

LEAD-FREE ENERGETIC MATERIALS

FULMINATION 2022

Euan McLean | Engineering & Technology Manger | 06/04/2022 | 12:20 – 12:50 | OME Stream

PURPOSE



To provide a high-level overview of the research and development programmes that are being conducted as a consequence of impending legislative restrictions on lead



01

INTRODUCTION

WHAT WE DO

CHEMRING ENERGETICS UK LTD | PART OF THE CHEMRING GROUP

Primary explosives and propellants

Extruded double-based (EDB) propellants for ejection systems, rocket motors, and gas generators; fully automated robotic manufacture of primary explosives for use in electro-explosive devices (EEDs)

Initiators

Electric fuseheads, igniters, electric detonators, non-electric detonators, stab detonators

High explosives

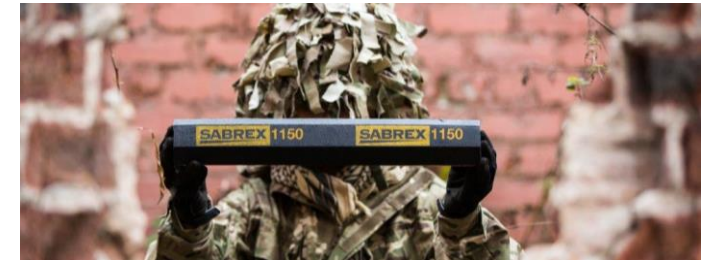
Linear cutting and shaped charges, plastic explosives, miniature detonating cord (MDC), mild detonating fuses, boosters, pellets, transmission cords

Rocket motors and cartridges

Rocket motors, EOD power cartridges, gas generators

Pyro-mechanical devices

Actuators, retractors, cable cutters, release bolts, safety and arming devices





02

REGULATION OF LEAD

EU AND UK REACH

REGISTRATION, EVALUATION, AND AUTHORISATION OF CHEMICALS

The European Chemicals Agency (ECHA) administers EU Regulation (EC) No. 1907/2006, concerning the Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) UK manufacture and import of chemicals now regulated under UK REACH; however, EU REACH continues to apply in NI

Registration of a chemical as a Substance of Very-High Concern (SVHC) and inclusion on the 'Candidate List' is the first step in the procedure for eventual inclusion in Annex XIV of REACH (the 'Authorisation List')

Lead exposure accounted for 24.4 million disability-adjusted life years (DALYs) of healthy life lost and 1.06 million deaths in 2017 (Institute for Health Metrics and Evaluation, 2017; World Health Organization, 2019)

ECHA's 11th recommended list of substances to move to Annex XIV, published February 2, 2022, includes lead (CAS 7439-92-1)

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Lead is a cumulative toxicant which affects neurological, skeletal, cardiovascular, renal, haematological, gastrointestinal, reproductive, respiratory, and endocrine systems

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The Occupational Safety and Health Administration (OSHA) have suggested that the acceptable blood lead level be reduced from 40 mg dl⁻¹ to between (5 to 10) mg dl⁻¹ (Schillaci, 2018)

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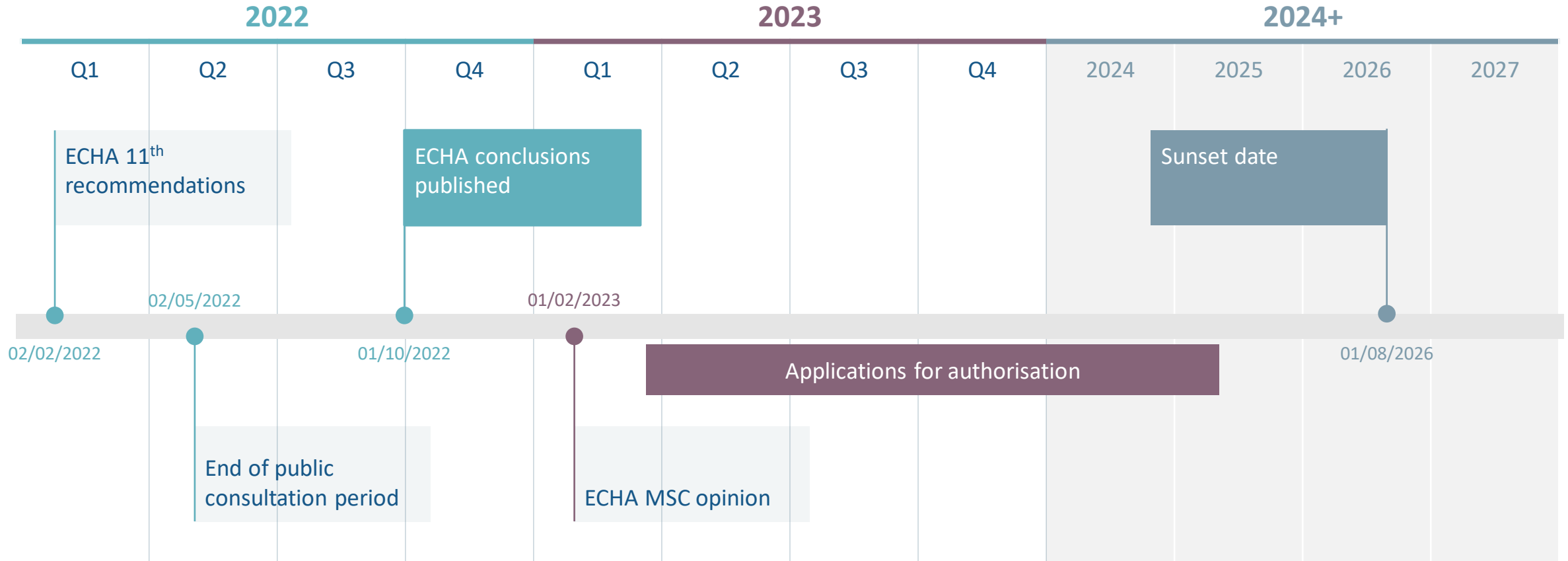
Lead styphnate and lead azide are SVHCs, lead nitrate and lead acetate (precursors to lead-based primaries and ballistic modifiers) are also listed as SVHCs, and elemental lead is used to sheath MDCs

