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AOP-64

IN-SERVICE SURVEILLANCE OF MUNITIONS CONDITION MONITORING OF ENERGETIC MATERIALS

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NATO LETTER OF PROMULGATION

27 February 2017

1. The enclosed Allied Ordnance Publication AOP-64, Edition A, Version 1, IN-SERVICE SURVEILLANCE OF MUNITIONS CONDITION MONITORING OF ENERGETIC MATERIALS, which has been approved by the nations in the AC/326 CNAD AMMUNITION SAFETY GROUP, is promulgated herewith. The agreement of nations to use this publication is recorded in STANAG 4675.

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RECORD OF RESERVATIONS

CHAPTER	RECORD OF RESERVATION BY NATIONS
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RECORD OF SPECIFIC RESERVATIONS

[nation]	[detail of reservation]

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CHAPTER 1 IN-SERVICE SURVEILLANCE OF MUNITIONS – CONDITION MONITORING

1.1. ABBREVIATIONS AND ACRONYMS

1.1.1. List of Abbreviation and Acronyms

AAT	Accelerated ageing test
AP	Ammonium perchlorate
ASTM	American Society for Testing and Materials
CTPB	Carboxy-terminated polybutadiene
DMA	Dynamic mechanical analysis
DPA	Diphenylamine
DSC	Differential Scanning Calorimetry
ESD	Electrostatic discharge
GAP	Glycidyl azido polymer
GC	Gas chromatography
GC/MS	Gas chromatography/Mass spectrometry
GPC	Gel permeation chromatography
HFC	Heat-flow calorimetry
HMX	Octogen
HPLC	High performance liquid chromatography
HTPB	Hydroxyl-terminated polybutadiene
ISS	In-service surveillance
NC	Nitrocellulose
NDT	Non-destructive test
PBX	Polymer-bonded explosives
QSPT	Quasi-static pressure test
RDX	Hexogen
RES	Remaining efficient stabilizer
SEC	Size exclusion chromatography
SEM	Scanning electronic microscopy
SIP	Safe interval prediction test
TGA	Thermo-gravimetric analysis
TLC	Thin layer chromatography
TMA	Thermo-mechanical analysis
TNT	Trinitrotoluene
UV	Ultraviolet

1.2. SCOPE

In-service Surveillance (ISS) becomes increasingly important with the relatively fast changes in storage conditions that may occur when the ammunition is used in world-wide operations. The need for monitoring is heightened because of stress from elevated ambient temperatures, high temperature stress field storage conditions, more transport shocks, more vibration, changing air pressure, and changes in humidity conditions.

It is preferred that the minimum amount of ammunition is destroyed in order to assess its usability in field operations. This focuses the demand on non-destructive methods and predictive methods. The decisive question is at what ageing state of the energetic material is the fulfillment of the military mission no longer possible?

This AOP provides standards for the procedures required to assess continued or extended service use of an item. This includes the essential chemical and mechanical degradation modes of energetic materials that should be measured, and it provides examples of ISS programs performed by different nations. This document is relevant to scientists or engineers looking for guidance on test procedures and for program managers seeking guidance on defining minimum inspection standards for service munitions.

Each nation should tailor its program to specific requirements and environments that apply to its inventory. It is not possible to prescribe a single protocol for each energetic material that will suit all nations.

1.3. RELATED DOCUMENTS

AECTP-100	Environmental Guidelines for Defence Material
AECTP-200	Environmental Conditions
AECTP-300	Climatic Environmental Tests
AECTP-400	Mechanical Environmental Tests
AECTP-600	The Ten Step Method for Evaluating the Ability of Material to meet Extended Life Requirements
AOP-7	Manual of Tests for the Qualification of Explosive Materials for Military Use
AOP-15	Guidance on the Assessment of the Safety and Suitability for Service of Munitions for NATO Armed Forces
AOP-46	The Scientific Basis for the Whole Life Assessment of Munitions
AOP-48	Explosives, Nitrocellulose based Propellants, Stability Test Procedures and Requirements using Stabilizer Depletion
AOP-4682	ENERGETIC MATERIALS, TEST METHODS FOR INGREDIENTS
AOP 62	In-Service Surveillance of Munitions General Guidance

AOP-63	In-service Surveillance of Munitions, Sampling and Test Procedures
STANAG 4115	Definition and Determination of Ballistic Properties of Gun Propellants Definition of Pressure Terms and Their Interrelationship for Use in the Design and Proof of Cannons and Ammunition
STANAG 4123	Methods to Determine and Classify the Hazards of Ammunition
STANAG 4147	Explosives: Chemical Compatibility of Ammunition Components with Explosives and Propellants (Non-Nuclear Applications)
STANAG 4157	Fuzing Systems: Test Requirements for Assessment for Safety and Suitability for Service
STANAG 4170	Principles and Methodology for the Qualification of Explosive Materials for Military Use
STANAG 4178	Test procedures for assessing the quality of deliveries of nitrocellulose from one NATO Nation to another.
STANAG 4324	Electromagnetic Radiation (Radio Frequency) Test Information to Determine the Safety and Suitability for Service of EEDs and Associated Electronic Systems in Munitions and Weapon Systems
STANAG 4370	Environmental Testing
STANAG 4487	Explosives, friction sensitivity tests
STANAG 4488	Explosives, shock sensitivity tests
STANAG 4489	Explosives, impact sensitivity tests
STANAG 4490	Explosives, electrostatic discharge sensitivity
STANAG 4491	Explosives, Thermal Sensitiveness and Explosiveness Tests
STANAG 4506	Explosive Materials, Physical/Mechanical Properties Uniaxial Tensile Test
STANAG 4515	Explosives, Thermal Characterization by Differential Thermal Analysis, Differential Scanning Calorimetric and Thermo Gravimetric Analysis
STANAG 4525	Explosives, Physical/Mechanical Properties, Thermomechanical Analysis (TMA) for Determining the Coefficient of Linear Thermal Expansion
STANAG 4540	Explosives, Procedures for Dynamic Mechanical Analysis (DMA) and Determination of Glass Transition Temperature
STANAG 4556	Explosives, Vacuum Stability Test
STANAG 4581	Explosives, Assessment of Ageing Characteristics of Composite Propellant containing an Inert Binder
STANAG 4582	Explosives, Nitrocellulose based Propellants, Stability Test Procedure and Requirements using Heat Flow Calorimetry

