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14. ABSTRACT These briefing charts are an overview of reduced toxicity, high performance monopropellant. Performance of hydrazine limits spacecraft payload, range, lifetime and operational response time. The focus is to replace SOTA Hydrazine with monopropellants based on energy dense ionic liquids.					
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REDUCED TOXICITY, HIGH PERFORMANCE MONOPROPELLANT

September 2011

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Current Propellant Safety Issues & Performance Drivers



- Hydrazine vapor toxicity can increase testing/operations costs:
 - System Handling/Fueling by certified crews in high level PPE
 - Monitoring system in field
- Vapor toxicity can limit transportation options
- Performance of hydrazine limits spacecraft payload, range, lifetime and operational response time



System Handling/Fueling

Desire improved volumetric impulse for greater capabilities and elimination of vapor toxicity with acceptable safety properties

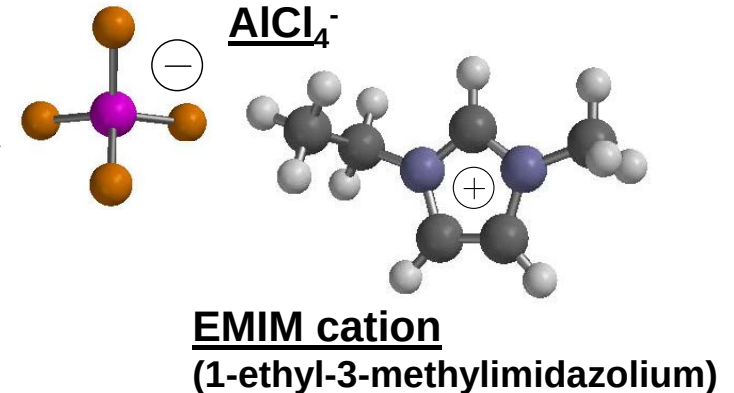


Energetic Ionic Liquids- Avenue to Hydrazine Replacement



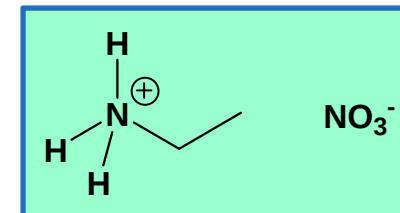
• History

- 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
Booster engines
DACS/ACS



**Energetic ionic liquids employed to produce
advanced monopropellant, AF-M315E**



AF-M315E Desirable Properties

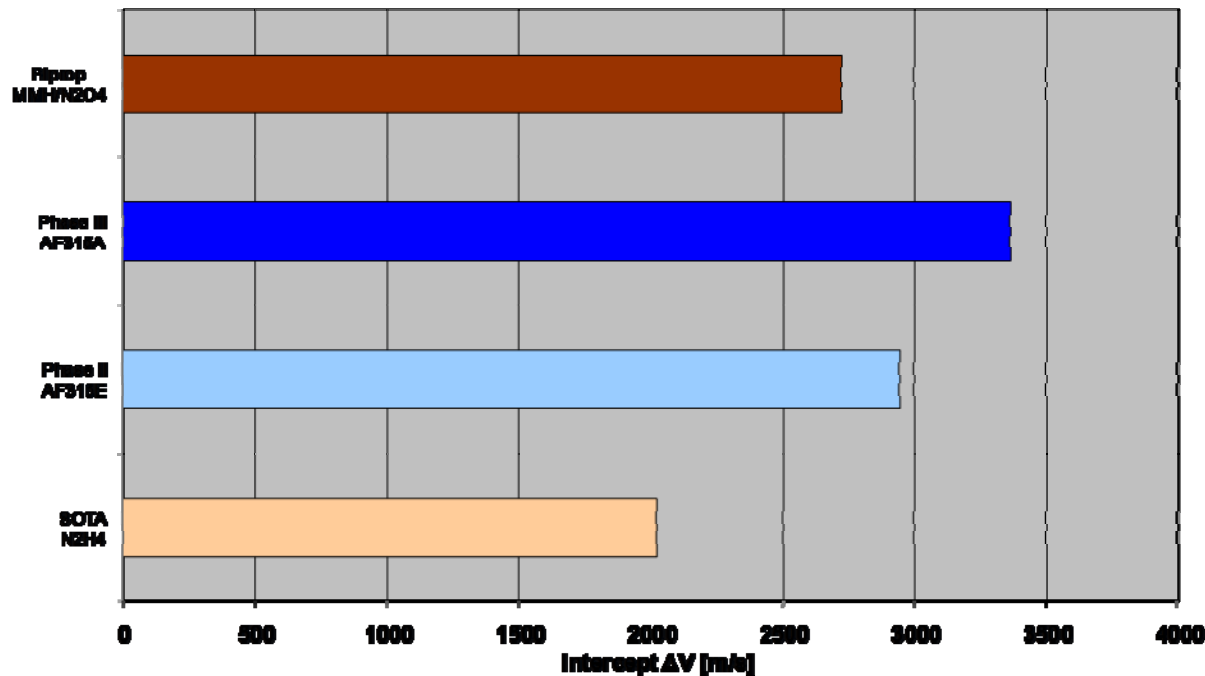
Challenging Initial Requirements

Characteristic	Objective
Density*Isp	3450 Ns/L [2.07 MPa-vac; exp=50]
Vapor toxicity	Does not exceed TLV (No SCBA in handling)
Exhaust carbon content	No soot in exhaust
Melting point	< 2°C
Detonability	Class 1.3 (Prefer 24 cards maximum in NOL)
Impact sensitivity	> 20 kg-cm minimum (E ₅₀)
Adiabatic compression	No explosive decomposition (pressure ratio of 35:1)
Thermal stability	< 2% by wt. decomposition (DOT)
Critical diameter	No propagation in lines of < 1.91 cm diameter