04

Whilst authorisations or military exemptions may be granted, worldwide demand for lead products is likely to contract significantly due to REACH and analogous legislation in the US and elsewhere

FORECAST TIMELINE

EXTRAPOLATED FROM LATEST PUBLISHED ECHA DATA AND COMBINED WITH EXPERIENCE OF PAST AUTHORISATIONS



LEAD REPLACEMENT PROGRAMMES

LEAD-FREE PRIMARIES AND EEDs, LEAD-FREE BALLISTIC MODIFIERS, AND LEAD-FREE MDC

Three primary lead-replacement workstreams

Initiators and EEDs

Several variants of lead styphnate and lead azide

Ballistic modifiers

Lead-based ballistic modifiers and compounds used in EDB

MDC

Elemental lead sheathing



Lead-free primaries and EEDs

WSTC0001 “LFIA”

WSTC0096 “LFIB”

CEUK/QinetiQ DBX-1 work

CEUK Phase 1 L-F programme



Lead-free ballistic modifiers

WSTC0508 BM study

Prototyping capability

UoE PhDs and Cambridge

PostDoc

Industry L-F BM Phase 1 programme



Lead-free MDC

BCAST development of tin-based MDC alloys



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L-F PRIMARIES AND EEDs

GENERAL OVERVIEW

OVERVIEW OF WORK COMPLETED UNDER WSTC0096 “LFIB” PROGRAMME AND PV-FUNDED DBX-1 WORK

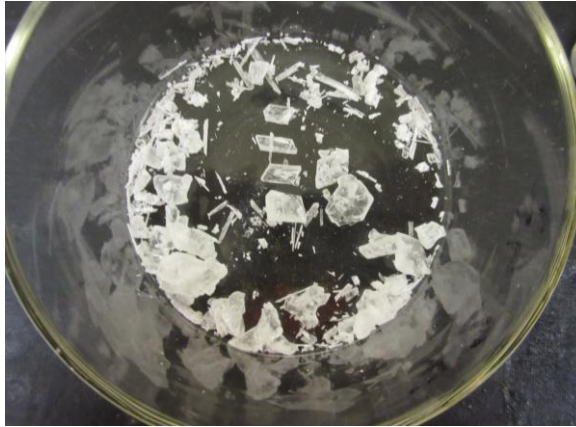
L-F candidates

Proposed deflagrative materials:

- EVAJAM
- KDNP

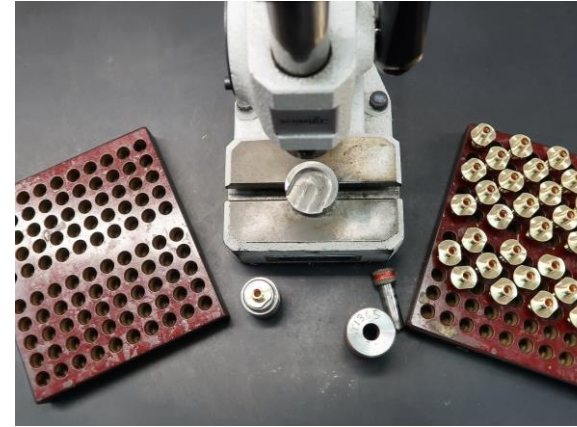
Proposed detonative materials:

- CaNT
- ROFNOR
- DBX-1



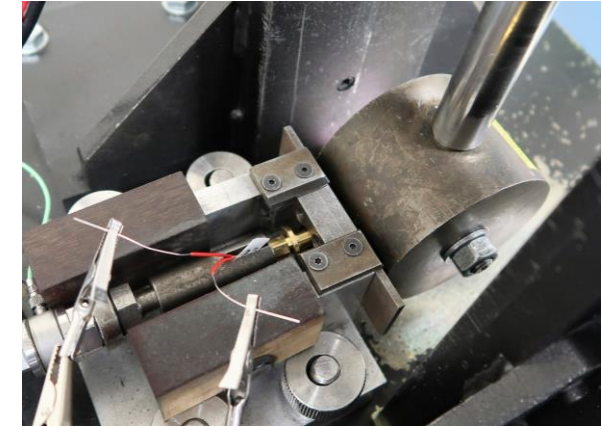
Synthesis

Lead-free candidate materials identified via WSTC0001 “LFIA”; material-level characterisation completed (EMTAP, thermal and chemical stability, etc.)