STANAG 4666 Explosives, Assessment of Ageing of Polymer Bonded Explosives (PBXs) Cast-Cured Compositions using Inert or Energetic Binders

1.4. GENERAL

1.4.1. Introduction

1. The essential part of any ISS programme is the assessment of the condition of the materials involved, particularly the energetic materials. The primary mode of degradation must be known and a measurable parameter that indicates that degradation must be identified if real confidence in the ISS program is to be established. For guidance on planning ISS refer to AOP-62 and for guidance on sampling and test procedures refer to AOP-63.

2. The primary purpose of ISS is to monitor the condition of in-service munitions and to demonstrate that the munitions will still function safely and reliably after exposure to the service environment. The ISS programme should allow validation and confirmation of the natural ageing effects predicted from the environmental trials programme. ISS provides real time results, so that if unacceptable degradation is identified in test samples, then such deterioration may be widespread amongst the population. In order to minimise the impact of this, the munitions selected for surveillance testing will normally be those from very early production that have experienced worst case service conditions ("Fleet Leaders" – See AOP-63). ISS programmes may also be used for extending the life of munitions for which no unexpected safety failure is likely.

3. The ISS programme should include critical examination involving non-destructive testing techniques, chemical/physical analysis and testing of materials and functional testing. Firings should be carried out at extreme service temperatures. For complex munitions such as missiles or torpedoes, the number that can be selected for an ISS programme is very limited. It is therefore essential that the maximum information is extracted from the investigation. When the store is simple, cheap and abundant then relatively large sample sizes can be taken allowing a high degree of confidence in the results.

1.4.2. Purpose

1. This AOP explains the physical and chemical mechanisms involved in the ageing of munitions and leading to their degradation. In particular the AOP describes the primary causes of instability in energetic materials (during ageing) with increasing in-service time. This AOP may repeat the principles of AOP-46 because the life assessment of munitions includes In-service Surveillance.

NOTE: AOP-46, The Scientific Basis for Whole Life Assessment, already refers to life assessment, life modelling and in-service surveillance. This series of documents

(AOP-62, AOP-63 and AOP-64) reinforces these aspects to provide a methodology for In-Service Surveillance that supports the principles of AOP-46.

1.4.3. ISS objectives

1. Explosive materials such as high explosives, propellants and pyrotechnics are used in weapon systems to perform a variety of functions. They provide the energy required to deliver the payload and produce the terminal effect. Because of their high energy content, these materials are sensitized and they can be initiated by stimuli such as heat, shock, friction, impact. Those stimuli can be encountered in service and their effects are assessed in ISS programs.

2. The objectives of an ISS program are:

   a. To ascertain the reliability, performance & safety of the munitions in the inventory.

   b. To provide reasonable assurance that only serviceable munitions are issued for use.

   c. To provide a comprehensive overview of the state of health of the inventory, thus allowing for necessary management decisions to be made and actions to be taken in a timely manner.

   d. To provide reasonable assurance those unserviceable munitions will still continue to be safe for storage, handling and transport only.

1.4.4. Degradation mechanisms (macroscopic effect of ageing)

The materials used in munitions can deteriorate in different ways. We can classify the different modes of degradation as follows:

a. <u>Thermochemical</u>

These failure modes may be defined as changes occurring in the chemical composition of materials resulting in unacceptable degradation of safety or functioning characteristics. Certain explosive compositions are inherently unstable and are continually undergoing slow decomposition even at ambient temperature. The decomposition reaction rate is altered by temperature and sometimes by other factors such as humidity. Examples of chemical failure modes include decomposition reactions of nitric ester propellants, (even when slowed down by the presence of stabilisers), corrosion of metals, incompatibility between materials and also the degrading effect of solar radiation on natural and synthetic organic materials such as rubbers and plastics.

b. Mechanical

Two principal mechanical failure modes can be identified. The first of these is fatigue, where under the action of cyclical loading, a crack is initiated and propagates leading to failure of the component. The second principal failure mode is due to the applied stress exceeding a threshold and breaking the component.

