DoD EPA DOE SERDP
Strategic Environmental Research and Development Program

NAVAIR

Lead Free Electric Primers

(Project Number 1331)

2007 NDIA Gun and Missile Systems
Conference and Exhibition

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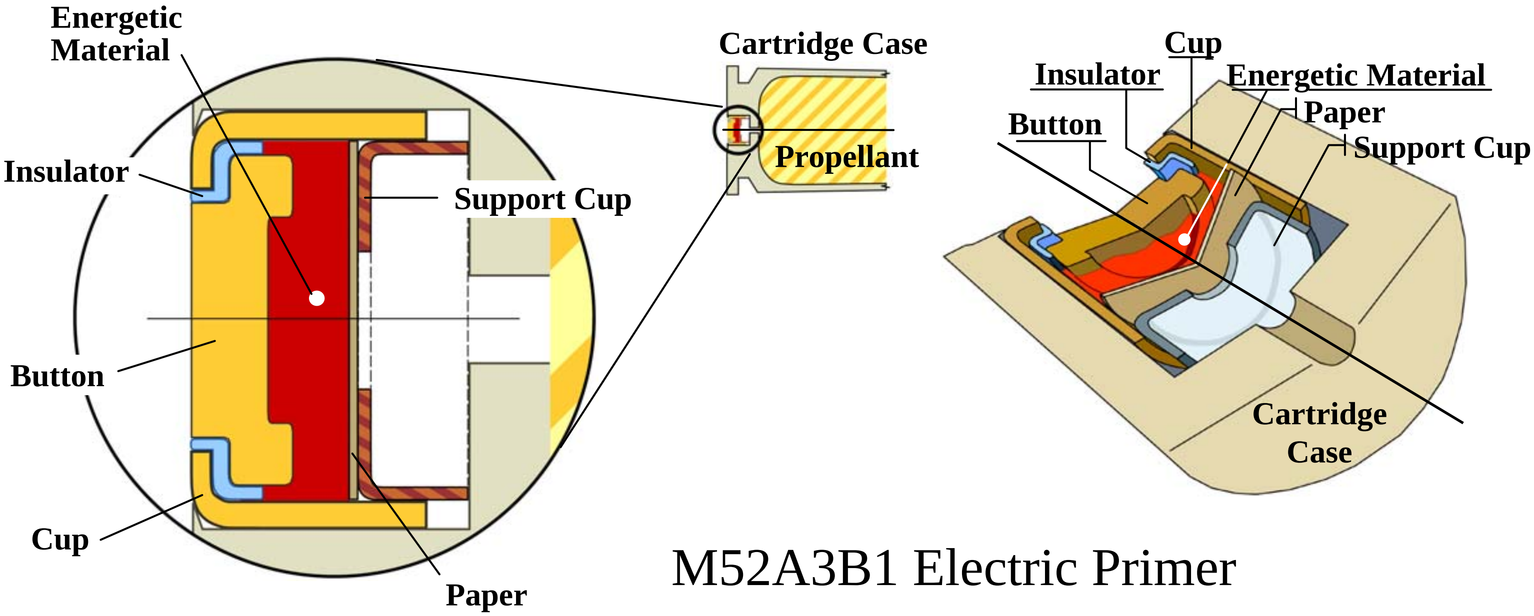
Approved for public release; distribution is unlimited

PROGRAM OBJECTIVE

The Objective of the SERDP Lead-Free Electric Primer (LFEP) Program is to Demonstrate the Feasibility of Substituting Metastable Interstitial Composite (MIC) Materials for the Lead Styphnate . . . Leading to the Development of a Safe, Reliable & Effective Lead Free Electric Primer (LFEP) for Use in Medium Caliber Ammunition



M52A3B1 Electric Primer

BACKGROUND / NEED

<u>Electrically Initiated Ammunition In-Service:</u>

- 20mm Ammunition
  - USN / USMC / USAF / NATO / FMS
  - Historically Over 1 Million Rounds per Year
  - (Peace Time Records)
- 30mm Ammunition – USA

Annual Production / Utilization

- Lead Styphnate – 1700 Pounds
- Barium Nitrate – 2000 Pounds

Environmental / Health Hazards Well Known / Documented

TECHNICAL APPROACH

Chemistry Focus

Material Characterization

Optimal Fuel/Oxidizer Ratio (Heat Treated MoO_3)

Material Mixing Processes - Solvent, Performance

Environmental Issues (Nano Particulate By-Products)

Primer Reliability

- Material Instability
  - Stability of MIC/Oxidizer + Additives
- MIC Primer Fabrication
  - Wet-Loading/Consolidation Process
- Aging

TECHNICAL APPROACH

Safety Issues

Primer Mixing Formulation and Processing Hazards
    HBSES, ESD, BAM
Production Line ‘Desensitization’

Manufacturing / Producibility Issues

Scalability
Safety
Cost
Reliability / Reproducibility

TECHNICAL APPROACH

All-Up Round Performance

- Primer Composite
  - Aluminum - Particle Size (Nano)
  - Oxidizer - MoO_3, Bi_2O_3
  - Mixing Process - Sonification
  - Additives - Carbon/Binder/Gas Generator
- Reproducibility
  - MIC Materials
  - Mixing Conditions
  - Composition
- Consolidation Process

ACCOMPLISHMENTS

Chemistry Focus

Nanocomposite Ingredients

Aluminum Powder	Size	Active Al
Technanogy	33 nm	48.8% (TGA @CL)
Technanogy	50 nm	64.8% (TGA @CL)
Nanotechnology	80 nm (116 nm)	82.7% (TGA @CL)
China Lake	208 nm	86.0% (TGA @CL)

Molybdenum Trioxide	Size
Climax	40 nm (BET @CL)
Aldrich	1.6 µm (BET @CL)

Bismuth Oxide	Size
Aldrich	320 nm (BET @ CL)
Skylighter	1-3 µm (BET @ LANL)
Sigma-Aldrich	< 10 µm

ACCOMPLISHMENTS

Chemistry Focus

LFEP Materials Summary

Binder	- Improved Pressed Pellet Integrity - Improved Ignition Reliability - Improved Handling Safety
Carbon	- Reliable Electric Ignition
Gas Generant	- Reduced All-Up Round Action Time - Optimal Amount

