Topics of Interest: Ageing & Cook-off

Dr Michael Sharp
TSO Energetic Materials

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Two Topics of Interest to the IM Community

IM & AGEING

- ✓ Consequences for IM
- ✓ Ageing Data

COOK-OFF

- ✓ SOA Document
  - Threat
  - Small-scale Tests

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IM and Ageing

New Energetic Materials are being introduced to help meet IM requirements (e.g. PBXs)

- The IM community requires more information on how these materials age

Self-ignition of M10 Gun PROPELLANT

Ähtäri Ammunition Depot in Finland

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IM and Ageing

Ageing and IM

Ageing of the energetic material may alter the hazard properties of the EM and thus affect the level of IM-ness.

- More Data Required

Safety Implications - IM assessment no longer valid?

Use of New Reduced Vulnerability EM

could alter the life expectancy of a munition

- More Data Required

Cost Implications - Impacts on CBA of IM

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NIMIC Ageing Programme

- To increase confidence NIMIC, in collaboration with the Nations, will undertake a review of Ageing
  - Share data on some selected materials (HTPB)
    - Critical ageing mechanisms, accelerated ageing trials, real time ageing
  - Comparison with more conventional fills
  - Techniques to determine ageing

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High Explosives

- **A large number of reduced vulnerability formulations have become available**

  - **Melt Cast PBX's**

    AFX-645, PAX-21, XF-13-153…

  - **PBX's**
    - **Information on ≈60 formulations* containing HTPB**
      - Great deal of interest HTPB ageing

    AFX-757, AFX-770, B-2170, B-2211 D, B-2248, CX-84, HEXABU 88, PBXN-109, PBXN-110, PBXW-115, ROWANEX-1100, ROWANEX-1301….

* NIMIC Energetic Materials Compendium

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Melt Cast vs. PBX

Mechanisms	Melt Cast EMs		Plastic Bonded EMs	
Binder Degradation	✗		✓	New Binders need evaluating
Degradation of Mechanical Properties	✓	Physical changes need evaluating (expansion of charges)	✓	Physical changes need evaluating
De-wetting	✗		✓	Interaction of polymers, fillers and bonding agents need to be determined
Migration	✗		✓	Plasticiser migration can be a problem
Explosive Filler Particle Morphology	✓	Possible concerns for hot environments	✓	Solvation of EM filler in residual solvent or plasticiser
Chemical Decomposition of EM Components	✗	Chemical compatibility of ingredients should not be a problem	✓	New Energetic binders and plasticisers with unknown long term stability
Crack formation	✓	Observed for TNT melt cast formulations	✓	Embrittlement of binder systems due to a number of the above mechanisms

Key: ✓ = potential concern ✗ = unlikely to be a concern

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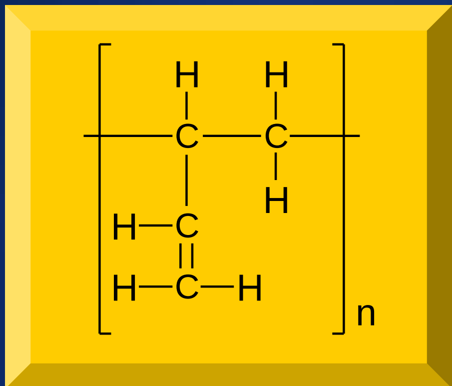
Melt Cast Formulations

Explosive	
Conventional TNT Fills	
TNT	Stockpile samples show no significant change in compressive strength for 20, 30, 40 years.
Comp B	No change in sensitiveness for samples up to 31 years old Some irreversible growth on thermal cycling
H-6	Slight cracking observed for 40 year old samples
Reduced vulnerability IM Formulations	
AFX-644	Exudation of D2 wax on thermal cycling
AFX-645	Evidence of suitability of service life in excess of 20 years
XF-13153	Stable ageing characteristics

HTPB Ageing – Critical Ageing Mechanism (SNL)



OXIDATION

Atm. O_2

Hardening – Surface Localised

Tensile Elongation Decreases

Increased Cross-link Density

Densification

Failure Criterion
50% Residual Elongation

80 Years Life

Inclusion of AP did not alter rate of ageing

Consequences for IM?