Loss of material may cause structural weakness or looseness between mating surfaces. The occurrence of fretting under these conditions between exposed explosive surfaces can lead to the possible formation of “hot spots” with subsequent ignition and/or explosive events. Explosive material in the form of dust may also occur under these conditions and can have a much higher sensitiveness than the parent bulk composition and lead to a hazardous condition.

c. Thermomechanical

This term applies to mechanical stresses in materials that are induced by thermal effects resulting in mechanical failure. A change of temperature in systems containing materials with different thermal properties, thermal diffusivity and coefficients of thermal expansion produces stresses within the materials and particularly at bonded surfaces. Coefficients of expansion of metals are much smaller than those of plastics and rubbers. Such problems are often encountered in case bonded rocket motors between propelling charge, liner and case or, in motors with loose charges, between charge and inhibitor. The results of differential thermal expansion and contraction of materials in munitions leading to dimensional changes can cause problems such as cracked explosive fillings or seal failures, the latter permitting ingress of moisture or exudation of explosive material. Cracking of TNT (trinitrotoluene) based compositions in the main fillings of munitions occurs due to thermomechanical stressing and is more severe when such fillings are bonded to the case material thus restricting volume contraction of the explosive on cooling.

In NATO nations, the bulk of surveillance activity on energetic materials is applied to nitrocellulose based propellants. The safe storage life of these propellants is directly related to the level of stabilizer present. If the stabilizer is depleted below a minimum acceptable level then the rate of decomposition of the propellant will accelerate rapidly with self-heating and, in extreme circumstances, spontaneous ignition may occur. This critical safety aspect explains the concentration of surveillance effort on this class of explosives. In practice, with a properly qualified propellant composition, the safe storage life can be significantly greater than the ballistic performance life for both gun and rocket applications.

1.5. APPLICATION

1.5.1. Chemical and physical ageing phenomena (microscopic effect of ageing)

1. The mechanical properties of the energetic materials may be degraded by different ageing phenomena. Those phenomena are linked to the mechanisms of degradation already cited. The principal ageing phenomena are:

   a. Oxidation of binder or charges (due to oxygen, possibly facilitated by moisture)
   b. Degradation of binder or Nitrocellulose (NC). With NC the reduction of chain length (decrease of molecular weight) results in decrease of mechanical strength
   c. Diffusion of mobile ingredients and contact components
   d. Action of chemical species produced by chemical decomposition
   e. Agglomeration or separation of particulate fillers in charges

2. The factors (impacting quantities) determining the extent of ageing includes:

   a. Time
   b. Temperature
   c. Moisture
   d. Oxygen
   e. Electromagnetic radiation (mainly UV)
   f. Air pressure
   g. Shocks

3. One of the most common failure modes resulting in the munitions becoming unsafe or unsuitable for service is the contamination of the internal environment of the weapon system by moisture, i.e. interactions/reactions of water with energetic materials.

4. The different chemical tests are listed by class of energetic materials in the appendix.

1.5.2. Failure modes and ageing phenomena of energetic materials

1. Single base gun propellant

Nitrate esters in propellants decompose very slowly at normal ambient temperatures, but more rapidly as the temperature and the relative humidity increases. However, the reaction is autocatalytic and therefore a stabiliser is required to react with the accelerating decomposition products to prevent autocatalysis. Measurement of the stabilizer depletion and Heat Flow Calorimetry (HFC) are the test methods most often employed to estimate ageing of NC based propellants. Propellant decomposition produces gases inside the propellant grain which will diffuse to the atmosphere at exposed surfaces.

2. Double base, triple base gun propellants and rocket propellants

As for single base propellant, stabilizer depletion and released gases (NOx) concentration can cause serious problems, as can migration of ingredients in the nitrocellulose matrix. This is particularly relevant to the migration of nitroglycerine or other plasticisers into inhibitors of rocket propellants; the flame resistance of the inhibitor is reduced with contact to nitroglycerine. Swelling of the inhibitor originating from this migration can occur and cause high stress concentrations with subsequent bond failures. The inhibitor may also become mechanically weak and softened due to plasticiser absorption. A build-up of internal gas pressure greater than the tensile strength of the grain will lead to cracking with serious consequences particularly for double base rocket propellant.

3. Composite propellant

   a. The qualities of composite propellants are directly related to the rubbery properties of the binder which is often hydroxyl-terminated polybutadiene (HTPB) or carboxyl-terminated polybutadiene (CTPB).

   b. Cross-link density seems to be an important indicator of the ageing states of the binder polymer and also the propellant. Polymers used in composite propellants, such as the commonly used HTPB are susceptible to oxidative cross-linking. This can lead to hardening and embrittlement of the propellant with associated loss of extensibility (strain capacity) and an increased propensity for cracking. The presence of moisture modifies the properties and ageing of HTBP/Ammonium Perchlorate (AP) composite propellants in practically all situations. In addition to influencing binder oxidation, moisture may affect the binder-filler interface.

4. Composite modified double base type

   The general term composite modified double base propellant is used to describe hybrid propellants that contain nitrate esters with, in addition, inorganic oxidants such as ammonium perchlorate to increase the energy. Test methods applied to double base propellants are also routinely applied to composite modified double base because the nitrate ester component is thought to be the least stable. Experience has shown however that the addition of oxidant may also introduce undesired extra reactions that reduce reliability or safety and which may not be identified by the usual test procedures. Rapid decomposition reactions have been observed in certain propellants after prolonged storage at high temperatures, 90°C and above. While above normal storage or operational temperatures, this situation could be seen in a rocket motor in close proximity to a fire, for example. It is recommended that a degree of caution is adopted in the ISS of propellants of this type.

