PERC
Purdue Energetics Research Center

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Purdue University Zucrow Labs
Energetics Laboratory

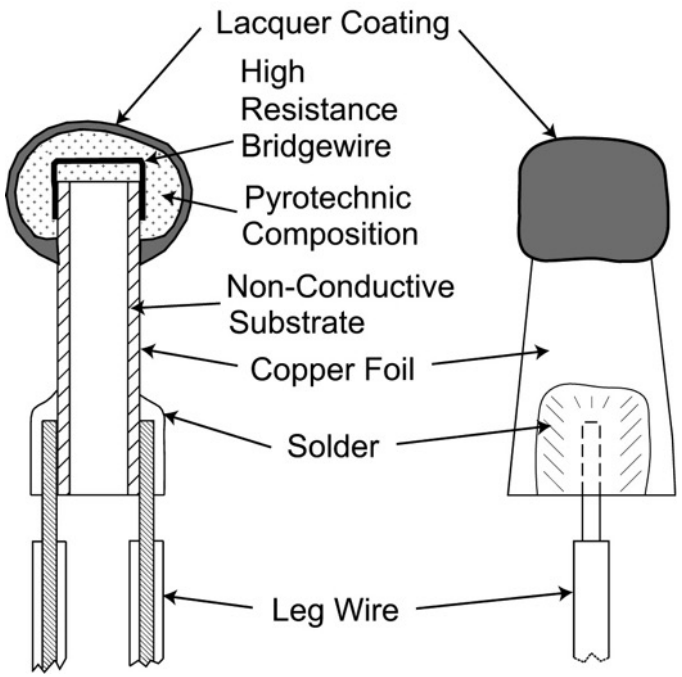
SERDP • ESTCP SYMPOSIUM
25 Years of ESTCP
2019 | Enhancing DoD's Mission Effectiveness

How can we have less toxic AND better energetic materials?

- Can we really have better energetic materials that are ALSO less toxic?
  - Maybe, with some effort, we can “have our cake and eat it too”!
  - Examples:
    - Lead free matches and primers
    - Less caustic solid rocket products
    - Additively manufactured gun propellants using less solvent (maybe)

Lead Free Electric Matches

- Electric matches used with pyrotechnics
- Nearly all current electric matches contain lead as thiocyanate, nitroresorcinate, or tetroxide
  - Produce lead containing smoke
- Can these materials simply be replaced with nanoscale thermites?
  - Not exactly



D. L. Naud, M. A. Hiskey, S. F. Son, J. R. Busse, and K. Kosanke, "Feasibility Study on theuse of Nano-scale Thermites for Lead-free Electric Matches," Journal of Pyrotechnics, Issue 17, pp. 65-75 (2003). http://www.jpyro.com/wp/?p=437

Lead Free Electric Matches

- Initial matches used ~40nm Al/MoO_3 in NC lacquer
  - Match ignited reliably
  - However, burn was too fast to ignite black powder reliably!
- Switched to larger nano-Al (~120 nm) & added secondary material
  - Larger Al is broader in distribution
  - Probably a good thing for this application
  - Match and black powder then ignited reliably!

Lead Free Electric Matches

- Compares well to standard electric match in performance
- Impact sensitivity better than Martinez match on LANL drop test
- Coatings mitigated nAl oxidation

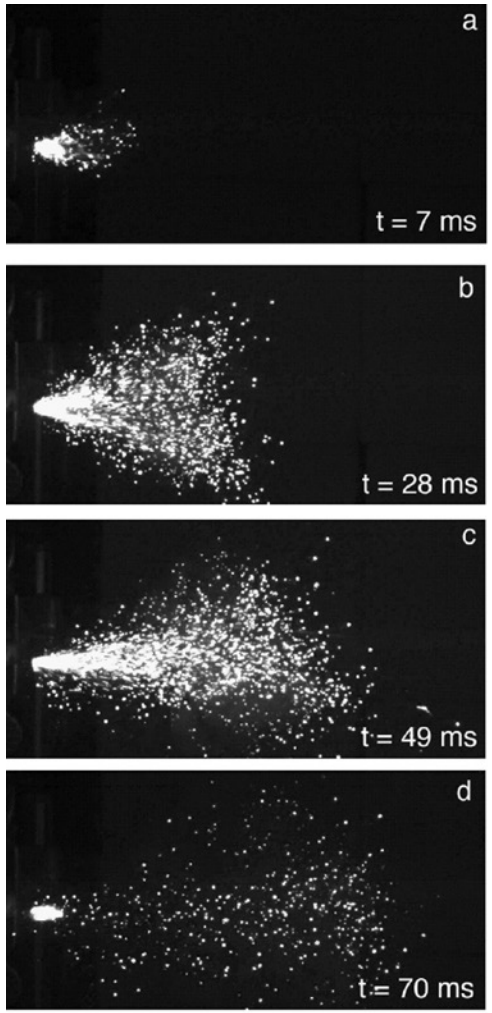


Figure 7. High speed video of a Martinez Minimatch.

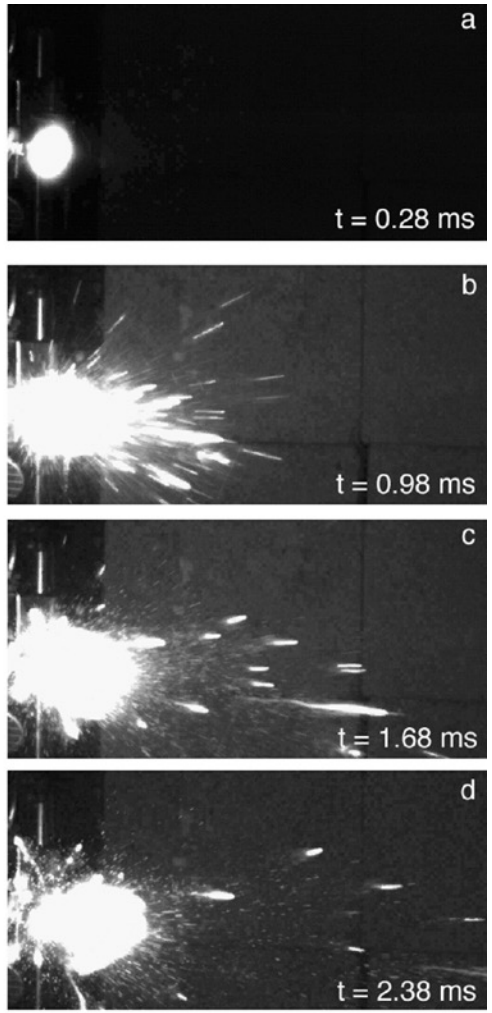
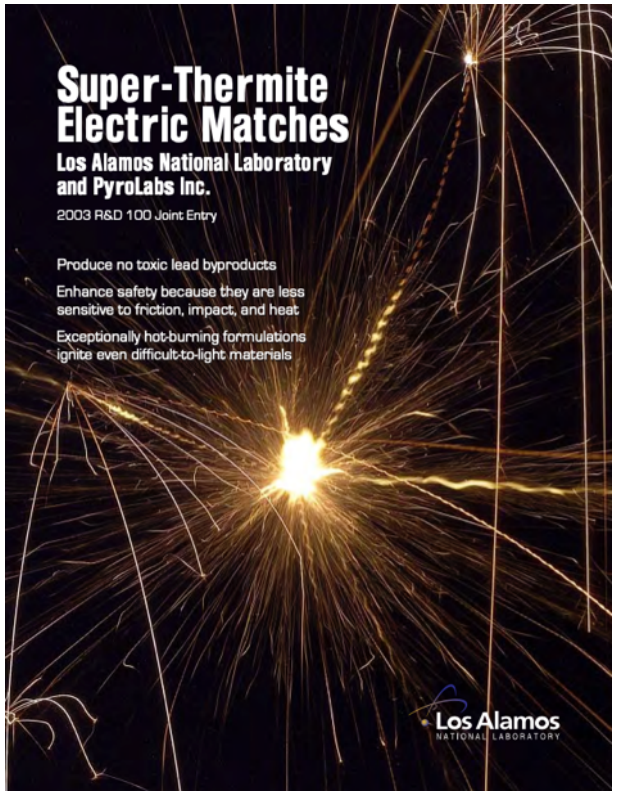


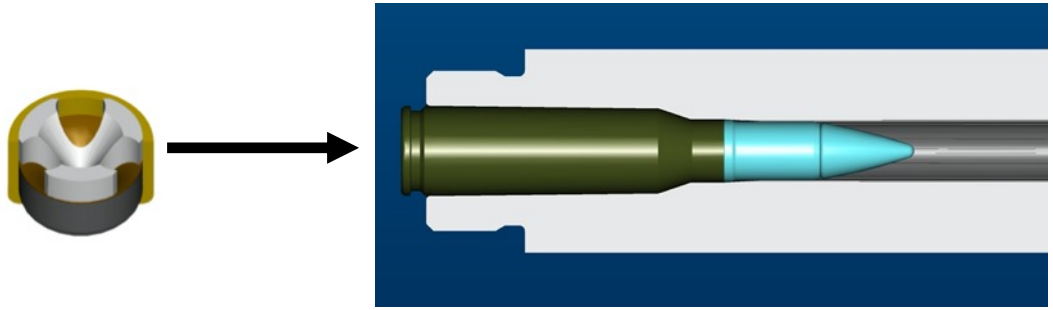
Figure 8. High speed video of a lead-free match.