- **Failure Criteria for IM?**
- **Other Ageing Mechanisms?**

HTPB Containing Formulations

- **PBXN-109 (RDX/AL/HTPB)**

  RDX from two different lots was investigated

  - **No trends observed for impact, friction, or ESD sensitivity**
  - **Mechanical properties – some changes observed but not thought to be significant**
  - **Shock sensitivity (LSGT) – one RDX lot appears to become more shock sensitive on ageing**

HTPB Containing Formulations

- **PBXN-110 (HMX/HTPB)**

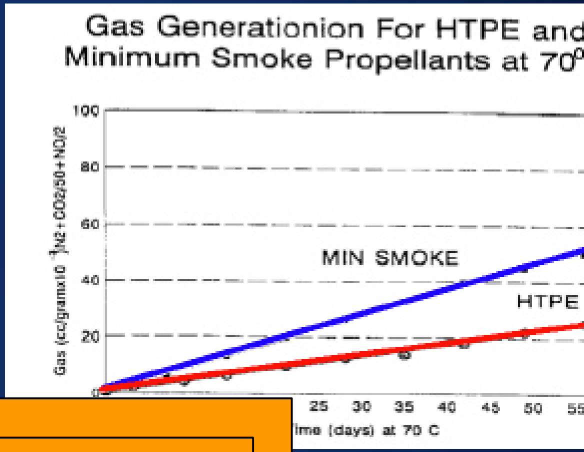
  Aged at 6 months at 70ºC (equivalent to 11 years at 21ºC)

  – Slight decrease in density
  – Mechanical properties:
    - Max stress increases
    - Max strain decreases
  – No changes to impact, friction, or ESD sensitivity observed
  – No significant changes in shock sensitivity

Samples still within specifications -
minimum expected life is 11 years at ambient

Rocket Propellant - HTPE Ageing

- **Ageing Data**
  - HTPE propellants reported to be very stable in extensive long-term ageing studies (7 years at 25ºC – no change in tensile strength, no stabiliser depletion observed)



At 25ºC For 3 years

- No Change in strain to failure at -40ºC
- No Observed Change in Burn rate

At 49ºC For 3 years

- Failure strain increases slightly
- No Observed Change in Burn rate

At 68ºC For 20 Weeks

- No Observed Change in Burn rate

The good news for IM is that it is thought that the move towards using plastic bonded energetic materials with better mechanical properties results in materials more likely to resist the effects of ageing

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Cook-off Review Document

- **CHWG – Agreed that the following topics should be in the review**

COOK-OFF SMALL-SCALE TESTS

MODELLING
What are the available models?

COOK-OFF REACTION MECHANISMS

EM CHARACTERISTICS & REACTION MECHANISM
PBXs vs. melt cast fills

PREDICTING REACTION VIOLENCE

DAMAGE
Characterisation

SCALING LAWS
Confinement & the relationship

EM KINETICS
Methods for measuring EM

APPLICATION OF MODELLING TO REAL PROBLEMS

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Cook-off The Threat

Heating Source	• Torching • EM Burning • Exhausts • Pyrotechnics	• Fuel Fire • Wood fire • Propane burner • Building Fire	• Hot Breach • Gun Battlecarry • Launcher • Nuclear plant • Aircraft debris • Remote fire • Aerodynamic Heating • Adjacent compartment fire	• Solar Heating • Steam leak
Regime	Fast Cookoff (FCO)		Intermediate Cookoff (ICO)	Slow Cookoff (SCO)
Temperatures (Order of magnitude)	1000 to 2000 °C	~1000 °C	100 to 300 °C	~ 100 °C
Heating rates (Order of magnitude)	50 to 100 °C/sec	1 to 20 °C/sec	25°C/hr to 50 °C/min	< 20 °C/hr

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Cook-off reaction Mechanisms

Thermal Conductivity

Melting point

Phase transitions

Decomposition Onset Temperature

Specific Heat Capacity

Coefficient of thermal expansion

Porosity

Phase transition kinetic parameters

DAMAGE

Unreacted Hugoniot data

Phase transition density changes

Time to explosion

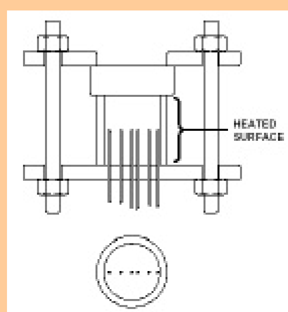
Chemical Kinetics Parameters

Mechanical Properties

- Shear Modulus
- Stress / Strain relationship
- Bulk Modulus
- Elastic Modulus
- Poisson's Ratio