**Focus- Replace SOTA Hydrazine with Monopropellants
Based on Energy Dense Ionic Liquids**



Ionic Liquid-based Monopropellants System Payoffs



Microsat Benefits

120 kg (95 kg propulsion system)
High delta-v required

**AF-M315E exceeds
SOTA monopropellant (45%)
and
bipropellant (8%)
Next generation exceeds
SOTA monopropellant (66%)
and
bipropellant (23%)**

- IL-based monopropellants confer higher system payoff in volume limited systems partly due to high density and reduction in system's inert mass fraction



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)



AF-M315E

Small-Scale Hazards



Test	AF-M315E	Desired
Hazard Class	1.3C (FHC)	1.3C (FHC)
Unconfined Burn (Open container/wood fire)	Test 1 and 3: No reaction Test 2: slow burn	No explosion
NOL Card Gap (O cards)	Negative (deformed plate)	Negative (deformed plate)
Drop Weight Impact Sensitivity (JANNAF Test Method)	126 Kg-cm (E ₅₀) Lot 32 Reference material: N-Propyl Nitrate (21 kg-cm)	>20 (E ₅₀) Kg-cm
Sliding Friction (Julius Peters –BAM)	352 N (5 consecutive “no go”)	>300N
Thermal (50 ml beaker @75°C/48 hours)	No reaction Wt. Loss < Wt. Volatiles	No reaction Wt. Loss< Wt. Volatiles
TGA (75°C/48 hours)	0.86 Wt % , Excluding Volatiles	<2.0 Wt%, Excluding Volatiles
Electrostatic Discharge	>1J	>1J



Direct Spill- Pan Fire Test

Purpose

Simulate an AF-M315E spill into a JP-8 fuel fire

Results

Test conducted on small-scale (15ml added to 1 gallon JP-8) failed to ignite propellant

At larger scale (1 liter added to 4 gallons of JP-8), denser propellant also falls to bottom of the pan and is ignited when JP-8 is nearly completely consumed

Once ignited (6 min. into test) the propellant exhibited a sporadic luminescent mild burn

AF-M315E is difficult to ignite at ambient pressure – only catalytic initiation is reliable

JP-8 Fire Prior to Propellant Addition



Ignition of Propellant Near End of Test

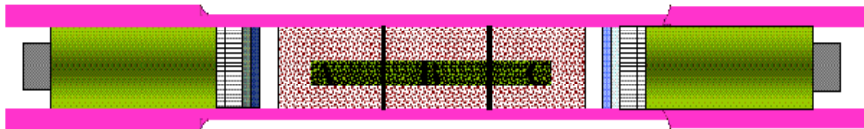




Confined Slow Cook-Off Test Design

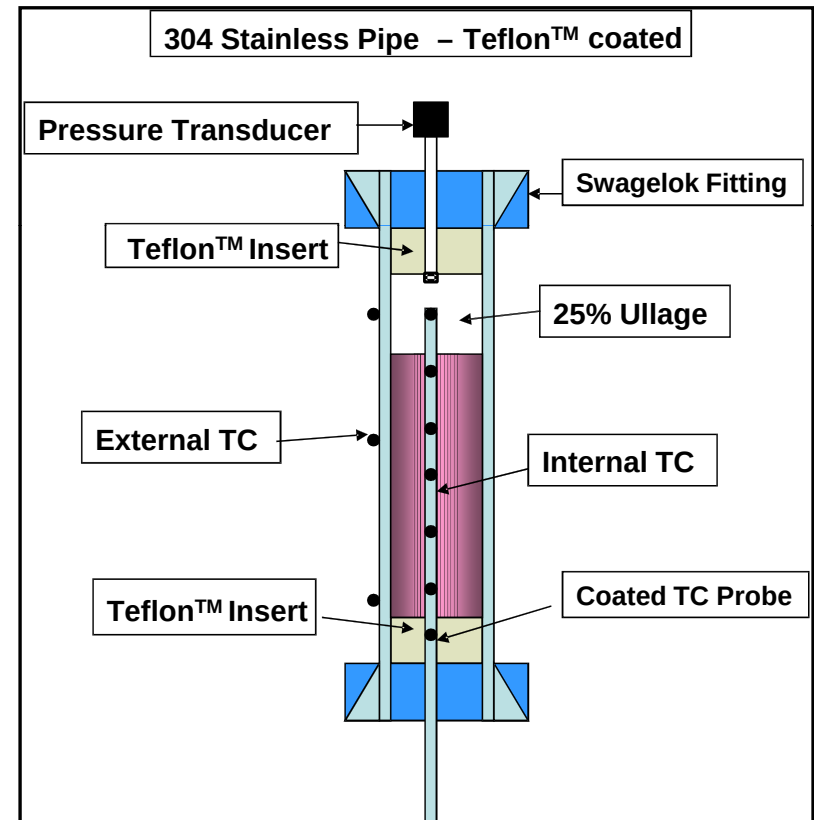


Adapted the Standard China Lake 2.54" Cook-Off Pipe in Conjunction with Alice Atwood @ NAWC



- Easier to adapt for liquid testing than the Small Scale Cook-Off Bomb (sealing is an issue)
- Desire internal thermocouples to determine critical temperature of AF-M315E
- Desire a pressure tap to determine rupture pressure
- Desire a burst pressure of ~34.5 MPa similar to a notional propellant tank
- Desire ullage and vertical orientation
- Scalable design ($L/D = 3$) to full-scale (17.8 cm and 34.3 cm diameter)
- Tested using direct heating

