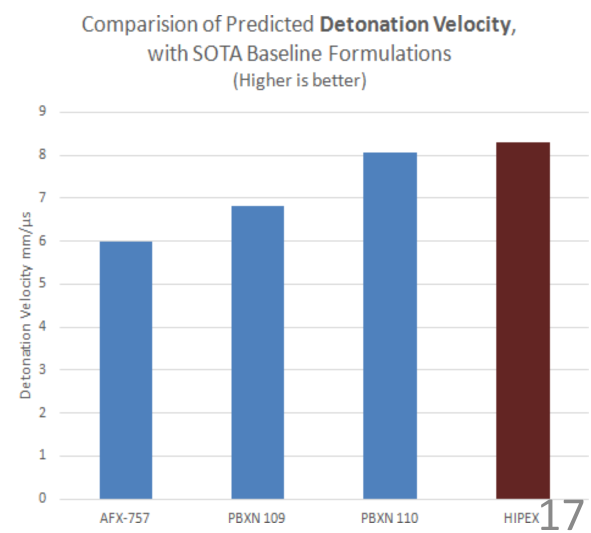
- SBIR program
- Aluminized explosive (HIPEX) (20-25% Al)
- *Safe* Class 1.4C high explosive
- Must be electrically “charged” prior to detonation or <u>will not detonate</u>
    - Charging creates voids and allows for detonation
- Flame temp.: 3350-3500 K
- Better mechanical properties than HIPEP from filler reinforcement
- Damage-tolerant high explosive
- HIPEX Cheetah v8 predictions indicate high potential



HIPEX:
Electrically Variable Explosive

		
HIPEX charge without "precharging" or sensitization. Shock from the booster charge doesn't cause any reactions and dissipates. No detonation, 1.3 or possibly 1.4 hazard class.	HIPEX charge with "precharging" causing potential changes such as microbubbles, Ohmic heating, charge storage, and/or nitric acid production (electrochemical response). Shock from booster causes exothermic reactions in these changes supporting and driving the shock up to detonation, 1.1 hazard class.	HIPEX charge with considerable "priming." Lots of changes occur prior to the shock. Shock transitions quickly to detonation. EVE may be primed enough to cause an enhanced detonation.





(Liquid) Monopropellants

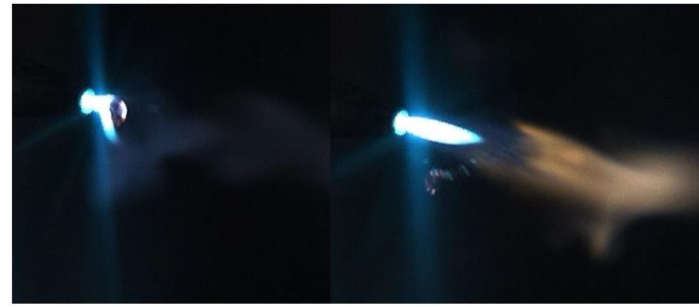
Green Electric Monopropellant Development

Video: GEM electrical ignition, approx. 50 msec duration Liquid Monopropellant Ignition and Combustion 10-mm Glass Vial High-Speed Video
~ 500 psi

- **AF-M315e** was developed by the Air Force beginning in the late 1980s.
  - *Green hydrazine replacement propellant*
- **GEM** was originally developed by DSSP in 2012 for oil/gas downhole use as a pumpable, low-velocity *gas generator/propellant.*

GEM and AF-M315e Ignitions

- GEM and AF-M315e are both flame insensitive; HAN-based monopropellants can be ignited:
  - Thermally or
  - With a catalyst
- GEM can also be ignited:
  - Electrically
  - As a plasma/ion source
- It can be used either in chemical mode or electrical mode, providing for a chemical burn with high thrust or operating like a PPT with high specific impulse.



Droplet passing through an oxy-acetylene torch flame had no reaction.

