High Performance Polymer-Bonded Explosive Containing PolyNIMMO for Metal Accelerating Applications

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Presentation Outline

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- Objective of Study
- Rationale & Methodology
- Energetic Polymer & Plasticisers
- Candidate Selection
- Candidate Assessment
  - Thermal Properties
  - Physical & Mechanical Properties
  - Hazard Properties
  - Shock Sensitiveness
  - Performance
- Summary
- Acknowledgements

Objectives of Study

- To develop new explosive compositions for metal accelerating applications which possess improved performance and lower vulnerability in comparison with currently available military explosives
- To develop and utilise fully energetic binder systems based on polyNIMMO
- Specifically, to at least match the performance of Octol 75/25 in terms of detonation pressure and metal accelerating ability whilst demonstrating reduced vulnerability

Rationale & Methodology - Formulation Rationale

- HMX chosen as energetic filler to maximise performance
  - Readily available
  - Higher density, detonation velocity & pressure
- Fully energetic binder systems evaluated
  - i.e. energetic polymer with energetic plasticiser
  - Binder contributes towards performance
  - Allows more latitude with level of solids loading to achieve trade-offs
    - eg performance vs hazard vs processing
- Programme addressed castable formulations
  - Ease of processing for medium to large warhead filling operations
  - Castable PBXs generally demonstrate better IM compliance
  - More binder present so better mechanical properties
  - Established processing technique

Rationale & Methodology - Formulation & Assessment Methodology

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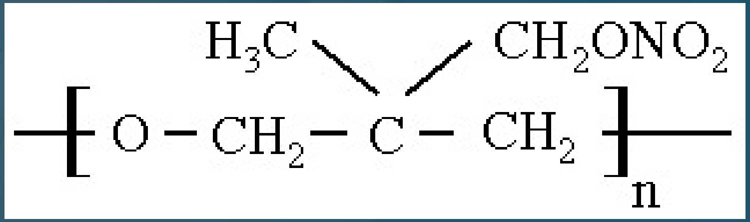
- PolyNIMMO binders plasticised with a range of energetic plasticisers
  - Butyl NENA
  - ROWANITE 8001 (K10)
  - GAPA
- Performance modelling to identify trends and narrow field of formulation and processing activities
- Series of initial compositions prepared on the small scale to investigate the effect of formulation variables and to screen in small scale tests:
  - Processing, hazard, thermal behaviour, mechanical properties
- Leading candidate down selected then manufactured on intermediate scale for further assessment:
  - Shock sensitiveness
  - Performance

Energetic Polymer and Plasticisers

Energetic Polymer

- PolyNIMMO Pre-polymer
  - a homopolymer of 3-nitratomethyl-3-methyl oxetane (NIMMO) possessing reactive terminal primary hydroxyl groups
  - can be cured using isocyanates to give rubbers
  - manufactured by ICI in the UK



n = 22

Viscosity at 40º C (poise)	560
Viscosity at 60º C (poise)	100
Hydroxyl value (mg KOH/g)	18-22
Molecular Weight (notional)	5500
Density (g/cm³)	1.26
Glass transition (º C)	-25
Heat of Formation (kCal/mol)	-73.9
Heat of Explosion (kCal/mol)	28.8
Temperature of Ignition (º C)	no less than 165º C

Energetic Plasticisers (1)

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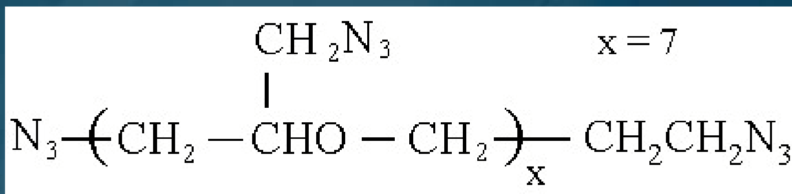
- Butyl NENA
  - The nitratoethylnitramine family (NENAs) contain both nitrate ester and nitramine functionalities
  - Traditionally used as plasticisers in gun and rocket propellants
  - Manufactured by NSWC Indian Head Division

$$C_4H_9 - \underset{\displaystyle NO_2}{\overset{|}{N}} - CH_2 - CH_2ONO_2$$

Appearance	Yellow Liquid
Composition	Butyl-NENA: 60-100% Metyl-nitroaniline: 0-1%
Density (g/cm^3)	1.2
Molecular Mass	207
Temperature of Decomposition (º C)	210
Melting Point (º C)	-27
Heat of Formation (kJ/mol)	-192
Heat of Explosion (J/g)	1083

Energetic Plasticisers (2)

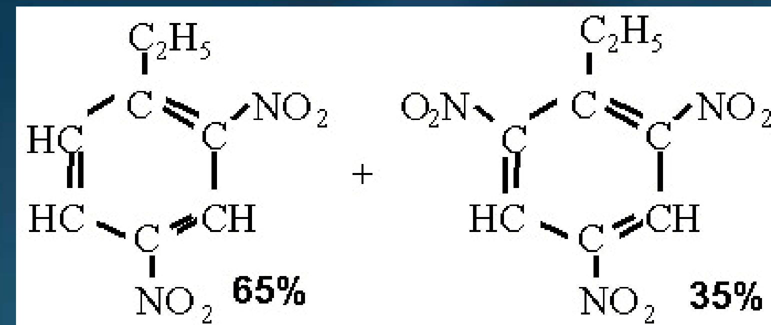
GAPA



Glycidyl azide polymer azide oligomer

Appearance	Pale Yellow Liquid or slightly ambered
Density (g/cm³)	1.27
Molecular Mass	805
Glass Transition (º C)	-69
Melting Point (º C)	-27
Heat of Formation (kJ/mol)	-227
Solubility	miscible with acetone and chlorinated solvents not miscible with water and aliphatic hydrocarbons

ROWANITE 8001 (K10)



Appearance	Clear, yellow to medium orange liquid
Composition	Dinitroethylbenzene: 65% Trinitroethylbenzene: 35%
Density (g/cm³)	1.363 ± 0.003
Molecular Mass	209
Temperature of Ignition (º C)	240
Melting Point (º C)	-40
Oxygen Balance (%)	-53
Heat of Formation (kJ/mol)	-402
Viscosity at 20º C (mPa.s)	38.5

Candidate Selection

Performance Modelling (1)