Small-scale tests

- Name and type of test
- Organisations which use the test
- Energetic materials for which there is data
- Principle
  - Sche
  - Dime
  - Instru
  - Heati
- Paramet
- Sample
- Limitatio
- References

GLASS-WINDOWED VEHICLE	Type of Test Direct Observation
 	**Organizations** QinetiQ, Fort Halstead **Energetics Tested** (RDX/HTPB 85:15) (RDX/TNT 60:40)

Principle

Glass windowed vehicle designed to allow direct observation of the changes to the explosive fill just prior to ignition.

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- Name and type of tes
- Organisations which
- Energetic materials f
- **Principle and physical description**
  - Schematics
  - Dimensions and confinement
  - Instrumentation employed
  - Heating rates and conditions
- Parameters measured
- Sample data
- Limitations
- References

Physical Description	
Dimensions:	41mm diameter by 55mm long tube
Confinement:	3.5 mm steel tube (41mm diameter by 55mm long) with a 19mm thick glass window at one end. The assembly was clamped between 2 flat steel plates of 10 mm thickness. Top plate, adjacent to glass, has a large diameter hole to allow direct observation. End plates clamped by 4 tie bars.
Instrumentation	Direct Observation - video recording through glass window. Six 'K' type mineral insulated thermocouples (1.5mm diameter) are fitted to the bottom plate. Data logging using Nicolet Odeyssey transient recorder with 10 Hz sampling rate. Video camera resolution = standard 625 PAL format (each pixel = 0.25 sq.mm of glass window)

Heating Method/ Conditions:	Heating rates of 20ºCmin^{-1}, 8ºCmin^{-1} and 3ºCmin^{-1} were achieved using a nickelchrome tape of ~4Wm^{-1} resistance connected to the 240V AC mains supply through a manually controlled variable transformer.
Sample mass/volume:	Explosive capacity approximately 100g.

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Measurements	
Parameters	**Instrumentation**
Location of Ignition	Direct observation
Physical changes / events leading to ignition	Direct observation
Degree/Violence of the reaction (some)	Fragment Analysis
Ignition temperature	Thermocouples
Temperature as a function of time	Thermocouples
Temperature profile across sample	Multiple thermocouples

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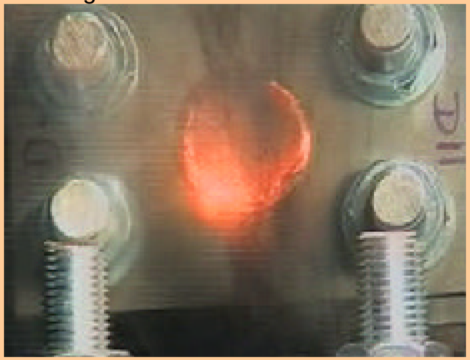
Sample data

RDX/HTPB samples – three explosions and 3 burning reactions.

Explosions resulted in shattering of the glass window and some damage to steel components, which remained relatively intact. Two slow heating experiments displayed a small thermal explosion but most of the EM was recovered. A further sample gave an explosion resulting in ignition and burning of the entire explosive. A further three samples ignited and the EM and was totally consumed. Concentric burning was observed from the outer edge starting about 160ºC. Burning was not continuous and was a process of repeated quenching re-ignition which increased in frequency. The figures below shows, the burning reaction and the residue obtained from the recovered vehicle.



Ignition of the EM

Residue from Cigar burning

In the majority of the experiments evidence of explosive oozing from under the glass window was observed at about 120ºC, which sometimes ignited.