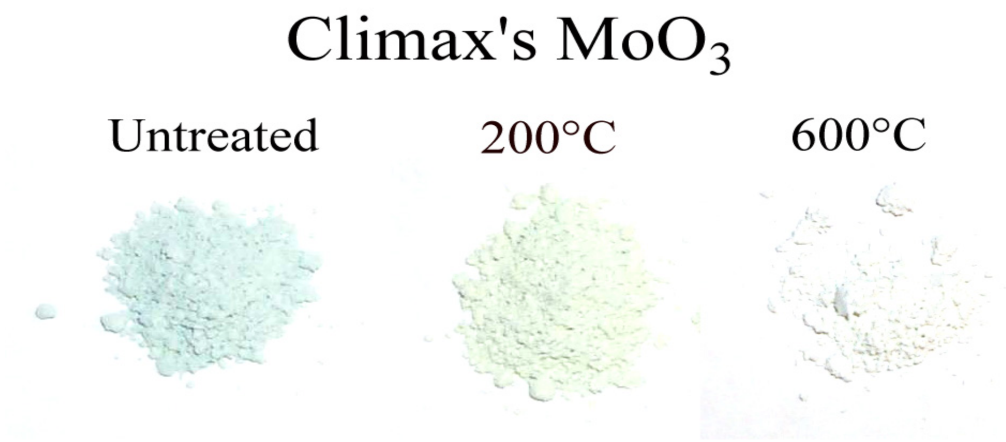
Multi-Vendor Al/MoO_3 Source Demonstration

All-Up Round Action Times
Technanogy, NSWCIH, NAWCWD

ACCOMPLISHMENTS

Chemistry Focus

Aging of the Oxidizer

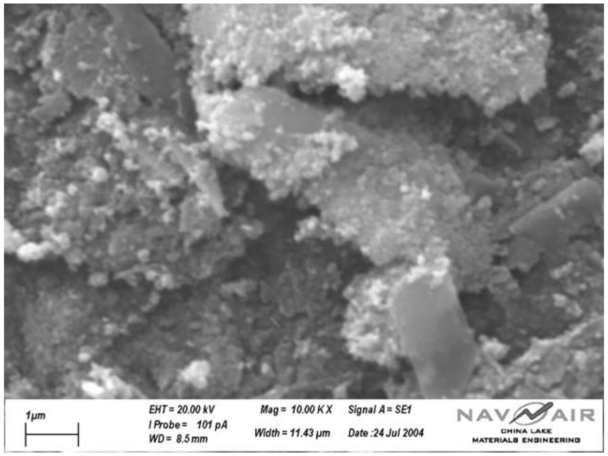


An obvious change occurs in the “as received” MoO$_3$ from the manufacturer, Climax. Freshly prepared samples of MoO$_3$ are white and have large surface areas (~ 45 m^2/g) as measured by BET. However, exposure to air over time results in a significant decrease in surface area (~ 20 m^2/g) and leads to a lime green coloration.

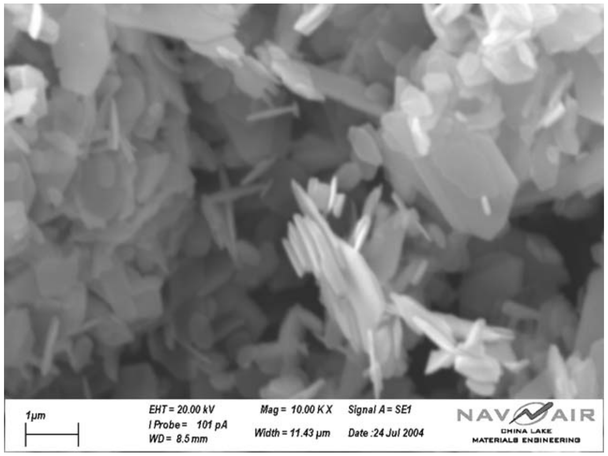
ACCOMPLISHMENTS

Chemistry Focus

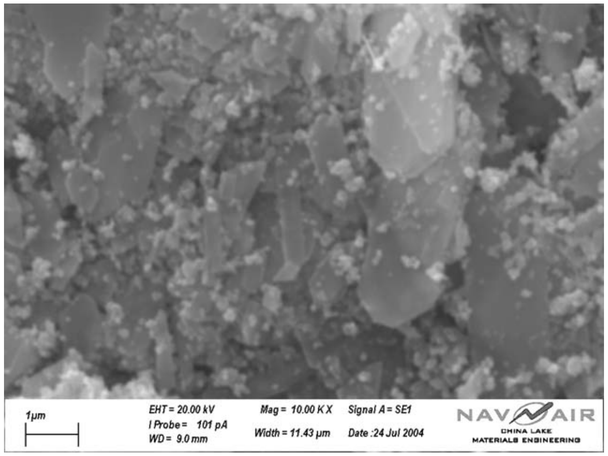
Heat Treatment of MoO_3



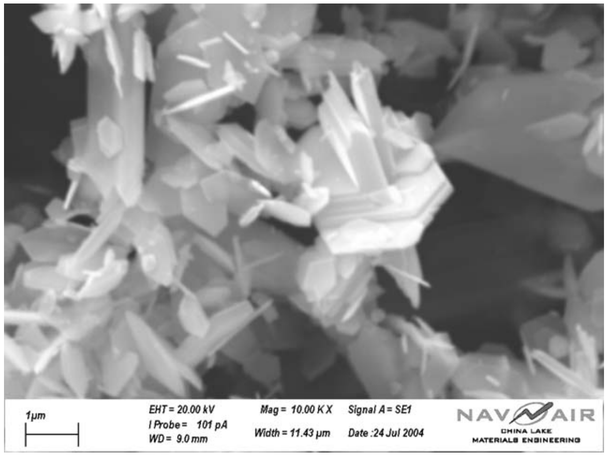
Untreated MoO_3 After 24 Days in Air



MoO_3 Heated to 500°C for 15 Minutes



MoO_3 Heated to 400°C for 15 Minutes



MoO_3 Heated to 400°C for 180 Minutes

ACCOMPLISHMENTS

Chemistry Focus

Heat Treatment of MoO_3

	Heat Treat Temperature					
	400 Degrees Centigrade		443 Degrees Centigrade		500 Degrees Centigrade	
Time (Minutes)	Morphology	Size (nm)	Morphology	Size (nm)	Morphology	Size (nm)
15					Orth (100%)	220
22			Orth (100%)			
30	Mono / Ortho				Orth (100%)	
60	Mono / Ortho					
120	Orth (100%)					
180	Orth (100%)	198			Orth (100%)	