R&D 100 Award Winner, "Super-Thermite Electric Matches" (2003)

Lead Free Primers

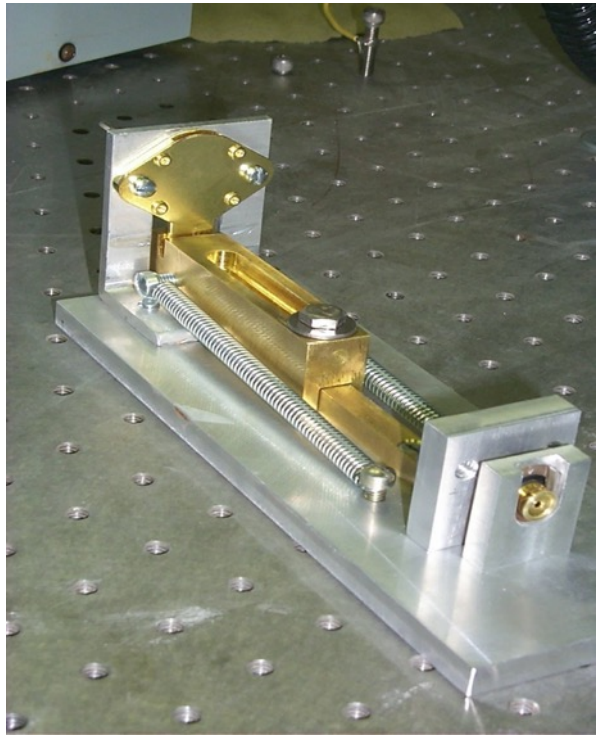
- Commonly used primers contain lead and antimony compounds
- This raises environmental concerns
- Lead Styphnate & PETN make up 30-40% of the formulation!
- Can these materials be simply replaced with nanoscale thermites?
  - Not exactly



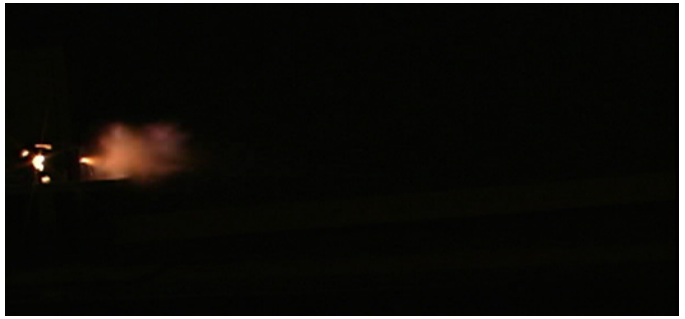
P. P. Ostrowski, M. M. Bichay, T. M. Allen, V. E. Sanders, and S. F. Son, "Recent Accomplishments in MIC Primer Development at NSWC/Indian Head," 41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit; Tucson, AZ; USA; 10-13 July 2005. pp. 1-11, 2005.

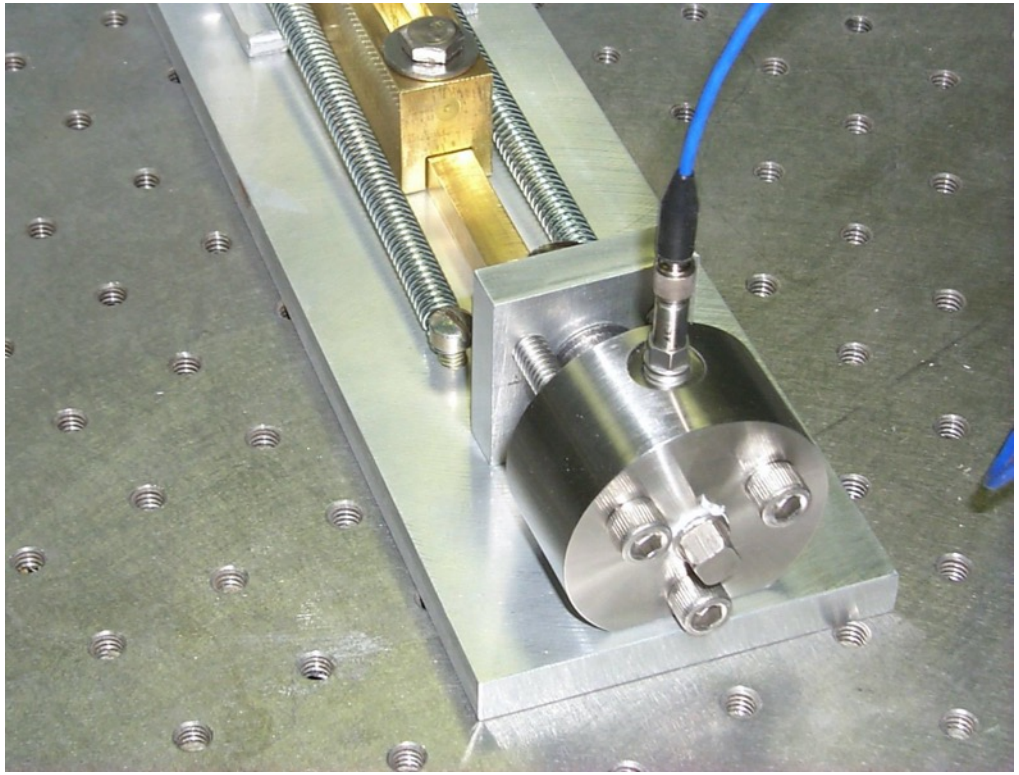
Lead Free Primers

- Testing performance



Open primer firing

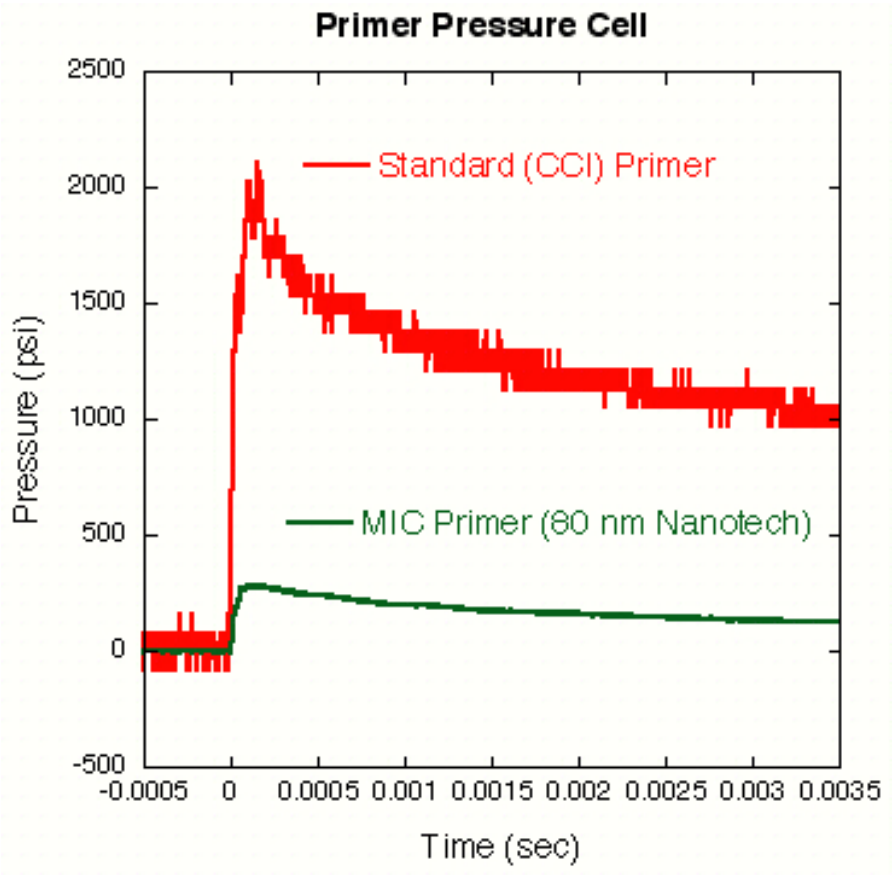




Primer pressure cell

Lead Free Primers

- Produced hot products, but pressure output ultimately not adequate
- Pressure can affect ignition significantly
- Ultimately gas generators were added to improve ignition of gun propellents.



