NATO STANDARD

AOP-4581

ENERGETIC MATERIALS, ASSESSMENT OF AGEING CHARACTERISTICS OF COMPOSITE PROPELLANTS CONTAINING AN INERT BINDER

Edition A, version 1

MARCH 2022

NORTH ATLANTIC TREATY ORGANIZATION

ALLIED ORDNANCE PUBLICATION

Published by the
NATO STANDARDIZATION OFFICE (NSO)

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NORTH ATLANTIC TREATY ORGANIZATION (NATO)

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NATO LETTER OF PROMULGATION

21 March 2022

1. The enclosed Allied Ordnance Publication AOP-4581, Edition A, version 1, ENERGETIC MATERIALS, ASSESSMENT OF AGEING CHARACTERISTICS OF COMPOSITE PROPELLANTS CONTAINING AN INERT BINDER, which has been approved by the nations in the CNAD Ammunition Safety Group (CASG - AC/326), is promulgated herewith. The agreement of nations to use this publication is recorded in STANAG 4581.

2. AOP-4581, Edition A, version 1, is effective upon receipt.

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4. This publication shall be handled in accordance with C-M(2002)60.

Dimitrios SIGOULAKIS
Major General, GRC (A)
Director, NATO Standardization Office

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RECORD OF RESERVATIONS

CHAPTER	RECORD OF RESERVATION BY NATIONS
Note: The reservations listed on this page include only those that were recorded at time of promulgation and may not be completed. Refer to the NATO Standardization Document Database for the complete list of existing reservations.	

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RECORD OF SPECIFIC RESERVATIONS

[nation]	[detail of reservation]

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CHAPTER 1 INTRODUCTION

1.1. AIM

The purpose of this agreement is to standardize accelerated ageing and testing protocol by which aged samples of composite propellant containing an inert binder can be assessed and compared.

1.2. AGREEMENT

The participating nations agree that the principles and methodology set out in ANNEX A, the procedure set out in ANNEX B and the test methods set out in ANNEX C constitute basic data for ageing behavior assessment of inert binder composite propellants.

1.3. GENERAL

This AOP describes an approach for accelerated ageing and testing of composite propellants. The approach described in this AOP consists in performing accelerated ageing in accordance with the procedure set out in Annex B and subsequently subjecting the aged composite propellants to chemical and mechanical tests using the methods described in ANNEX C. The procedures described in this AOP may also find application to polymer bonded explosives (PBX) with inert binder. Later on the first publication of STANAG 4581, the STANAG 4666 also reported studies on the assessment of PBX ageing.
This AOP covers accelerated ageing and testing of composite propellants with inert binders. It may also be applicable to some PBX compositions.
This AOP does not cover the evaluation of the equivalent life or service life as a whole, but only the ageing and testing of composite propellants. Because propellants have different compositions and properties, there is no single chemical method that can be applied in all cases. The applicability of each of the methods set out in ANNEX C will have to be specified.

1.4. WARNING

This agreement calls for the use of substances and test procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and in no way absolves the user from statutory obligations relating to health and safety at any stage during use.

1.5. RELATED DOCUMENTS:

1. STANAG 4506: Explosives, Physical/Mechanical Properties, Uniaxial Tensile Test.
2. STANAG 4540: Explosives, Procedures for Dynamic Mechanical Analysis (DMA) and Determination of Glass Transition Temperature.
3. STANAG 4515: Explosives, Thermal Characterization by Differential Thermal Analysis, Differential Scanning Calorimetry and Thermogravimetric Analysis.
4. STANAG 4487: Explosives, Friction Sensitivity Tests.
5. STANAG 4489: Explosives, Impact Sensitivity Tests.
6. STANAG 4490: Explosives, Electrostatic Discharge Sensitivity Tests.
7. STANAG 4491: Energetic Materials, Thermal Sensitiveness and Explosiveness Tests – AOP-4491
8. ASTM D 2240-00: Standard Test Method for Rubber Property - Durometer Hardness.

ANNEX A TO
AOP-4581

ANNEX A PRINCIPLES AND METHODOLOGY

A.1. GENERAL

1.1 The approach proposed in the present AOP makes it possible to evaluate the ageing behavior of composite propellants on the basis of the results of accelerated ageing. A single-temperature ageing and testing protocol is provided to allow comparisons between aged samples of composite propellants containing inert binders.

NOTE A1: It is recognized that multi-temperature conditioning and testing could result in a more complete assessment of ageing behavior. Therefore the accelerated ageing procedure, as specified in ANNEX B, can be applied to additional and/or other temperatures and durations, provided that the conditions of ageing are clearly stated in the test results.

1.2 Because the ageing mechanisms may be substantially modified by the presence of nitrate esters in the binder, the scope of the agreement is restricted to inert binder propellants. These binders consist primarily of carboxy-terminated polybutadiene-acrylonitrile (PBAN), carboxy-terminated polybutadiene (CTPB) and hydroxy-terminated polybutadiene (HTPB). The oxidizer of these propellants generally consists of ammonium perchlorate.

1.3 Because some properties (particularly mechanical) can be highly altered by humidity and the presence of oxygen, it is critical that the ageing conditions are well controlled:

- The container must be hermetically sealed.
- The moisture content of the propellant must be analyzed by a suitable method (ex. Karl Fischer) and recorded.
- The propellant should be in an environment similar to the all-up configuration. If it is not known, then the volume of air present around the aged propellant is recommended to be approximately 80/20 sample/air volume.