MoO_3 Heat Treatment Study Analysis

- Determine Optimal Time and Temperature for Conversion
  - ✓Total Orthorhombic Phase Conversion
  - ✓Minimal Particle Size Growth
- X-Ray Diffraction To Determine Material Phase
- SEM To Determine Particle Size and Morphology

ACCOMPLISHMENTS

Chemistry Focus

Ultrasonic Mixing

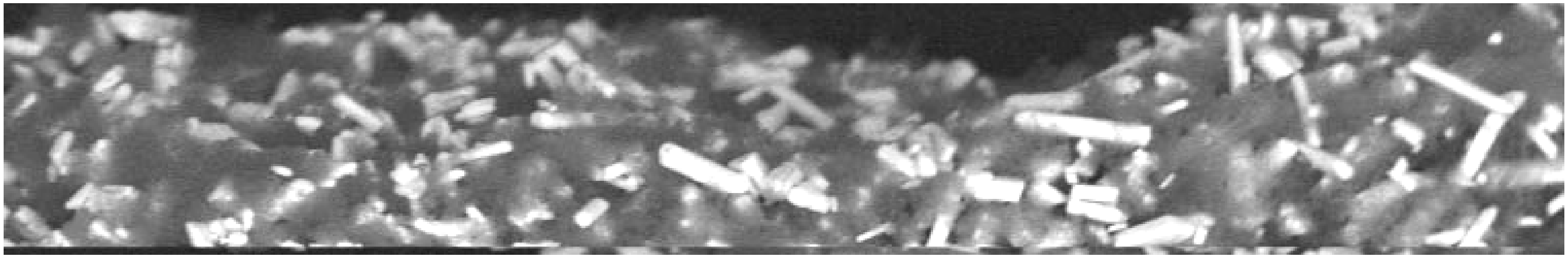
Determine Aging vs Different Mix Processes

- Dry Mixing – Mechanical Shaker for 2 Minutes
- Ultrasonic Bath
  - Sonicate Al/MoO_3 for 15 Minutes
  - Sonicate Mixture for 1 Hour
- Ultrasonic Horn (100W, 400W)
  - Sonicate Mixture for 0.5 to 2 min.
- Mixing Process Monitoring
  - TGA of MIC

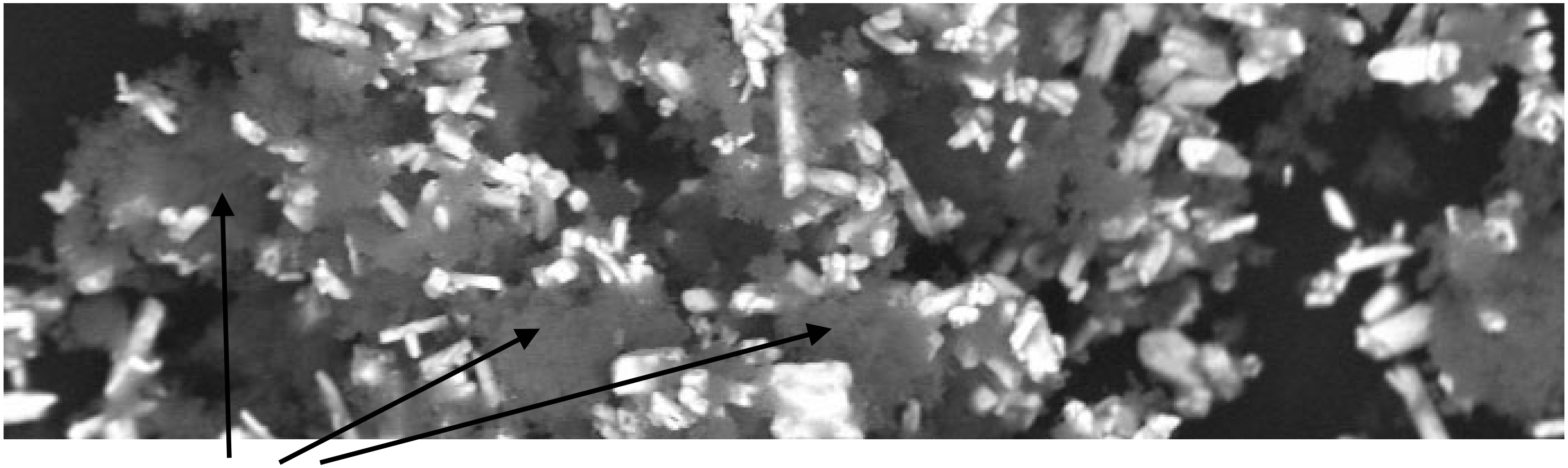
ACCOMPLISHMENTS

Chemistry Focus

Solvent Effect in Mixing
Hexane Versus i-PrOH



Hexane



Poorer Mixing

i-PrOH

ACCOMPLISHMENTS

Chemistry Focus

400W Sonic Mixing
75% Amplitude 0.5s pulse, 1 min.

	Molybdenum Trioxide MoO_3			
Aluminum Powder	**Climax 40 nm**		**Aldrich 1.6 mm**	
	Hexane	**i-PrOH**	**Hexane**	**i-PrOH**
Al (35 nm)	Good			
Al (50 nm)	Good		Good	
Al (80 nm)	Good		Good	

	Bismuth Trioxide Bi_2O_3					
Aluminum Powder	**Aldrich 320 nm**		**Skylighter 1-3 mm**		**Sigma-Aldrich < 10 mm**	
	Hexane	**i-PrOH**	**Hexane**	**i-PrOH**	**Hexane**	**i-PrOH**
Al (35 nm)				**Poor**		
Al (50 nm)	Good	**Poor**		**Poor**	Good	**Very Poor**
Al (80 nm)	Good	**Poor**	**Very Good**	**Good**	Good	
Al (208 nm)					Good	
Al (5 mm)	Good					