Modified Slow Cook-Off Pipe





Sub-Scale Slow Cook-Off Tests



Joint US Air Force/Navy Design

Test Conditions

- Ramp at 10 deg C/min to 60 °C
- Soak for three hours
- Ramp at 0.05 °C/min to cook-off

Results

Two tests performed, giving mild case bursts at 48.3×10^5 – 55.2×10^5 MPa with few fragments

Critical temperature at 2.54 cm diameter was determined to be approximately 140°C

Highest temperatures recorded were in the liquid phase near the liquid/gas interface—probable location of event initiation

Pre-Test 2.54 cm Cook-Off Pipe Assembly



Post Test Cook-Off Hardware





Full-Scale Slow Cook-off Test



Test Conditions

- Soak at ambient temperature.
- Ramp at 0.05 deg C/min to cook-off

17.8 cm Test Results

- No detonation, but strong case burst in center- large fragments recovered; both case ends intact
- Thermocouple data showed,
 - Thermal runaway at $\approx 140^{\circ}\text{C}$; similar to small-scale tests
 - Failure temperature $\approx 146^{\circ}\text{C}$
- The highest temperatures were near the propellant surface

17.8 cm OD Steel Vessel



Top End of Steel Pipe – Post Test





Full-Scale Slow Cook-off Testing

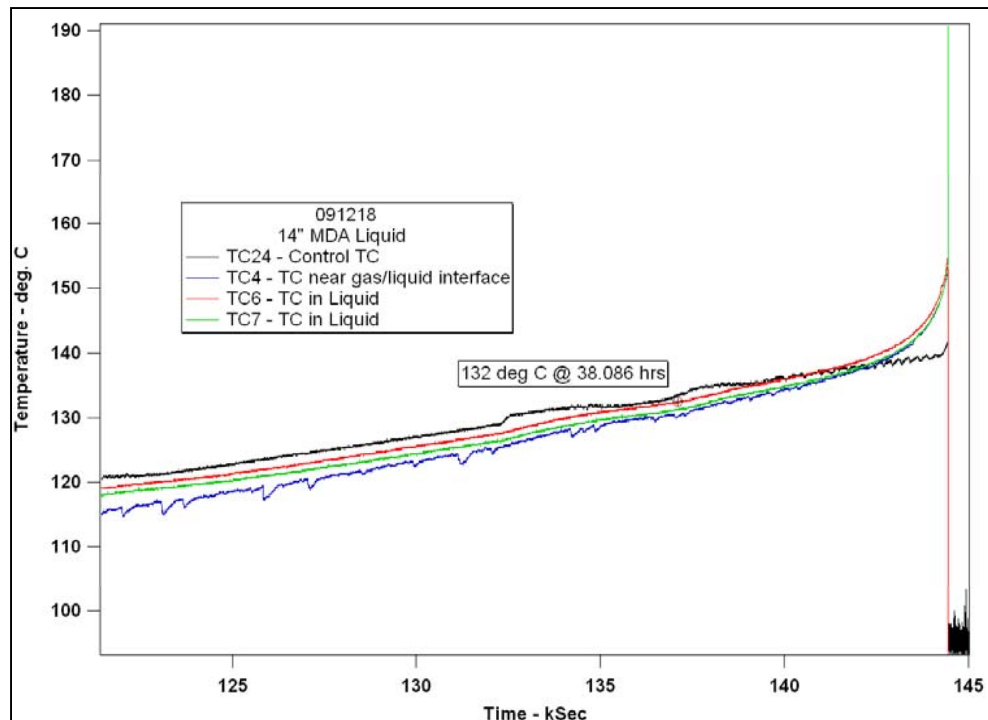


34.3 cm Test

Self-heating started at approximately 132°C – much better than model prediction

Highest temperature near the propellant liquid/gas interface

Failure occurred at approximately 140°C



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34.3 cm OD Steel Vessel



