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

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Presentation Outline

- 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
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
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

\[
\text{H}_3\text{C} - \text{O} - \text{CH}_2\text{C} - \text{CH}_2\text{NO}_2 \]

\[n = 22\]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 40°C (poise)</td>
<td>560</td>
</tr>
<tr>
<td>Viscosity at 60°C (poise)</td>
<td>100</td>
</tr>
<tr>
<td>Hydroxyl value (mg KOH/g)</td>
<td>18.22</td>
</tr>
<tr>
<td>Molecular Weight (notional)</td>
<td>5500</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.26</td>
</tr>
<tr>
<td>Glass transition (°C)</td>
<td>-25</td>
</tr>
<tr>
<td>Heat of Formation (kCal/mol)</td>
<td>-73.9</td>
</tr>
<tr>
<td>Heat of Explosion (kCal/mol)</td>
<td>28.8</td>
</tr>
<tr>
<td>Temperature of Ignition (°C)</td>
<td>no less than 165°C</td>
</tr>
</tbody>
</table>
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

\[
\text{C}_4\text{H}_9\text{N} \quad \text{CH}_2 \quad \text{CH}_2\text{ONO}_2
\]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Yellow Liquid</td>
</tr>
<tr>
<td>Composition</td>
<td>Butyl-NENA: 60-100%</td>
</tr>
<tr>
<td></td>
<td>Methyl-nitroaniline: 0-1%</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>1.2</td>
</tr>
<tr>
<td>Molecular Mass</td>
<td>207</td>
</tr>
<tr>
<td>Temperature of Decomposition (^\circ) C</td>
<td>210</td>
</tr>
<tr>
<td>Melting Point (^\circ) C</td>
<td>-27</td>
</tr>
<tr>
<td>Heat of Formation (kJ/mol)</td>
<td>-192</td>
</tr>
<tr>
<td>Heat of Explosion (J/g)</td>
<td>1083</td>
</tr>
</tbody>
</table>
Energetic Plasticisers (2)

**GAPA**

\[
\text{CH}_2\text{N}_3 \quad x = 7
\]

\[
\text{N}_3\text{-CH}_2\text{-CHO - CH}_2\text{-CH}_2\text{N}_3^x
\]

Glycidyl azide polymer azide oligomer

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Pale Yellow Liquid or slightly ambered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm(^3))</td>
<td>1.27</td>
</tr>
<tr>
<td>Molecular Mass</td>
<td>805</td>
</tr>
<tr>
<td>Glass Transition (°C)</td>
<td>-69</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>-27</td>
</tr>
<tr>
<td>Heat of Formation (kJ/mol)</td>
<td>-227</td>
</tr>
<tr>
<td>Solubility</td>
<td>miscible with acetone and chlorinated solvents, not miscible with water and aliphatic hydrocarbons</td>
</tr>
</tbody>
</table>

**ROWANITE 8001 (K10)**

\[
\text{C}_2\text{H}_5
\]

\[
\text{NO}_2 \quad 65\%
\]

\[
\text{O}_2\text{N}
\]

\[
\text{NO}_2 \quad 35\%
\]

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Clear, yellow to medium orange liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Dinitroethylenbenzene: 65% Trinitroethylenbenzene: 35%</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>1.363 ± 0.003</td>
</tr>
<tr>
<td>Molecular Mass</td>
<td>209</td>
</tr>
<tr>
<td>Temperature of Ignition (°C)</td>
<td>240</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>-40</td>
</tr>
<tr>
<td>Oxygen Balance (%)</td>
<td>-53</td>
</tr>
<tr>
<td>Heat of Formation (kJ/mol)</td>
<td>-402</td>
</tr>
<tr>
<td>Viscosity at 20°C (mPa.s)</td>
<td>38.5</td>
</tr>
</tbody>
</table>
Candidate Selection
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 (ButylINENA, K10 and GAPA)
- Comparisons made with predictions for Octol 75/25 and PBXN-110
Expert Code Performance Modelling
(50/50 PolyNIMMO / plasticiser ratio)

- Butyl NENA
- Octol 75/25
- GAPA
- K10
- PBXN-110

Velocity of Detonation (m/s)

Solids Loading (% volume)
Expert Code Performance Modelling
(50/50 PolyNIMMO / plasticiser ratio)

- Octol 75/25
- Butyl NENA
- GAPA
- K10
- PBXN-110

Detonation Pressure (GPa)
Solids Loading (% volume)
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

- 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 = 8437 m/s
    - Predicted Detonation Pressure = 32.4 Gpa

- Focus on assessment of Butyl NENA plasticised PBX designated RF-67-43
Processing
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
Limit of processability

**ROWANITE 8001**
- Solids 76% v/v
- (82.17% w/w)
- Pot Life ~ 120 mins

**Butyl NENA**
- Solids 77% v/v
- (83.96% w/w)
- Pot Life ~ 200 mins

**GAPA**
- Solids 72% v/v
- (79.56% w/w)
- Pot Life > 250 mins
RF- 67- 43 Thermal Properties
Thermal Properties Assessment (1)

- **Vacuum Stability**
  - 100°C 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 30°C to 400°C at a rate of 10°C per minute
    - Major Exotherm = 275.84°C
    - Minor Exotherm = 185.48°C
Glass Transition Temperature using DSC
- Heating samples from -150°C to 30°C at a rate of 10°C per minute
- PBX below this temperature will become Hard and Brittle
- Glass Transition Temperature, T_g ~ -69.0°C (92.9°F)
RF- 67- 43 Physical & Mechanical Properties
Physical Properties Assessment