Poor – Material Separation (Al from Oxidizer) Was Observed

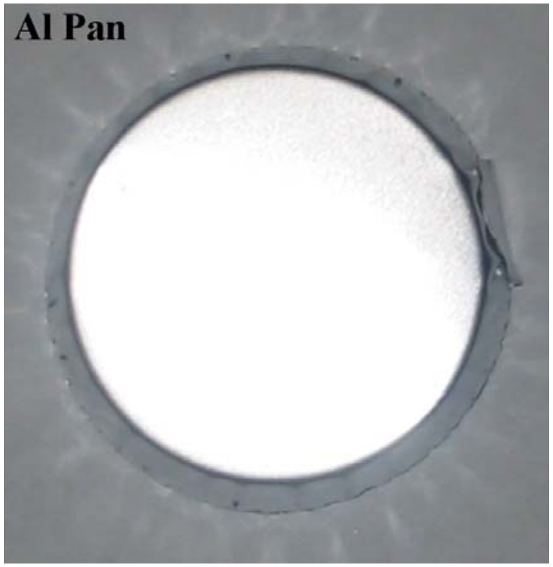
Good – Little or No Material Separation

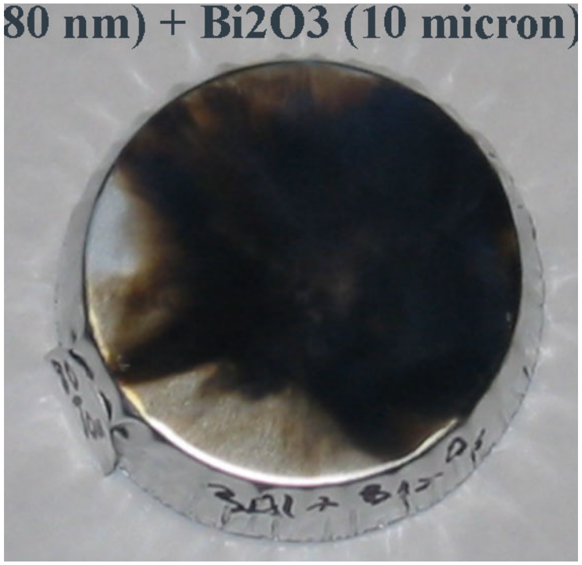
Very Good – No Material Separation, Rapid Precipitation, Easy Isolation (Filtration)

ACCOMPLISHMENTS

Chemistry Focus

Pan Test
50-55 mg of Al/Bi_2O_3


Al Pan


80 nm) + Bi2O3 (10 micron)

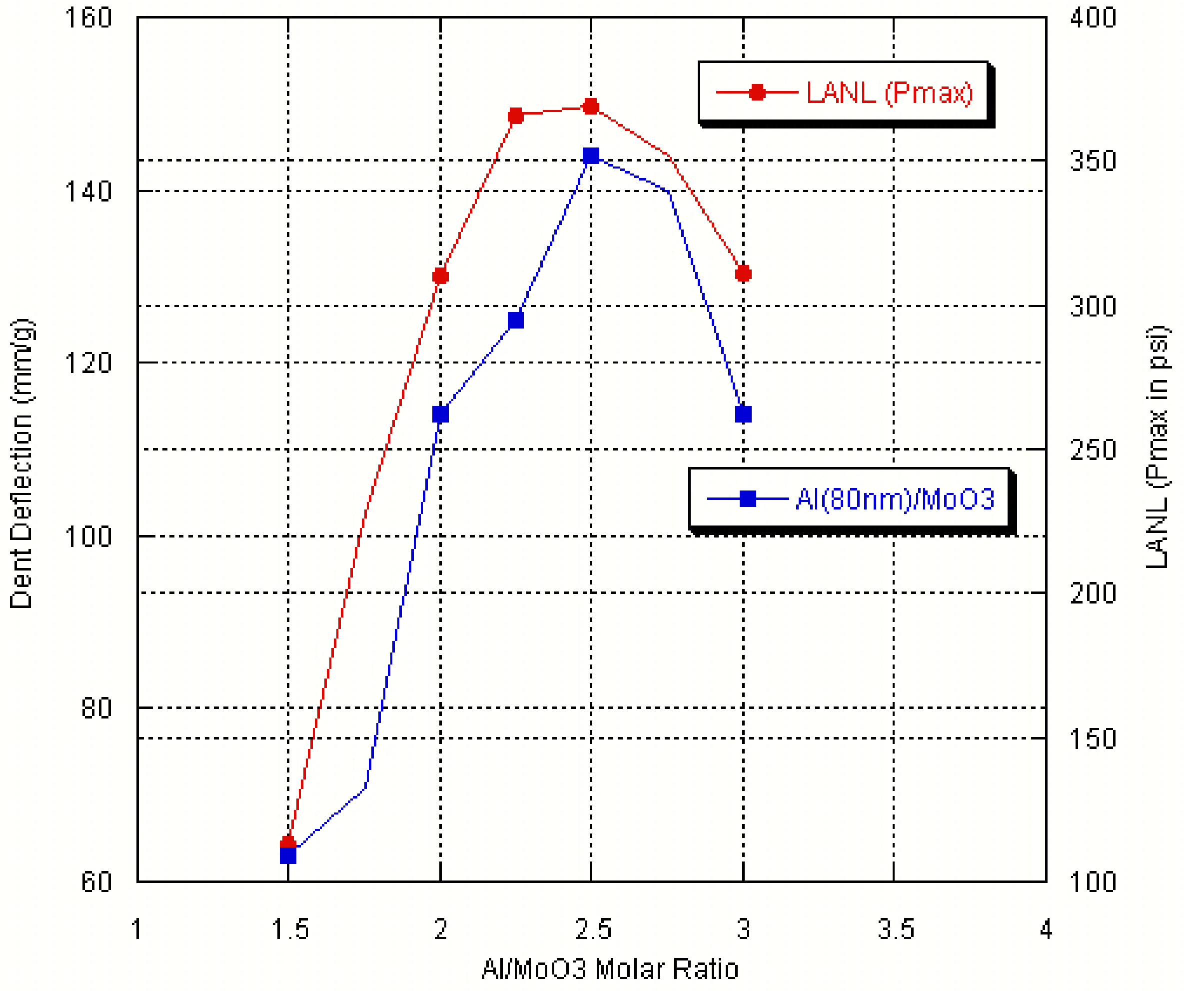

Al (80 nm) + Bi2O3 (Sky) / i-PrOH


Al (80nm) + Bi2O3 (Sky) (Hexane)


Al (80 nm) + Bi2O3 (320 nm)

ACCOMPLISHMENTS

Optimization of Al(80nm)/MoO_3 (Cl) by LANL Pressure Cell Versus Pan Deflection



Optimization results were similar for both methods.

