

In-service Chemistry

by Libbie Bush

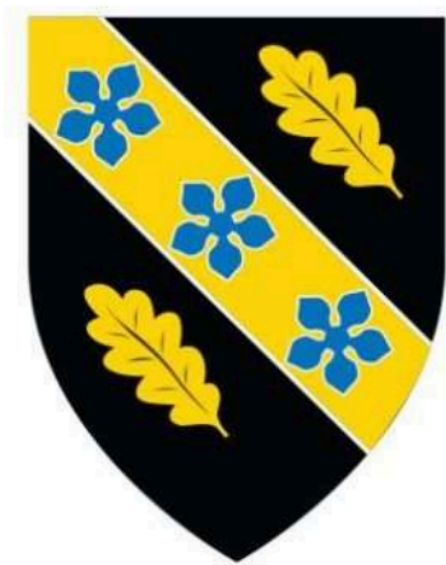
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Energetic Material Lifecycle In-Service Chemistry

L6 -OME Chemistry of OME (ACDA6020)

2223155

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Abbreviations

NC - Nitrocellulose

NG - nitro-glycerine

COMP B – Composition B

TNT —2,4,6-Trinitrotoluene

RDX — Cyclotrimethylenetrinitramine

HPLC — High-Performance Liquid Chromatography

FTIR — Fourier Transform Infrared Spectroscopy

EMTAP — Energetic Materials Technology Assessment Program

NATO — North Atlantic Treaty Organization

STANAG — Standardization Agreement

Abstract

Energetic materials possess high energy densities that render them thermodynamically unstable, yet they remain usable due to kinetic constraints that limit decomposition under controlled conditions. The stability of these materials is strongly influenced by molecular structure and functional group chemistry, with nitrate esters generally exhibiting greater instability than aromatic nitro compounds. During storage and service life, slow decomposition processes occur, which may be accelerated by chemical ageing mechanisms such as impurity accumulation and autocatalytic reactions. These processes can reduce activation energy barriers, leading to a progressive loss of kinetic stability and increased sensitivity. Such degradation has direct implications for safety, performance, and Insensitive Munition compliance. This paper highlights the importance of understanding ageing-driven decomposition mechanisms and emphasises the role of systematic in-service surveillance and condition monitoring, as defined in NATO STANAG 4675, to support continued safety assurance and informed life-assessment of munitions.

Introduction

During the lifecycle of an energetic material, it is influenced by different chemical principles that can be grouped into four key stages explain in Figure 1: design, manufacture, in-service surveillance and disposal. This report focuses on chemical principles within in-service surveillance that determine the material's stability, ageing behaviour, compatibility, and performance reliability during its operational service life.

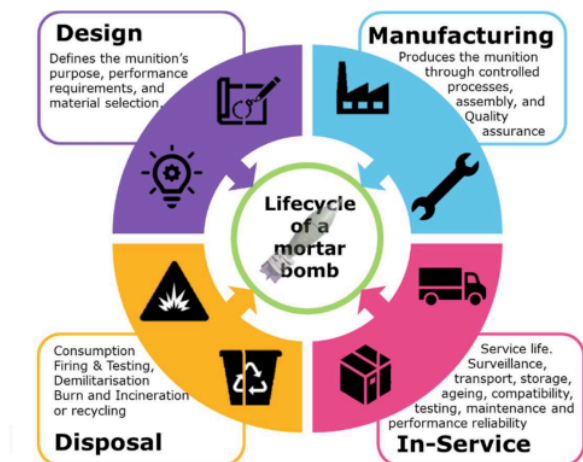


Figure 1 - Lifecycle of a Mortar Bomb

To illustrate these principles, this report uses the example of an 81mm mortar bomb, as shown in Figure 2, focusing on the high explosives and propellants within the bomb.