Reaction was a detonation

Bikini gauges indicate >103 kPa @ 50ft

Fragments thrown > 185 m

Punched hole in end cap

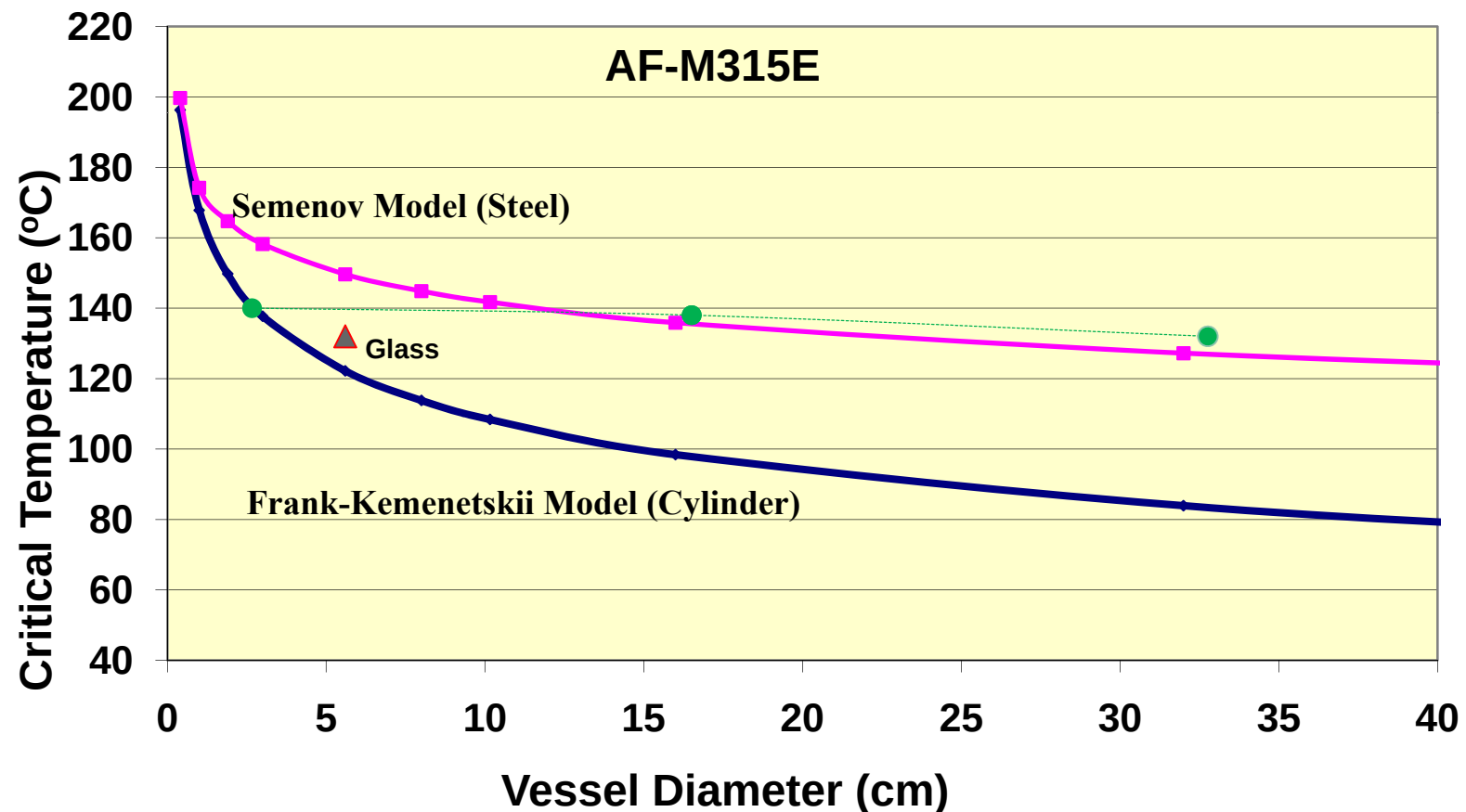


Critical Temperature Models for AF-M315E



Critical Temperature Models Appear Conservative for Larger Diameters

- Convection takes place in liquids
- Models are heavy functions of E_a which is not predicted well by traditional small unconfined tests



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Final Hazard Classification Testing



Test data included: Small-Scale Hazard Data, Single package, External Fire and Super Large Scale Gap Test (SLSGT)

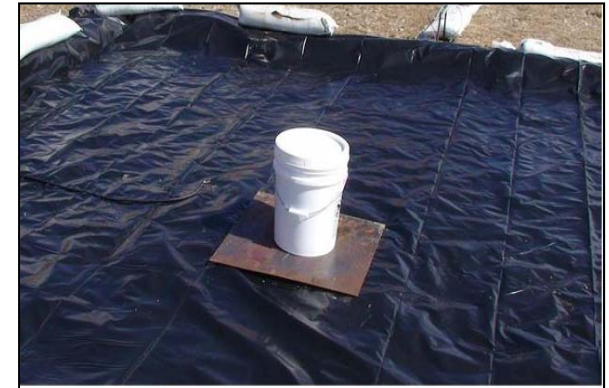
Single packaging tests

Two packaging configurations identified exhibiting no reaction in single package tests performed in triplicate with a C-4 Donor

- 18.9 liter composite pail containing 25 kg of propellant in a 75.6 liter drum over-pack
- 3.8 liter poly container (4.54 kg) in a 18.9 liter plastic pail over pack

Single Package Test

Overpacked 3.8L Container



Post Test





Single Package Testing



Overpacked 18.9 Liter Container



Post Test



Overpacked 3.8 Liter Container



Post Test



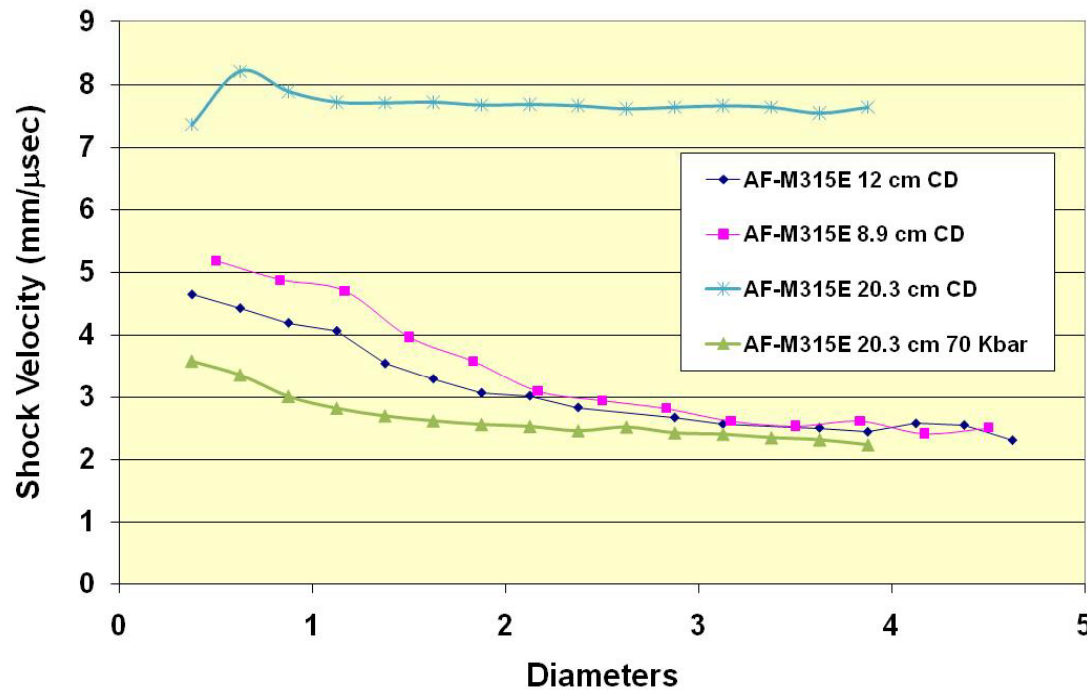


Super Large Scale Gap Test



Critical Diameter is between 10.16 and 17.78 cm ID

- Shock decayed to sonic velocity at 70 kbars shock input (1.27 cm Steel Confinement)
- Witness plate deformed (no detonation)
- Helps differentiate Class 1.1 and 1.3 for propellants