Optimal performance achieved at a 2.5 Al/MoO_3 ratio.

Best performance for fuel rich composites.

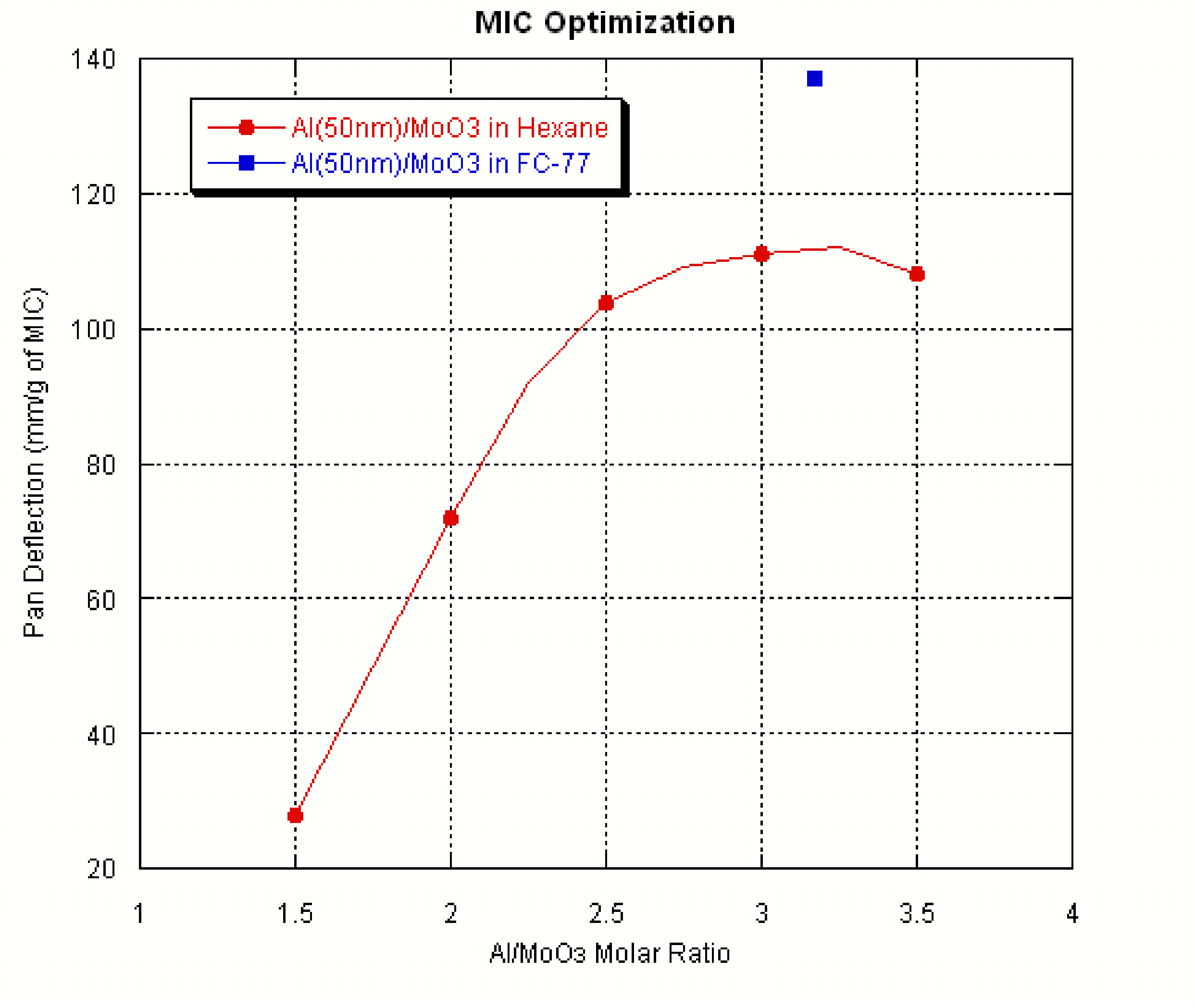
$2\ Al + MoO_3 \rightarrow Al_2O_3 + Mo$

Stoichiometric at 2:1

Pan Deflection Test is a rapid screening tool for MIC performance

ACCOMPLISHMENTS

MIC Performance Testing As Measured By Al Pan Dent Deflection



Al(50 nm)/MoO_3(44nm)
400 W Ultrasonic Horn
2 minute @ 75% Ampl
Pulse Length = 0.5 sec

Performance using FC-77 as a solvent exceeds hexane by > 20%

Cause under investigation

ACCOMPLISHMENTS

Safety Status:

- Standard Handling Safety Tests Completed
  - MIC/BTATZ/Kel-F/C Composition Has Reduced Sensitivity
    - ESD/Friction/Impact Effects Moderated Formulation by Kel-F Binder
- Conduct Safety Tests on Altered Primer Formulation
  - Al/Bi_2O_3/BTATZ/Kel-F/C Composition
    - Determine if Mix Sensitivity Moderated by Kel-F Binder
- Develop Formulation Process – Reduce Hazardous Operation
  - Focus on Handling, Processing and Desensitization

ACCOMPLISHMENTS

Safety Status:

Handling and Safety Concerns

Issue: ESD and friction sensitivity of MIC materials, particularly Bi_2O_3, has raised concerns in handling safety

Approach: Utilize safety tests for ESD and friction that are sensitive enough to rank primer formulations for handling.

Establish “wet” loading procedures that minimize handling and reduce sensitivity during processing.