Safety Video

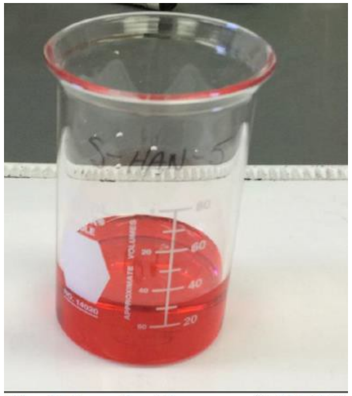
Liquid pulsed-plasma thruster

Formulation

- *S-HAN-5* precursor
- *Ships as 1.4C, 30-kg cartons*

Constituents	Weight Percent (%)
Hydroxylammonium Nitrate	80-95%
Ammonium Dihydrogen Phosphate	0-1%
Ammonium Nitrate	0-5%
2,2'-dipyridyl, 2,2'-bipyridyl	0-1%
Water	0-2%

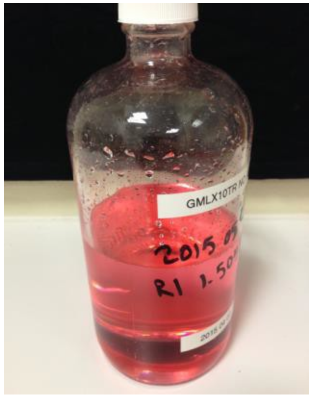
S-HAN-5



Liquid Propellant Precursor (S-HAN-5)

Constituents	Weight Percent (%)
Hydroxylammonium Nitrate	65-75%
Ammonium Dihydrogen Phosphate	0-1%
Ammonium Nitrate	0-7%
5-Aminotetrazole	0-3%
2,2'-dipyridyl, 2,2'-bipyridyl	0-1%
Cycloamylose; polysaccharide	15-25%
Water	0-4%

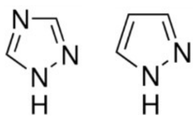
GEM



Characteristics, Optimized for Propulsion

Metric	*GEM Mod 3*	*NTO/Hydrazine (MR = 1.21)*
Vacuum Specific Impulse (50:1 expansion, 300 psi)	283.0 s	331.3
Theoretical Density	1.575 g/cc	1.205 g/cc
Density-Specific Impulse	445.7 g*s/cc	399.2 g*s/cc
Vapor Pressure (kPa)	~0.003	5 / 101
Boiling Point, °F	>220	71/237
Toxicity	Very Low	High

124-T and pyrazole both add Isp and stability.