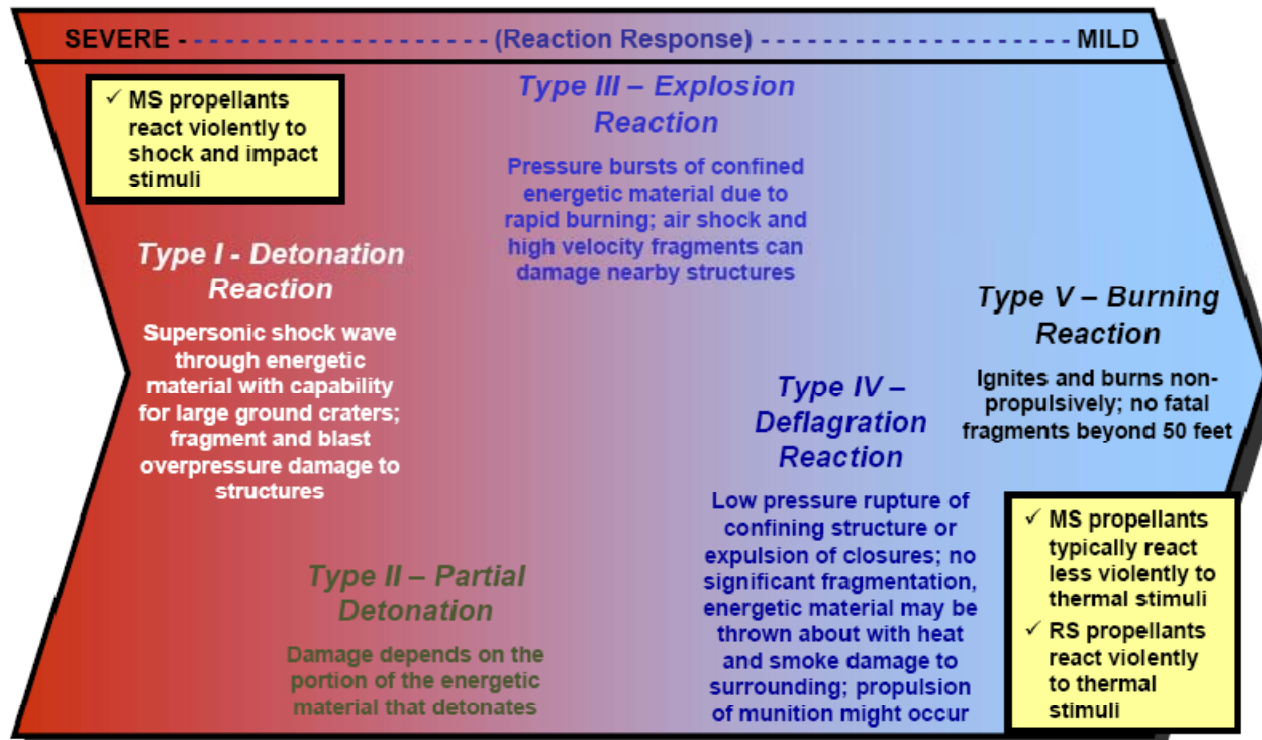




External Fire Test



Type V – Burning Reaction Desired



Pre-Test Configuration





External Fire Test



Results

- 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 776 °C

Type V – Burning Reaction!

Post Test



Sequence of Events

TIME	EVENT	TIME	EVENT
1:11	POP	5:54	TEST ITEM BURNING
1:27	POP	6:01	TEST ITEM BURNING
1:38	POP	6:22	TEST ITEM BURNING
1:43	POP	7:04	TEST ITEM BURNING
2:00	POP	7:13	TEST ITEM BURNING
2:02	POP	8:07	TEST ITEM BURNING



Substance Final Hazard Classification



US Dept. of Transportation Granted a HD 1.3C Designation For Two Packaging Configurations of AF-M315E

Packaged AF-M315E Received Final Hazard Classification of 1.3C in August 2010

U.N. PROPER SHIPPING NAME AND NUMBER:
Propellant, liquid, UN0495

- **18.9L composite pail containing 25 kg of propellant in a 75.6L drum over-pack (EX2010060551)**
- **3.8L poly container (4.54 kg) in a 18.9L plastic pail over-pack (EX2010060549)**

Over-packed 3.8L Container



Over-packed 3.8L Container

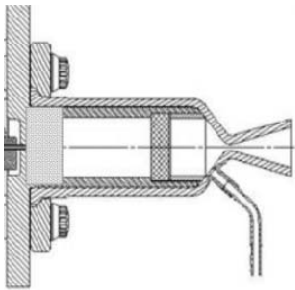




Spacecraft Chemical Propulsion Demonstration



- Technology development oriented
- Employing advanced catalyst ignition



SOTA	N_2H_4
Propellant	AF-M315E
System Goal	3450 Ns/L
Demo Objectives	18 N, <i>30 minute cumulative life</i>
Challenges	Catalytic reactivity, high temp & oxidation resistant components (catalyst substrate, bedplate, throat)