Less Caustic Rocket Propellant Products

- TRADITIONAL PROPELLANT HAS NOT CHANGED MUCH SINCE 1954

$$Al + NH_4ClO_4 + Rubber \rightarrow H_2 + CO + HCl + Al_2O_3 + N_2$$

Al-Li

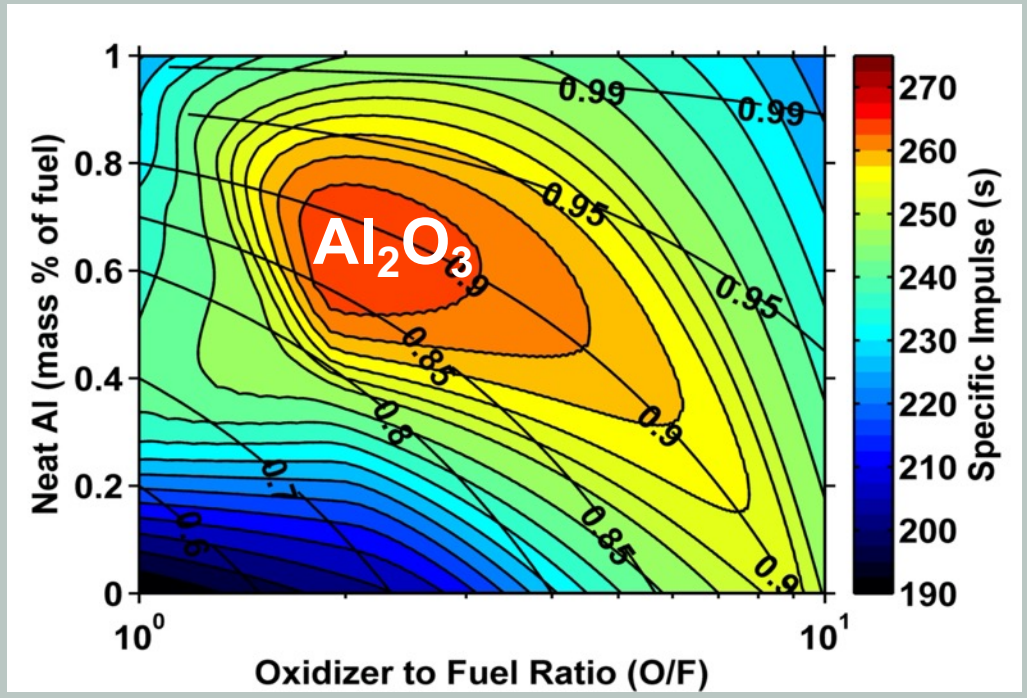
B. C. Terry, T. R. Sippel, M. A. Pfeil, I. E. Gunduz, and S. F. Son, "Removing Hydrochloric Acid Exhaust Products from High Performance Solid Rocket Propellant Using Aluminum-Lithium Alloy," *J. Hazardous Materials*, Vol. 317, pp. 259-266, 2016.

B. C. Terry, I. E. Gunduz, M.A. Pfeil, T.R. Sippel, and S.F. Son, "A Mechanism for Shattering Microexplosions and Dispersive Boiling Phenomena in Aluminum–Lithium Alloy Based Solid Propellant," *Proceedings of the Combustion Institute*, 36 (2), pp. 2309-2316, 2017.

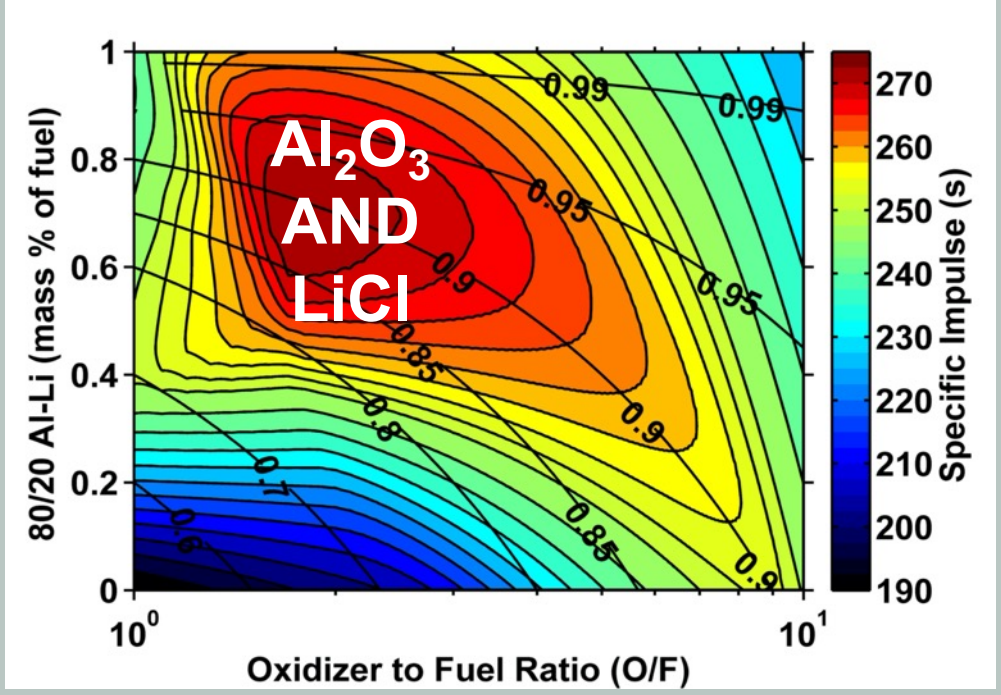
Some slides from Dr. Brandon Terry, Adranos

