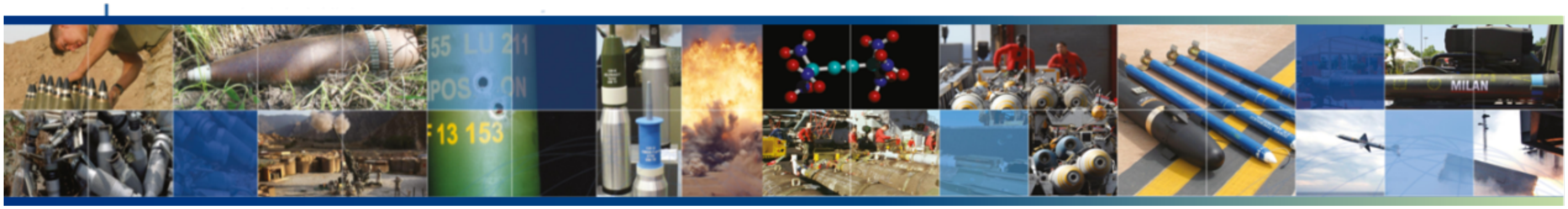
MSIAC Munitions Safety Information Analysis Center

Supporting Member Nations in the Enhancement of their Munitions Life Cycle Safety



Qualification and Energetic Materials Challenges

IMEMTS

Portland, OR, USA

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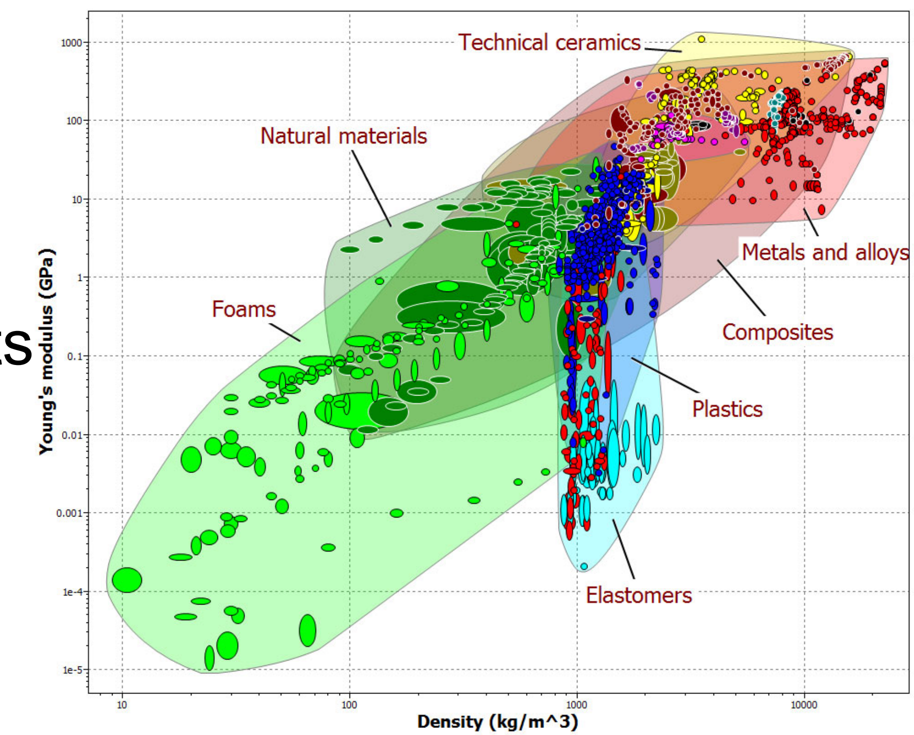
Outline

- Introduction
- MSIAC Workshops – The Repeating Issue
- Materials in Munitions
- Models & Benefits
- Current Testing Requirements
- How to Move Forward



Multiple materials present in munitions
Visualising the bulk engineering materials in property space (ρ vs ε)
https://www.grantadesign.com/products/ces/find.htm

Material Properties Data & Modelling

- NIMIC/MSIAC workshops
  - Cook Off
  - Shaped Charge Jet
  - Fragment Impact
  - XDT
  - Sympathetic Reaction
- Gaps highlighted

Models

- Software exchange (1993)
- Lack of input conditions (1992)
- Improve models through collaboration (2004)

Material Characterisation - Mechanical

- Requirement for high strain rate properties (1992)
- Strain rates at temperature and pressures (2000)

Material Characterisation - Thermal

- Data needed at elevated temperatures (1993)
- Collaborative database on energetic & inert material properties (2004)
- Prioritise and identify standardised material data sets for SCJ (2014) and thermal (2016)

- Few explosives have all experimentally determined observables[1]
- Why?
  - Improved models
  - Technology provides wider access to capability (Moore's Law)
  - No data collection (needs don't match requirements)

1. Peterson J. R., Wight, C. A. "An Eulerian-Lagrangian Computational Model for Deflagration and Detonation of High Explosives", (**2012**), 159, 2491-2499.