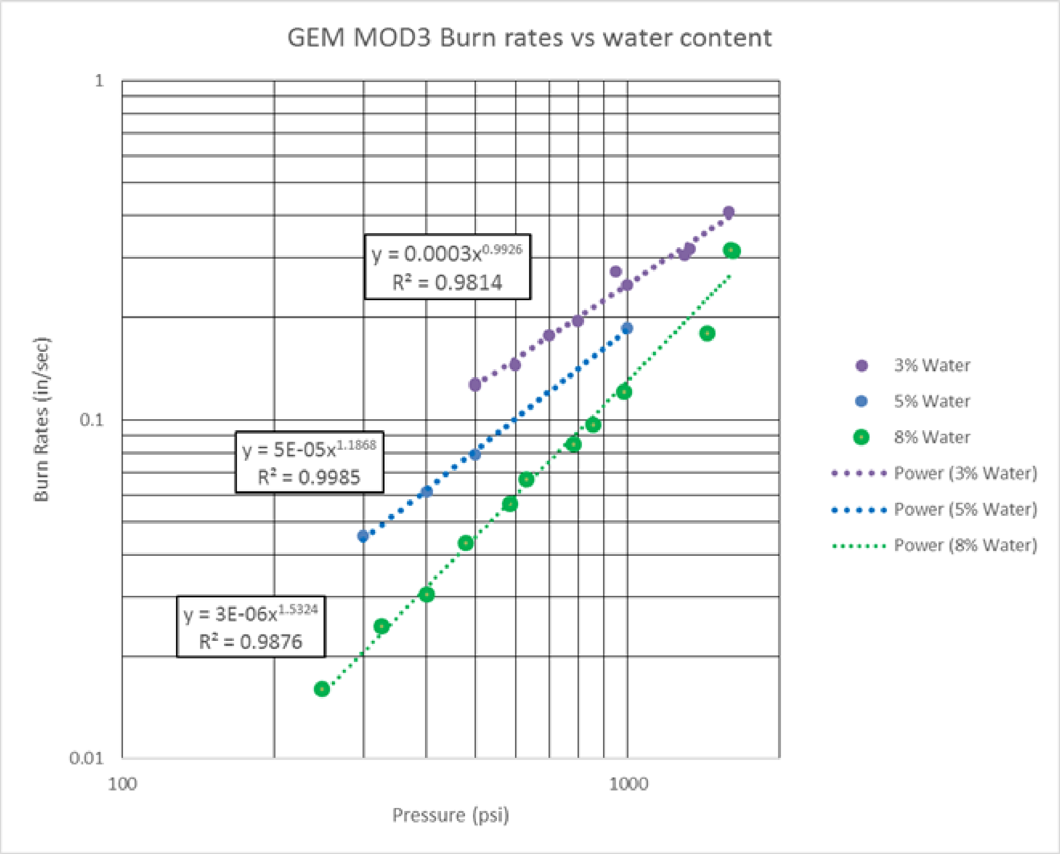


1,2,4-triazole and 1,2-diazole (pyrazole) stabilize HAN, add performance, in GEM3

Goal	*Parameter*	*AF-M315E*	*GEM Mod 3*
↑	Theoretical Isp, sec	266	*283*
↑	Actual Density (measured), g/cc	1.46	*1.505*
↓	Dynamic Viscosity, centipoise	23	*19*
↓	Ignition Delay (hot glass surface at 450°C), millisec	900	*200*
↑	Time to Fume-off at 150°C, hours	1.5	*19*
↓	Carbon Content, wt%	7.65	*7.39*

GEM Ballistics and Water Content

- Ballistics and viscosity of GEM can be easily modified as required for different applications.
- Gelling the propellant is also done for certain applications.