Less Caustic Rocket Propellant Products

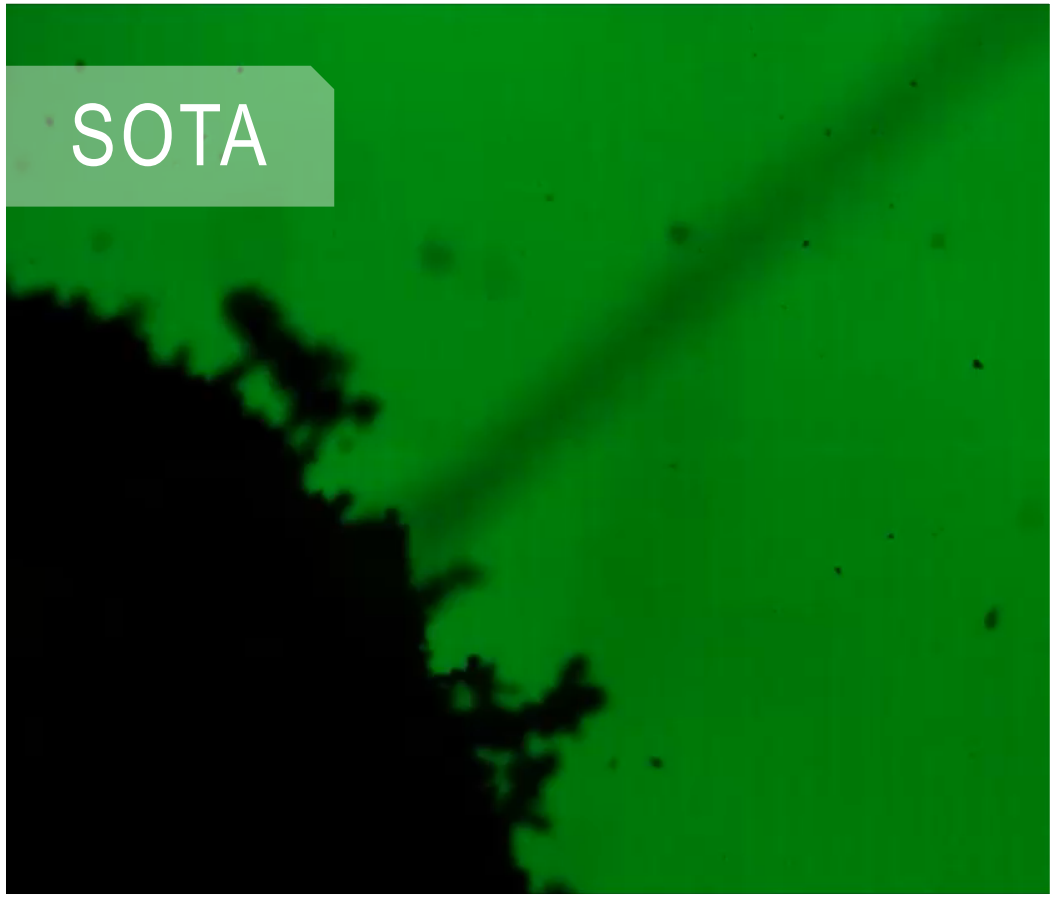
NEAT ALUMINUM



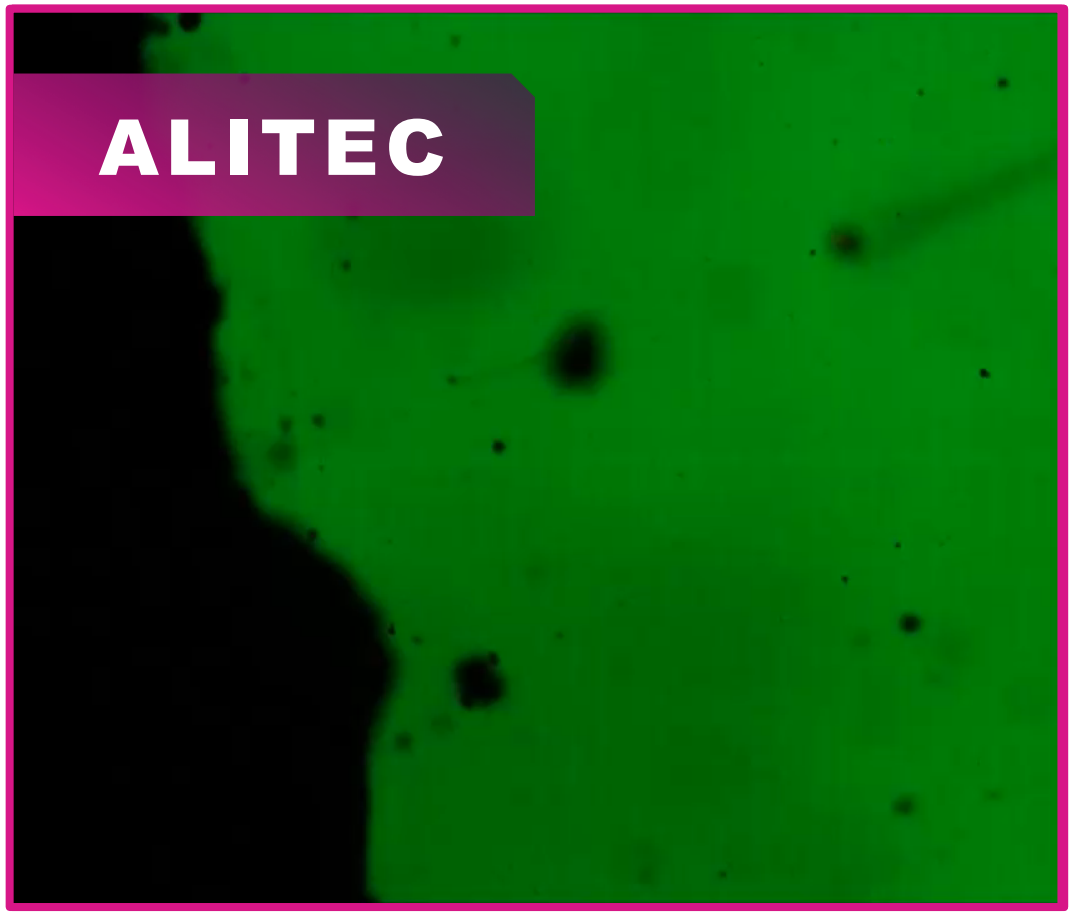
80/20 AL-LI ALLOY



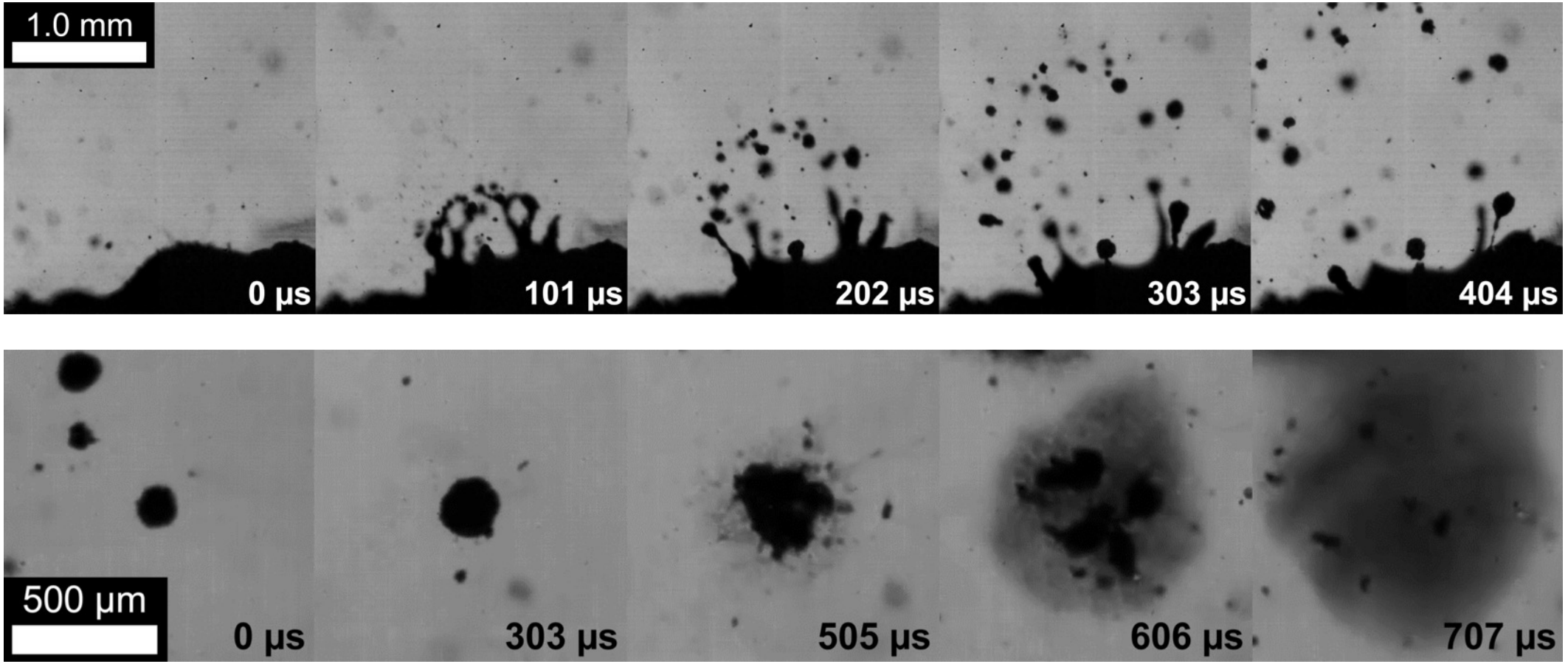
Less Caustic Rocket Propellant Products



VS.