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- Performance parameters modelled with In-house EXPERT computer programme based on the Kamlet Model
  - Determines detonation characteristics of energetic materials which consist of C, H, N and O only
  - Model predicts:
    - heat of detonation, gas evolved on detonation and average molecular mass of the evolved gaseous products
  - Model then gives predicted
    - Velocity of detonation and detonation pressure
- Modelling conducted on formulations with:
  - Solids loading range of 74 to 77% v/v
  - Plasticiser/polyNIMMO ratios of 70/30, 60/40 and 50/50
  - Three different plasticiser types (ButylNENA, K10 and GAPA)
- Comparisons made with predictions for Octol 75/25 and PBXN-110

Performance Modelling (2)

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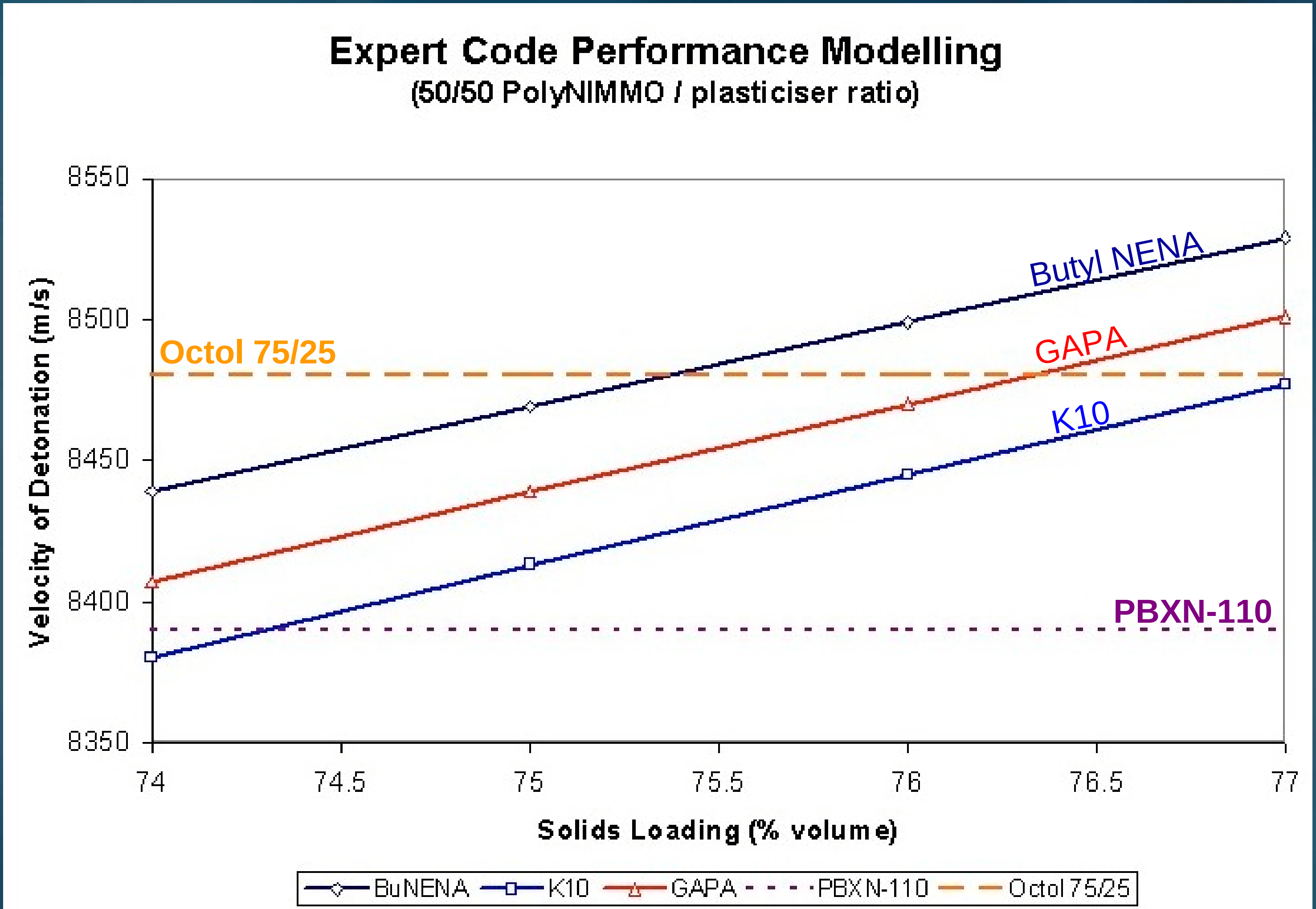
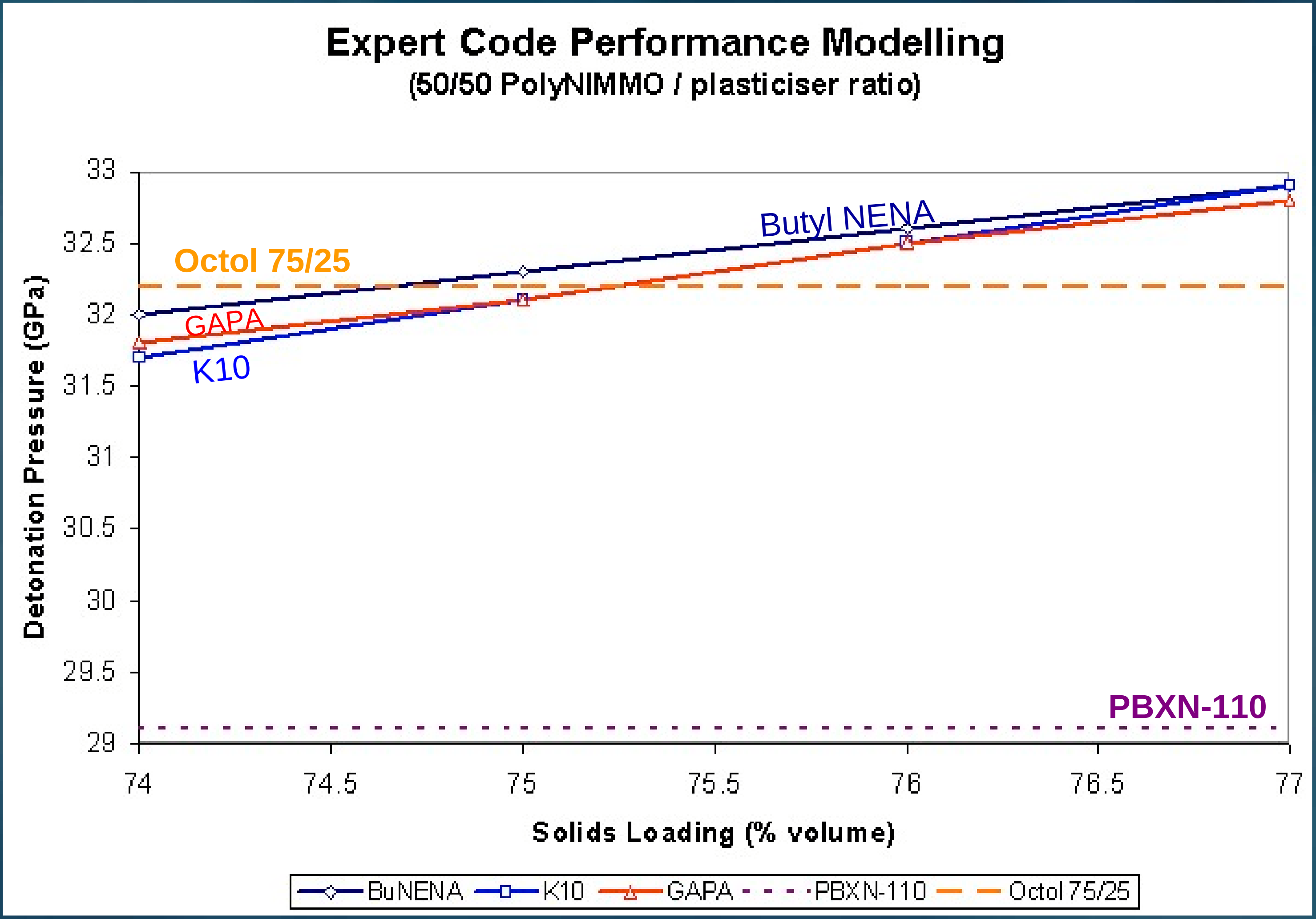