Fabrication

Fabrication of a range of EEDs, including fuseheads, igniters, actuators, and detonators using the lead-free candidate materials



Evaluation

Evaluation of performance using vented vessels, witness plate tests, Langlie method, actuator pendulum testing (thrust, energy, functioning time, etc.) at hot (A1), cold (C2), and ambient



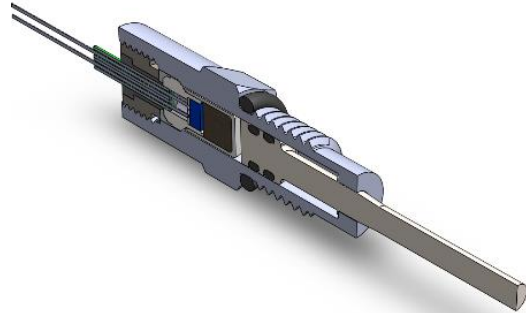
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L-F PRIMARIES AND EEDs

PROPOSED DEFLAGRATIVE MATERIALS

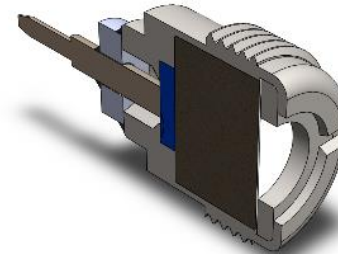
EVAJAM

Aqua-tetrakis(4-amino-1,2,4-triazole-N)-copper(II) chloro-tetrakis(4-amino-1,2,4-triazole-N)-copper(II) triperchlorate



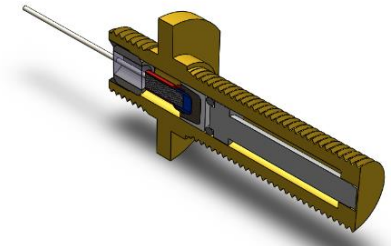
Actuator trials (pressed igniter)

~7 % failure rate



Buttered igniter trials

No successful firings during Langlie assessment



Actuator trials (fusehead)