What types of parameters

Physical	Chemical	Thermal	Mechanical
State (s, l, g)	Enthalpy of formation (kJ mol^{-1})	Thermal conductivity (W g^{-1}.K^{-1})	Tensile strength (MPa)
Density (g cm^{-3})	Enthalpy of combustion (kJ mol^{-1})	CTE (µm m^{-1})	Compressive strength (MPa)
Molecular weight (g mol^{-1})	Enthalpy of detonation (kJ mol^{-1})	Specific heat capacity (J g^{-1}.K^{-1})	Complex modulus
Melting point (°C)	Solubility (mg L^{-1})		
Boiling point (°C)			
Decomposition temperature (°C)			
Hazard	**Shock**	**Performance**	
Impact (J)	Gap (GPa)	Detonation velocity (km s^{-1})	
Friction (N)	Shock velocity (km s^{-1})	Detonation pressure (GPa)	
ESD (J)	Particle velocity (km s^{-1})	Critical diameter (mm)	
	Run distance (mm)	Gurney energy (kJ kg^{-1})	

What are the challenges?

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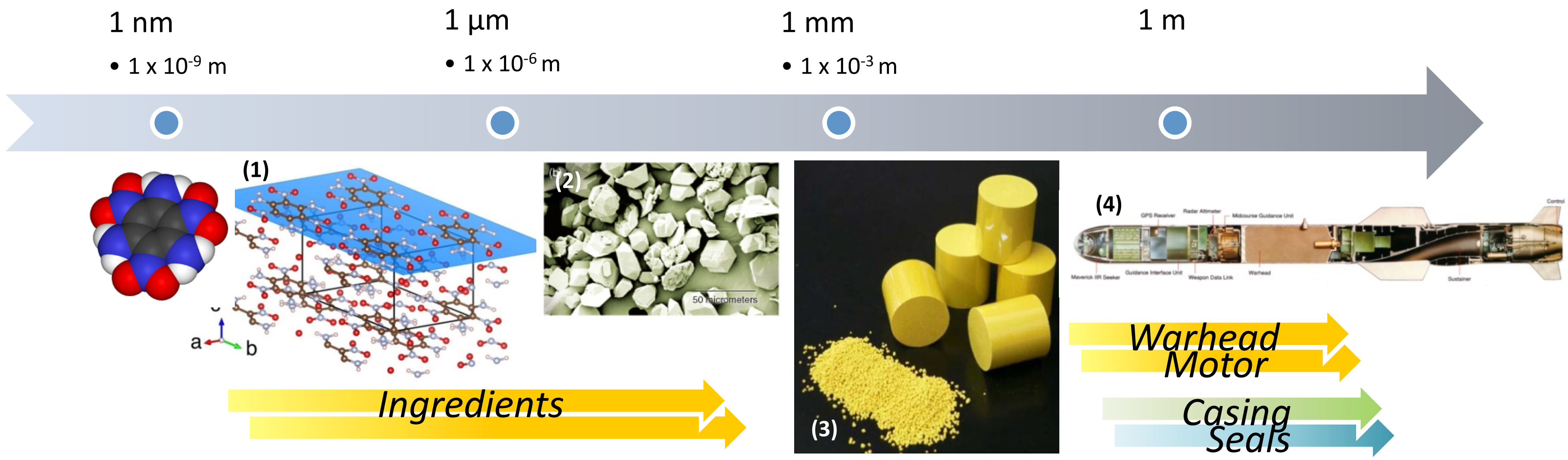
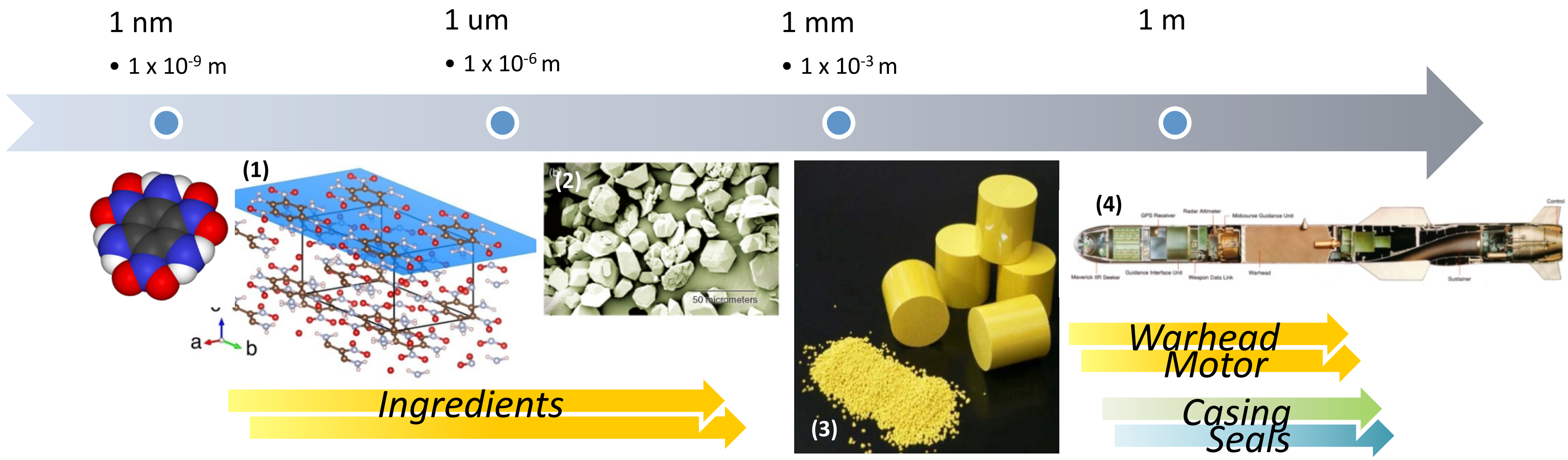