Performance Modelling (3)



Performance Modelling (4)

- All other factors (solids loading, polymer/plasticiser ratio) being equal predicted performance in terms of and follows following trend:
  - V of D: Butyl NENA > GAPA > ROWANITE 8001
  - $P_{cj:}$ Butyl NENA > GAPA = ROWANITE 8001
- Conclusion (all other factors being equal) target performance level can be achieved with lower HMX solids loading with a Butyl NENA binder than with GAPA or ROWANITE 8001 binders
- Modelling results used to scope small scale formulation, processing and assessment programme
  - Different HMX blends evaluated and solids loading increased incrementally
  - Plasticiser/polymer ratio assessed for each plasticiser

Candidate Formulation Down-Selection

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- GAPA plasticiser quickly eliminated as binders too viscous
  - Resultant solids loading too low to achieve desired performance level
- Field of study reduced to Butyl NENA and ROWANITE 8001 formulations
- Candidate formulations taken forward for screening tests
  - Butyl NENA plasticised Research Formulation designated RF-67-43
    - Solids loading level = 77% v/v (83.92% m/m) HMX
    - Predicted V of D = 8531 m/s
    - Predicted Detonation Pressure = 32.9 GPa
  - ROWANITE 8001 plasticised Research Formulation designated RF-67-49
    - Solids loading level = 76% v/v (82.17% m/m) HMX
    - Predicted V of D = 8437m/s
    - Predicted Detonation Pressure = 32.4 Gpa
- Focus on assessment of Butyl NENA plasticised PBX designated RF-67-43

Processing

Processing Assessment (1)