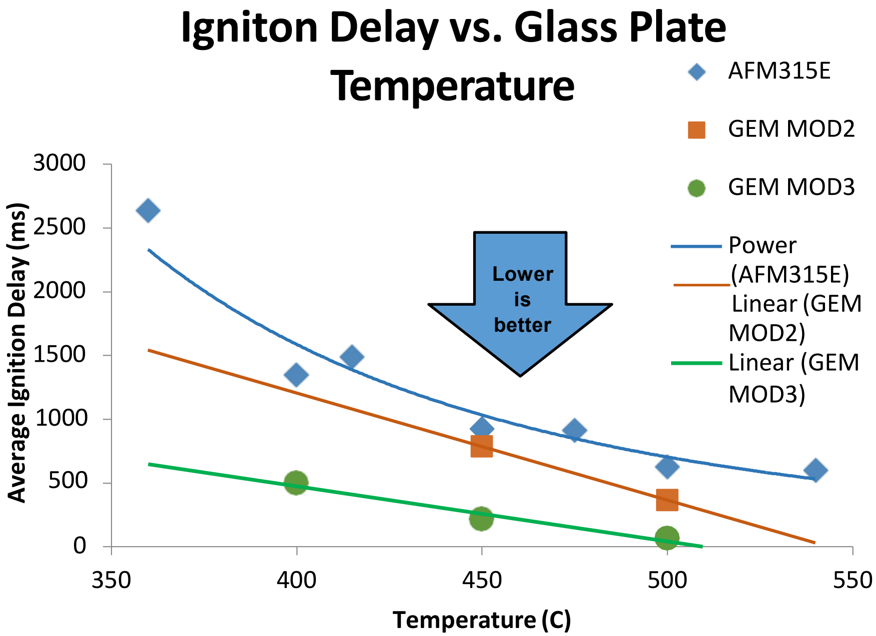


Monopropellant Performance

Parameter	Hydrazine	AF-M315E	LMP103S	NOFBX	**GEM MOD3**
Description	Heritage monoprop	Air Force HAN-based monoprop	ADN-based monoprop	Nitrous oxide fuel blend (similar to NA-7)	**DSSP HAN-based monoprop**
DOT Hazard Classification	UN2029 (class 8 corrosive)	1.4C Energetic substance	1.4S (FHC) 1.3C substance	Detonable	**1.4C Energetic substance**
Theoretical $I_{sp\text{-}vac}$ [sec] (p_c = 300psia, ε = 50)	236.8	261	252	320	**284**
Density [g/cc] @ 25°C	1.01	1.465	1.24	0.55	**1.579**
Density-I_{sp} [g-s/cc]	235.1	382.4	312.5	176	**426**
Boiling Point [°F]	236.3	>212	248	<70	**>212**
Freezing Point [°F]	35.6	<-7.5	-120 (ADN condensation @ 19.4)	-112	**<-4**
Vapor Pressure @ 25 °C kPa	1.91	1.4	15.09	5169	**0.003 calculated**
Toxicity	High	Very low*	Low	Low	**Very low**

Thermal Ignition of Ionic Monopropellants

- Hot plate testing was done with a drop of propellant dropped onto a heated glass slide, and ignition delay was measured at various temperatures.

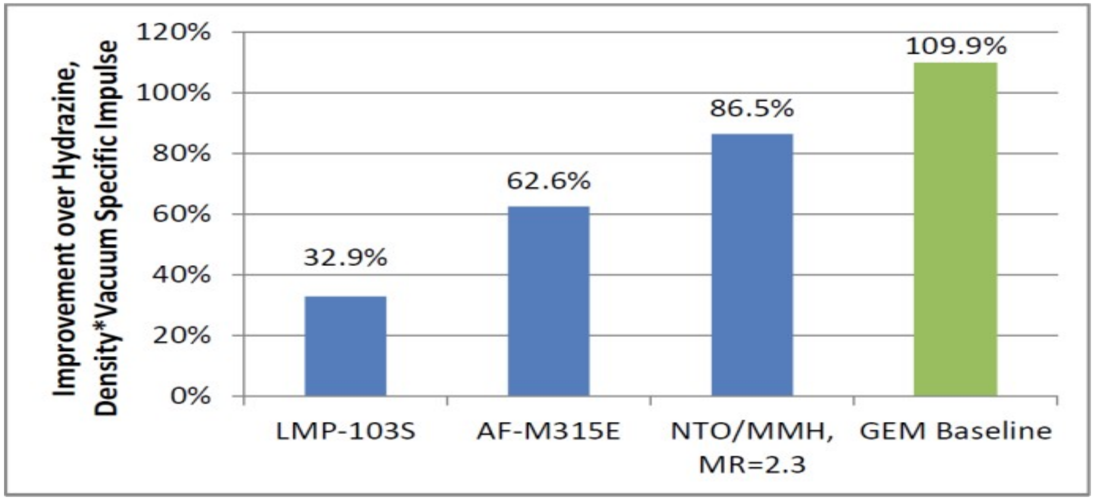


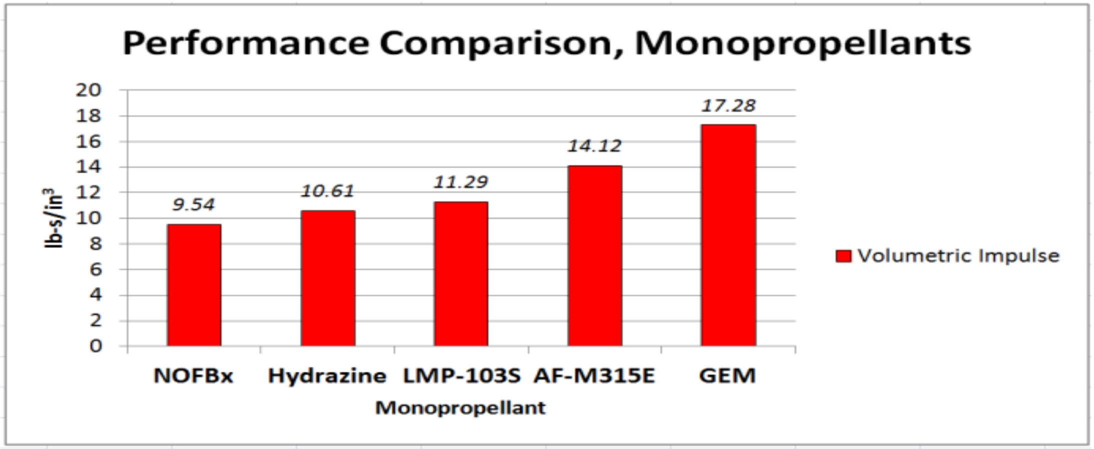
Video: GEM Drop Tests
500 °C/932 °F
GEM ~64 msec, AF-M315E ~625 msec