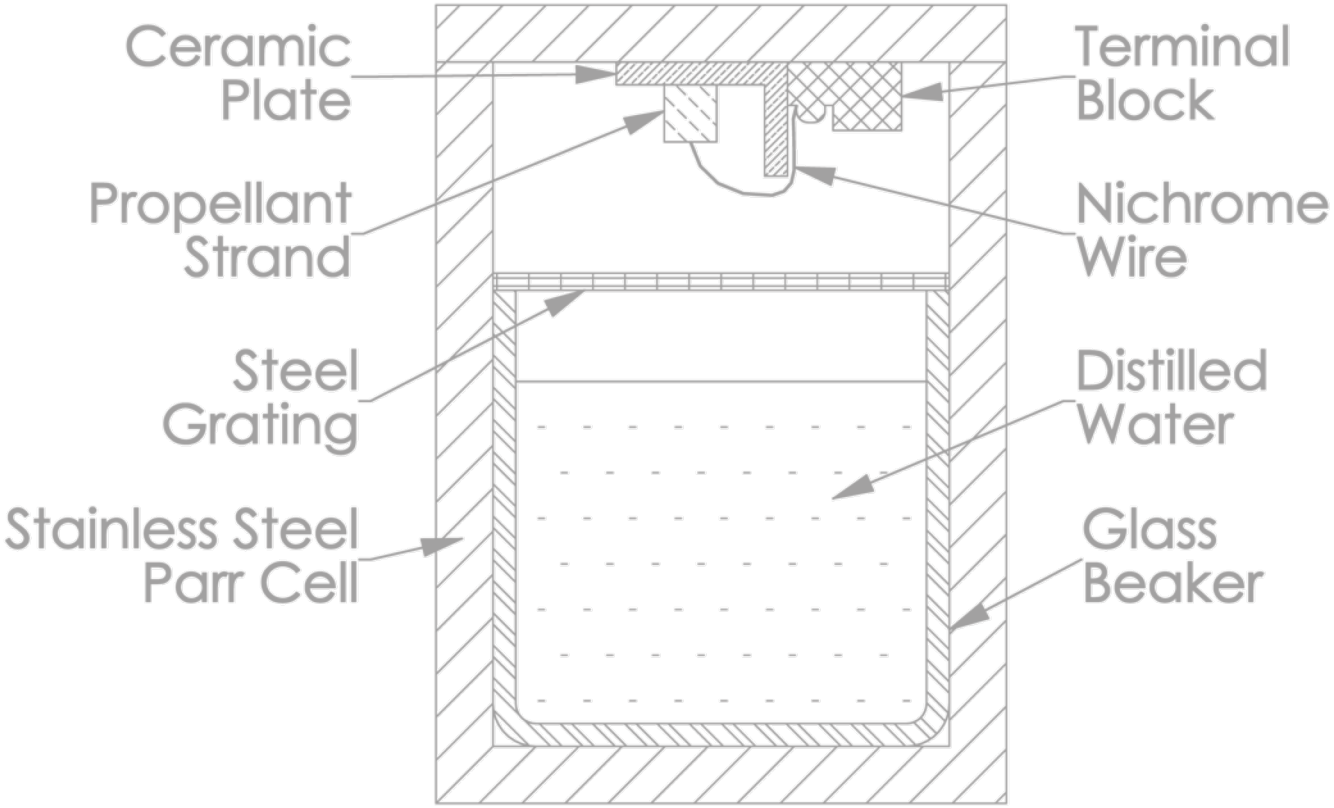
Less Caustic Rocket Propellant Products



Al-Li MICROEXPLOSIONS

Less Caustic Rocket Propellant Products

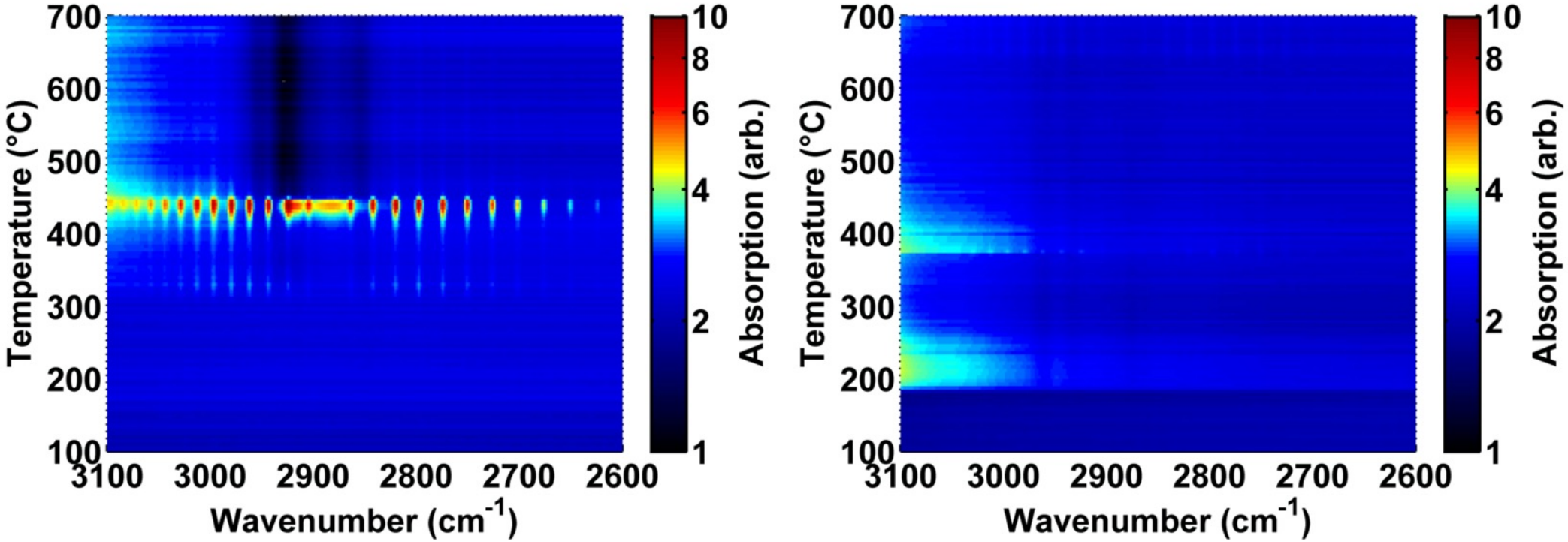
WET BOMB COMBUSTION



75.5 ± 4.8% reduction in acidity

Less Caustic Rocket Propellant Products

DSC/TGA COUPLED WITH MS/FTIR



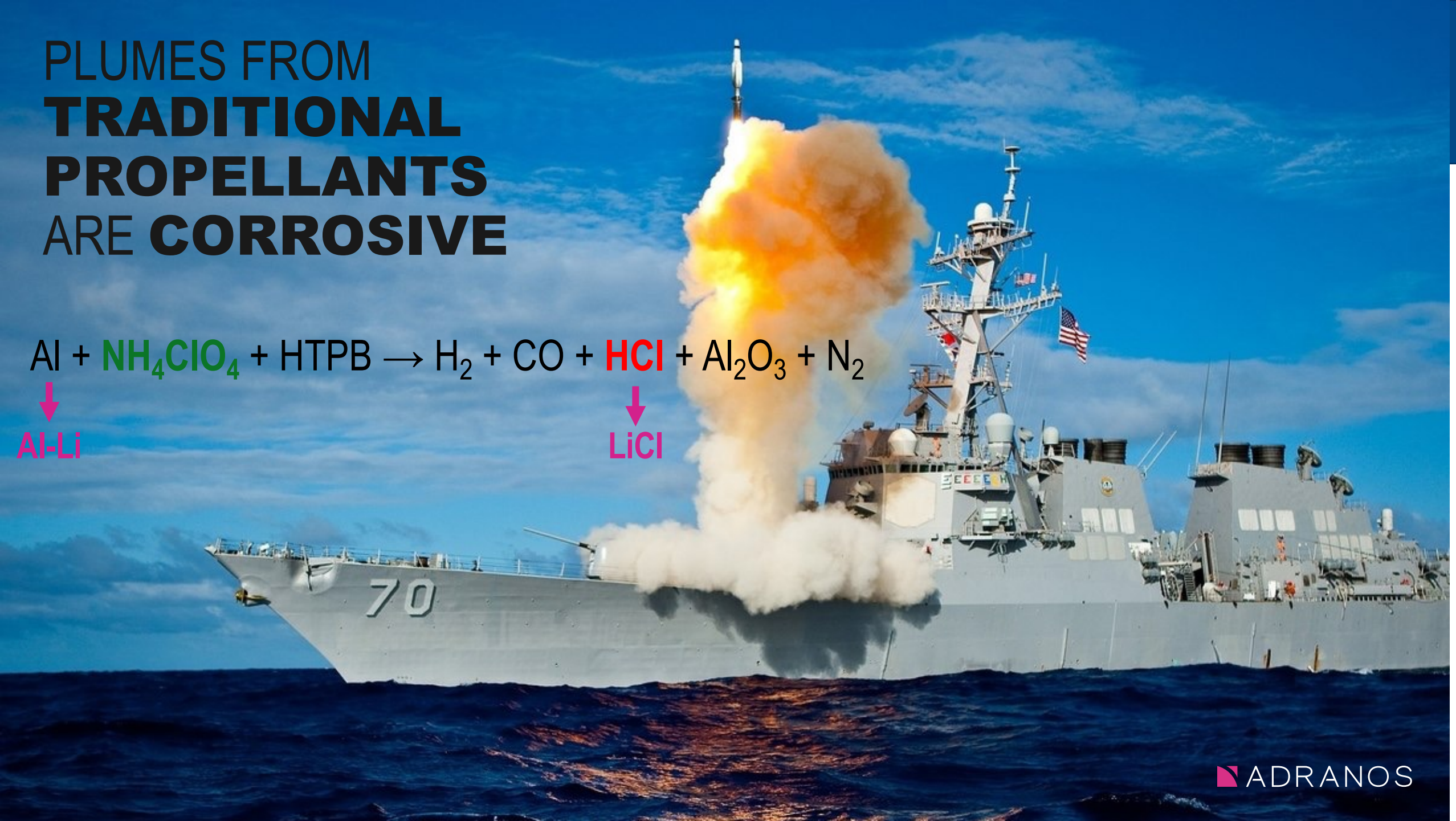
No HCl Evolution Detected Using DSC/TGA with Online MS/FTIR

PLUMES FROM **TRADITIONAL PROPELLANTS** ARE **CORROSIVE**

$$Al + NH_4ClO_4 + HTPB \rightarrow H_2 + CO + HCl + Al_2O_3 + N_2$$

Al → Al-Li

HCl → LiCl



ADRANOS

Less Caustic Rocket Propellant Products

- Challenges:
  - Uncoated Al-Li oxidizes in air/moisture
  - Domestic supplier not available
  - Available Al-Li was not spherical
- Adranos is addressing these issues with a proprietary coating
  - Domestic source obtained
  - Spherical Al-Li fabricated
  - This has allowed scaling and motor tests
- Improved performance due to lower MW, lower 2 phase flow losses and improved combustion efficiency