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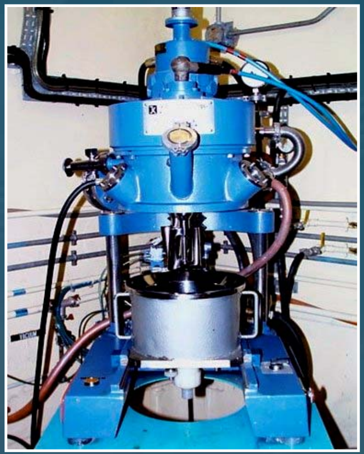
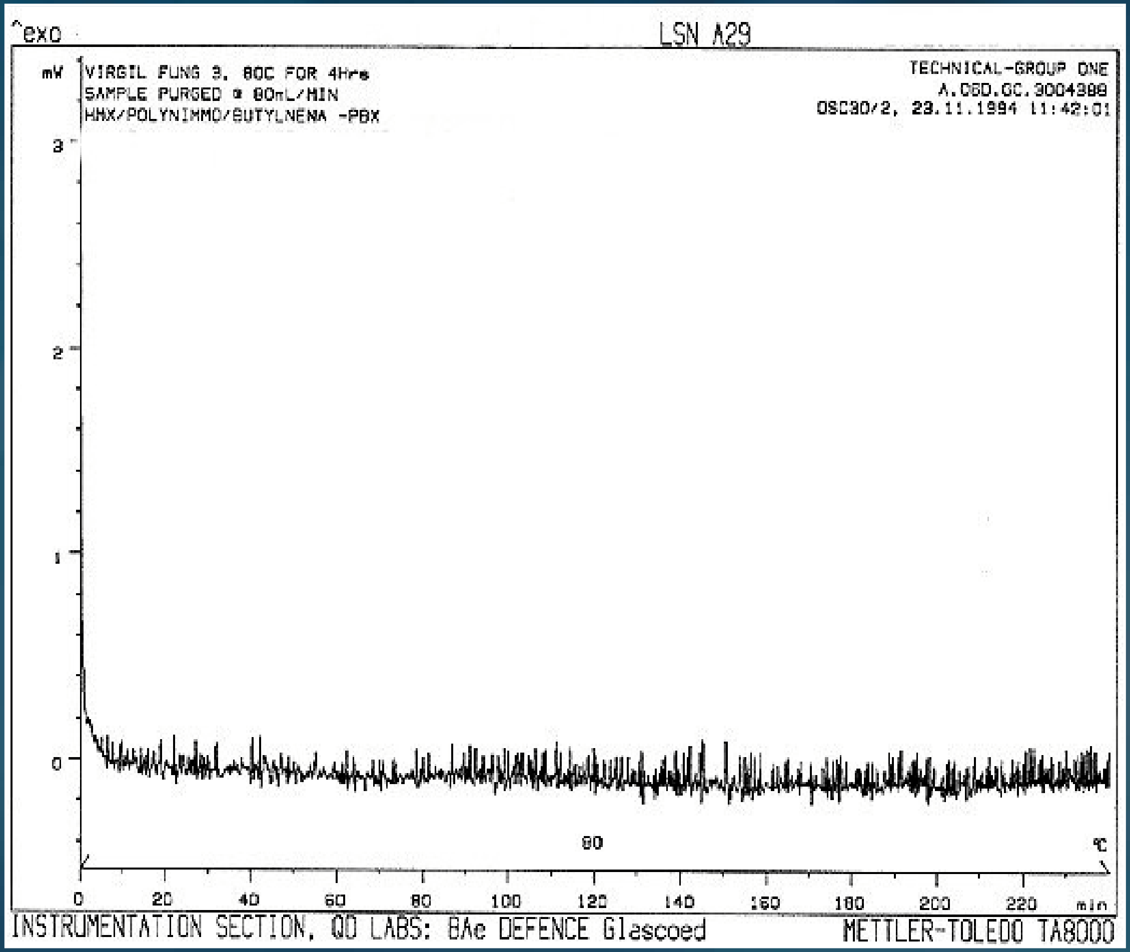
- Small scale mixes were prepared using vertical incorporator
  - initially 1.6Kg increasing to 5Kg
- Effect of formulation variables on process behaviour and end-of-mix (EOM) viscosity (all other factors being equal)
  - Solids loading level - higher the solids loading, higher the EOM viscosity
  - Plasticiser type - lower viscosity plasticiser yields a lower EOM viscosity
  - Polymer/plasticiser ratio
    - lower polymer/plasticiser yields a lower EOM viscosity
    - lower polymer/plasticiser ratio reduces mechanical strength
    - too high a plasticiser level can give rise to migration and exudation
  - Mixing temperature - higher the mixing temperature, the lower the EOM viscosity (but must consider pot-life issues)
- Assessment criteria
  - End of mix viscosity (Brookfield viscometer)
  - Pot-life; time taken to reach 20 kPoise (2kPa.s)
  - Cure Time; time to reach constant Shore A hardness
  - Cured charge quality; density & % Theoretical Maximum Density (TMD)
  - Thermal stability; DSC with sample maintained at 80°C for 4 hours

Processing Assessment (2)



HKV5 High Shear Mixer

Viscosity Measurement



DSC trace

Processing Assessment (3)

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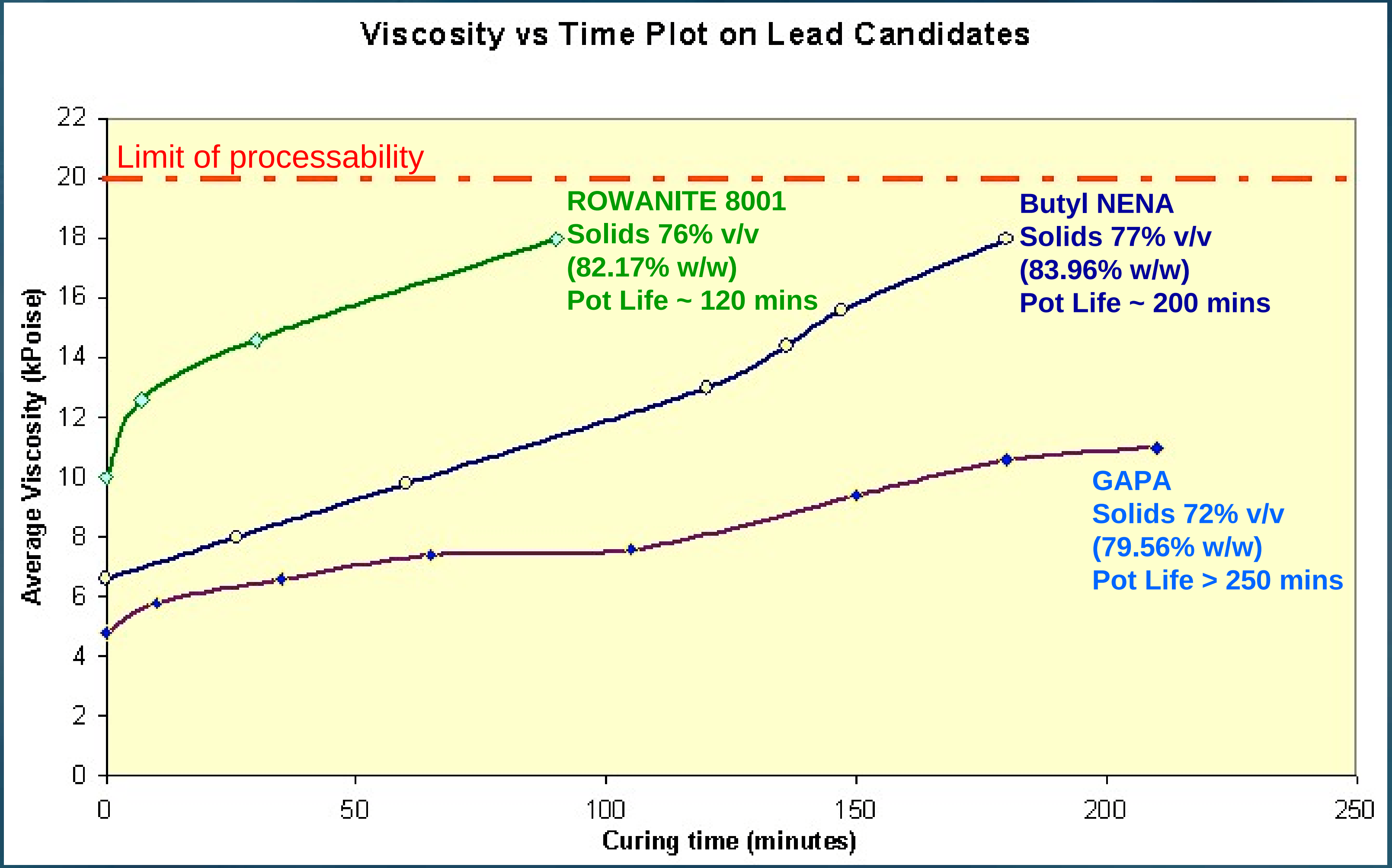
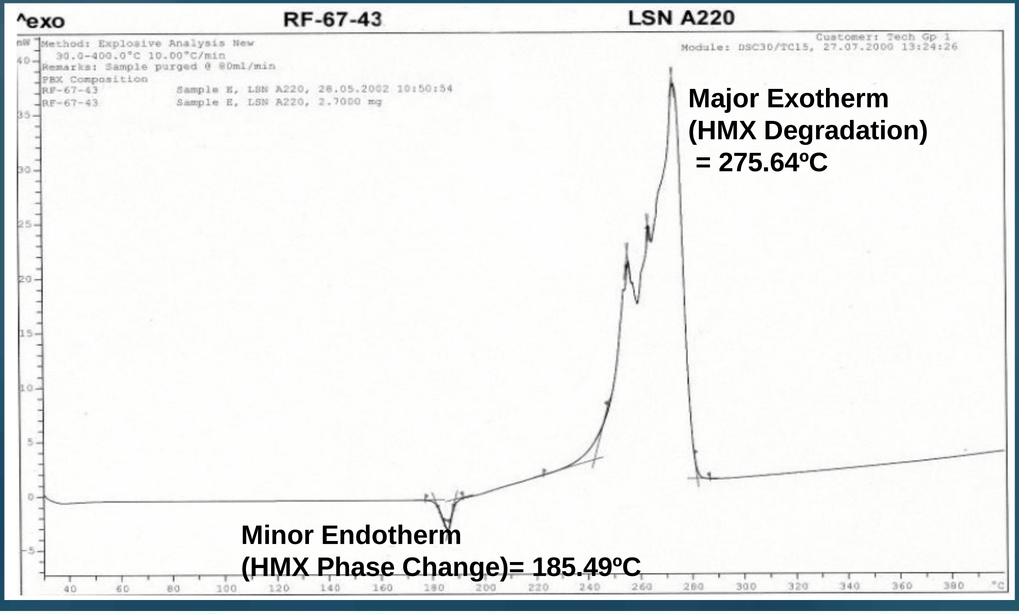