Small-scale tests

- Name and type of test
- Organisations which use the test
- Energetic materials for which there is data
- Principle and physical description
  - Schematics
  - Dimensions and confinement
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Summary

NIMIC will continue working on these projects

Participation amongst the NIMIC nations is welcome

Contact NIMIC for more details on these Topics

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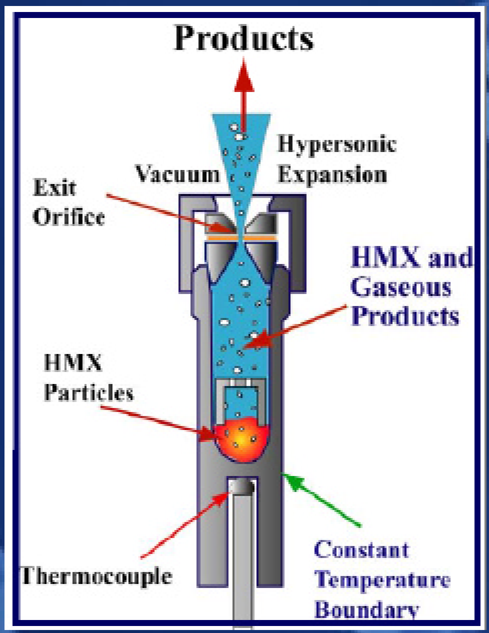
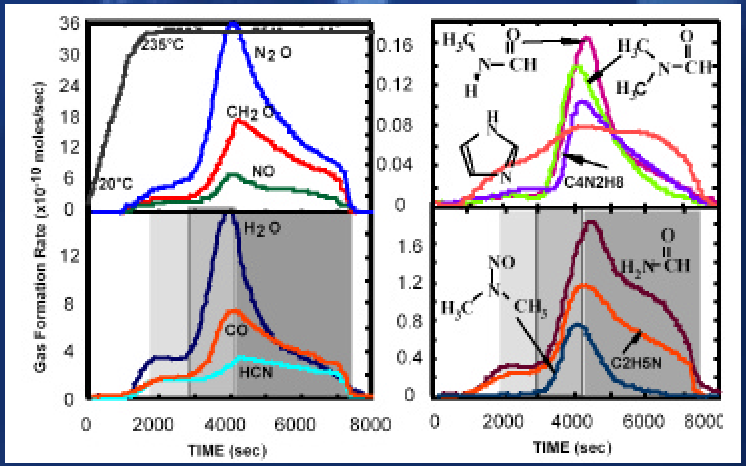
Simultaneous Thermogravimetric modulated-beam mass spectrometry (STMBMS)





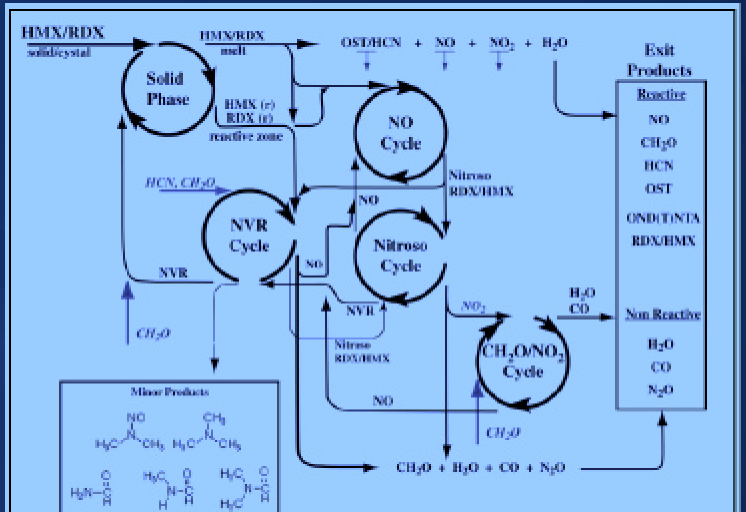


Figure 4. Reaction scheme showing the physical and chemical processes that control the thermal decomposition of RDX and HMX.

"Thermal decomposition of HMX: morphological and chemical changes induced at slow decomposition rates." R. Behrens; 12th International Detonation Symposium, August 11 - 16, 2002;

BA

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Need Techniques to Determine Consequences of Ageing on IMness

- **Use Small-scale Testing and Modelling Data**
  - **Need to determine what properties are changing and how they impact IM Characteristics**
    - **Particularly interested in changes in mechanical properties in plastic bonded materials**
    - **Increases in shock sensitivity**
    - **Increases in porosity**
  - **Useful tests and models have been identified**

Small-Scale Testing and Modelling Workshop, Jan. 2000

Cook-off Test Datasheets

Mechanical stimuli – identified useful tests