~80 % failure rate using all-fire threshold established by Langlie assessment

~40 % failure rate using increased all-fire level

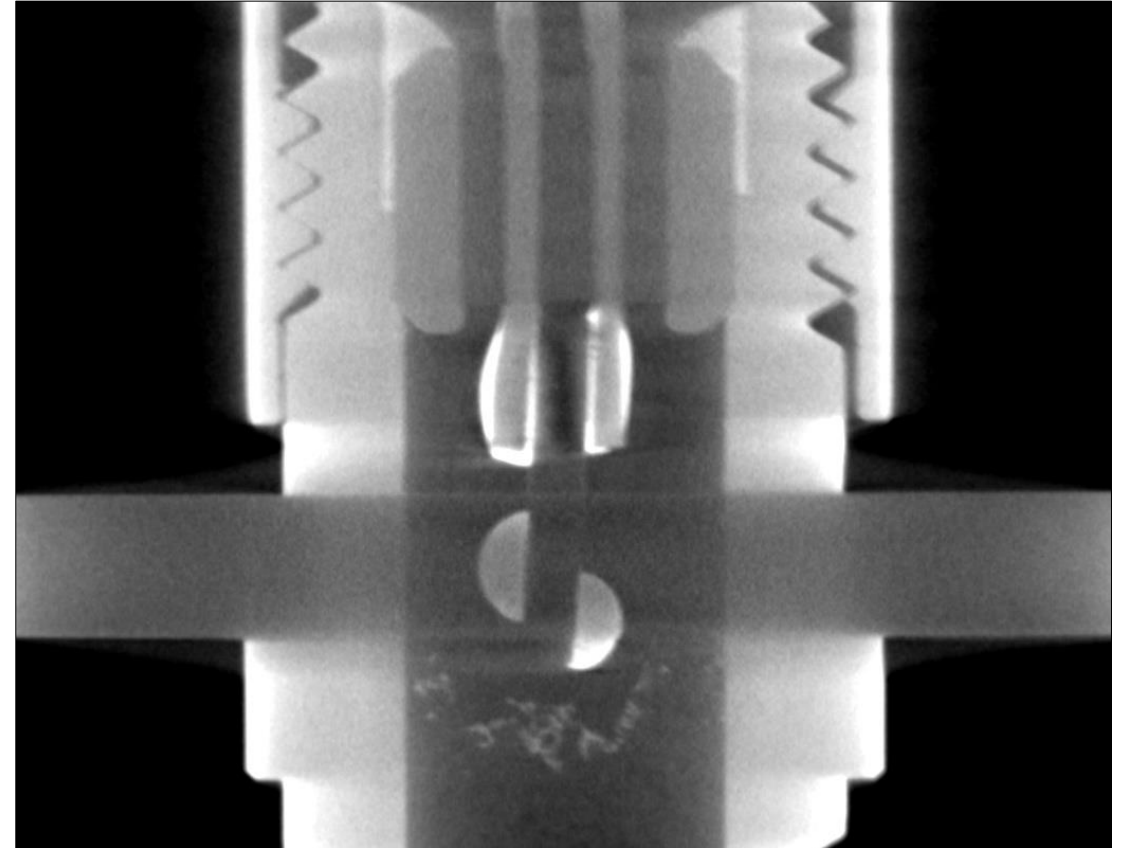
EVAJAM

Langlie all-fire assessment

1.54 A for 10 ms at $T_0 \rightarrow$
3.58 A for 10 ms at $T_0 + 6$ months

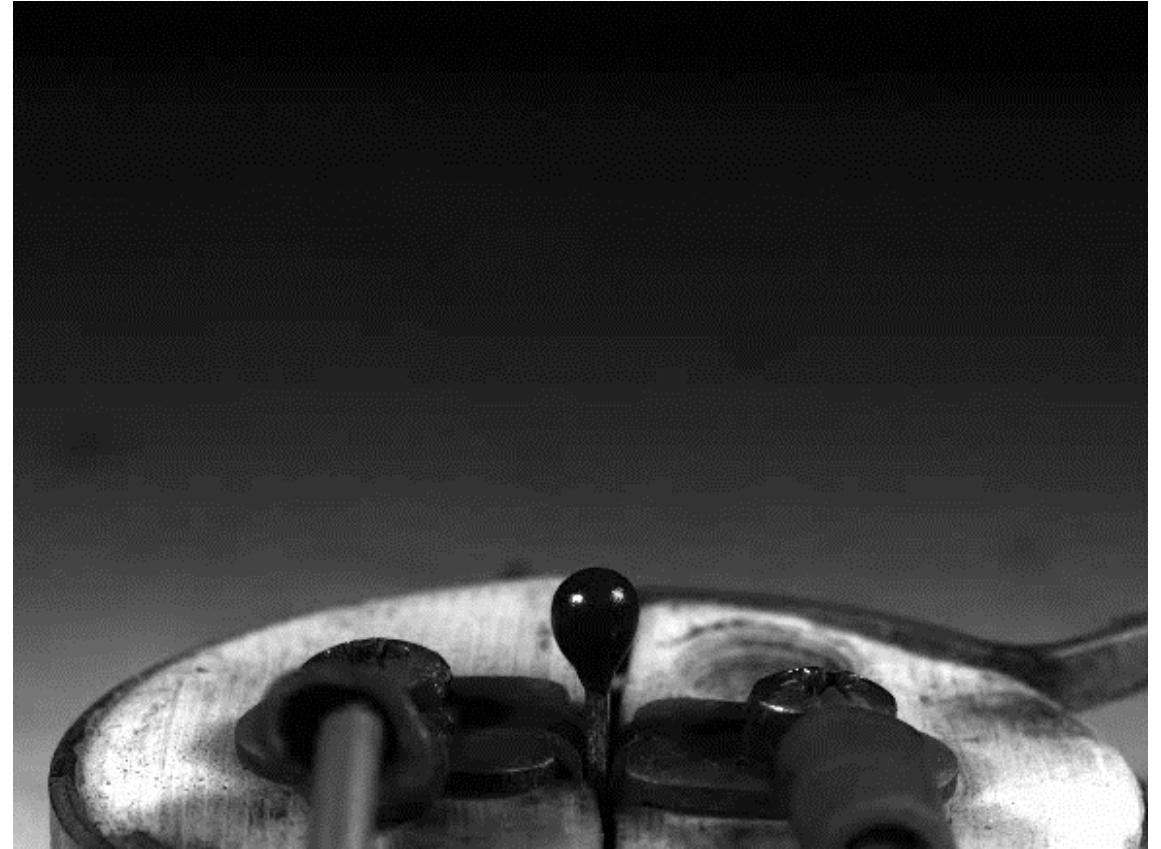
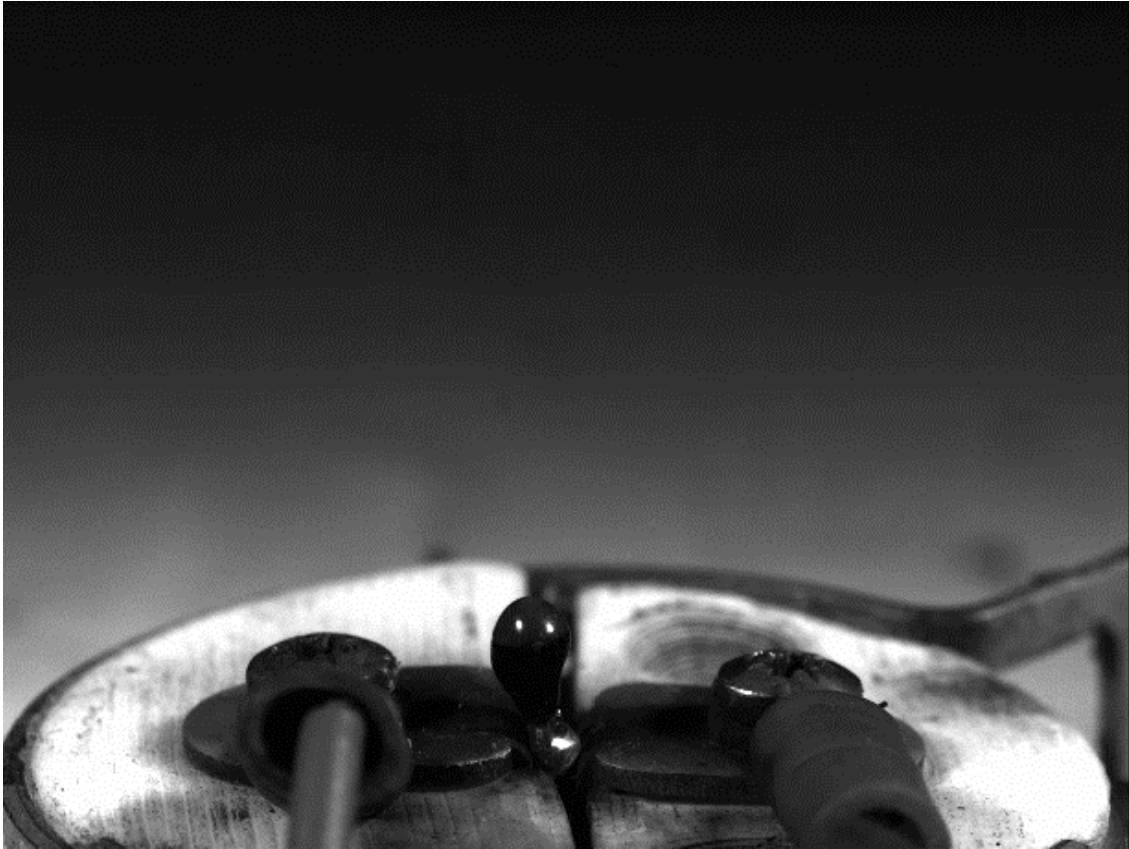
Test equipment and test setup ruled out
Radiographic (CT) inspection conducted to rule
out assembly errors