- Multiple materials present within munitions
  - Focus on energetic materials (this presentation)
- Understanding required across all scales
  - Material properties (physical, chemical, mechanical) to system response
- From single molecule to warhead
  - Scale – 10 orders of magnitude (nm to m)
  - Mass – 6 orders of magnitude (mg to kg)

1. Luscher, D. J. et al, *Crystals* **2017**, 7(5), 138
2. Heller, A. Science & Technology Review **2009**, 4-10
3. Price, D. IMEMTS, **2010**,
4. Kopp, C. AGM-84E SLAM, **1988**

Current Situation - Munition



- Testing focussed on performance and safety in storage, transport and service
  - STANAG 4123 / UN Hazard Classification
  - AOP-15 / Safety & Suitability for Service
  - STANAG 4439 / Insensitive Munitions
- Criteria for tests can be binary - usually pass/fail
  - Limited number of tests
  - High costs
- Reliance on ‘whole body of evidence’ for assessment

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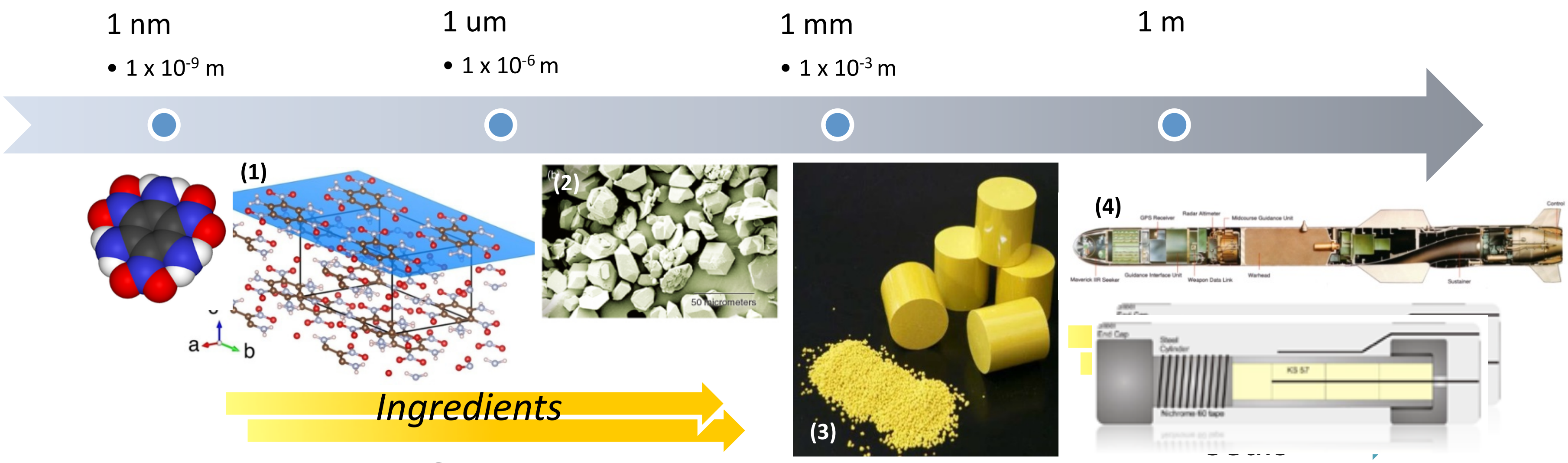
Current Situation - Sub-scale