5. Booster explosive

Booster explosives are used to transmit and augment the reaction initiated by the primary explosive. For Trinitrotoluene (TNT) based secondary explosive compositions, a potential failure mode is exudation. The exudate may be incompatible with contact materials and sensitive to external stimuli (e.g. impact and friction).

a. Melt cast explosive, high explosive

For melt cast explosive, TNT exudation is a failure mode which should be monitored. The exudate may be incompatible with contact materials. The commonly used ingredients hexogen (RDX), octogen (HMX) and TNT all possess excellent long term chemical stability and are not expected to change to any measurable extent with properly formulated explosive compositions.

b. PBX cast cured or pressed explosives

Polymer bonded explosives (PBX), in which the energetic material commonly is bound in a rubbery binder, are being used increasingly in warheads. Polybutadiene binders (such as HTPB) are often used and these can degrade in the same way as composite propellants, resulting in embrittlement and cracking of the composition. There may also be an energetic binder such as Glycidyl-azide-polymer (GAP). The presence of moisture is again of significance although the typical fillers (RDX or HMX) are much less water-sensitive than AP.

The primary method of degradation of PBX is oxidation. Oxidation releases free radical species from the binder. Those species are able to subsequently react in the condensed phase of the heterogeneous polymer. These polymeric free radicals may cause cross-linking and molecular weight increase or decrease.

The migration of plasticizer may lead to heterogeneous mechanical properties.

c. Primary explosives

Primary explosives are mostly ionic compounds having high melting points so exudation is not a problem. The main potential failure modes are due to material incompatibilities and moisture ingress. The former should be eliminated by standard screening tests and choice of materials. The reaction of moisture with initiatory substances such as lead azide can lead to non-functioning failure.

d. Pyrotechnics compositions

Traditional pyrotechnic compositions, in comparison to the organic nature of the other types of energetic material, are physical mixtures of inorganic ingredients, occasionally with polymeric binder. However several oxidisers (e.g. sodium nitrate) used in-service compositions (e.g. illuminating flare) are hygroscopic and some fuels (e.g. magnesium) are readily hydrolysed by moist air. This may result in the development of internal gas pressure in stores, which in the case of hydrogen leads to a flammability hazard. The adsorption of moisture can also lead to physical and chemical changes due to the partial solution of ingredients of the compositions, changes in the density or shape of the consolidated product, cracking and crystallisation of salts on the surfaces of the composition. The performance of pyrotechnic devices is often adversely affected by moisture ingress.

e. Liquid propellant (nitrate ester type)

Decomposition of the nitrate ester is the main effect on ageing with subsequent depletion of stabilizer. The presence of metallic impurities may catalyse this reaction.

f. Combustible items

Combustible items include celluloid and nitrofilms, cartridge and combustible cases. Combustible cartridge munitions, which contain nitrocellulose, were developed to protect the propellant charge, to reduce the weight of ammunition and to improve the ballistics efficiency of the gun (increased firing rate).

Although nitrate esters and stabilizer migrate from the propellant into the combustible cartridge or combustible case, a small concentration of the same stabilizer is present also in the combustible item to protect the nitrocellulose from oxides of nitrogen in a similar manner to the stabilization of propellant.

An issue however is the degradation of the mechanical properties of the combustible cases with plasticizer migration, which can affect the functionality of the system. In addition, the plasticizer migration into the combustible case means that the propellant formulation is no longer as manufactured, and therefore performance can be affected.

g. Polymers

Natural and synthetic materials such as rubbers, adhesives and polymers deteriorate in a variety of ways in different environments. Small changes in composition can lead to considerable changes in the ageing behaviour of the materials. In general, they are more or less sensitive to temperature, moisture, oxygen and solar radiation, particularly the ultra-violet part. However they can be quite sensitive to the order of exposure to different environments. The deterioration of rubbers in natural exposure can vary depending on whether they are exposed early to strong solar radiation which forms a protective skin or whether there is regular rainfall which may wash away autocatalytic products of decomposition.

Absorbed moisture will tend to plasticise an adhesive or polymeric structure, thus changing the glass transition temperature. The stress and the failure strain may either increase or decrease. Moisture can also displace the adhesive from the interface with the adherent. In particular, it affects joints involving metals which may react to form hydroxides or oxides, reducing joint strength.

ANNEX A CLASSIFICATION OF FAILURE MODES AND AGEING PHENOMENA BY TYPE OF ENERGETIC MATERIAL

A.1. SOLID GUN PROPELLANT

A.1.1. Single base gun propellant

Ageing phenomena	Possible effects	Tests	Reference	Notes
Breakdown of the CO-NO_2 bond in nitrate ester	• Heat generated	• Heat Flow Calorimetry (HFC)	STANAG 4582	[I] (a)
	• Gas (NOx) evolved	• Visual • Fume test • Abel heat test • Mass loss at 90°C	 AOP 7 (US, GE) AOP 7 (UK) AOP 7 (GE)	 [N] (c) [N] (c) [N] (d)
	• Stabilizer depleted	• High Performance Liquid Chromatography (HPLC) • Gas Chromatography (GC), Thin Layer Chromatography (TLC)	AOP-48, AOP-7	[I] (b) [N]
NC Chain scission	• Decrease of mechanical strength	Gel permeation chromatography (GPC)	STANAG 4178 test 13	[I] (g)
	• Change in ballistic properties	Ballistic Closed vessel test	STANAG 4115	[I] (f)
Uptake of moisture		Water content (Karl-Fischer titration)		[N]
Uptake of nitroglycerine (where contact with double base type is possible)	• Stabilizer depleted faster than expected	HPLC	AOP-48	[I]

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations
- (a) HFC measures total heat produced by all reactions. Assumptions are necessary to allow 10 years sentencing. Applicable to all NC-based propellant types and stabilizers used for them

- (b) Stabilizer analysis by HPLC is historically the most commonly applied test. Assumptions are required about stabilizer daughter products (consecutive reaction products of the added stabilizer) to allow 10 years sentencing.