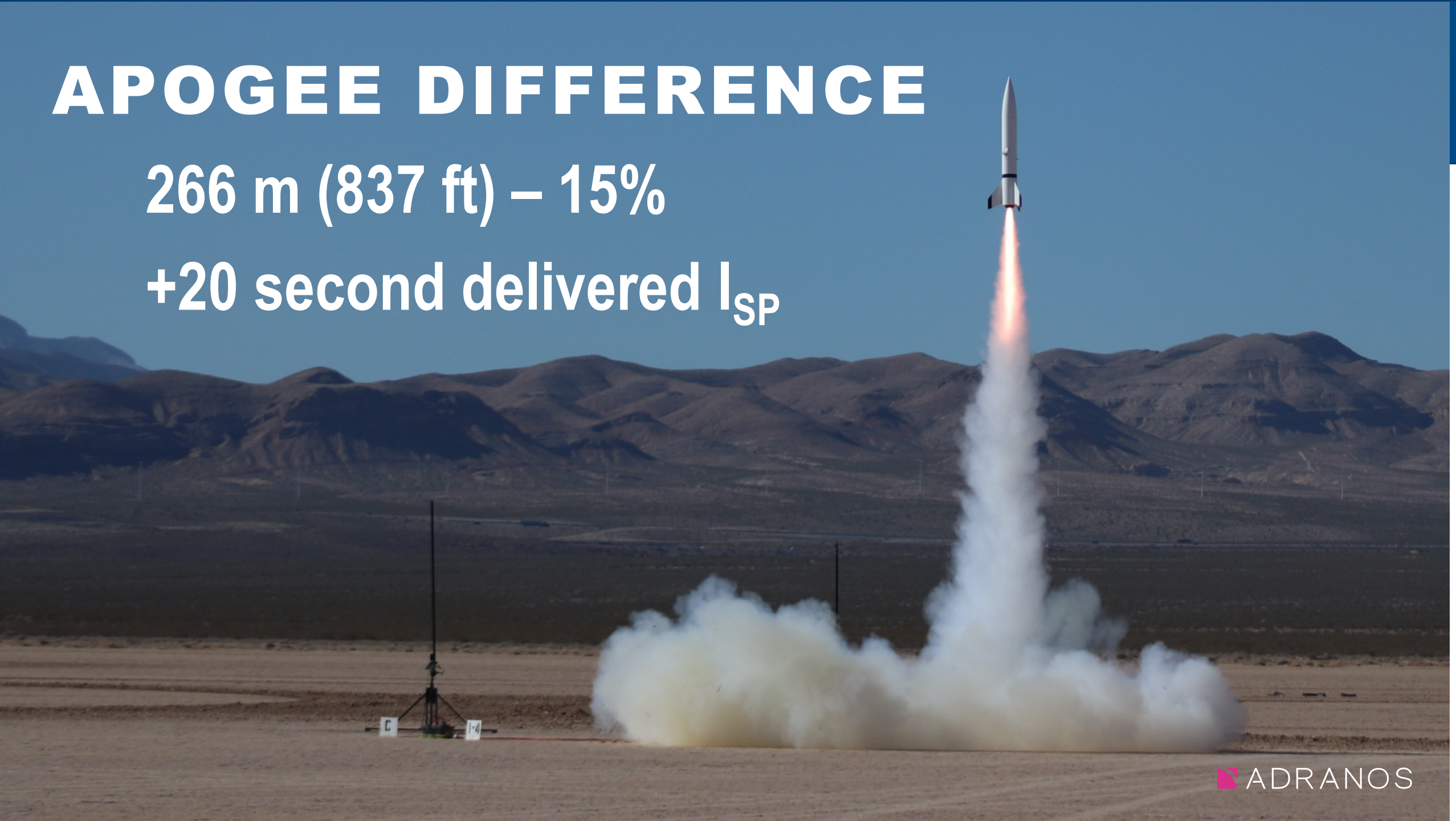
ALITEC Static Test Fires

Motor	SOTA Baseline	ALITEC
2 x 4	$c^* = 1399 \pm 27$ m/s (91% efficiency)	$c^* = 1524 \pm 6$ m/s (97% efficiency)
4-Inch CP	$c^* = 1391 \pm 60$ m/s (91% efficiency)	$c^* = 1539 \pm 6$ m/s (98% efficiency)
	c_f efficiency = 91% ± 4%	c_f efficiency = 95% ± 2%
	$I_{SP} = 202 \pm 10$ s (Ideal = 238 s)	$I_{SP} = 236 \pm 4$ s (Ideal = 256 s)

APOGEE DIFFERENCE

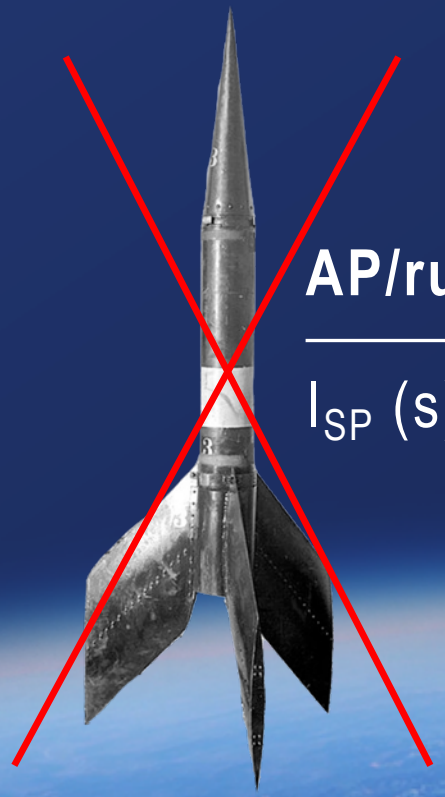
266 m (837 ft) – 15%

+20 second delivered I_{SP}



ADRANOS

HISTORY OF SOLID MOTOR PERFORMANCE



AP/rubber

I_{SP} (s)

1940s

AP/Al/rubber

+12s

1954

ALITEC

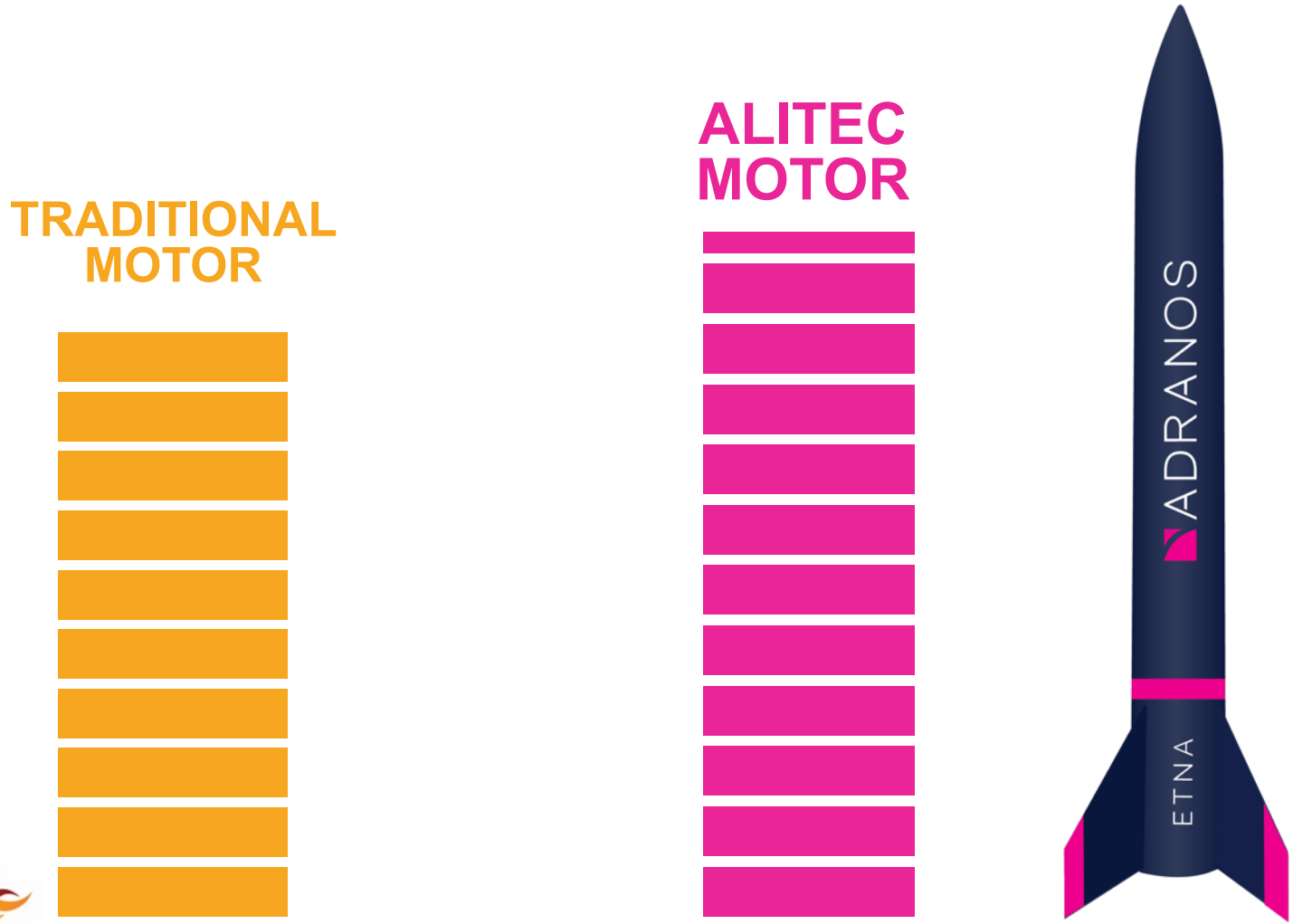
+20s

2019

Could this be more significant than aluminized propellants?!

ADRANOS

Less Caustic Rocket Propellant Products



11%

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Looking Ahead: Less Solvent in Gun Propellants

- DoD gun propellant fabrication processes generate significant solvent waste, it is desirable to reduce environmental impact
  - Decrease the use of volatile solvents or other wastes for legacy or novel formulations
  - Enable non-solvent formulations using novel material systems and approaches
  - Lower overall energy use

- DoD is interested in novel additive manufacturing (AM) approaches for gun propellants to meet current and future mission requirements
  - Tailored combustion and mechanical characteristics
  - Reduced sensitivity to impact, shock, heat, friction.
  - Consistent function (low/high operating temperatures)
  - Ultimately resulting in higher performance

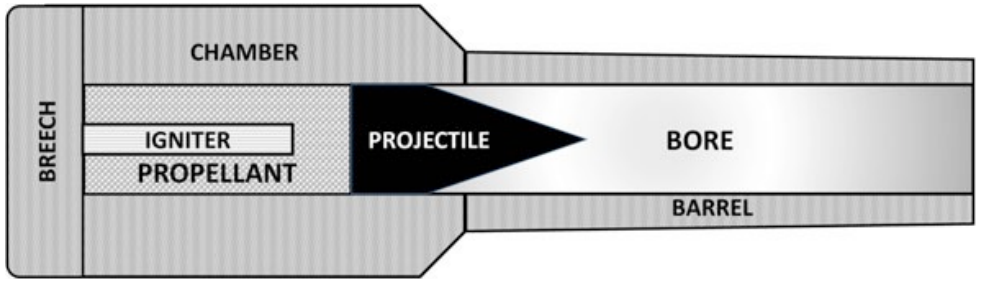
Technical Objectives

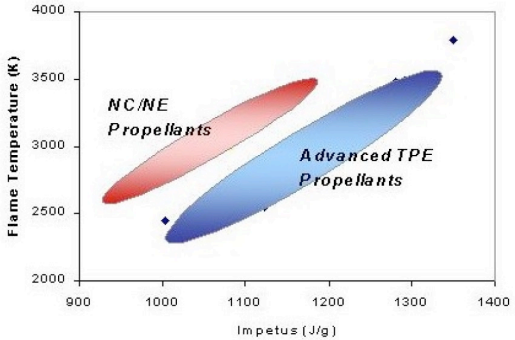
- Implement a new AM method developed by our group suitable for printing sensitive extremely viscous solids
- Characterize the propellant material viscosity with solvent amount for solvent based systems and temperature for thermoplastic elastomer systems and how it affects 3D printing
- Investigate printed structure mechanical properties, layer adhesion, microstructure
- Quantify printed propellant performance
- Relate printed part properties to printing and material parameters
- Assess the reduction in environmental impact and lifecycle