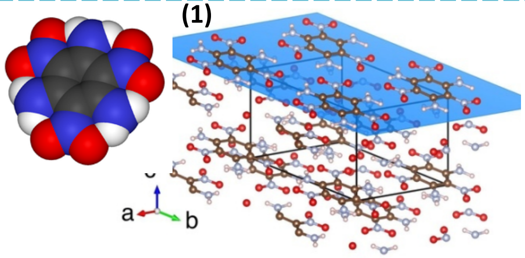


- Experiments performed to elucidate response to a hazard
- Some tests determine scientific understanding whilst other provide pass/fail
  - Friability
  - EMTAP 36 (UK Fragment Impact)
- All results are compared against existing EM knowledge
- Difficult to use information for prediction of munition response

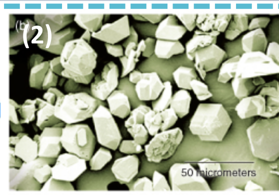
Qualification

TRL1 | *Material Properties* | *AOP-7* | TRL9

(1)

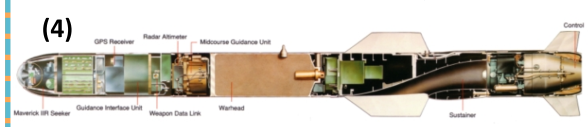


(2)



(3)

(4)



MSDS

Hazard Classification

- Development cycle – no requirement to fully characterise materials
- Testing focussed on performance and safety
- AOP-7
  - Qualification for inclusion of energetic material in a military munition
- Hazard Classification
  - Assessment for transportation
- Material Safety Data Sheets
  - Some physical and chemical properties

Known Issues
EM down selection based on performance

AOP-7

- Qualification of new EM based on assessment of **safety** and **performance**
  - Agreed minimum data set
  - Whether the EM characteristics change during the lifecycle
  - Information on the chemical and physical properties *shall* be provided
  - Compliance with National H&S requirements *shall* be provided
    - MSDS
    - EHDS
- Shall
  - Can be interpreted as not mandated

- Chemical, Physical and Mechanical Properties:
  - **Stability & Thermal Characterization**, Variation of Properties with Age, **Compatibility**, Density, Melting Point, Thermal Characterisation, Glass Transition Point and **Mechanical/Rheological Properties**
- Hazard Assessment
  - **Ignition Temperature**, **Explosive Response when Ignited (Confined and Unconfined)**, **Electrostatic Discharge**, **Impact**, **Friction**, and **Shock**
- Performance Assessment:
  - Detonation Velocity and **Critical Diameter**
- Those indicted in bold are mandatory qualification data or properties

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Qualification Program

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Category	Test Performed	Criteria
Stability Characterisation	Vacuum Thermal Stability	< 2 cm^3 gas
	Thermal Stability	No change
Thermal Characterisation	Thermo gravimetric analysis	
	Self Heating (onset)	
	Compatibility	< 2 cm^3 gas
Ignition Temperature	Woods Metal Bath	
	Henkin Time to Explosion	
	Critical Temperature	> 82 °C
	1-L Cook Off	
Explosive Response	Variable Confinement (SCO)	Deflagration or less
	Variable Confinement (FCO)	Deflagration or less
	Small Scale Burn	Less than explosion
Sensitivity Tests	ESD	No reaction at 0.25 J
	Impact	
	Friction	> 96 N
	Shock Sensitivity	
	Cap Test	
Chemical, Physical, Mechanical	CTE	
	Density	
	Growth	1 %
	Exudation	0.1 %
	Young's Modulus	
	Compressive Strength	
	Strain @ Max Stress	
	Cube Cracking	No fissures
Variation with Age	Ageing protocol	
Toxicity Evaluation	MSDS	
Performance Properties	Detonation Velocity	
	Dent Depth	
	Explosivity of Dust	
	Critical Diameter	

- US Example
  - IMX-104 qualification
  - Zunino et al (IMEMTS 2012)
- Greater testing requirements than AOP-7 minimum
- Tests
  - Included chemical & physical parameters
- Gaps
  - Not reported
  - C_P
  - Wedge

Material Safety Data Sheet

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- Global Harmonised System
  - EU requirement CLP (EU1272/2008)
  - Information gathered by manufacturer for Material Safety Data Sheet (MSDS)
  - 16 sections including Hazards, Transport and….
- Chemical & Physical Properties
  - Section 9
  - No consistency in reported information
    - From 0/20 to 18/20
  - Data usually only gathered at one temperature and/or pressure
    - 25°C (not consistent)
    - 133.3 hPa (also not consistent)
- So how can we measure the parameters?