ACCOMPLISHMENTS

Safety Status:

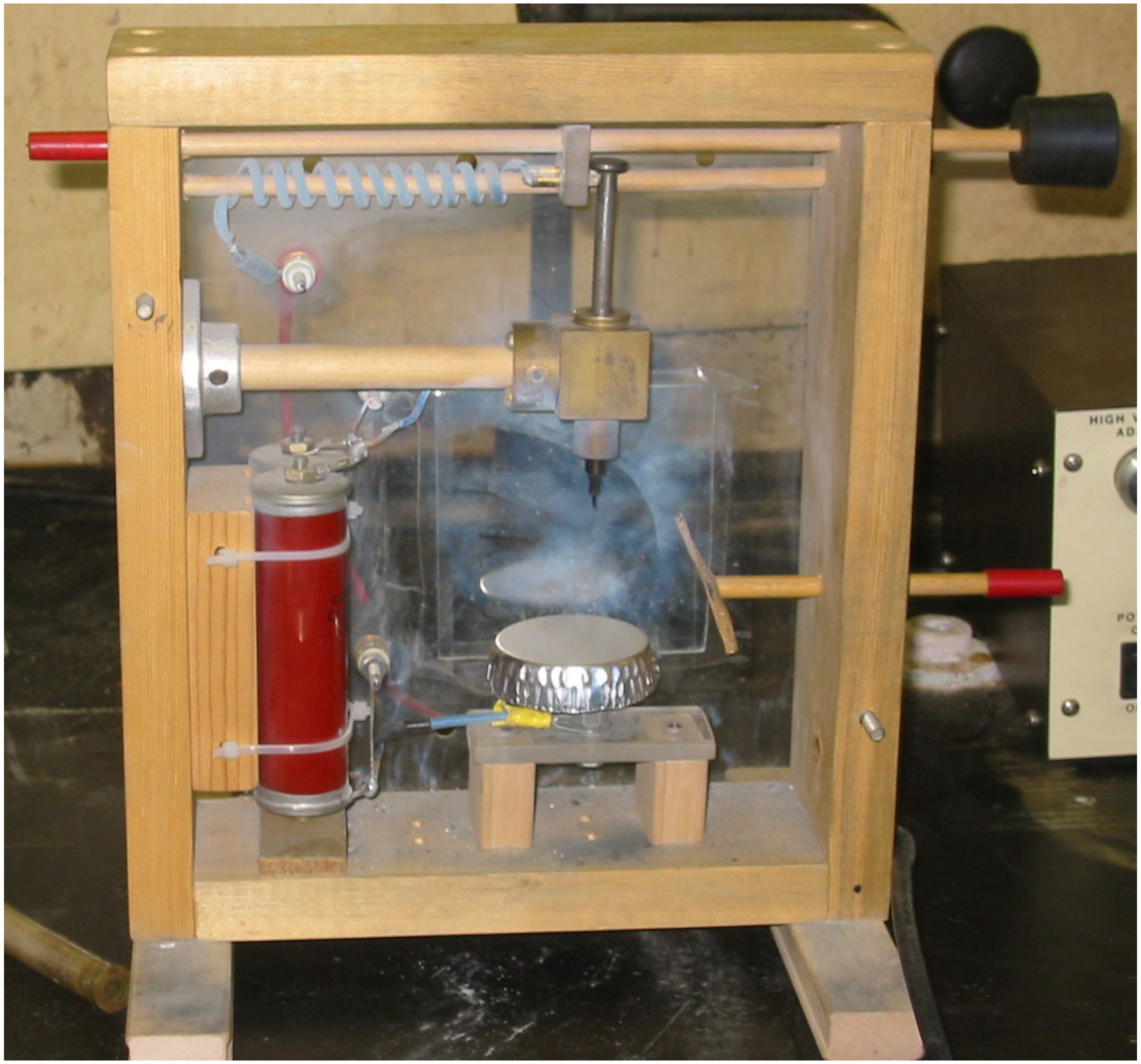
Electrostatic Discharge (ESD) Sensitivity

Power Supply = 0-5KV

Capacitance = Variable
0.02, 0.04, 0.22 μF

Energy Range =
2.75 to < 0.001 Joules

Variable Electrode Gap



ACCOMPLISHMENTS

Safety Status:

Friction Sensitivity Data Al Composites

Mixture	6/6 NF @	Low Fire Point	Sample Size	Notes
PETN	42N		~35mg	Burn Mark and NOx Generation
M-52 Primer Mix	4N		~2 mg	Moderate snap, spark
Al(80)/Moly/BTATZ/KelF	9N		~2 mg	Moderate snap, spark
Al(80)/Moly/KelF		0.05N	~2 mg	Extremely loud snap, spark
Al(80)/Moly		0.05N	~2 mg	Extremely loud snap, spark
Al(80)/BiO		0.05N	~2 mg	Extremely loud snap, spark
Al(80)/AgIO3/KelF		0.05N	~2 mg	Extremely loud snap, spark
Al(80)/AgIO3		0.05N	~2 mg	Extremely loud snap, spark

BAM Friction Tester

Relative friction sensitivity of energetic materials generated by mechanically rubbing between roughened surfaces

Range = 0.05N to 10N on small BAM

5.0N to 360N on standard BAM

ACCOMPLISHMENTS

Primer Reliability

Chemical Instability
    Stability of MIC (Al/MoO_3)
    Material Aging (H_2O) – atmospheric, chemical, contamination

MIC Mixing Process – Ultrasonic Mixing

Loading and Pressing
    Density
    Electrical Properties (C)
    Physical Integrity (Binder)

ACCOMPLISHMENTS

Primer Reliability

Loading Procedures

Both LFEP Loading Procedures Utilize MIC Pastes that are Loaded and Pre-Consolidated (Incrementally), Dried and Given Final Consolidation After Drying

- Solvent-Based Primer Loading Process
  - MIC Formulation and Hexane (1:1 by weight)
- Water-Based Primer Loading Process
  - Nano Al Treated with Methyltrichlorosilane
  - Heat Treatment of the MoO_3

Issue - Treatment of MIC Materials to Enhance Handling Safety May Adversely Affect Primer Performance

ACCOMPLISHMENTS

Al (80 nm)	0.163g
$NH_4H_2PO_4$	0.042g
Bi_2O_3 (320 nm)	0.963g
Gum Arabic	0.059g
Water	25 ml