Change was only apparent when using
fusehead-type actuators – suggesting possible
composition shrinkage over time in storage



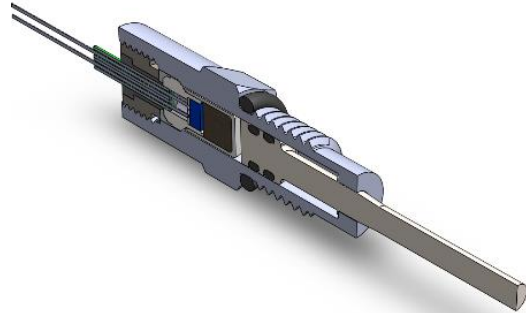
HIGH-SPEED VIDEO (40,000 fps)

EVAJAM FUSEHEAD (LEFT) COMPARISON WITH IN-SERVICE FUSEHEAD (RIGHT)



KDNP

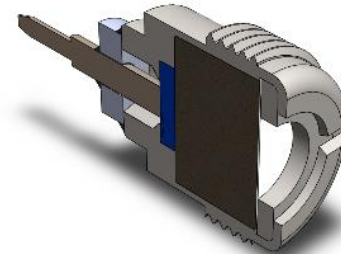
Potassium 5,7-dinitro-[2,1,3]-benzoxadiazol-4-olate 3-oxide



Actuator trials (pressed igniter)

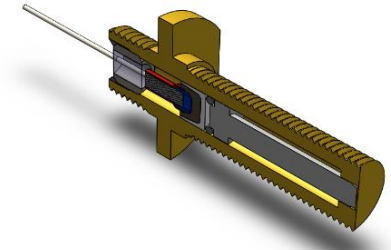
All devices functioned successfully

Relatively consistent functioning time across temperature range



Buttered igniter trials

All devices functioned successfully



Actuator trials (fusehead)

All devices functioned successfully

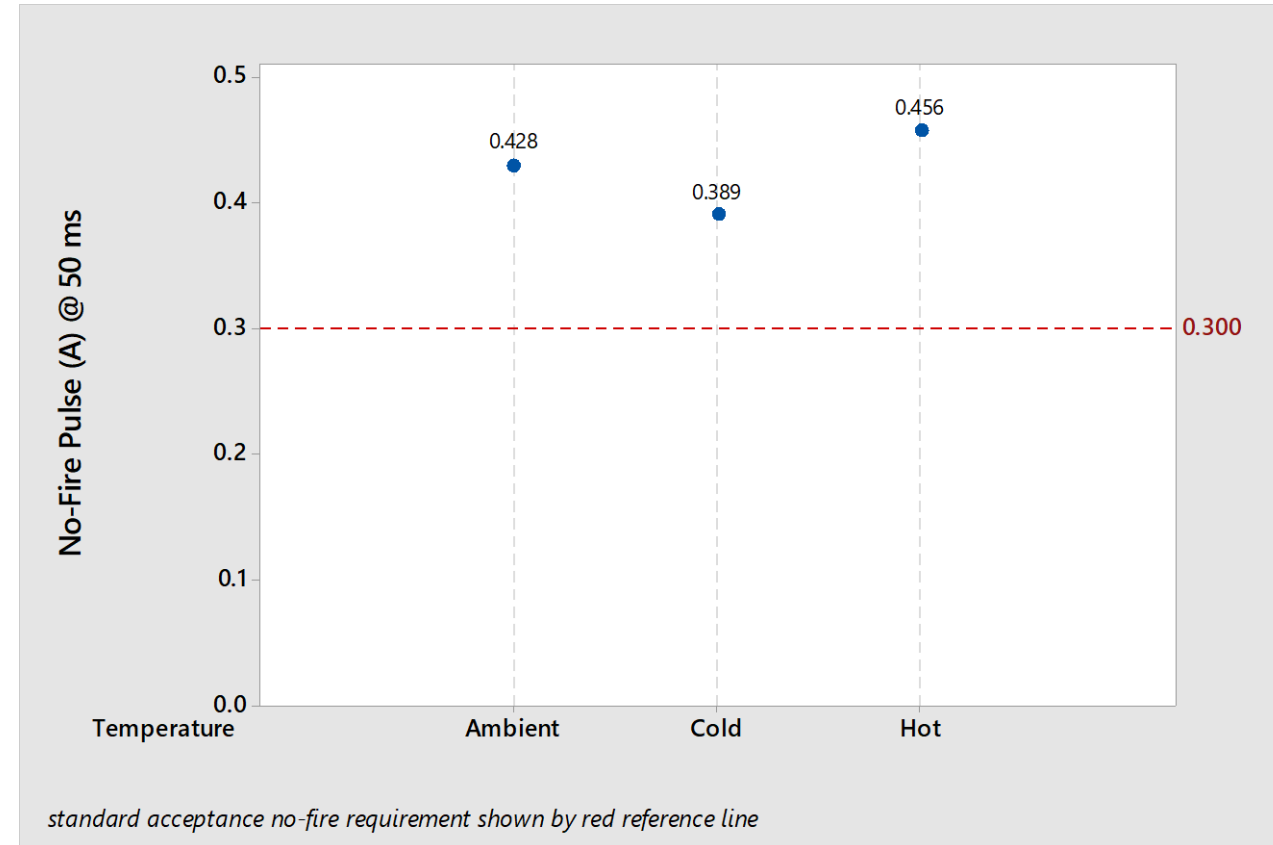
Consistent functioning time across temperature range