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

a)	Appearance	Form: crystalline Colour: light yellow
b)	Odour	No data available
c)	Odour Threshold	No data available
d)	pH	No data available
e)	Melting point/freezing point	Melting point/range: 67 - 70 °C
f)	Initial boiling point and boiling range	No data available
g)	Flash point	155.0 °C - closed cup
h)	Evaporation rate	No data available
i)	Flammability (solid, gas)	No data available
j)	Upper/lower flammability or explosive limits	No data available
k)	Vapour pressure	133.3 hPa at 157.7 °C 1.3 hPa at 102.7 °C
l)	Vapour density	No data available
m)	Relative density	No data available
n)	Water solubility	No data available
o)	Partition coefficient: n-octanol/water	No data available
p)	Auto-ignition temperature	No data available
q)	Decomposition temperature	No data available
r)	Viscosity	No data available
s)	Explosive properties	No data available
t)	Oxidizing properties	No data available

9.2 Other safety information
No data available

1. Sigma-Aldrich “2,4-Dinitrotoluene”, (**2015**), Safety Data Sheet.

Whole Body of Evidence

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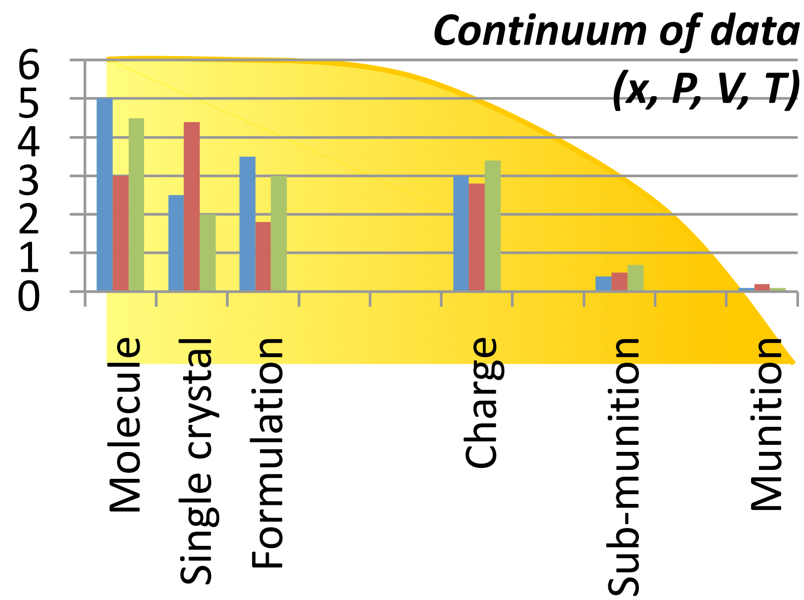
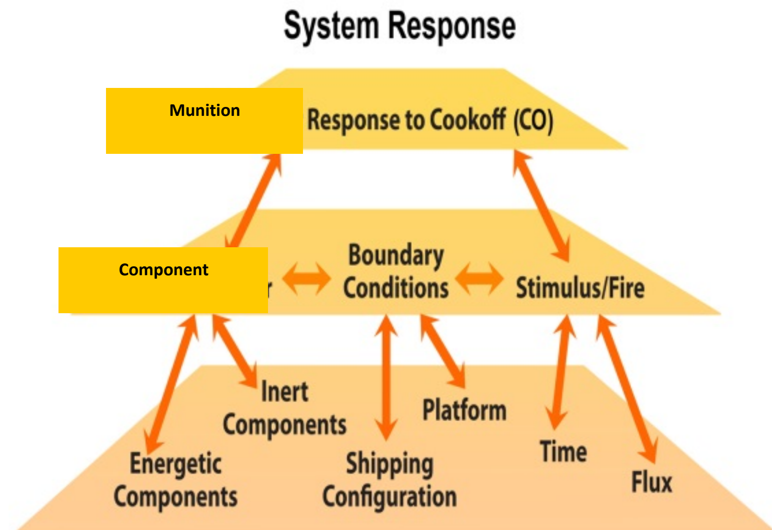
- Understand munition response to key abnormal threats include
  - Thermal
  - Shock
  - Impact
- Discrete data sets available
  - Relates to specific tests
- Therefore we use
  - Models to test our understanding…but
  - Do we have the right information