Liquid Engine Alternative Propulsion Development Program (LEAP-DP)



Technology Development

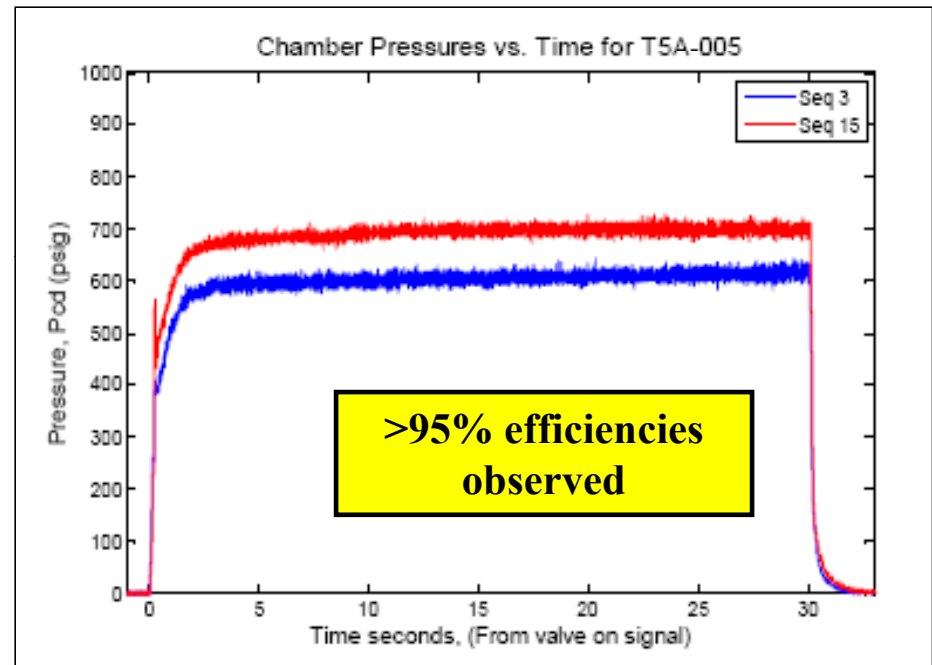
Demonstrate a survivable thruster to meet spacecraft monopropellant goal:
3450 Ns/L [2.07 MPa-vac; exp=50]

- 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

20 N Brassboard Thruster Pulses



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



Propellant Performance Characteristics



	LMP-103S	AF-M315E	Hydrazine
Flame Temperature	1600°C	1900°C	600°C
Isp	252 (theor) 235 sec (delivered)*	266 (theor) ~250 sec (delivered)	220-224 sec (1N thrusters)
Density (g/cc)	1.24*	1.465	1.01
Density Isp Increase over N ₂ H ₄	30%*	50%	-
Preheat Temperature	300°C nominal	370°C nominal	315°C Capable of cold starts (5°C)
Minimum Operational Temperature	10 – 50 °C	< 0 °C System dependent – Propellant becomes viscous, but no precipitation or phase change occurs.	5 - 50 °C
Minimum Storage Temperature	-7 °C	Very low (<22°C) Forms a glass – no crystallization occurs	1°C (Freezing Point) Reheated for re-use

*Anflo, K. and Mollerberg, R., "Flight Demonstration of New Thruster and Green Propellant Technology on the PRISMA Satellite" ACTA Astronautica, Vol. 65, Nov.-Dec. 2009

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Compatibility and Handling



Propellant	LMP-103S	AF-M315E
Thruster Materials Compatibility	High combustion temperature and oxidative environment - high temperature, corrosion resistant refractory metal (Ir and Re) chamber materials needed.	High combustion temperature and oxidative environment - high temperature, corrosion resistant refractory metal (Ir and Re) chamber materials needed.
System Materials Compatibility	Compatible with most COTS materials currently used for N ₂ H ₄ systems. Propellant is basic – compatible with many metals.	Limited material compatibility driven primarily by HAN content and acidity
Handling & Safety	Significantly reduced toxicity removes the need for SCAPE suits	Low toxicity and vapor pressure allow handling with only basic PPE Propellant will not crystallize if concentrated



Status



- Broad range of safety and hazard characterization completed on USAF advanced monopropellant AF-M315E
- AF-M315E has demonstrated significantly reduced toxicity compared to spacecraft monopropellant hydrazine with much higher performance
 - Promises lower testing/operations costs, improved operational responsiveness
 - Leading to next generation systems with increased spacecraft payload, range, and lifetime
- The FHC test data package accepted by DOT for a packaging specific hazard classification of 1.3C for AF-M315E



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Back-Up Slides



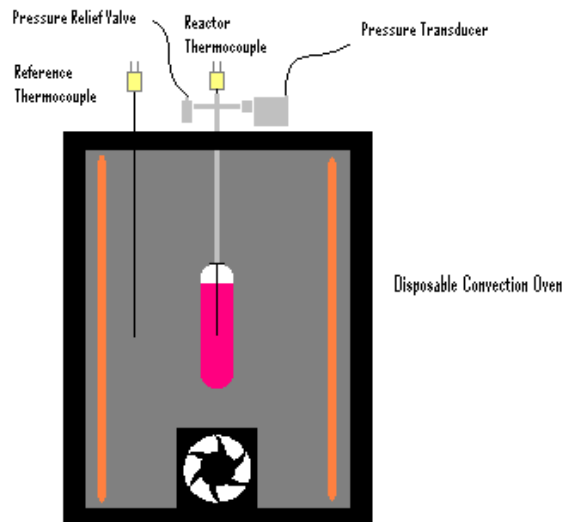


Confined Slow Cook-Off Tests



-Background-

- Wanted Critical Temperature Curve of AF-M315E for Propellant Processing – Similar to 1-Liter Cook-off Test for Melt-Castable Explosives
- New Cook-Off Test Apparatus Designed for Confinement and Propellant Compatibility
 - All Glass High Pressure Vessels
 - Teflon™ or Teflon Coated Couplings and Thermocouples
 - Kraton™ Coated Stainless Steel Tubing
 - Pressure Tap