RF- 67- 43 Thermal Properties

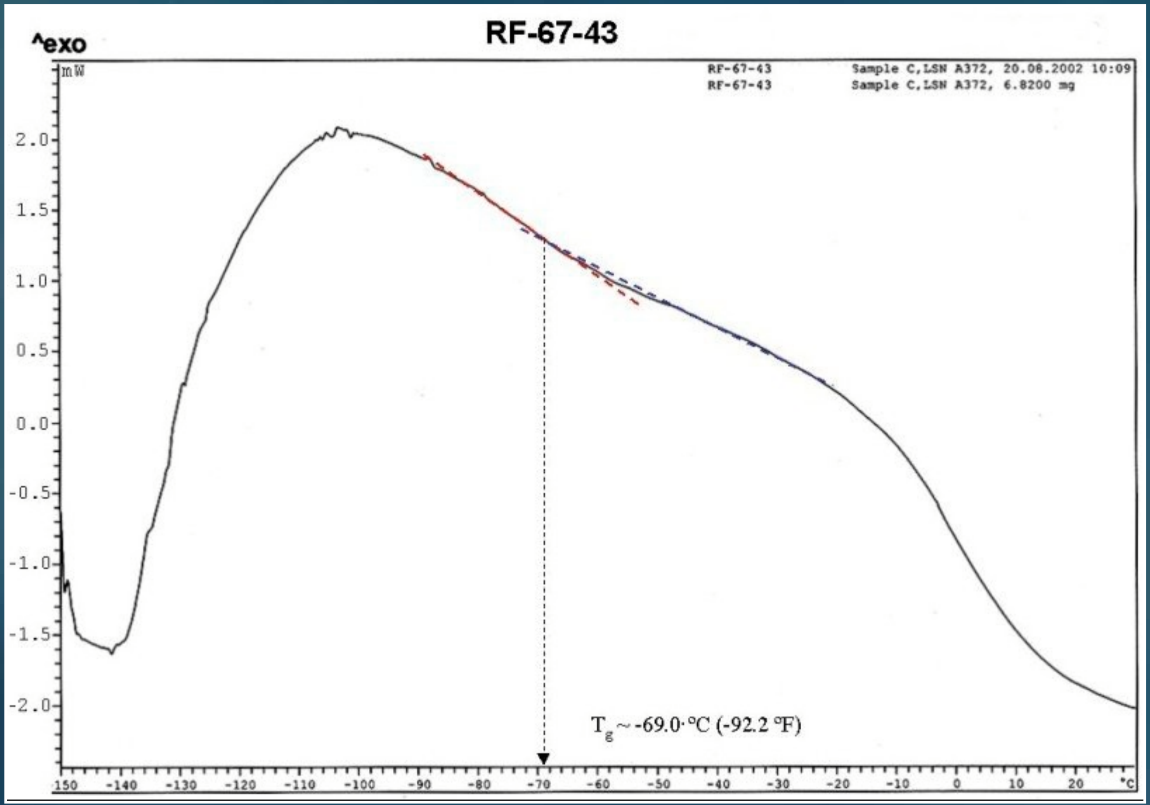
Thermal Properties Assessment (1)

- Vacuum Stability
  - 100ºC for 48 hours (MIL-STD-1751A method 1061)
  - Pass criterion: 2 ml of gas / gram of sample maximum
    Result = 0.16 ml of gas / gram of sample
- DSC
  - Heating samples from 30ºC to 400ºC at a rate of 10ºC per minute
    - Major Exotherm = 275.84°C
    - Minor Exotherm = 185.48°C



Thermal Properties Assessment (2)

- Glass Transition Temperature using DSC
  - Heating samples from -150ºC to 30ºC at a rate of 10ºC per minute
  - PBX below this temperature will become Hard and Brittle
  - Glass Transition Temperature, Tg ~ -69.0°C (92.9°F)