Al and $NH_4H_2PO_4$ in 10 ml of H_2O sonicated for 30 s

Bi_2O_3 and Gum Arabic in 15 ml of H_2O sonicated for 30 s

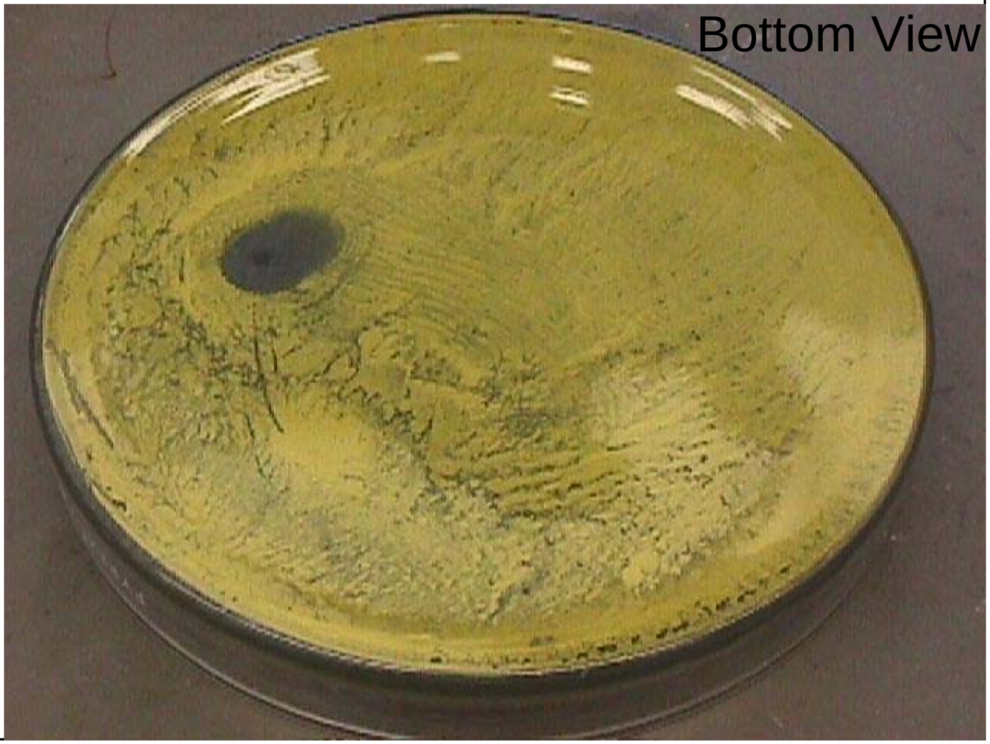
2 Components mixed and sonicated for 1 minute

Transferred into an Petri dish and air dried.

Result: Separation of Al and Bi_2O_3 during drying process

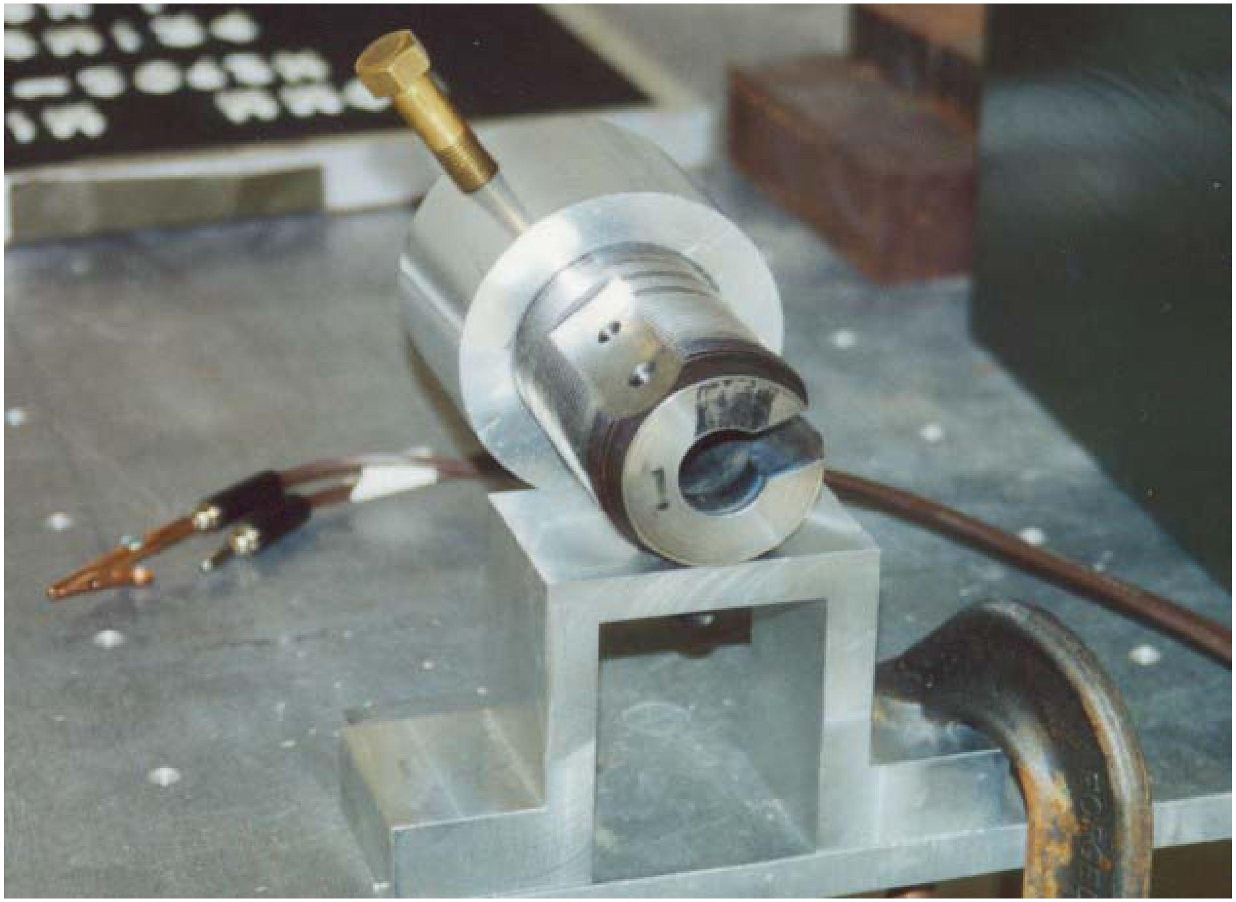
Conclusion: Phase separation will lead to highly variable primer performance


Top View


Bottom View

ACCOMPLISHMENTS

All-Up Round (AUR)



Primer Electrical Resistance Measurement & Test Firing Fixture

ACCOMPLISHMENTS

All-Up Round (AUR)

Issue: Primer performance may vary depending on environmental conditions found in storage and operation.