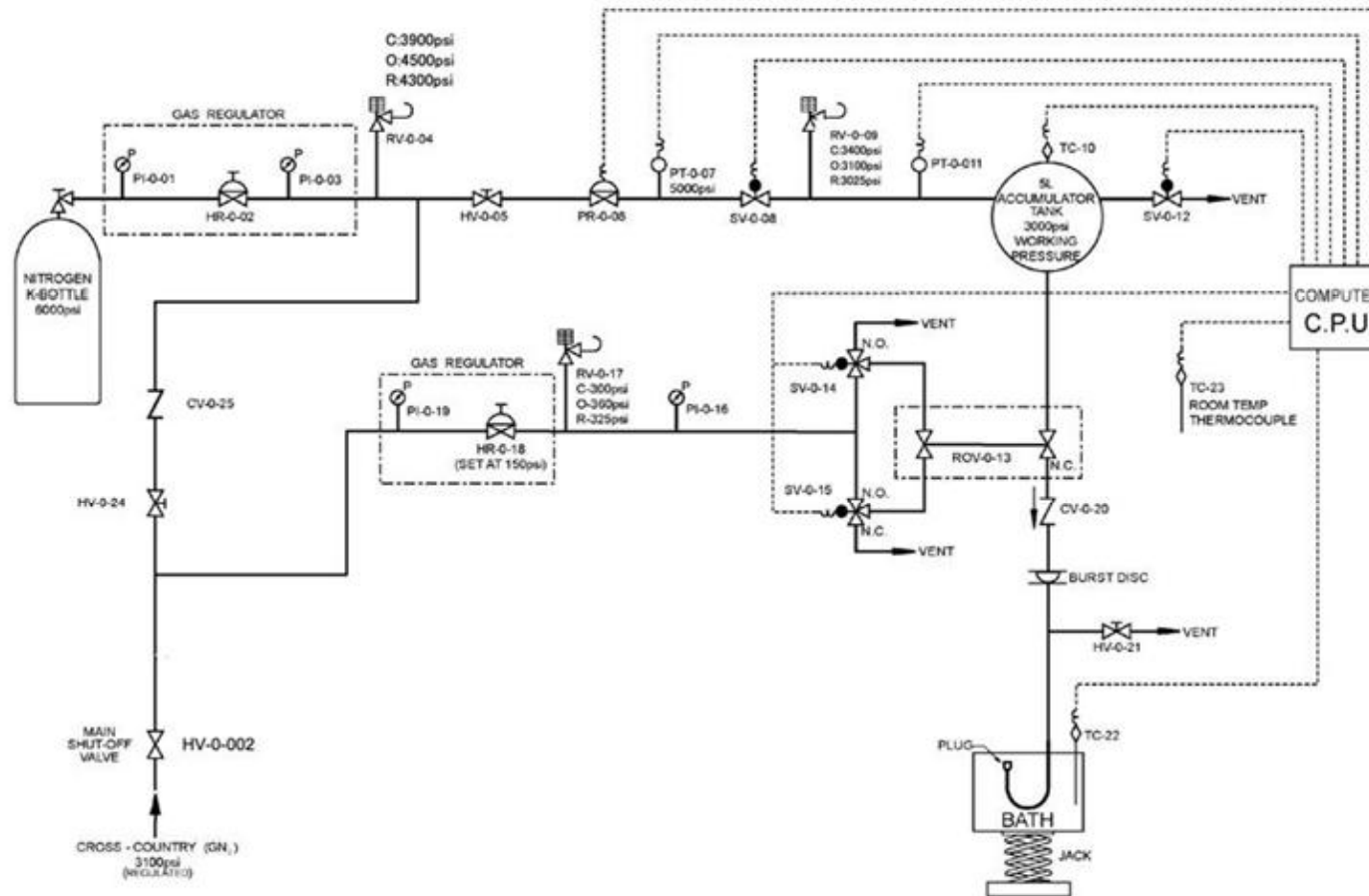
Confined Cook-Off Test Design



250 ml Confined Cook-Off Oven Assembly



U-Tube Adiabatic Compression

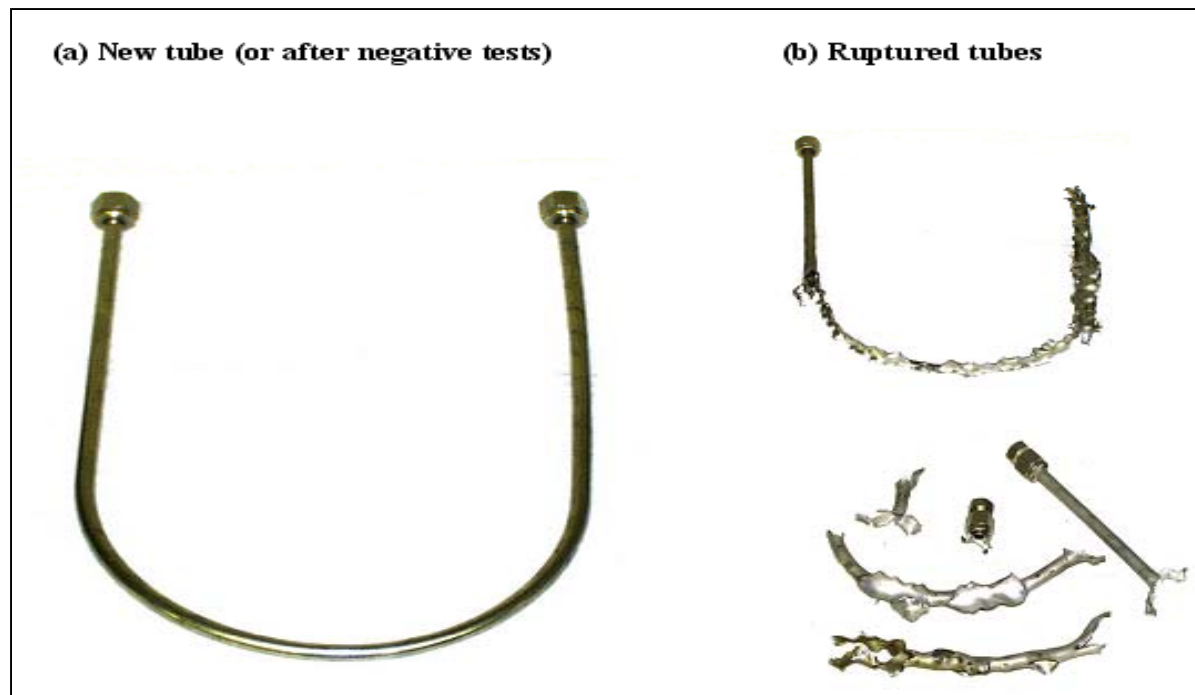




Adiabatic Compression - continued -



- 3 ml samples are placed in tube
- tube may be heated in a ball bearing bath to desired temperature
- high pressurization rate with N_2 achieved with fast acting valve and a rupture disk