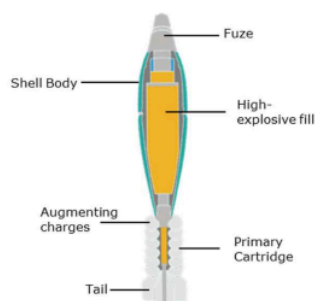


Figure 2 - Mortar Bomb [1]

The high explosive used in this example is Composition B (comp B), which is made up of 59.5% RDX, 39.5% TNT and 1% wax. [2] The Primary cartridge uses a double-base propellant containing nitroglycerine (NG) and Nitrocellulose (NC), and the augmenting charge case is made from NC, then filled with ball power which is a single-based propellant with spherical grains. [3]

Thermal stability and ageing

Metastability and Slow Decomposition

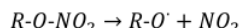
Energetic materials have a high energy density compared to their decomposition products, making them thermodynamically unstable. This is partially due to the reactive covalent bonds within the molecular structure. However, the function groups also dictated the stability, for instance nitrate esters being much more unstable than aromatic nitro groups. Despite this, under controlled conditions, they can be kinetically stable as they have high activation energy barriers that require a stimulus, meaning the decomposition is very slow over time. However, chemical ageing processes can accelerate these decomposition pathways and reduce the activation energy and therefore kinetic stability over time, increasing their sensitivity. [4]

Autocatalytic Decomposition

An autocatalyst is a substance that speeds up a chemical reaction while also being a product of the reaction itself. The more autocatalysts form, the faster the reaction accelerates, creating a feedback loop that will continue to accelerate until it has fully decomposed or until an external stimulus slows the reaction. [5]

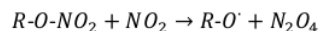
Autocatalysts are most common in nitrate esters, as they are unstable. Over time they naturally decompose slowly. This initial reaction of a general nitrate ester is shown in Equation 1.

Equation 1 - Initial Autocatalyst decomposition reaction



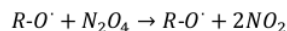
The NO_2 is formed from the initial reaction this then reacts with another nitrate ester group to form N_2O_4 shown in Equation 2

Equation 2 - Autocatalytic decomposition reaction 2



The N_2O_4 then reform two NO_2 shown in Equation 3 which can react with two more nitrate esters, the process continues.

Equation 3 - Autocatalytic decomposition reaction 3



After each reaction, the amount of NO_2 doubles and the process accelerates. If this reaction is not controlled it could cause runaway reactions, as well as the activation energy lowers the more autocatalysis that forms, causing the material to lose its kinetic stability and become less predictable [6]

Arrhenius Equation

The Arrhenius equation describes the exponential dependence of chemical ageing rate on temperature and activation energy. The equation is shown below in Equation 4

Equation 4 - Arrhenius Equation [7]

$$k = Ae^{-E_a/RT}$$

k : Rate constant

A : Pre-exponential factor

E_a : Activation energy

R : Gas constant

T : Temperature (in Kelvin)

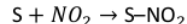
This equation shows that a small increase in temperature can produce a large increase in decomposition rate and therefore service life. As T increases E_a/RT becomes less negative, and the reaction rate increases, so there is more decomposition happening in the material. This shows the importance of having strict temperature control during storage to maintain kinetic stability for Long-term storage. [8]

Stabilisation Chemistry

Stabilisers are essential additives that tend to be aromatic amines that are added to single and double-based propellants. Their main function is to control the decomposition of nitrate esters by reacting with NO_2 , removing it from the system, and inhibiting the production of autocatalysts.

The stabiliser and NO_2 reaction has a lower activation energy than the nitrate ester and NO_2 , meaning that the NO_2 favours the reaction with the stabiliser and blocks the formation of autocatalysis. The general equation for this is shown in Equation 5 where S represents a stabiliser [9]

Equation 5 - Stabiliser reaction



Stabilisers act as a chemical clock to the ageing processes, as they are slowly consumed over time in the reaction above. They are not there to stop the breakdown of nitrate ester but delay it; they will still degrade over time. This method just slows down that reaction. They are a good way to show the product is ageing, as the amount of the stabiliser left shows the speed at which the nitrate esters are degrading [10]

Comb B ageing

TNT is an aromatic nitro compound that has relatively low sensitivity and chemical stability. RDX is a nitramine with high detonation power. The combination of these two high explosives is often used as it offers the performance of RDX with the stability of TNT. TNT softens at around 80 °C, while RDX remains solid up to about 200 °C. This means RDX can partially dissolve into TNT at these temperatures, and when it cools causes Recrystallization, wax migration and void formation. [11] This changes the packing arrangement and alters the lattice energy, causing areas where strain can increase and sites for hot spots that lower the activation energy, making the material much less kinetically stable. When the TNT softens, it can also produce an oil that can seep through the shell creating the appearance of 'Sweeting' [12]

