Characterisation of aged Polymer Bonded eXplosives - Development of STANAG 4666

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Overview

1. Introduction Lifetime
2. History of STANAG
3. Workshop in Finland (2005)
4. Reference documents - Techniques
5. Aim of STANAG
6. What is changing, making material critical
7. Conclusion
8. Acknowledgement
Lifetime

Out-of-Area operations

IM - signature

Package

New Energetics

Life-cycle costs

Environment

Surveillance – what / how / frequency

Tracking / tracing

Condition logging

Lifetime / safety / functionality

IMEMTS - Miami, 15-18 October 2007
Insensitive Munitions

- RNLA had not yet insensitive munitions
- TNO advised RNLA on adequate protection

Anti tank weapon at the back of jeep in Afghanistan: 1 bullet on AT-4 could be fatal
Transport conditions - example
Current-future activities for SG1

• In 2003 a survey of the member nations was conducted to determine which standards are needed

• Those high on the list include;

  • Standardization of surveillance activities
  • Update of ingredients specifications and methods
  • Standard to cover “Ageing of PBXs”
History of STANAG 4666

• MSIAC workshop – May 2005

• Start for AC-326-SG 1 – CNG to set up a new document;

  The aim of this agreement is to standardize accelerated ageing and testing protocol by which aged samples of PBX’s, cast-cured compositions using ‘inert’ or ‘energetic’ binders can be assessed and compared.

• Title STANAG 4666 :
  Explosives: Explosives, assessment of ageing of Polymer Bonded Explosives (PBX’s) cast cured compositions using inert or energetic binders

• Custodian nation : The Netherlands - TNO
Areas to cover by the working group in Finland

- What other specifications do people use to look at ageing of PBXs
- What is the aim/goal of this STANAG
- Can the STANAG help to fill gaps in STANAG 4170
- What is the scope of materials covered by this STANAG, e.g. for cast-cured inert binder PBXs only, pressed, etc
- Is only an update of STANAG 4581 required?
- Can/should sentencing criteria be suggested/included
- Is the STANAG to be designed to help find the critical ageing mechanisms of the PBX (e.g. a decision tree) or is this assumed prior to application?
NAVSEA 8020.C

- Spells out mandatory requirements to qualify new energetic materials for USA usage
- Accelerated ageing is an essential part of the qualification process
- Conditions of ageing;
  - 60°C, 1, 2, 4, 6, 8 months, sealed containers
  - 70°C: 1, 2, 4, 6 months, sealed containers
  - 25°C, 30% RH - until final (type qualification)

*Compositions based on polyester binders are aged under controlled 30% RH*
NAVSEA 8020.C

Requirements to meet qualification include:

• No substantial change in:
  • Ignition temperature (DTA)
  • Impact sensitivity
  • Friction sensitivity
  • Shock sensitivity
  • Stabiliser/antioxidant level (% change)

• >20% change in mechanical properties may require further tests

• Safe(shelf) life at 25°C – minimum 20% stabiliser remaining at 20 years

• Safe use(service) life - <20% change in post-cure properties, no substantial change in shock sensitivity, no fissures after 30 days at 60°C in x-ray fissure test
PBX – energetic materials /// binders

HTPB

O=C\(\text{CH}_2\text{CH}_3\)

Poly-Urethane

RDX

NTO

HMX
CAST PBX

- 80 – 90 % solid load
- 10 – 20 % binder
- Binders: HTPB, GAP, PolyNimmo, PolyGlyl, PolyGlyl, HTPE (future ?)
- Energetic Material
  - RDX, HMX, RS-RDX, AP, AI, AN, TATB, NTO, DOA, DOS, IPD, TMETN, BDNPA/F, TEGDN
  - FOX-7, CL-20, AND, GAP-azide
What is leading to IM properties vs Ageing ?

• Mechanical properties
• Friability
• Sensitivity
• Burning / detonation process
• One or two (or even more) IM compositions in a article
• Influence of humidity on one component or all
• Taking into account all stabilizers ?
First line of test methods

- Molecular weight (diffusion processes / hardening) [GPC]
- Detonation velocity
- Porosity (ultrasound sufficient enough ?)
- Flyer impact
- Focusing on energetic part or binder ?
- What is maximum ageing temperature
- Ignitability – separate or ignition train
STANAG 4581 - Contents

• Accelerated ageing conditions
  • Bulk block sample
  • “Sealed” condition
  • Only one temperature – 60°C, 3/6 months

• How to prepare test samples from aged ‘bulk’ material

• Chemical analysis methods
  • Sol content
  • Cross link density
  • HPLC analysis of antioxidant content
  • GC analysis of plasticiser content

• Mechanical tests
  • Uniaxial tensile test (STANAG 4506)
  • Dynamic Mechanical analysis (DMA) (STANAG 4540)
  • Shore Hardness (ASTM D2240-00)

• Refers to many other STANAGS for actual testing methods
Tests methods

Possible new methods in STANAG 4666 edition 1

• Tests for filler-binder interface
• Dilatometry (pressure)
• Microscopy (SEM, optical, FTIR imaging)
• TMA (expansion)
• Friability (critical dp/dt, critical velocity, number of repeats/velocities….)
• Small scale sensitivity tests – one company uses ESD as key screening method
• Hardness techniques – shore hardness, DMA, others?
• Shock sensitivity
Proposed test methods in draft STANAG 4666

CHEMICAL TESTS
• 1A Measurement of the soluble fraction
• 1B Measurement of crosslink density
• 1C Measurement of antioxidant content (HPLC)
• 1D Measurement of plasticizer content

MECHANICAL TESTS
• 2A Uniaxial tensile test
• 2B Dynamic mechanical analysis
• 2C Measurement of Shore A hardness
• 2D Thermal Mechanical Analyses
Cont’d

**THERMAL TESTS**
- 3A Differential Scanning Calorimetry
- 3B Thermogravimetry
- 3C Pressure Vacuum Stability Test
- 3D Heat Flow Calorimetry (HFC)

**OTHER TESTS**
- 4A Scanning Electron Microscopy
- 4B Shock Sensitivity
- 4C Friability Test
- 4D FTIR spectroscopy
Examples for new techniques
SEM
Thermal analysis (TG-SDTA)
Kinetics

- The applied heating rates are: 0.25 K/min; 0.5 K/min; 1 K/min; 2 K/min; 5 K/min; 7.5 K/min; en 10 K/min
Ignition temperature

![Graph showing the relationship between heating rate and ignition temperature.](image)

- **Ignition temperature**
  - X-axis: Heating rate / (K/min)
  - Y-axis: Ignition / °C

- Heating rate data points:
  - 0.0 K/min: Ignition temperature is approximately 220 °C
  - 2.0 K/min: Ignition temperature is approximately 260 °C
  - 4.0 K/min: Ignition temperature is approximately 270 °C
  - 6.0 K/min: Ignition temperature is approximately 275 °C
  - 8.0 K/min: Ignition temperature is approximately 280 °C
  - 10.0 K/min: Ignition temperature is approximately 290 °C
Aged at 60 / 70 / 80 C

Decomposition profile is changing as function of ageing temperature
Discussion / Conclusion
Discussion / conclusion

- Proposed test methods has to be evaluated
- Additional tests are advisable to be performed on different compositions by participating countries
- First edition of STANAG will be set-up and forwarded to the SG-1 members
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