KDNP

Langlie all-fire and no-fire results comparable to in-service fusehead (RD1349)

Higher no-fire threshold and slightly higher all-fire threshold – suggests that KDNP is slightly less sensitive to thermal stimuli

Fairly consistent at hot (A1), cold (C2), and standard ambient





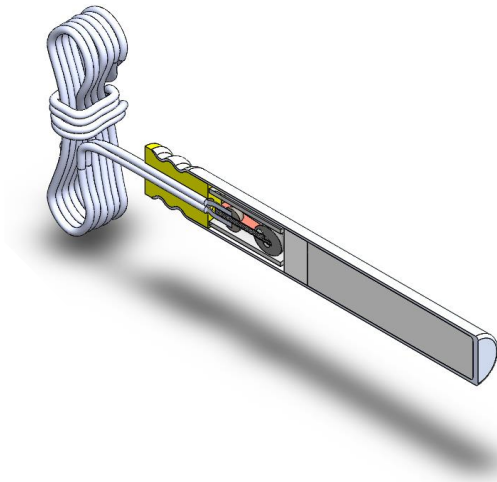
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L-F PRIMARIES AND EEDs

PROPOSED DETONATIVE MATERIALS

CaNT

No takeover from
fusehead to CaNT
Detonator tube split
and CaNT dispersed



Calcium 5-nitriminotetrazolate

ROFNOR

Successful takeover from fusehead to ROFNOR

No takeover from ROFNOR to PETN; detonator tube split and PETN dispersed

Similar results observed historically during trials using detonators filled only with lead styphnate priming charge

Catena-[dodecakis(μ -4H-1,2,4-triazol-4-amine)-tetracopper(II) octa-perchlorate dihydrate]



DBX-1



Copper(I) 5-nitrotetrazolate
All detonators functioned
(6/6)

Small diameter detonator
with low priming charge is
considered most difficult to
initiate

Demonstration of fully lead-
free detonator using EVAJAM-
based fuseheads



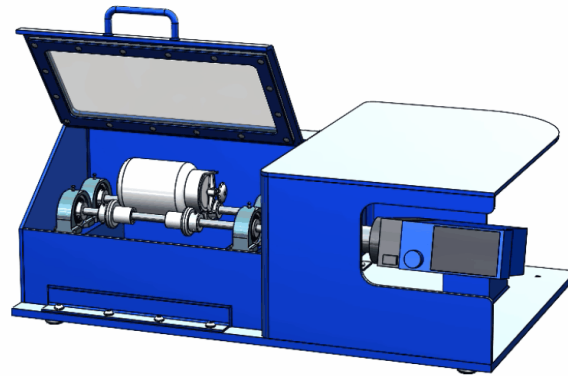
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L-F PRIMARIES AND EEDs

CURRENT/FUTURE WORK

CURRENT/FUTURE WORK

Chemring-funded Phase 1 lead-free primaries and EEDs programme now underway and nearing completion



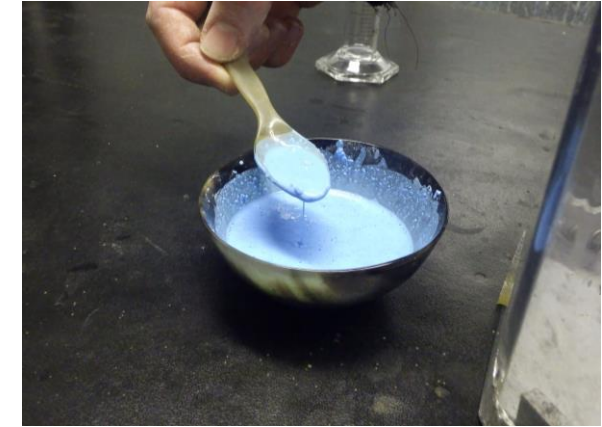
Ball milling

Ball milling of several existing and new candidate materials for use in μ s-response detonators and to improve manufacturing utility in dips and butters



Further syntheses

Synthesis and characterisation of materials identified from further literature searching; continue to explore and understand scale-up requirements



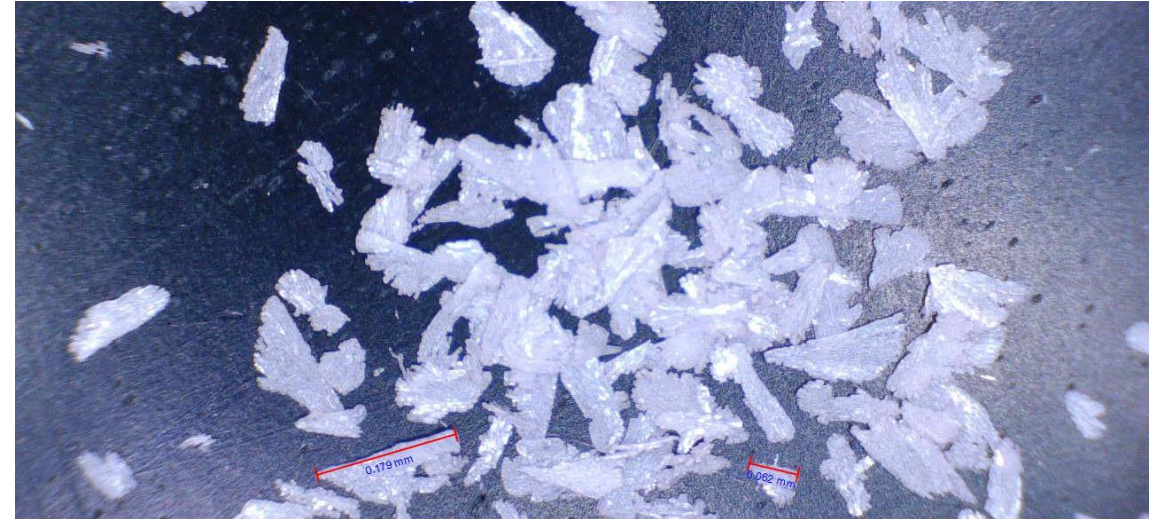
Close-out recommendations

Repurpose ROFNOR as a lead styphnate (deflagrative) composition; further evaluate promising candidates