Approach: Promising primer formulations are verified by loading in AUR’s and conducting PVAT testing at ambient and cold temperatures that would be most detrimental to performance.

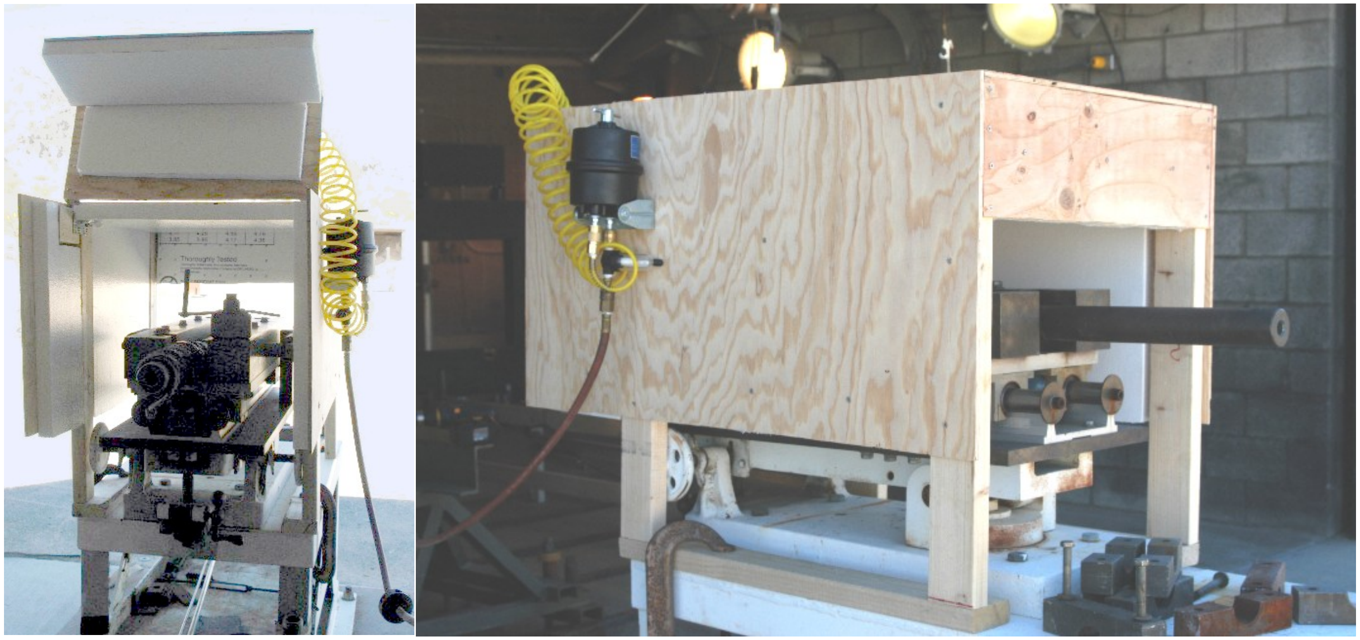
ACCOMPLISHMENTS

All-Up Round (AUR)

Cold Temp Test Setup

Cold Temp AUR Test Conditions

- All Rounds Cold Conditioned
- Liquid Nitrogen Used To Cool Breech and Barrel within Shroud
- Dry Air Used to Remove Moisture around Breech



ACCOMPLISHMENTS

All-Up Round (AUR)

Formulation Identity	Firing Test Date	Initial Temperature (ºF) of Primer	Primer Test Temperature (ºF)	Action Time (msec)	Chamber Pressure (ksi)	Velocity (fps)
KTHU-22	2 Mar 05	Ambient	Ambient	Within Spec	Within Spec	Within Spec
KTHU-22	4 Apr 05	Ambient	Ambient	Within Spec	Within Spec	Within Spec
KTHU-47	23 Jun 05	Ambient	Ambient	Within Spec	Within Spec	Within Spec
KTHU-53	23 Jun 05	Ambient	Ambient	Within Spec	Within Spec	Within Spec
KTHU-57	27 Sept 05	Ambient	Ambient	Within Spec	Within Spec	Within Spec
KTHU-22	20 Oct 05	Cold Temperatures	Cold Temperatures	Within Spec	Within Spec	Within Spec
KTHW-24	24 Oct 05	Cold Temperatures	Cold Temperaures	Exceed Spec	Within Spec	Within Spec

ACCOMPLISHMENTS

Manufacturing/Producibility:

Coordinated efforts with the Army’s ammunition procurement office, Joint Munitions Command, and the Navy’s medium caliber ammunition program office, PMA-242, to begin the technology transition process.

Scalability
Handling Safety
Cost
Reliability/Reproducibility

PARTNERING

- MIC Joint Service Working Group-Government
  - Los Alamos National Laboratory
  - Lawrence Livermore National Laboratory
  - Sandia National Laboratory
  - Eglin Air Force Base
  - NAWCWD-China Lake
  - NSWC-Indian Head

- MIC Joint Service Working Group-Industry
  - GDOTS Canada Inc
  - ATK
  - Novacentrix

TRANSITION PLAN

Following Successful Development & Demonstration of a Medium Caliber LFEP the Navy, & Likely the Army, will Pursue the Follow-On Development, Qualification & Production of Environmentally Favorable Primers for Military Ammo Applications.

ESTCP began FY07 and partnering with:
Primer and Ammunition Manufacturers-
Lake City Ammunition and Armament Plant and GDOTS Canada Inc.
Materials Manufacturers-Novacentrix

Production and handling studies will be the focus of the first year of ESTCP. Investigators will work with industry to ensure a cost effective, viable production method for mass production of Lead-Free Electric Primers.

The qualification process will include industry buy in and Low Rate Initial Production. The LRIP lot will be thoroughly evaluated.

Questions?