  According to AOP 48, HPLC is the preferred method, with other methods (e.g. GC, TLC) being allowed if they show equivalent precision and are able to differentiate between different stabilizers, their daughter products and other propellant ingredients.

  TLC is used additionally by Germany.

  GC is used by France only for single base gun propellant stabilized by Diphenylamine (DPA). The goal is to give a first result of the stabilizer consumption with a low-cost method. If the result isn't relevant HPLC is required.
- (c) and (d) long standing national test methods.
- (e) The terms Gel Permeation Chromatography (GPC) and Size Exclusion Chromatography (SEC) are used equivalently and mean the same polymer analytical technique.
- (f) Closed vessel test used for testing gun propellants (infrequent use in surveillance)
- (g) Suitable sample preparation (usually extraction of other components following national procedures) may be required prior to performing GPC Analysis of Nitrocellulose according to STANAG 4178.

A.1.2. Double base, triple base gun propellant

Ageing phenomena	Possible effects	Tests	Reference	Notes
Breakdown of the CO-NO_2 bond in nitrate ester	• Heat generated	• HFC	STANAG 4582	[I]
	• Gas (NOx) evolved	• Abel Heat Test	AOP-7	[N]
		• 80° Self-heating Test	AOP-7	[N]
		• Methyl Violet Test (120°C)	AOP-7	[N]
		• 65.5° Red Fume Test	AOP-7	[N]
		• B&J test (115°C)	AOP-7	[N]
	• Stabilizer depletion	• HPLC or GC	AOP-48	[I]
NC Chain scission	Embrittlement and reduction in mechanical strength	GPC (SEC),	STANAG 4178 test 13	[I]
		Quasi-Static Pressure Test (QSPT) for embrittlement of AP grains		[N] [a]
		Tensile test	STANAG 4507	[I]
	Change in ballistic properties	Ballistic Closed Vessel Test	AOP-7 STANAG 4115	[I]
Uptake of moisture	Slow hydrolysis of some additives	GC determination of Water (and residual solvent)		[N]
		Karl-Fischer titration		[N]
Others	Changes in colour,	Visual examination		
	Grains become brittle or powdery			
	Exudation of nitroglycerine			

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations
- [a] QSPT is a test performed by Germany

A.2. SOLID ROCKET PROPELLANT

A.2.1. Double base, triple base gun propellant

Ageing phenomena	Possible effects	Tests	Reference	Notes
Breakdown of the $CO-NO_2$ bond in nitrate ester	• Heat generated	• HFC	STANAG 4582	[I]
	•Gas (NOx) evolved	• Abel Test	AOP-7 (UK)	[N]
		• 80° Self-heating Test	AOP-7 (UK)	[N]
		Methyl Violet Test (120°C)	AOP-7 (US)	[N]
		• 65.5° Fume Test	AOP-7 (US)	[N]
		• B&J test (115°C)		[N]
	• Stabilizer depletion	•HPLC	AOP-48	[I]
NC Chain scission	Decrease of molecular weight	GPC	Under development	[a]
	Embrittlement and reduction in mechanical strength	Tensile test	STANAG 4507	[I]
	Change in ballistic properties	Strand Rate Burning Test	AOP-7	[I]
		Ballistic Closed Vessel Test	STANAG 4115	[I]
Diffusion of plasticizer, and other mobile additives	Change in mechanical and visco-elastic (glass transition temperature) properties	Tensile test, Dynamical Mechanical Analysis	STANAG 4507	[I]
	Change in ballistic properties	Strand rate burning	AOP-7	[I]
	Incompatibility issues with contact materials	HFC, Stabilizer loss, ThermoGravimetric Analysis (TGA), Differential Scanning Calorimery (DSC)	STANAG 4147	[I]
	Nitroglycerine migration into charge inhibitor coating	HPLC		[I]
Uptake of moisture	Slow hydrolysis of some additives	GC determination of Water (and residual solvent)	National (US)	[N]
		Karl-Fischer titration		[N]
Others	Changes in colour, grains become brittle or powdery	Visual examination		[N]
	Exudation of nitroglycerine			

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations
- [a] Nations can orient their GPC method with STANAG 4178 as a guidance

A.2.2. Composite propellant

Ageing phenomena	Possible effects	Tests	Reference	Notes
Oxidation of binder	Depletion of anti-oxidant	HPLC analysis	STANAG 4581	[I]
Increase in cross link density (HTPB)	Hardening occurs	Sol-gel determination Shore A Hardness	STANAG 4581	[I]
Decrease in cross link density (polyether)	Softening occurs	Sol-gel determination	STANAG 4581	[I]
		Shore A Hardness	STANAG 4581	[I]
Uptake of moisture	Agglomeration of AP	Karl Fischer titration		[N]
	Degradation of Aluminium			
	Gas evolution leading to crack	Non-Destructive Test (NDT)		[N]
Change to polymorphism of oxidant	Dewetting with binder, dimensional change			[N]
Diffusion of plasticizer, surface agent or other mobile additive	Change in mechanical and visco-elastic (glass transition temperature) properties	Tensile test, DMA	STANAG 4506 STANAG 4540	[I]
	Change in ballistic properties	Strand Rate Burning Test	AOP-7	[I]
		DMA	STANAG 4540	[I]
	Incompatibility issues with contact materials	HFC, Stabilizer loss, TGA, DSC	STANAG 4147	[I]
Mechanical damage due to shock, vibration or thermal cycling	Void formation	NDT	According to National procedures	[N]
	De-wetting of filler	NDT		
	Loss of bond line integrity	Dimensional measurement Peel test		