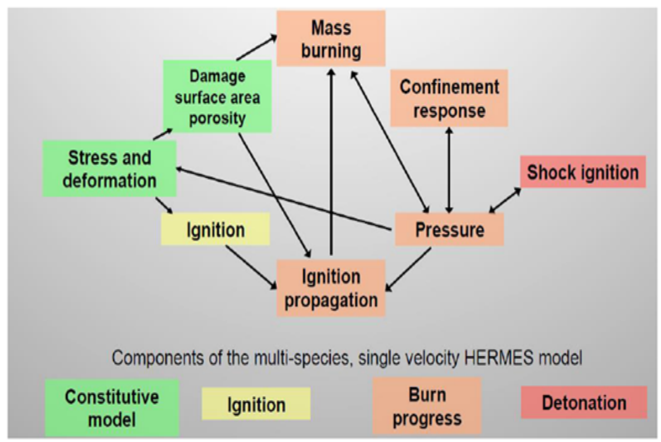




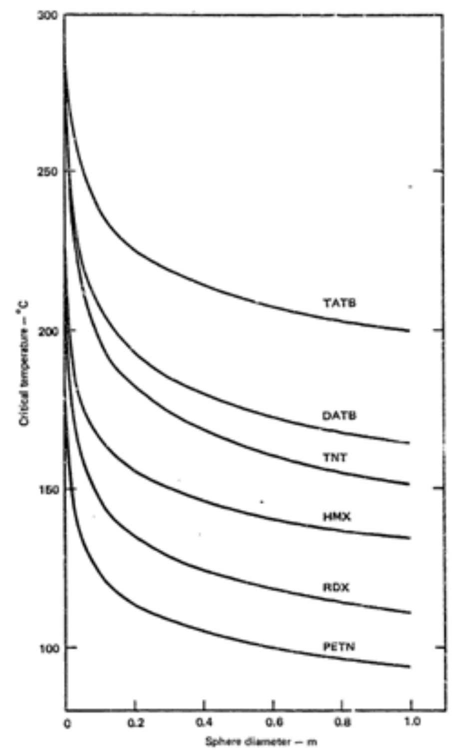
Development of a scaling hierarchy for cook off hazards
Atwood, A. *et al*. (**2010**), IMEMTS, Munich

Models

- Greater reliance on modelling for
  - Simulation
  - Safety assessment
  - Ultimate aim →
    - ➢ Prediction
- Development of computational tools for simulating abnormal thermal events (e.g.)
  - Critical Temperature[1]
  - ALE3D[2]
    - ➢ LLNL
  - Eularian & Lagrangian[3]
    - ➢ University of Utah
  - Multiple codes
    - ➢ SNL
- Thermal Hazards
- Time to ignition
  - Thermal & physical parameters
  - Chemistry
  - Confinement - complex



The HERMES model components
Development of thermal violence cookoff tests at AWE
Cook, M. (**2016**), SoCO, Atlanta



$$\frac{E_a}{T_m} = R \ln\left[\frac{a^2 \rho Q Z E_a}{T_m^2 \lambda \delta R}\right]$$

Critical temperature[1]

1. Rogers, R. N. Thermochimica Acta, (**1975**), 11, 131-139
2. McClelland, M. A., Tran, T. D., Cunningham, B. J., Weese, R. K., Maienschein, J. L.. "Cookoff Response of PBXN-109: Material Characterization and ALE3D Model", (**2000**), JANNAF, Monterey, CA.
3. Peterson J. R., Wight, C. A. "An Eulerian-Lagrangian Computational Model for Deflagration and Detonation of High Explosives", (**2012**), 159, 2491-2499.