Catalyst Ignition Video

Performance

- Volumetric Isp
- Price point

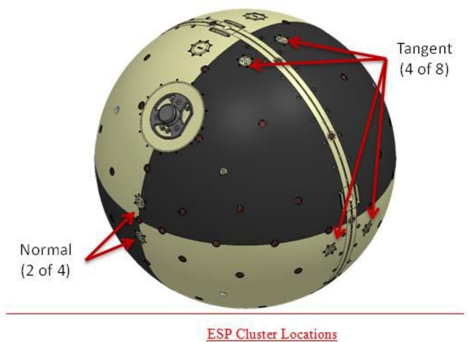


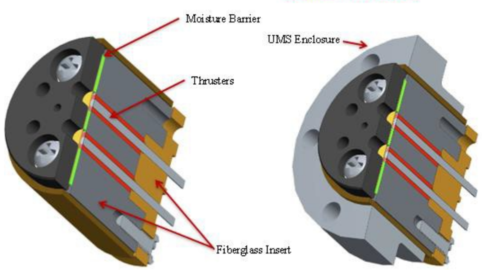


EXAMPLE USES

1st HAN Propellant Flown In-Space 2014

SpinSat





Metric	Value
Impulse Bit (early life, ~10 pulses)	0.35 mN*s
Impulse Bit (midlife, ~100 pulses)	0.4 mN*s
Impulse Bit (late life, ~250 pulse)	0.45 mN*s
Specific Impulse (lifetime averaged)	300 s
Total Impulse per Thruster	0.15 N*s
Pulse to Pulse Variability	5-10%

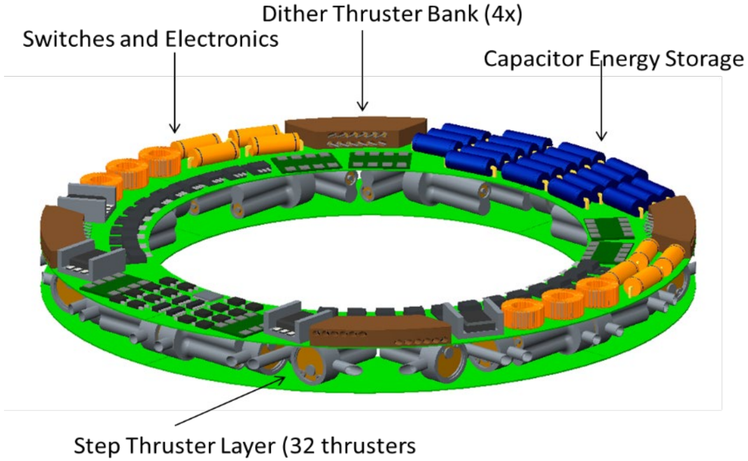
Reference - http://www.spaceflight101.com/spinsat.html

Next In-Space 2019

NASA's Green Propellant Infusion Mission: GPIM

Led by Ball Aerospace, with Aerojet developed AF-M315e thrusters.

Application Precision ACS



Metric	Electric Solid Microthrusters Test Data
Pitch, Yaw Thrust	Peak capability, 1.8 N/0.41 lbf
Roll Torque	Peak capability, 0.26 N*m/2.25 lbf
Total Rotational Energy	247.6 in*lb*s / 28.0 J*s
Minimum Impulse Bit	Dithers can fire ~0.1 mN*s
Response Time	Dithers respond in ~1 ms
Flight Mass	First prototype 3.5 lb / 1.59 kg (2015)
Operating Frequency	System produces a MIB every .05s
Envelope	Fits inside envelope
Power Draw	Maximum power draw is 1.6 kW
Thrust Variability	<10% on final batch
Service Lifetime	13 years proven, >20 yr. expected
Max Operating Pressure	0.05 torr (200,000 feet alt.)