- TIL of 35:1 pressure ratio desired

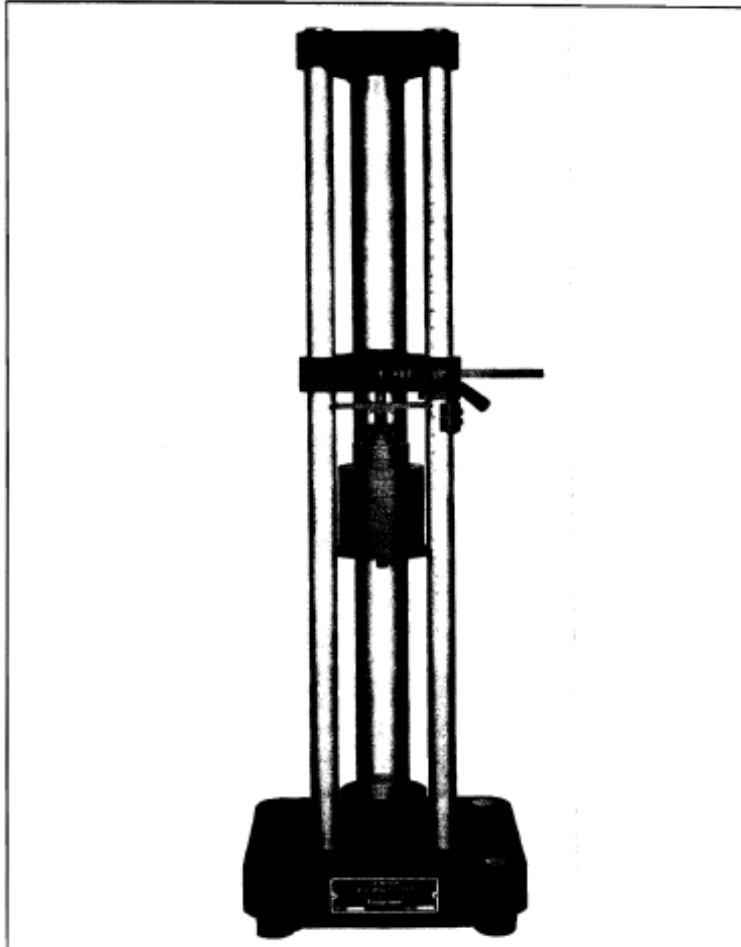




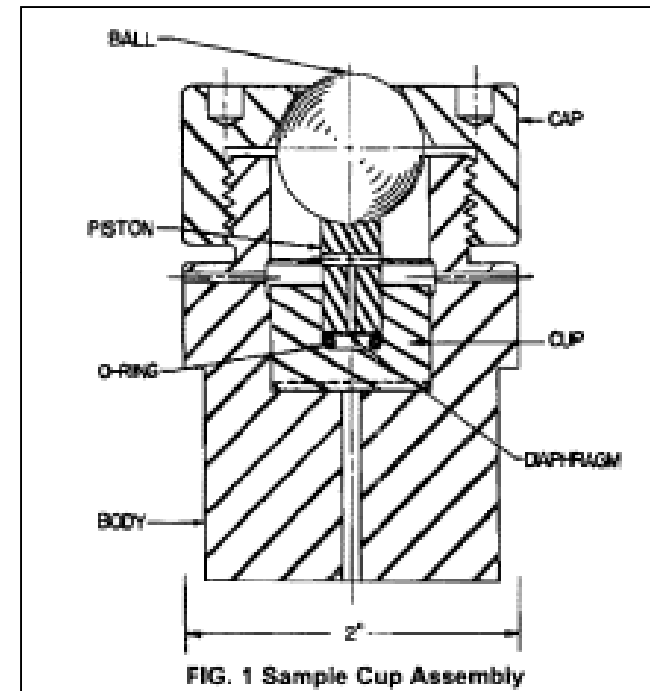
JANNAF Liquid Impact Test



Olin Mathieson Drop-Weight Impact Tester



Liquid Sample Cell Assembly



- Test is a form of adiabatic compression
- N-propyl nitrate reference material
 - Calibrated with water