Benefits of Modelling

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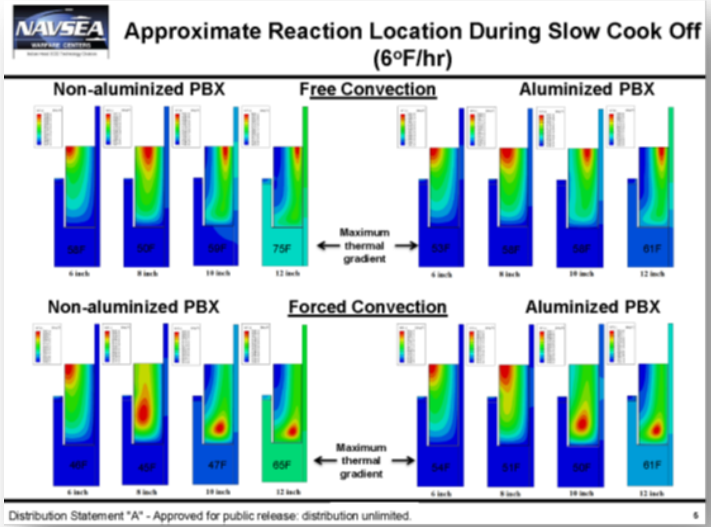
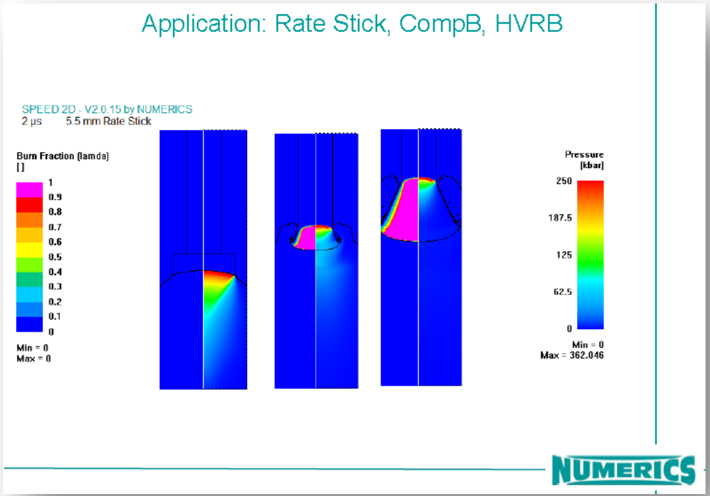


Clark, K. (**2016**), SoCO, Atlanta



Hartmann, T; Rottenkolber, E. (**2014**), SCJ, Brest

- Assess interdependence of, and sensitivity to changes in, variables
  - Size
  - Volume
  - Materials
  - External conditions
- Test mechanistic understanding
- Increases confidence in observed behaviour
- Provides insight into reaction that can not always be observed experimentally
  - Time to reaction
  - Location of reaction
  - Reaction growth
  - But cannot reliably predict reaction violence

Modelling Requirements

- Requirement to populate model(s) with experimental data as [$f_n(T)$] and [$f_n(P)$]
  - Coefficient of Thermal Expansion[1]
  - Specific Heat Capacity
    - Solid phase[1]
    - Gaseous phase[2]
  - Shear Modulus[1]
  - Bulk Modulus[1]
  - Reaction kinetics, detonation[1]
  - Condensed Phase Activation Energy[2]

Temperature
-60 °C to 500 °C
(model dependent)
Pressure
0.1 MPa to 50 GPa
(model dependent)

- Good models need
  - Well defined experiments
  - Information on the boundary conditions
  - An iterative development cycle supported by progressive experimental design and testing programme
- Discussion
  - Mismatch in requirement to obtain data

1. McClelland, M. A., Tran, T. D., Cunningham, B. J., Weese, R. K., Maienschein, J. L.. "Cookoff Response of PBXN-109: Material Characterization and ALE3D Model", (**2000**), JANNAF, Monterey, CA.
2. Peterson J. R., Wight, C. A. "An Eulerian-Lagrangian Computational Model for Deflagration and Detonation of High Explosives", (**2012**), 159, 2491-2499.

Methods for Obtaining Parameters

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- Chemical & Physical Properties
  - MSDS
    - Density, vapour pressure (if recorded)
  - AOP-7
    - Onset of decomposition; Ageing includes mechanical properties
- Parameters still required
  - Function of temperature (e.g. -60 to 120°C – material dependent)
  - Determine other factors from these selected parameters e.g. critical temperature, enthalpy of formation

Enthalpy of Combustion	ΔH_c	kJ mol^{-1}	ASTM D 4809	liquid hydrocarbon fuels	Bomb Calorimetry

MSIAC Methods for Obtaining Parameters

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Thermal		**Units**			
Vapour pressure	P_{vap}	hPa			
Heat Capacity	C_p	$J\ g^{-1}.°C^{-1}$			
Thermal Conductivity	λ	$W\ cm^{-1}.°C^{-1}$			
Coefficient of Thermal Expansion	*CTE*	$\mu m\ m^{-1}.°C^{-1}$			
Activation Energy	E_a	$kJ\ mol^{-1}$			
Physical					
Density	ρ	$g\ cm^{-3}$			
Enthalpy of Combustion	ΔH_c	$kJ\ mol^{-1}$	ASTM D 4809	liquid hydrocarbon fuels	Bomb Calorimetry