Surveillance, Testing and Traceability

Surveillance programs confirm the chemical stability, safety and performance of a product while it is in service through regular testing and inspection. Samples should be withdrawn from a lot to test stabiliser depletion, moisture content, burn rate, and thermal stability using tools such as heat-flow calorimetry, HPLC, FTIR and EMAP testing, as well as test firing in accordance with STANAG 4675. [13] This data should be traceable throughout its life to see how chemical ageing has affected the product and its performance reliably, to give guidance on whether the material is considered safe to remain in service or no longer meets the chemical requirements [14].

Evaluation

Chemical ageing cannot be eliminated from a lifecycle only managed. As the service life of a product increases, the uncertainty in the thermal and kinetic stability, and the design assumption at the start of its lifespan may not be applicable. The functional group and bond chemistry of a molecule determines the ageing characteristics and the underlying chemistry within this. Inadequate in-service control accelerated the degradation process and created a material that becomes hard to control, safe degradation. Understanding the chemical principles and monitoring is key to ensuring a long and safe service life and performance reliability

Conclusion

Energetic materials are thermodynamically unstable but kinetically constrained under controlled conditions. Chemical ageing, including slow and autocatalytic decomposition, reduces kinetic stability and increases sensitivity over time. Effective in-service surveillance is therefore essential to manage safety, performance, and service-life risks

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Appendix

Energetic Material In-Service Chemistry

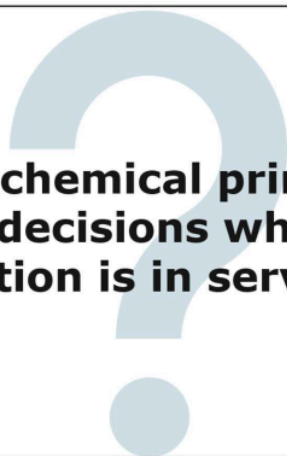
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Libbie Bush (2223155),



In - Service

Libbie Bush





**How do chemical principles
Govern decisions while the
Munition is in service**

Munition Life Cycle



Design



Manufacture



In Service



Disposal

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What is in-service



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Service life



BAE SYSTEMS

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Stabilisers

- Extend safe life
- Control ageing
- Help detect ageing
- Prevent autocatalysis



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Autocatalysis

- Catalyst speeds up reactions without being used
- *autocatalyst*
Autocatalysis is a product of the reaction
- Accelerates itself in a loop until it is interrupted

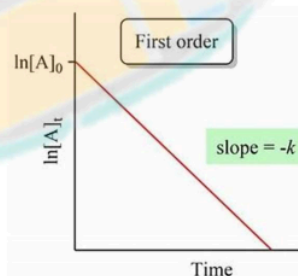


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Arrhenius equation

$$k = A \cdot e^{\frac{-E_a}{RT}}$$

- Reaction Rate (k)
- Activation Energy (E_a)
- Temperature (T)
- Rate Constant (R)



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Double-Based Propellant

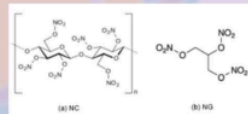


Stabiliser
Depletion

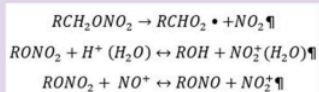
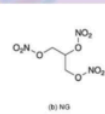


Migration

Nitrocellulose
NC



Nitroglycerin
NG



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Aging in COMP B

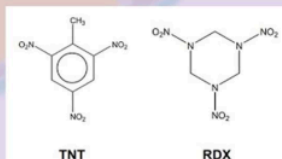


'Sweetening'



recrystallises

Composition – RDX/TNT 60/40%
with small amounts of wax



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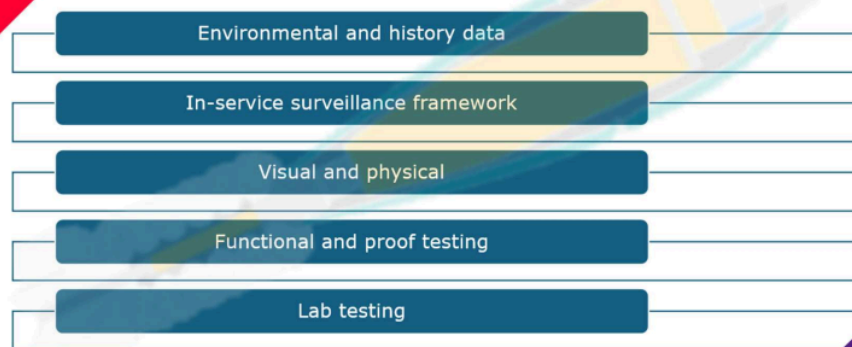
Why ^{the} Traceability is important