RF- 67- 43 Physical & Mechanical Properties

Physical Properties Assessment

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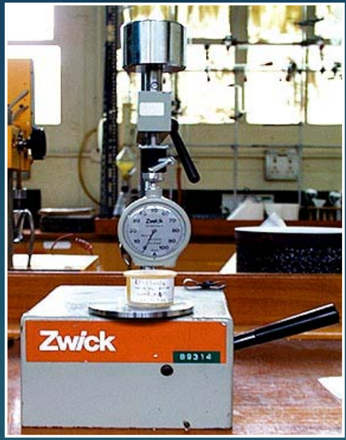
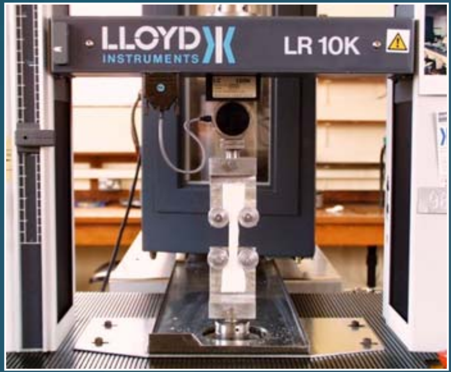
- Density
  - Density of cured explosive is measured using the oil displacement method
  - Density of RF-67-43 = 1.74 g/cm^3 (99.6% TMD)



- Shore A Hardness
  - Shore A Hardness of RF-67-43 = 20-25

- Mechanical Properties
  - Maximum load (N), maximum stress (N/mm^2), strain at maximum load (%), load at break (N), stress at break (N/mm^2)
  - 10 test pieces tested at ambient temperature to obtain an average result

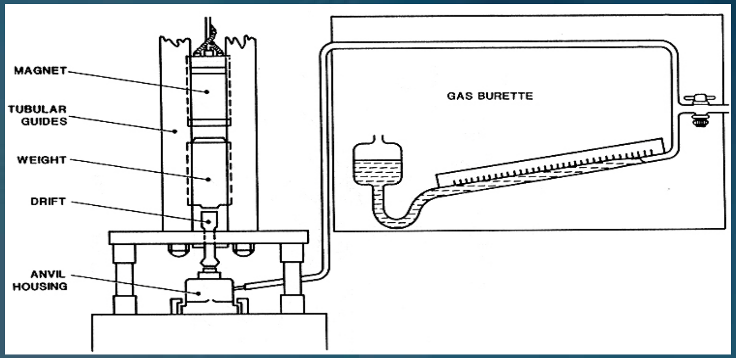


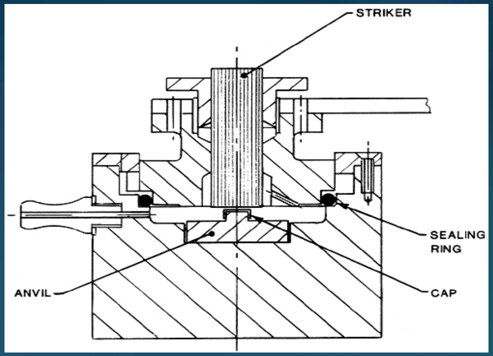
Max Load (N)	Max Stress (N/mm^2)	Strain at Max Load (%)	Load at Break (N)	Stress at Break (N/mm^2)
10.32	0.0839	25.15	5.419	0.0442

RF- 67- 43 Small Scale Hazard Properties

Sensitiveness to Mechanical Impact and Friction

- Rotter Impact Test (EMTAP Test No.1A)





Rotter Impact Testing Apparatus **Testing Mechanism**

Mallet Friction Test (EMTAP Test No.2)

- Strike HE sample on steel surface with steel-tipped mallet (100 strikes); record Ignition (sparks or flame; a "crack" as some or all trace reacts)
- Sentencing criteria
  - No ignition = 0% (frictionally insensitive)
  - Up to six ignitions = 50% (frictionally insensitive)
  - More than six ignitions = 100% (very sensitive)

Summary of Small Scale Hazard Properties

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Test	EMTAP Test No.	Result
Sensitiveness to Mechanical Impact	1A	F of I = 90
Mallet Friction	2	50%
Rotary Friction	33	F of F = 5
Ignition by Electrostatic Spark	6	NO IGNITION AT 4.5J
Temperature of Ignition	3	200°C
Ease of Ignition	4	FAIL TO IGNITE
Behaviour on Inflammation	5	IGNITES AND SUPPORTS TRAIN STEADILY THROUGHOUT