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations

A.2.3. Composite modified double base type

Ageing phenomena	Possible effects	Tests	Reference	Notes
Breakdown of the $CO-NO_2$ bond in nitrate ester	Heat generated Gas (NOx) evolved	HFC	STANAG 4582	[I]
	Stabilizer depleted	HPLC analysis	AOP-48	
NC Chain scission	decrease of mechanical strength	GPC (SEC)	under development	
	Changes in mechanical properties	Tensile test, DMA	STANAG 4506, STANAG 4540	[I]
	Change in ballistic properties			
Diffusion of plasticizer, surface agent or other mobile additive	Change in mechanical and visco-elastic (glass transition temperature) properties	Tensile test, DMA	STANAG 4506, STANAG 4540	[I]
	Change in ballistic properties	Small-scale burning test		
	Incompatibility issues with contact materials	HFC, Stabilizer loss, TGA, DSC	STANAG 4147	[I]

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations

A.3. EXPLOSIVES

A.3.1. Booster explosive

Ageing phenomena	Possible effects	Tests	Reference	Notes
Decomposition of nitro-compounds	Build-up of impurities, which can cause instability	Vacuum stability	STANAG 4556	[I]
		Melting point (setting point)	AOP-4682	[I]
Incompatibility with contact materials over long time period	Sensitive metal salts and other sensitive compounds may be produced	Visual examination		[N]
	Stability may be degraded	Impact and friction testing	STANAG 4489, 4487	[I]
		Vacuum stability at 100°C	STANAG 4147	[I]
Exudation of mobile species	May deposit energetic compounds on surface or into threads	Visual examination		[N]
Water uptake	Salt formation, agglomeration, degradation	Water content by Karl Fischer titration		[N]
		Weight loss on drying		[N]

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations

A.3.2. Melt Cast explosive, high explosive

Ageing phenomena	Possible effects	Tests	Reference	Notes
Decomposition of nitro-compounds	Build-up of impurities, which can cause instability	Vacuum stability	STANAG 4556	[I]
Incompatibility with contact materials over long time period	Sensitive metal salts may and other sensitive compounds be produced (TNT with lead compounds; Ammonium nitrate with metals)	Impact and friction testing	STANAG 4489, 4487	[I]
	Stability may be degraded	Vacuum stability at 100°C	STANAG 4147	[I]
Exudation of mobile species (e.g. wax)	May deposit energetic compounds on surface or into threads	Visual examination		[N]
Gassing from aluminised filling	Hydrogen gas build-up in severe cases			
Water uptake	Salt formation, agglomeration, degradation	Water content by Karl Fischer titration		[N]
		Weight loss on drying		[N]
Polymer chain scissioning in melt-cast PBX	Loss in mechanical strength	GPC (SEC)		[N] [a]
Polymer chain scissioning in melt-cast PBX	Loss in mechanical strength	GPC (SEC)		[N] [a]

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nation
- [a] STANAG 4178 may be applicable or provide a basis for developing a procedure

A.3.3. PBX Cast cured

Ageing phenomena	Possible effects	Tests	Reference	Notes
Oxidation of binder	Hardening occurs	Shore A Hardness	STANAG 4666	[I]
Uptake of moisture	Agglomeration of explosive filler causes hardening	Karl Fischer test and Visual inspection		[N]
Increase in cross link density	Hardening occurs	Sol-Gel determination	STANAG 4666	[I]
Decrease in cross link density	Softening occurs	Sol-Gel determination	STANAG 4666	[I]
	Change in mechanical and visco-elastic (glass transition temperature) properties	TMA, DMA, DSC for glass transition temperature	STANAG 4515 STANAG 4540 STANAG 4525	[I]
Change to polymorphism of explosive filler	De-wetting with binder, dimensional changes	Scanning Electronic Microscopy (SEM)	STANAG 4666	[I]
Diffusion of plasticizer, surface moderant or other mobile additive	Change in mechanical properties	HPLC or GC analysis	STANAG 4666	[I]
	Incompatibility issues with contact materials	Vacuum stability test	STANAG 4147	[I]
Mechanical damage due to shock, vibration or thermal cycling	Void formation	NDT		[N]
		Tensile strength	STANAG 4506	[I]
	De-wetting of filler	Dimensional measurement tests, NDT		[N]
	Increase in sensitivity to shock, impact, friction, or ESD	Impact and friction test, ESD test, Shock test	STANAG 4487, 4488, 4489, 4490	[I]