Thermobaric Explosive

Liquid monopropellant explosives allow incompatible materials to be combined to modify shock waves.

T=0
GEM Detonation

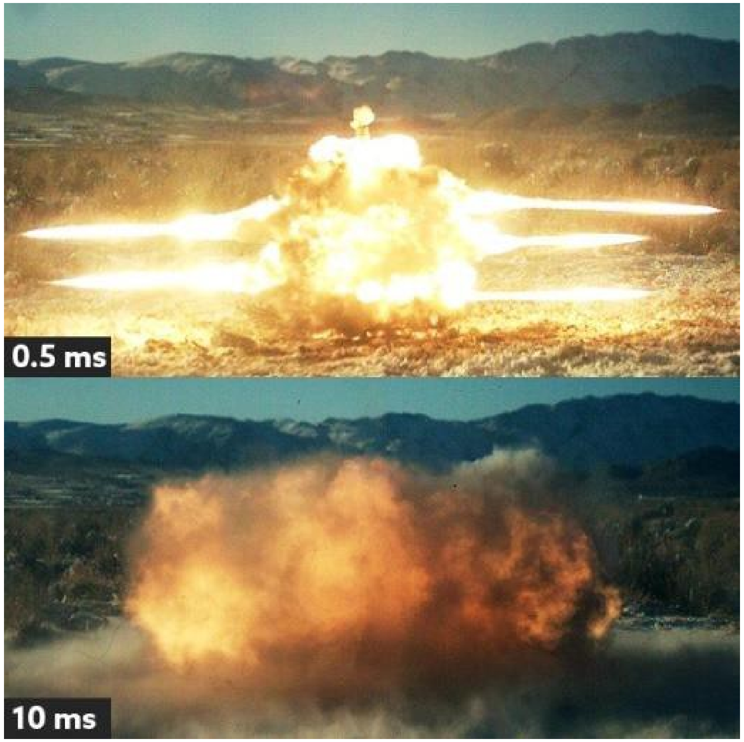
T=+10ms
Mg ignition

T=+20 ms

T=+30ms
Mg burn out

Enhanced Oil Recovery and Waterless Fracking

- SBIR commercialization
- First liquid propellant in the oil industry.
  - Pumpable and injectable
    - Burn propagation in fractures of <70 microns (human hair)
- Development focus
  - Well stimulation tool
  - Propellant-enhanced shaped charges



Oil tool above ground test, shaped charges fire following by GEM ignition.

Liquid Avalanche Explosives

GEM has slow shock wave for heaving wet "maritime" snow.
GEM is Class 1.4c requiring less magazine storage setback acreage than currently used Class 1.1 explosives.

Measured Overpressure

at Radius (kPa)		
Blast at surface	*3m*	*6m*
Emulsion	25.5	6.5
Liquid GEM	31.7	13.1
Gelled GEM	31.7	13.1

	Vertical Shockwave Speed (ft/s)	**Horizontal Shockwave Speed (ft/s)**
Emulsion	1331	1595
GEM	1392	1550
Gelled GEM	1690	1641

Snow Pit Dimensions

Blast Surface	*Width (m)*	*Depth (m)*
Emulsion	0.81	0.53
Liquid GEM	1.07	0.53
Gelled GEM	1.07	0.53

Blast 0.45m *below surface*	*Width (m)*	*Depth (m)*
Emulsion	1.88	1.02
Liquid GEM	2.49	1.35
Gelled GEM	2.62	0.94

Muzzle Flash Simulation

- Army SBIR contract
- Replace blank rounds and battlefield with "non-pyrotechnics"
  - Better
    - Realistic-IR
    - Multi-fire
  - Safer
    - Minimal injury risk
  - Green
    - No Pb contamination from primers
  - Faster
    - No policing empty shell casings after training
    - No magazine storage/tracking required
    - 400x less material handling
- SBIR Commercialization
  - Live entertainment, theme parks, concerts, weddings, etc.

Thank You