- Where has the product been
- What has the product experienced
- How is the product ageing so far
- Is it still safe



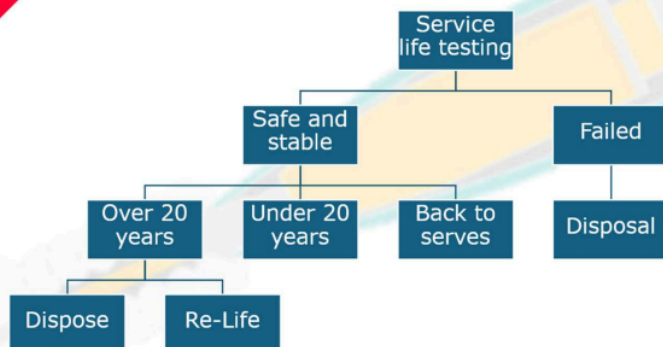
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Testing and Surveillance



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Testing and Surveillance



Questions?

 **BAE SYSTEMS**

FINAL GRADE

68/100

GENERAL COMMENTS

Engagement with Literature 12/15

Your reflection demonstrates strong engagement with appropriate literature, including peer-reviewed journals, textbooks, and NATO/defence standards, which are generally well selected and relevant to in-service chemistry. Sources are mostly integrated into the discussion rather than listed descriptively.

However, the presentation shows more limited evidence of literature engagement, with references present but not consistently used to support specific claims during delivery. Across both components, there are also technical referencing issues (e.g. missing access dates, formatting inconsistencies) that prevent a higher mark.

To improve: Ensure all claims in the presentation are explicitly supported by sources, and apply full IEEE consistency (including access dates) across all written work.

Knowledge and Understanding 14/20

The reflection shows strong chemical understanding at L6, particularly in explaining metastability, autocatalytic decomposition, stabilisation chemistry, and the role of activation energy and kinetics. Terminology is mostly accurate and explanations are clear.

In contrast, the presentation lacks chemical depth, relying on general descriptions with limited use of precise technical language and little explicit chemical reasoning. This imbalance reduces the overall mark despite the strength of the written work.

To improve: Bring the same level of chemical precision and depth from the reflection into the presentation, particularly when explaining mechanisms and ageing behaviour.

Cognitive and Intellectual Skills 16/25

In the reflection, you demonstrate analytical thinking by linking chemical ageing mechanisms to safety, sensitivity, and service-life decision-making, and by recognising that ageing can be managed but not eliminated.

The presentation, however, remains largely descriptive, with limited analysis and little interrogation of cause-and-effect relationships. Opportunities to evaluate alternatives, limitations, or uncertainties were not fully taken during delivery.

To improve: Move beyond “what happens” in the presentation and focus more explicitly on why certain chemical pathways or surveillance decisions matter compared with alternatives.

Practical Application Skills 15/25

Your reflection demonstrates good applied understanding of how chemistry informs in-service surveillance, stabiliser monitoring, and service-life decisions, with clear links to real OME contexts and standards.

The presentation applies this knowledge only at a surface level, with limited realistic examples and insufficient operational detail. While practical constraints are acknowledged, they are not explored in depth during delivery.

To improve: Include more concrete, realistic examples in the presentation (e.g. decision thresholds, failure criteria, or surveillance outcomes) to strengthen applied credibility.

Transferable Skills 11/15

The reflection is clearly structured, professional, and easy to follow, with a strong academic tone and logical progression of ideas.

The presentation delivery was weaker, with signs of limited preparation, spelling/grammar issues on slides,

and reduced clarity at times. These issues detract from the communication of otherwise sound ideas.

To improve: Improve slide accuracy, rehearse technical explanations more thoroughly, and ensure confident, well-prepared delivery that matches the quality of the written work.

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