- **Density**
  - Density of cured explosive is measured using the oil displacement method
  - Density of RF-67-43 = 1.74 g/cm³ (99.6% TMD)

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

- **Mechanical Properties**
  - Maximum load (N), maximum stress (N/mm²), strain at maximum load (%), load at break (N), stress at break (N/mm²)
  - 10 test pieces tested at ambient temperature to obtain an average result

<table>
<thead>
<tr>
<th>Max Load (N)</th>
<th>Max Stress (N/mm²)</th>
<th>Strain at Max Load (%)</th>
<th>Load at Break (N)</th>
<th>Stress at Break (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.32</td>
<td>0.0839</td>
<td>25.15</td>
<td>5.419</td>
<td>0.0442</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Test</th>
<th>EMTAP Test No.</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitiveness to Mechanical Impact</td>
<td>1A</td>
<td>F of I = 90</td>
</tr>
<tr>
<td>Mallet Friction</td>
<td>2</td>
<td>50%</td>
</tr>
<tr>
<td>Rotary Friction</td>
<td>33</td>
<td>F of F = 5</td>
</tr>
<tr>
<td>Ignition by Electrostatic Spark</td>
<td>6</td>
<td>NO IGNITION AT 4.5J</td>
</tr>
<tr>
<td>Temperature of Ignition</td>
<td>3</td>
<td>200°C</td>
</tr>
<tr>
<td>Ease of Ignition</td>
<td>4</td>
<td>FAIL TO IGNITE</td>
</tr>
<tr>
<td>Behaviour on Inflammation</td>
<td>5</td>
<td>IGNITES AND SUPPORTS TRAIN STEADILY THROUGHOUT</td>
</tr>
</tbody>
</table>
RF-67-43 Shock Sensitiveness
Shock sensitteness 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

- Witness plate (228.6mm × 228.6mm × 9.53mm thick)
- Pentagon Pellets
- PMMA Disks
- Det holder
- Main Charge
- LSGT Tube (ID 36.5mm, OD 47.63mm, Long 139.7mm)
- Long Cardboard Tube (ID 50.8mm, OD 56.64mm, Long 215.9mm)
- PMMA Disks (Diameter 50.8mm, Height various)
- Small Cardboard Spacer (ID 47.63mm, OD 50.8mm, Long 19.05mm)
- Air gap 1.6mm
- Witness plate (228.6mm × 228.6mm × 9.53mm thick)

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

- ICI #8 Detonator
- Pentolite Pellets (Diameter 50.8mm, Height 25.4mm)
- PMMA Disks (Diameter 50.8mm, Height various)
- Long Cardboard Tube (ID 50.8mm, OD 56.64mm, Long 215.9mm)
- LSGT Tube (ID 36.5mm, OD 47.63mm, Long 139.7mm)
- Small Cardboard Spacer (ID 47.63mm, OD 50.8mm, Long 19.05mm)
Comparison of UK and US Large Scale Gap Test Results for RF-67-43

<table>
<thead>
<tr>
<th></th>
<th>UK EMTAP Test No.22</th>
<th>MIL-STD-1751A Method 1041 (NOL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detonator</td>
<td>L2A1</td>
<td>ICI #8</td>
</tr>
<tr>
<td>Donor Pellet</td>
<td>1 off Tetryl (density = 1.5 g/cm³)</td>
<td>2 off Pentolite (density = 1.56 g/cm³)</td>
</tr>
<tr>
<td>Attenuator</td>
<td>PMMA</td>
<td>PMMA</td>
</tr>
<tr>
<td>Witness Plate</td>
<td>Mild Steel (10.00mm thick)</td>
<td>Mild Steel (9.53mm thick)</td>
</tr>
<tr>
<td>Sample Density</td>
<td>1.74 g/cm³</td>
<td>1.74 g/cm³</td>
</tr>
<tr>
<td>Result (50% Point)</td>
<td>39.4mm (155 cards)</td>
<td>41.1mm (162 cards)</td>
</tr>
<tr>
<td>Result (P_g)</td>
<td>~ 33.8 kbar</td>
<td>33.1 kbar</td>
</tr>
<tr>
<td>Other results for comparison</td>
<td>RDX/TNT Type A, 50% point ~ 199 cards P_g = 20 kbar</td>
<td>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</td>
</tr>
<tr>
<td>Reference</td>
<td>EMTAP Manual Test No.22</td>
<td>NIMIC Excel Spreadsheet on Gap Tests version 1.3</td>
</tr>
</tbody>
</table>
RF- 67- 43 Performance
Performance Assessment (1)

- **Velocity of Detonation (unconfined)**
  - Test sample dimension = 25.4mm diameter × 227mm long
  - density = 1.74 g/cm³
  - 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/cm³
  - 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
This work package was conducted under the sponsorship of the US Navy’s Insensitive Munitions Advanced Development - High Explosives (IMAD-HE) Program

- **NSWC Indian Head**
  - Karen Burrows
  - Anh Duong
  - Heather Gokee
  - Al Gillis
  - John O’Connor

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  - Alan Watkins
  - Gwyn Sayce
  - Glascoed Laboratory
  - Summerfield Laboratory
  - Fast Event Facility