MSIAC Methods for Obtaining Parameters

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  - MSDS
    - Density, vapour pressure (if recorded)
  - AOP-7
    - Onset of decomposition; Ageing includes mechanical properties
- Parameters still required
  - Function of temperature (e.g. -60 to 120°C – material & model dependent)
  - Determine other factors from these selected parameters e.g. critical temperature, enthalpy of formation

Thermal		**Units**	**Existing Methods**	**Notes**	**Equipment**
Vapour pressure	P_{vap}	hPa	ASTM E 1782		Differential Scanning Calorimetry or Differential Thermal Analysis
Heat Capacity	C_p	$J\ g^{-1}.°C^{-1}$	ASTM E 1269		Differential Scanning Calorimetry
Thermal Conductivity	λ	$W\ cm^{-1}.°C^{-1}$	ASTM E 1225		Longitudinal Heat Flow
			ASTM C 518		Heat Flow Meter Apparatus
Coefficient of Thermal Expansion	*CTE*	$\mu m\ m^{-1}.°C^{-1}$	ASTM E 831 STANAG 4525	Thermochemical analysis	Thermal Mechanical Analyser (TMA)
			ASTM E 2716		Sinusoidal Modulated Temperature Differential Scanning Calorimetry
Activation Energy	E_a	$kJ\ mol^{-1}$	ASTM E 1614 STANAG 4147		Thermogravimetry Using Ozawa/ Flynn/Wall Method
			ASTM E 698	Thermally unstable materials	Differential Scanning Calorimetry
Physical					
Density	ρ	$g\ cm^{-3}$	ASTM D 792		Displacement
			ASTM D 1217		Pycnometry
Enthalpy of Combustion	ΔH_c	$kJ\ mol^{-1}$	ASTM D 4809	liquid hydrocarbon fuels	Bomb Calorimetry

Discussion

- Data
  - Capability exists to better characterise materials
  - Request for chemical, physical and mechanical information is usually much later in the qualification process (type qualification)
  - Propose at an earlier stage in development (pre-AOP-7)
- Modelling
  - Modelling is being used throughout munition development
    - Design
    - Safety assessment
    - Prediction
  - Access to codes and models across most MSIAC nations
  - Capability to run simulations is now faster and cheaper
- Benefits
  - Reduced time in development
  - Greater insight into internal behaviour
  - Improved assessment of time to reaction
  - Well-posed models enable easer design modifications
  - Increased confidence in assessed response level
  - Helps assess programme risk

Stakeholders

Manufacturers
Design Authorities
Safety Authorities
Modellers
Experimentalist

MSIAC

Supporting Munitions Safety

How is MSIAC helping?

- Enabling exchange of information
  - Workshops
- Generating guidance on models and methodology
  - L-195 (Babcock & van der Voort)
  - L-213 (Babcock)
- Data reviews
  - L-198 (Andrews)
- Repository for data
  - Energetic Materials Compendium (EMC)
- Developing models
  - TEMPER
- Promoting discussion

Acknowledgements

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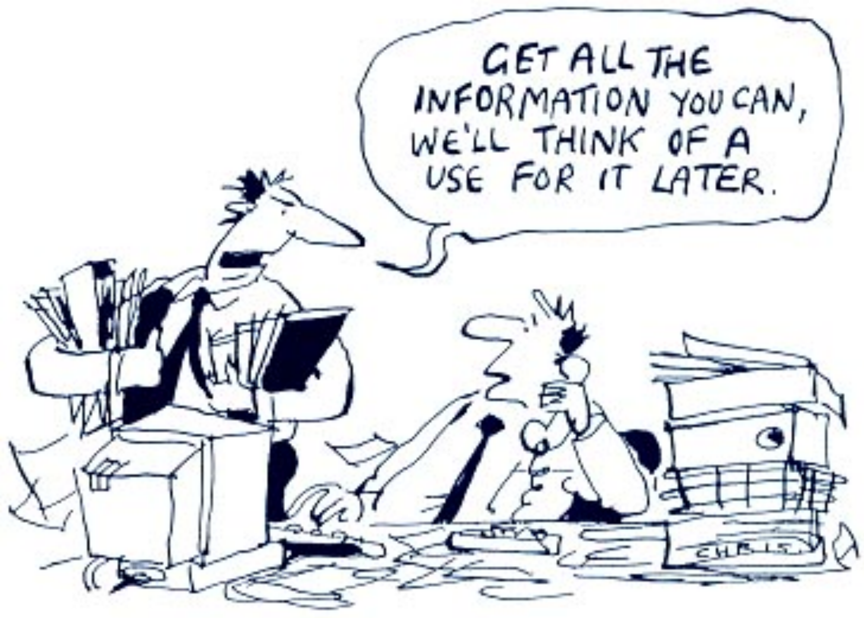

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