A.3.4. Pressed explosives

Ageing phenomena	Possible effects	Tests	Reference	Notes
Uptake of moisture	Loss of cohesiveness	Karl-Fischer test and visual inspection		[N]
Change to polymorphism of filler	Dimensional changes	Scanning Electronic Microscopy	STANAG 4666	[I], [a]
Mechanical damage due to shock, vibration or thermal cycling	Void formation	NDT		[N]
		Tensile strength	STANAG 4506	[I]
	De-wetting of filler	Dimensional measurement tests, NDT		[N]
	Increase in sensitivity to shock, impact, friction, or ESD	Impact and friction test, ESD test, Shock test	STANAG 4487, 4488, 4489, 4490	[I]

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations
- [a] Nations can orient the Scanning Electronic Microscopy method with STANAG 4666 as a guidance

A.3.5. Primary explosives

Type	Ageing phenomena	Possible effects	Tests	Reference	Notes
Primary Lead or Silver Azides Lead styphnate Tetrazene Blackpowder Percussion cap composition Conducting cap composition	Uptake of moisture	Slow chemical decomposition of principal ingredient leading to reduced efficiency or even failure	Chemical analysis, Karl-Fischer titration, weight loss on drying		[N]
Azides (especially)	Long term incompatibility with contact materials	Formation of highly sensitive salts with metals (e.g. Copper azide)	Visual examination for corrosion of contact components		[N]

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations

A 4. PYROTECHNIC COMPOSITIONS

Ageing phenomena	Possible effects	Tests	Reference	Notes
Uptake of moisture	Caking or dissolution of metallic salts	Oven drying at 103°C	National methods depending on exact pyro composition	[N]
	Build-up of acidity (blackpowder)	Titration		[N]
	Corrosion of metallic contact materials	Visual examination		[N]
	Build up of hydrogen gas (Al, Mg compositions, forming Al and Mg oxides and hydroxides)	Visual (distortion of packaging) Free Mg Test Gas analysis		[N]
	Build up of phosphine gas (Red phosphorus containing compositions)	Gas analysis, GC/MS, Trace analysis by e.g. Draeger tube	STANAG 4679 (closed vessel test)	[N]
	General impairment of performance	Functioning test (e.g. burning rate in a tube)		[N]
Oxidation	Reduction in free metal content (Al, Mg) or reduction in fuel element (B, P) leading to impaired performance	Chemical analysis Atomic absorption spectroscopy	National methods depending on exact pyro composition	[N]
	Change in temperature of ignition	Burning Rate Test,	STANAG 4491	[I]
		Proof firing		[N]
		DSC	STANAG 4515	[I]
others	Unreliability caused by any of the above factors	Functioning test,	This is most often used in ISS	[N]
		Proof firing		

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations

A 5. LIQUID PROPELLANT (nitrate ester type)

Ageing phenomena	Possible effects	Tests	Reference	Notes
Breakdown of the CO-NO_2 bond in nitrate ester	Heat generated	HFC	STANAG 4582	[I]
	Stabilizer depleted	HPLC, GC	AOP 48	[I]
Uptake of moisture		Karl-Fischer titration		[N]
Presence of metallic impurities from contact materials	May degrade stability	Chemical analysis, Atomic absorption or emission spectroscopy		[N]

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations

A 6. COMBUSTIBLE CARTRIDGE AND CASES

Ageing phenomena	Possible effects	Tests	Reference	Notes
Breakdown of the CO-NO_2 bond in nitrate ester	Heat generated	HFC	STANAG 4582	[I]
	Stabilizer depleted	HPLC, GC	AOP 48	[I]
NC Chain scission	Embrittlement and reduction in mechanical strength	Tensile test, DMA	STANAG 4507 STANAG 4540	[I]
Uptake of moisture		Karl-Fischer titration		[N]
Diffusion of plasticizer, and other mobile additives	Change in mechanical and visco-elastic (glass transition temperature) properties	Tensile test, DMA	STANAG 4507 STANAG 4540	[I]
	Change in ballistic properties	Burning rate (strand burning, closed vessel)	AOP-7	[I]
	Nitrate ester migration	HPLC, GC	AOP 48	[I]

- [I] denotes an internationally recognised test which has been documented in published standards (e.g. STANAG, ISO, ASTM)
- [N] denotes a national test, often with long experience in use but not necessarily approved by other nations

A 7. NON-ENERGETIC USE OF POLYMERS

Such polymers can have special functioning in munition systems as sealing or spring functioning. These functions determine strongly the type of inspections and surveillance. The list below gives only a few examples with typical ageing phenomena and subsequent effects.

Type	Ageing phenomena	Possible effects	Tests	Reference	Notes
Polyurethane	Oxidation	Hardening, dimensional changes as swelling or permanent setting	Visual inspection		
Foams, O-rings, and others		Consumption of anti-oxidants and other stabilizers (UV)		ASTM D6042 as a guidance	
Phenolic mouldings	Oxidation	Hardening, dimensional changes	Visual inspection		
		Acidic vapour in enclosed spaces			
Polyolefins (polyethylene foam and mouldings)	Loss of plasticizer	Hardening , cracking	Visual inspection		
Vinyl polymer (Polyvinyl chloride)	Loss of plasticizer	Hardening , cracking	Visual inspection		
Acrylic Polymer (Polymethyl methacrylate)		Cracking	Visual inspection		
Silicone polymer		Hardening, dimensional changes, powdering	Visual inspection		
Rubber	Oxidation, loss of plasticizer and anti-oxidant	Hardening, dimensional changes		ASTM D4676, ASTM D1992	
Paint and varnish	Oxidation (embrittlement of oil type)	Low molecular mass species evolved in enclosed spaces		ASTM D2832	