RF- 67- 43 Shock Sensitiveness

Comparative US/UK Shock Sensitiveness Assessment

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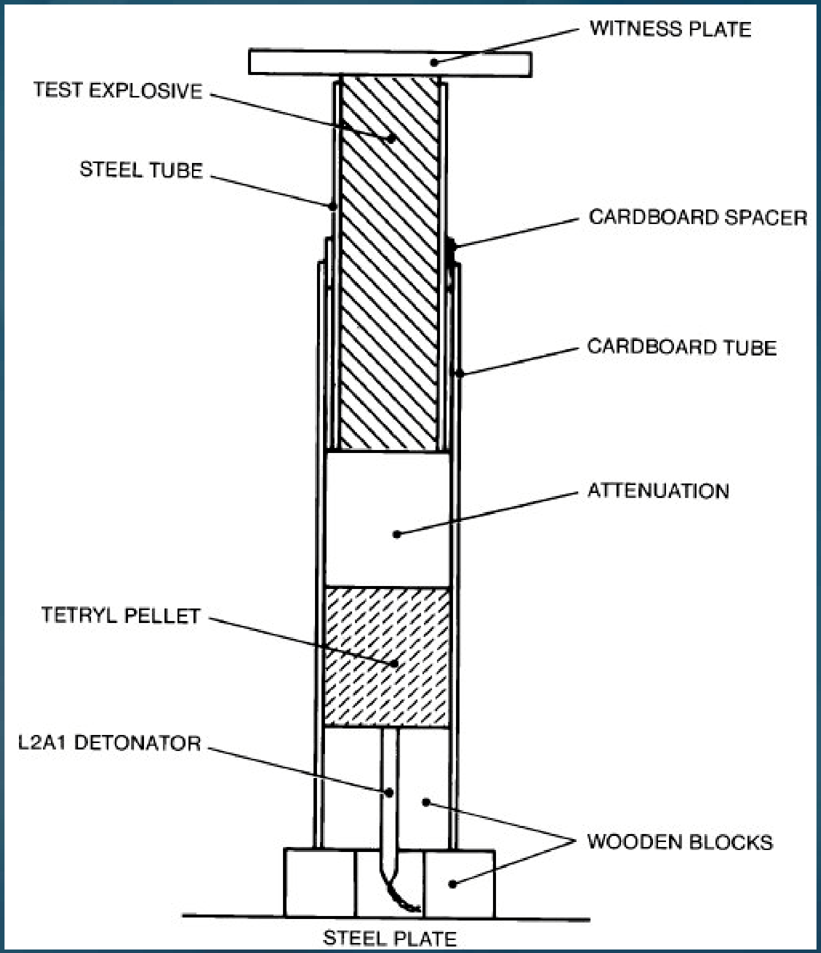
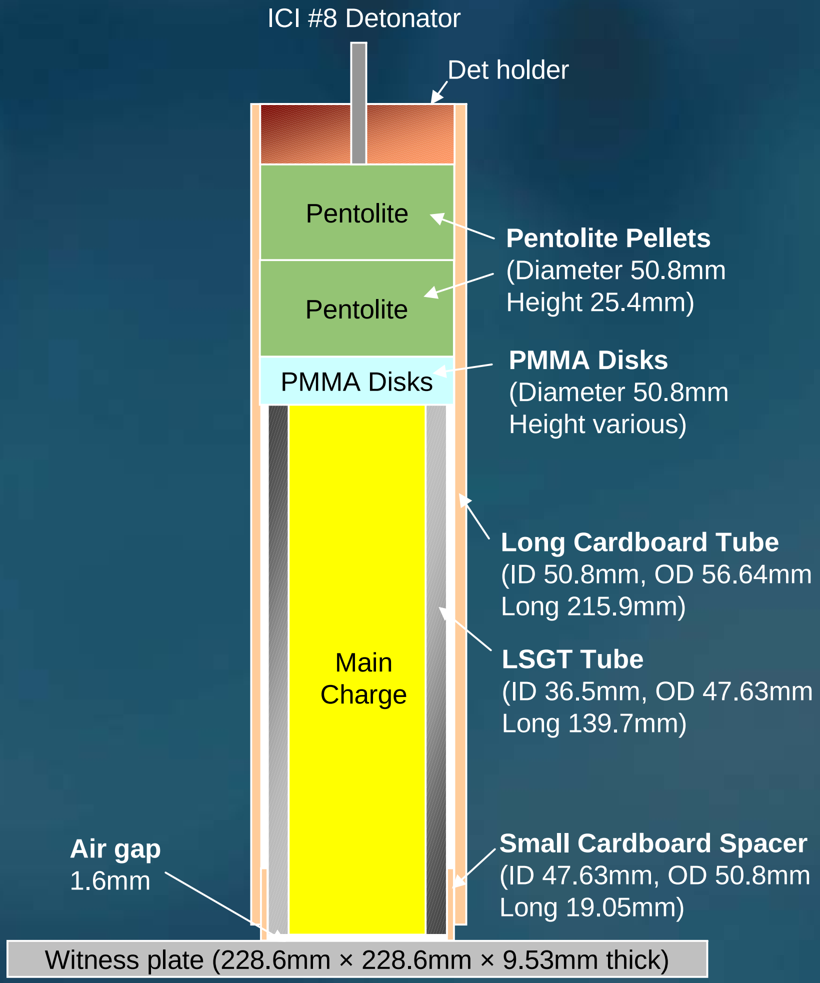
- Shock sensitiveness as measured in the large scale gap test (LSGT) conducted as an initial assessment of vulnerability
- Both UK and US test methods were carried out as they are not identical
- Both tests were performed in the Fast Event Facility (FEF) at RO Defence, Chorley with NSWC Indian Head personnel in attendance
- NSWC supplied major hardware and booster pellets for the US test which were flown in from the US
- Parallel approach allowed comparative assessment of US and UK large scale gap tests techniques on the same explosive composition filled under identical conditions
- Close co-operation between US and UK assessment teams established

Comparison of UK and US Large Scale Gap Test Configurations



UK: EMTAP Test No.22



US: MIL-STD-1751A Method 1041 (NOL)

Comparison of UK and US Large Scale Gap Test Results for RF-67-43

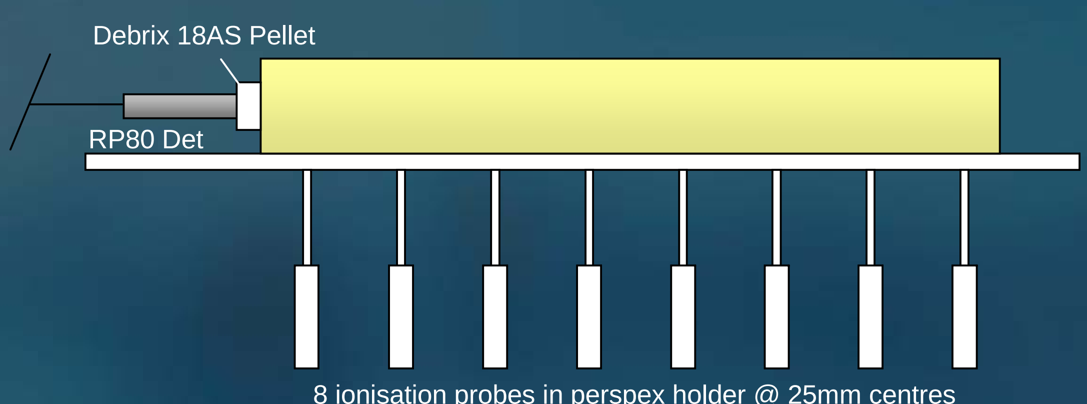
	UK EMTAP Test No.22	MIL-STD-1751A Method 1041 (NOL)
Detonator	L2A1	ICI #8
Donor Pellet	1 off Tetryl (density = 1.5 g/cm³)	2 off Pentolite (density = 1.56 g/cm³)
Attentuator	PMMA	PMMA
Witness Plate	Mild Steel (10.00mm thick)	Mild Steel (9.53mm thick)
Sample Density	1.74 g/cm³	1.74 g/cm³
Result (50% Point)	39.4mm (155 cards)	41.1mm (162 cards)
Result (P_g)	~ 33.8 kbar	33.1 kbar
Other results for comparison	RDX/TNT Type A, 50% point ~ 199 cards P_g = 20 kbar	PBXN-110, 50% point ~ 154-178 cards P_g = 27.0-36.8 kbar Octol 85/15 50% point = 236 cards P_g = 14.5 kbar
Reference	EMTAP Manual Test No.22	NIMIC Excel Spreadsheet on Gap Tests version 1.3