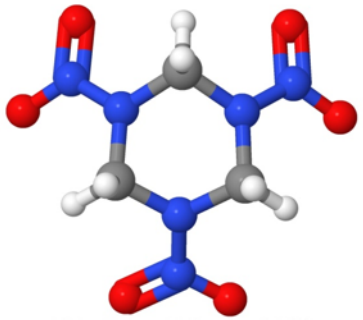
Technical Background

Gun Propellants

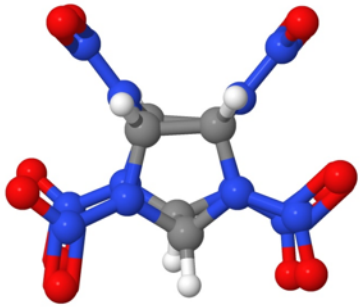
- Generate gas at high rates to propel a projectile down a barrel
- Typical formulations use nitrocellulose (NC) as the main component
  - Single base uses only NC – simple
  - Double base has added nitroglycerin – higher impetus
  - Triple base further includes nitroguanidine – lower flame temperature to protect barrel
- NC dissolves/gels with solvents to form the propellants
- Solvent-less formulations could be used with a plasticizer like diethylene glycol dinitrate (DEGDN), migration issues
- Thermoplastic elastomer (TPE) systems avoid solvents also and can be melted with energetics such as nitramines or high nitrogen for insensitive formulations







cyclotrimethylenetrinitramine (RDX)



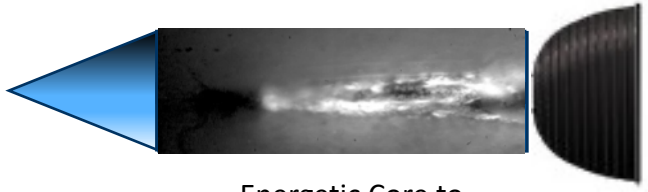
Hexanitrohexaazaisowurtzitane (CL-20)

Why Additive Manufacturing (AM) of Gun Propellants?

Unique Structures Inaccessible to Traditional Methods

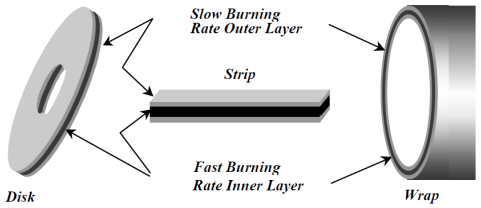
Solid Rockets

3D Variable Port Geometry for Thrust Control



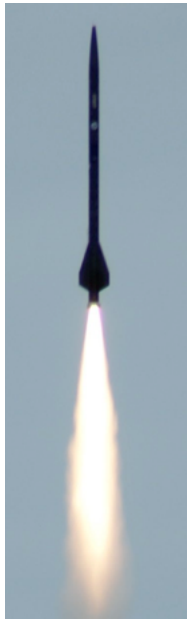
Energetic Core to Increase Range

Gun Propellant



Graded microstructure, composition, or novel geometry to modify properties

Fabrication on Demand

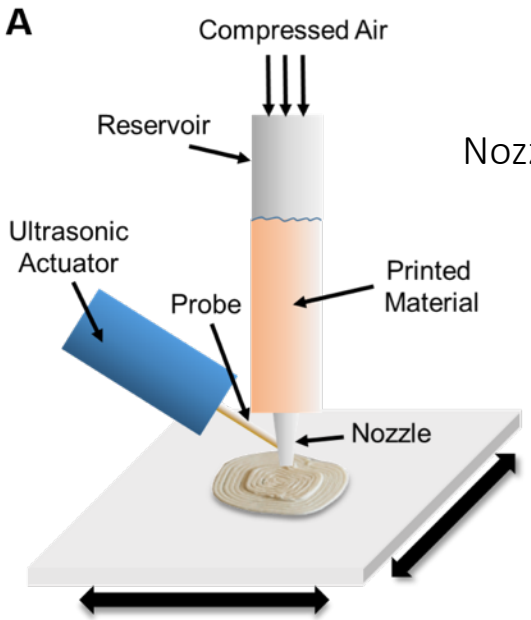


Store only raw materials, print depending on the requirements, minimum waste

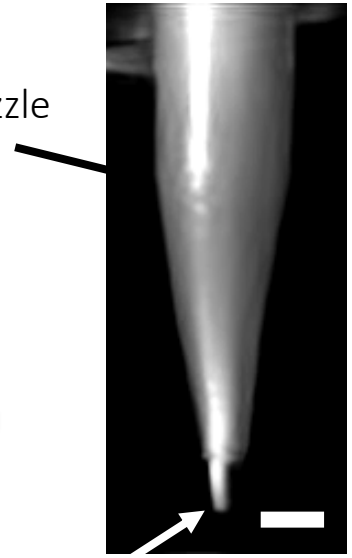
- S. Isert, C. D. Lane, I. E. Gunduz, S. F. Son, "Tailoring Burning Rates Using Reactive Wires in Composite Solid Rocket Propellants", Proc. Combust. Inst., 36(2), 2283-2290 (2017).
- US Patent Pending.

Vibration Assisted Printing

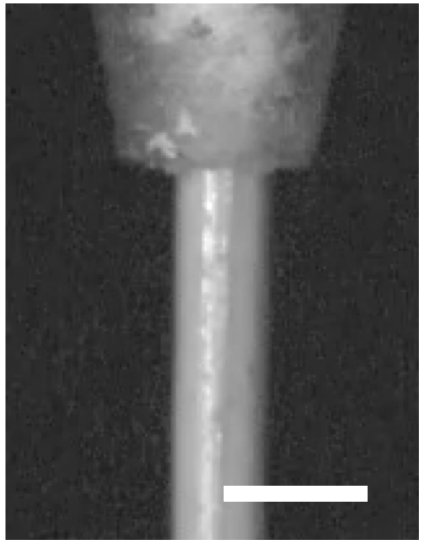
- Direct write approach
- The print nozzle is resonated to enhance displacements
- Vibrations assist flow by reducing effective friction at the exit
- Can print at high solids loading, minimal supports
- Reduce nozzle size for features with high resolution
- High flow/print speed, enhanced up to 3 orders of magnitude
- Low porosity in final parts

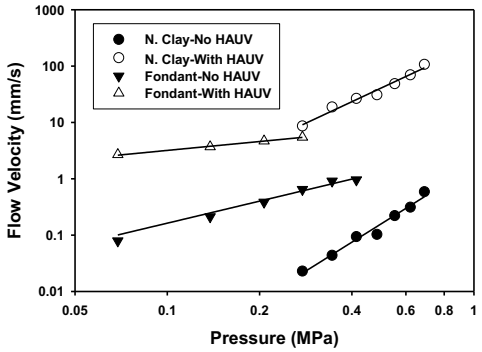


Nozzle Vibrations



Flow Control





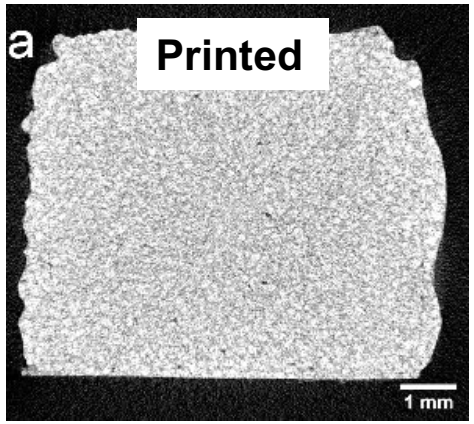
Nozzle Tip Vibration Amplitude: 16 µm, Scale Bar: 1 mm

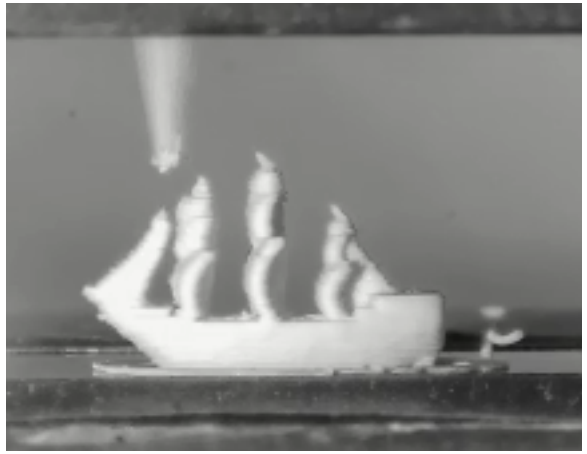
I. E. Gunduz, M. McClain, P. Cattani, G. T.-C. Chiu, J. F. Rhoads, S. F. Son, "3D Printing of Extremely Viscous Materials Using Ultrasonic Vibrations", Additive Manufacturing, 22, 98-103 (2018).