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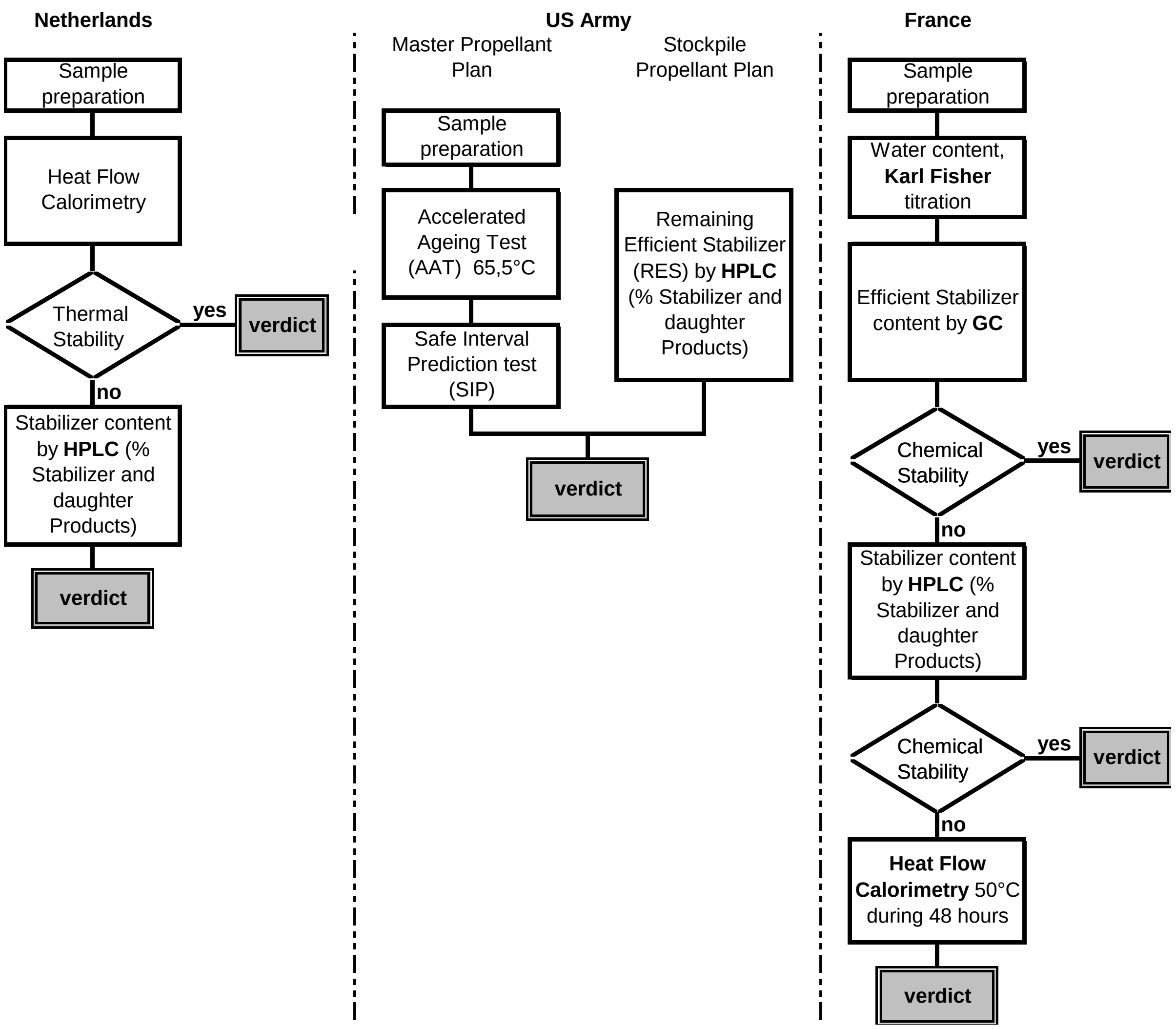
ANNEX B FLOW CHART – EXAMPLE OF ISS PROGRAM

This diagram provides examples of ISS Condition Monitoring programs and is intended to be illustrative of how test methods may be applied for certain energetic material types. The nation's ISS program presented here may be modified. Each nation should tailor its program to specific requirements and environments that apply to its inventory. It is not possible to prescribe a specific protocol that will suit all nationsText.

Example : Single base gun propellant stabilized by Diphenylamine (DPA).



Notes:

1. Heat Flow Calorimetry at 80°C during 10.6 days is an internationally accepted method described in STANAG 4582 Heat Flow Calorimetry at 50°C during 48 hours is a national procedure described in the French instruction MAT 2423 about ISS of ammunitions.
2. France: the Karl Fischer titration is only performed for 120 to 155 mm calibre ammunitions.
3. US Army: Information from U.S. Army Propellant Management Guide, prepared by US Army Defence Ammunition Centre
4. SIP: The test measures the decrease of initial stabilizer using High Performance Liquid Chromatography (HPLC) at regular intervals. The test is run at 65.5°C, like the AAT. Each sample also is tested prior to aging and the level of remaining effective stabilizer (RES) is determined.
5. US Army: The remaining effective stabilizer (RES) level is determined in duplicate for both the Stockpile Propellant sample and for the Master Propellant sample. A comparison for the propellant lot identifies errant behaviour between the fielded propellant and stored propellant, and provides the basis along with SIP testing of the Master Propellant sample.

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