SILVER AZIDE

SAMPLE	GRADE	IGNITIONS
B/N 07-09-21	Fine	0/5 at 67.5 mJ, 0/4 at 1,200 mJ
B/N 09-09-21	Intermediate	0/6 at 18 mJ, 1/1 at 65 mJ
B/N 13-09-21	Coarse	0/6 at 23 mJ, 1/2 at 30 mJ

Confirmatory samples of RD1303 (same capacitor, etc.) gave 1/1 results at 360 mJ, 120 mJ, 15 mJ, and 12 mJ



In all cases, CEUK silver azide appears less sensitive than RD1303 and results indicate that coarse silver azide is more sensitive to ESD than fine material; this is despite coarse, non-acicular materials usually being less ESD sensitive than fine explosives and silver azide ESD sensitiveness often being quoted in μJ -levels

MILLING

CHEMRING BALL MILL APPARATUS

1. Rollers

1 x driven, 1 x idle, designed to prevent axial movement and reduce vibration

2. Milling jar

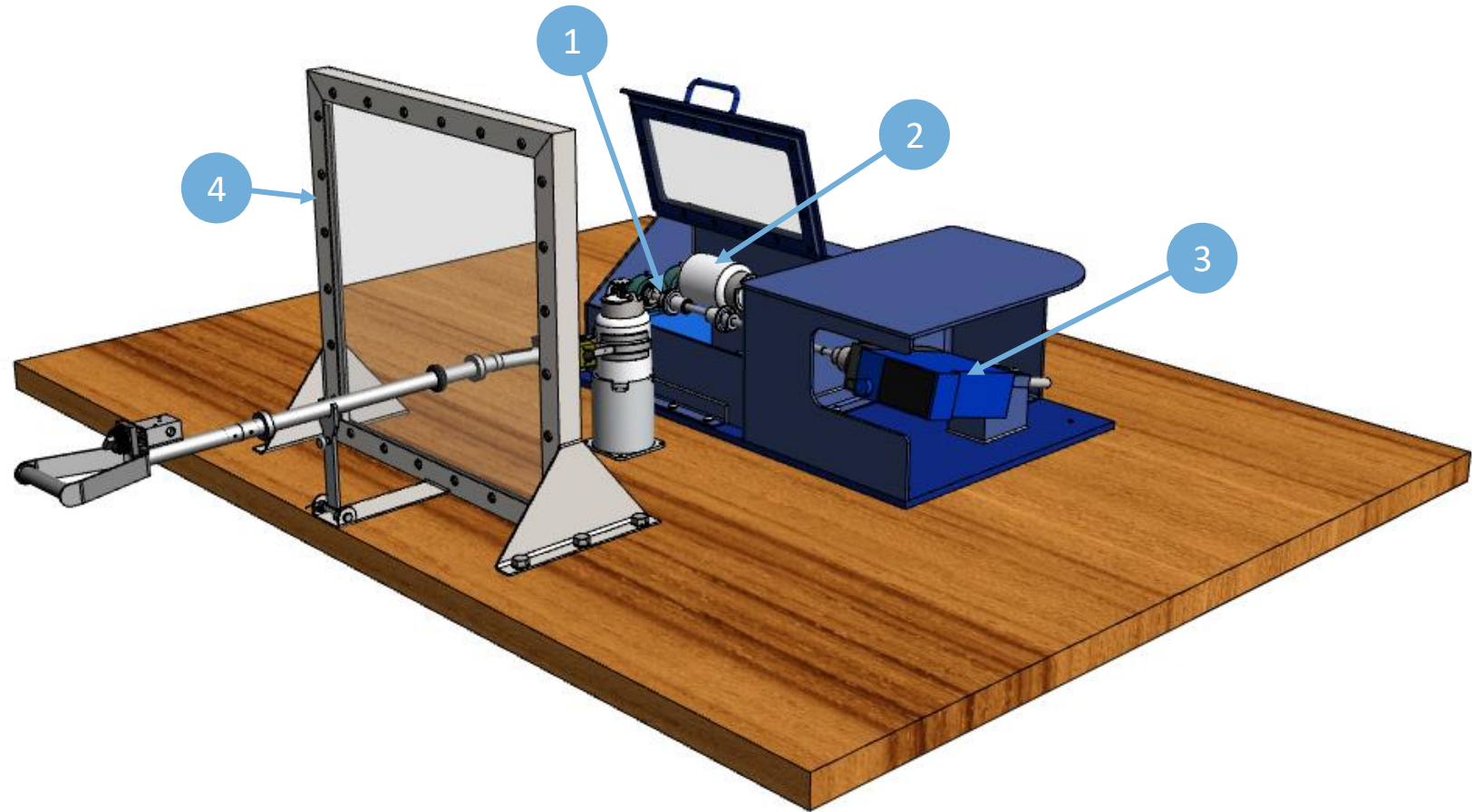
Contains isopropyl alcohol wetted primary and grinding media

3. Motor

Remotely-controlled motor with precise rotational control

4. Safety screen and pneumatic gripper

Hands-off manipulation and use of apparatus (loading, unloading, sieving, etc.)