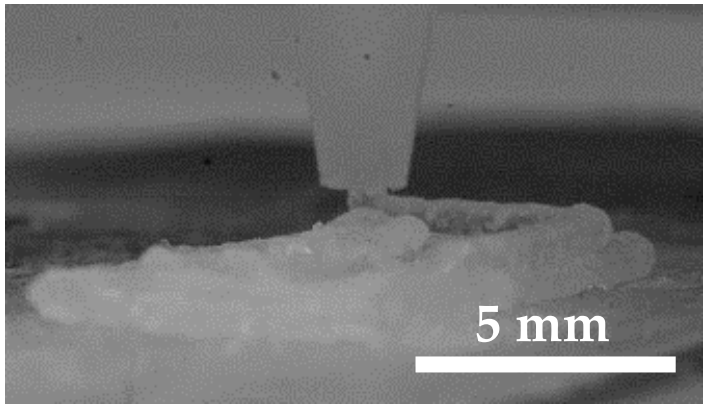
Vibration Assisted Printing

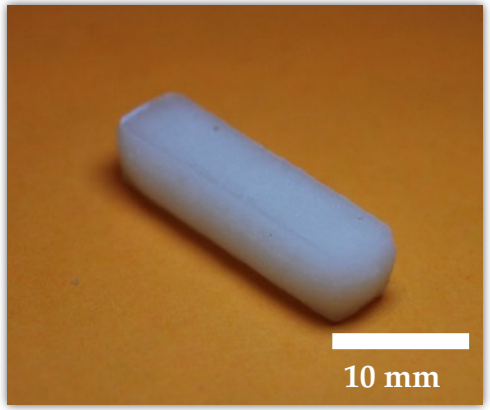
- Printed highly viscous (μ>10000 Pa·s) materials
- Printed AP composite solid propellants
- Lower porosity compared to cast samples
- Uniform microstructure with no signs of layering (good layer to layer adhesion)

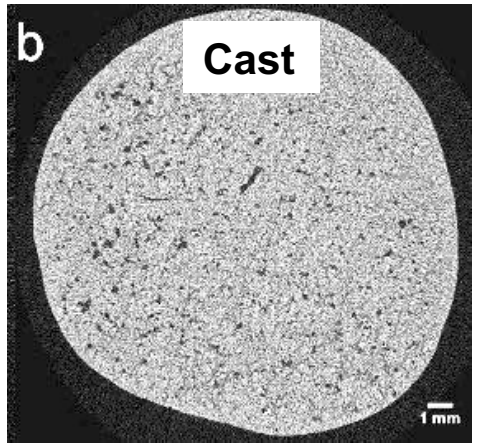
X-ray Micro-CT







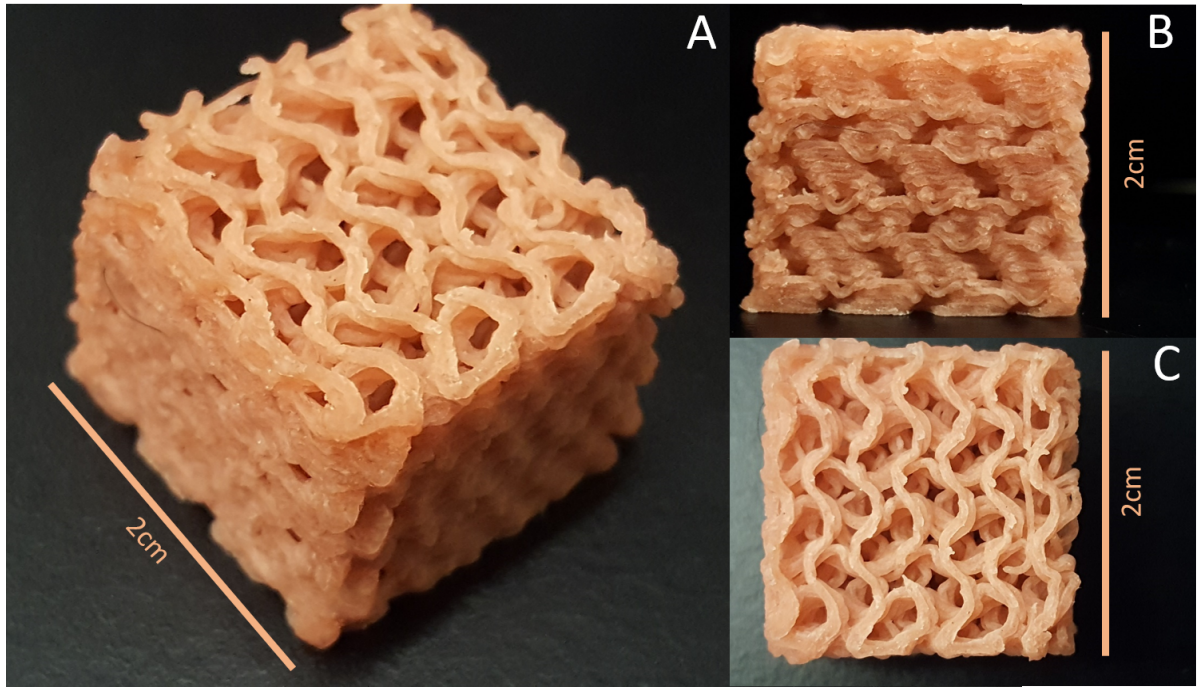


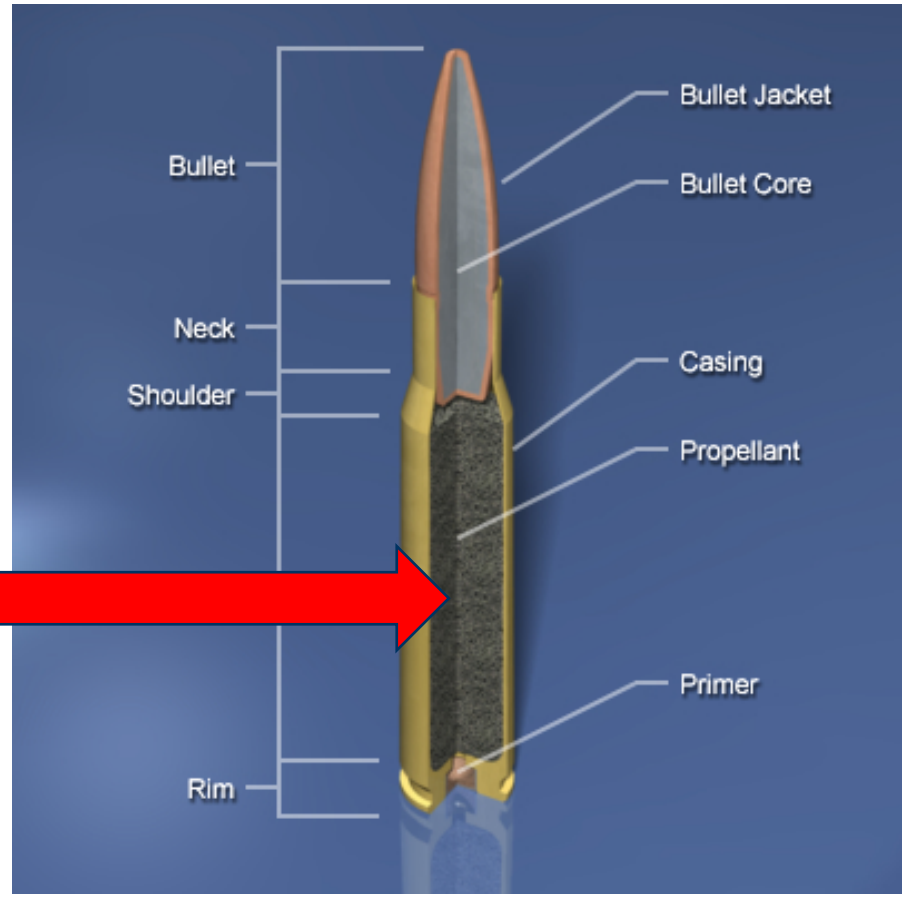


M. S. McClain, I. E. Gunduz, S. F. Son, "Additive Manufacturing of Ammonium Perchlorate Composite Propellant with High Solids Loadings", Proc. Combust. Inst., In press (2018).

Vibration Assisted Printing: Unique Structures

- Here's an example of unique structures that will be possible





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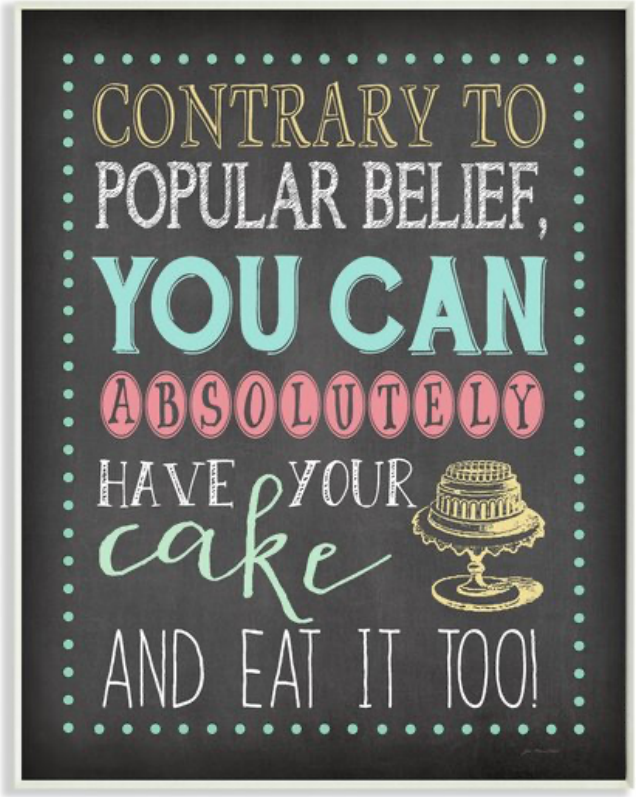
Summary

- With effort, there are opportunities to improve both toxicity and performance
- Three example areas were reviewed