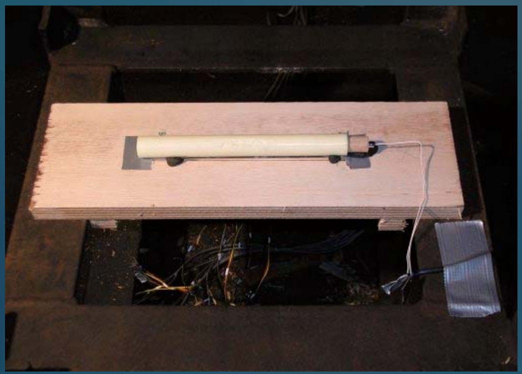
RF- 67- 43 Performance

Performance Assessment (1)

- Velocity of Detonation (unconfined)
  - Test sample dimension = 25.4mm diameter × 227mm long
  - density = 1.74 g/cm^3
  - V of D measured by triggering ionisation probes (8 off - 25mm apart)
  - 6 firings carried out
  - Mean Velocity of Detonation of RF-67-43
    - = 1% above PBXN-110*
    - = 0.2% below Octol 75/25*
  - Predicted Detonation Pressure using the Cook Equation, $P = 0.00987 \times r \times D^2 / 4$
    - = 5.8% above PBXN-110*
    - = 4.3% below Octol 75/25*

* NIMIC EMC version 3.0

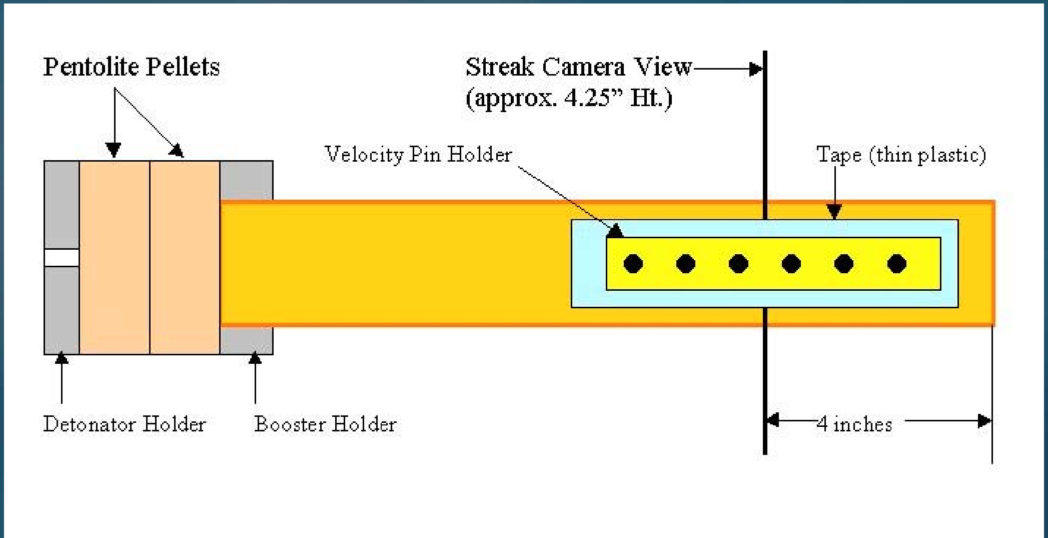


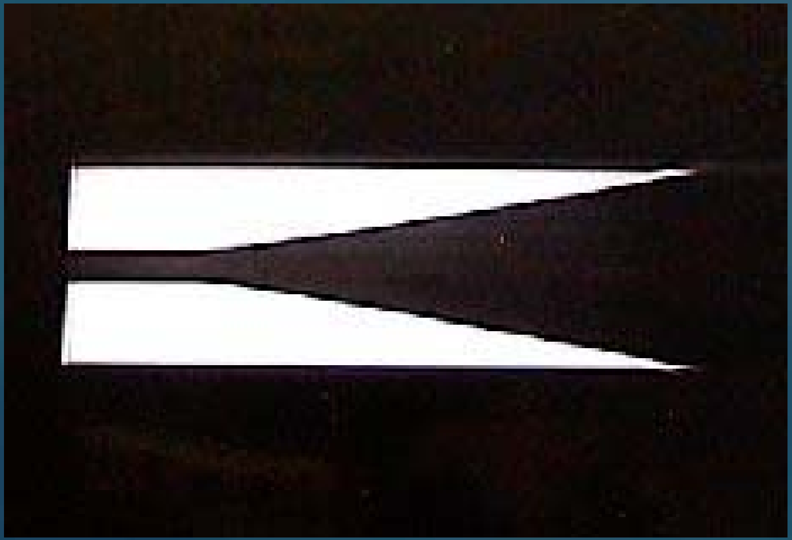


Performance Assessment (2)

- Cylinder Expansion
  - MIL-STD-1751 (USAF) Method 16
  - 5 firings carried out
  - Density = 1.75 g/cm^3
  - Mean Gurney Velocity (19mm) of RF-67-43
    - = 7% above PBXN-110*
    - = 5.4% above Octol 75/25*

* NIMIC EMC version 3.0





Summary

- Close US/UK co-operation has been established on comparative testing techniques and assessment criteria for secondary explosives
- A comparison has been made of the properties and processing behaviour of a series of castable PBXs with polyNIMMO binder systems plasticised with butyl NENA, ROWANITE 8001 (K10) and GAPA
- A candidate PBX, designated RF-67-43, utilising a polyNIMMO binder plasticised with butyl NENA was down selected and has been successfully scaled up to 5kg batch size for assessment
- Processability and cure behaviour satisfactory
- Mechanical properties adequate
- Small scale hazard properties and thermal stability satisfactory
- Shock sensitiveness (from LSGT) on a par with PBXN-110, significantly lower than Octol
- Performance encouraging
  - Improvement over PBXN-110
  - Approaching that of Octol 75/25

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