MILLING

CHEMRING BALL MILL APPARATUS

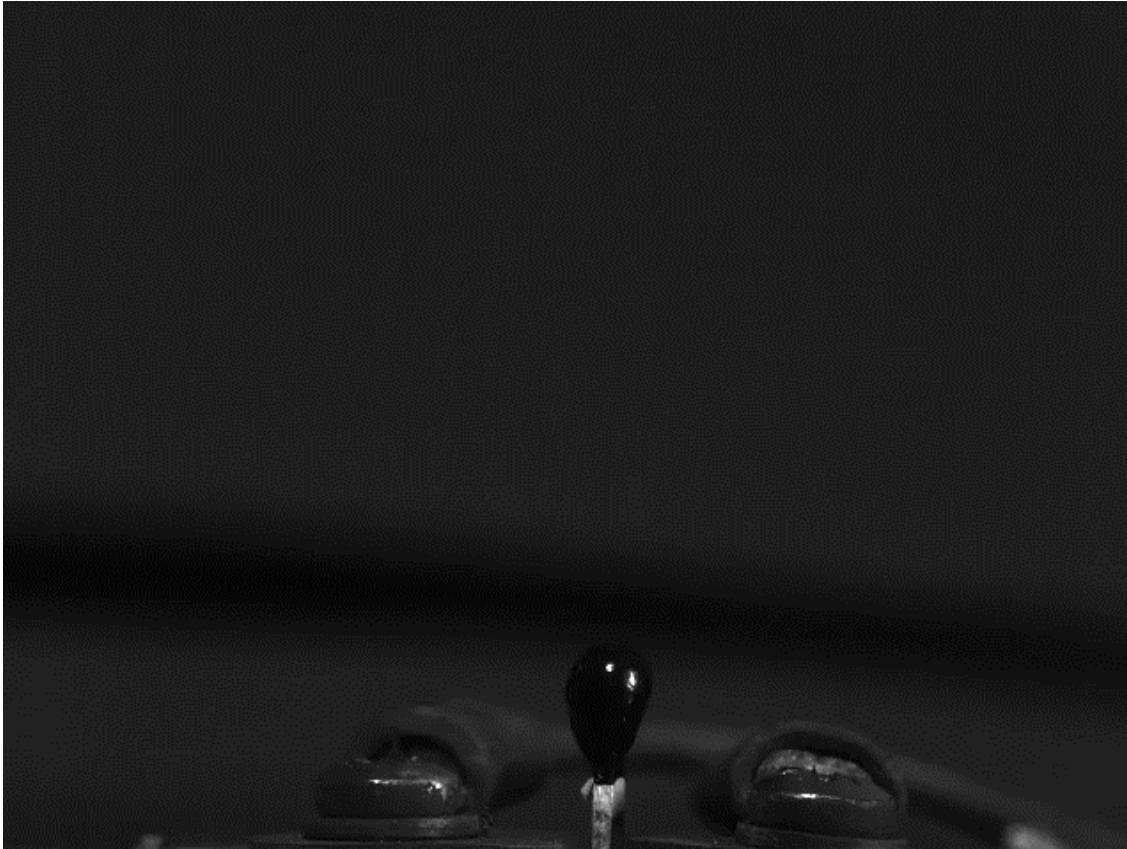


Initial commissioning trials underway and all risk assessment work completed for live trials

Minor remedial work planned to correct shaft runout and improve stability of milling jar during operation

ROFNOR

TRIALS USING ROFNOR IN DEFLAGRATIVE ROLE



01

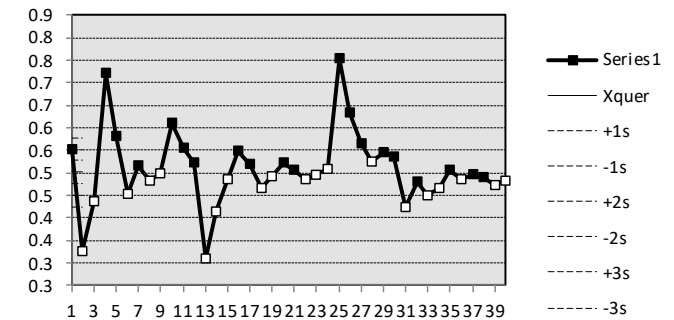
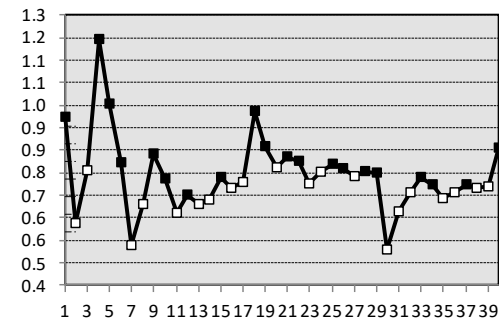
Good processability when used as a fusehead butter (using butyl acetate, ethyl cellulose, and potassium chlorate)

02

Lanlige all-fire at 1 A for 10 ms and Langlie no-fire at 0.4 A for 10 ms – comparable to in-service fusehead

03

Qualitatively, looks very promising using HSV – very energetic output over short duration ($\sim 75 \mu\text{s}$)



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Euan McLean | Engineering & Technology Manger | Euan.McLean@ChemringEnergetics.co.uk