1.4 The presence of transition metals such as iron might catalyze the breakdown of polymeric binder during ageing, resulting in cracking of the material. Therefore if transition metals are present, an analysis of the materials is recommended. Induced coupled argon plasma atomic emission spectrometry is a suitable analytical method for the determination of transition metals but other methods could be considered.

A.2. PROPERTIES ALTERED BY AGEING

Ageing can give rise to many phenomena, which may modify the ageing behavior of composite propellants.
For example:

- Oxidation of the binder leading to hardening which is generally increased by the presence of air and is therefore greater at the surface than at the center.
- Degradation of the binder by the rupture of chains.

- Migration of species (plasticizer and/or liquid catalyst) towards free surfaces can lead to material hardening and to a higher sensitivity.
- Solid fillers like ammonium nitrate or ammonium perchlorate can undergo various surface phenomena like absorption of moisture, partial dissolution followed by recrystallization or even temperature-based phase transitions. Any of these phenomena could modify the ageing behavior of the composite propellant as a whole.

A.3. CONTROL METHODS

The chemical and mechanical methods described in ANNEX C make it possible to identify the changes in the key parameters set out in paragraph **A.2.**

- The measurement of residual antioxidant levels enables a qualitative assessment of the state of binder degradation. However, there is not always a direct relationship between the residual antioxidant level and the propellant mechanical properties.
- The measurement of soluble fraction or crosslink density enables an assessment of how far the degradation reactions may occur either by rupture of chains or increase in crosslink density. There is a direct relationship between these parameters and the propellant mechanical properties.
- The measurement of plasticizer content at different locations will indicate any migration.

NOTE A-2: The migration of other species such as liquid catalysts may also occur but are not dealt with in this AOP.

- The measurement of tensile mechanical properties enables failure and response properties to be measured at specific temperatures and crosshead rates.
- The use of dynamic mechanical analysis (DMA) enables propellant viscoelastic behavior to be assessed.
- The measurement of Shore A hardness allows the change in this property to be determined.

Other tests may be conducted such as:

- Evaluation of thermal properties by DSC or DTA (STANAG 4515) or other methods (STANAG 4491, 4666).
- Sensitivity tests (impact, friction, electrostatic discharge, thermal sensitivity) (STANAG 4489, 4487, 4490, 4491, 4666).
- Analysis for transition metals by induced coupled argon plasma atomic emission spectrometry or any other suitable method.

Specific chemical methods for certain types of antioxidants and plasticizers are fully described in ANNEX C.

With respect to mechanical properties, only the specific conditions and results sheets are described. The assessment of the results is discussed in ANNEX D.

ANNEX B TO AOP-4581

ANNEX B ACCELERATED AGEING PROCEDURE

B.1. PRINCIPLE

The propellant is placed in the form of a block in a sealed conditioning system and artificially aged at the prescribed temperature and duration. For single-temperature assessments, 60°C for 3 and 6 months (minimum) is recommended.

NOTE B-1: It is recognized that multi-temperature conditioning and testing could result in a more complete assessment of ageing behavior. Therefore the accelerated ageing procedure, specified below, can be applied to additional and/or other temperatures and durations for the purpose of multi-temperature assessments. In all cases, the conditions of ageing should be clearly stated in the test results.

NOTE B-2: It is assumed that a temperature of 60°C enables acceleration of ageing without any changes in mechanisms.

NOTE B-3: It is important to avoid ageing too small samples of propellant and it is recommended to perform the ageing in bulk.

NOTE B-4: Propellant blocks may be wrapped with aluminum foil or another inert wrap during ageing periods to limit propellant surface attack by moisture and oxygen. Ageing in chemically-compatible, hermetically-sealed containers may be used, especially for those propellants that have surfaces readily attacked by moisture and oxygen.

NOTE B-5: Surface effects due to ageing may be assessed.

B.2. APPARATUS

2.1 Conditioning boxes or packs suited to the volume of the sample and hermetically sealed. Alternatively, aluminum foil or other inert wrap may be used to enclose the sample.

2.2 Oven maintained at 60 ±1°C for the required duration.

B.3. AGEING METHOD

Propellant samples should be aged in block. A typical example is given in Figure 1 and the note attached to this figure. Precondition the propellant blocks for a month at a relative humidity < 15% at ambient temperature. Place them flat in the conditioning box or pack or wrap in aluminum foil or an inert wrap and close tightly. Alternatively, cast rectangular ageing test propellant blocks into preformed aluminum foil or paper or other chemically inert sheet containers generating essentially hermetic seals on five surfaces. Place in an oven at 60°C for the required time (3 and 6 months). Upon completion of ageing, remove the enclosed samples from the oven and allow cooling to ambient temperature. The visual presence of cracks, voids and other flaws should be noted.

In order to avoid surface effect, a minimum depth of 20 mm should be removed from all surfaces of the bulk sample. This removal is intended to avoid localized irregularities influencing quality of bulk propellant ageing test specimens extracted from aged propellant blocks. These 20 mm pieces can be used to perform ageing profile assessment due to surface effects. Ageing sample propellant blocks should be large enough to readily extract 5 JANNAF Class C tensile specimens (test 2A), 3 dynamic mechanical analysis (DMA) bars (test 2B) and 4 Shore A hardness discs (test 2C). The remainder can be utilized for various chemical tests (tests 1A to 1D) and perhaps for plasticizer and/or antioxidant migration analyses. Figure 1 illustrates propellant block size and test specimen descriptions suitable for use in propellant ageing studies. More compact ageing test blocks may be used as long as the appropriate test sample set can be easily obtained from each block.

ANNEX B TO
AOP-4581

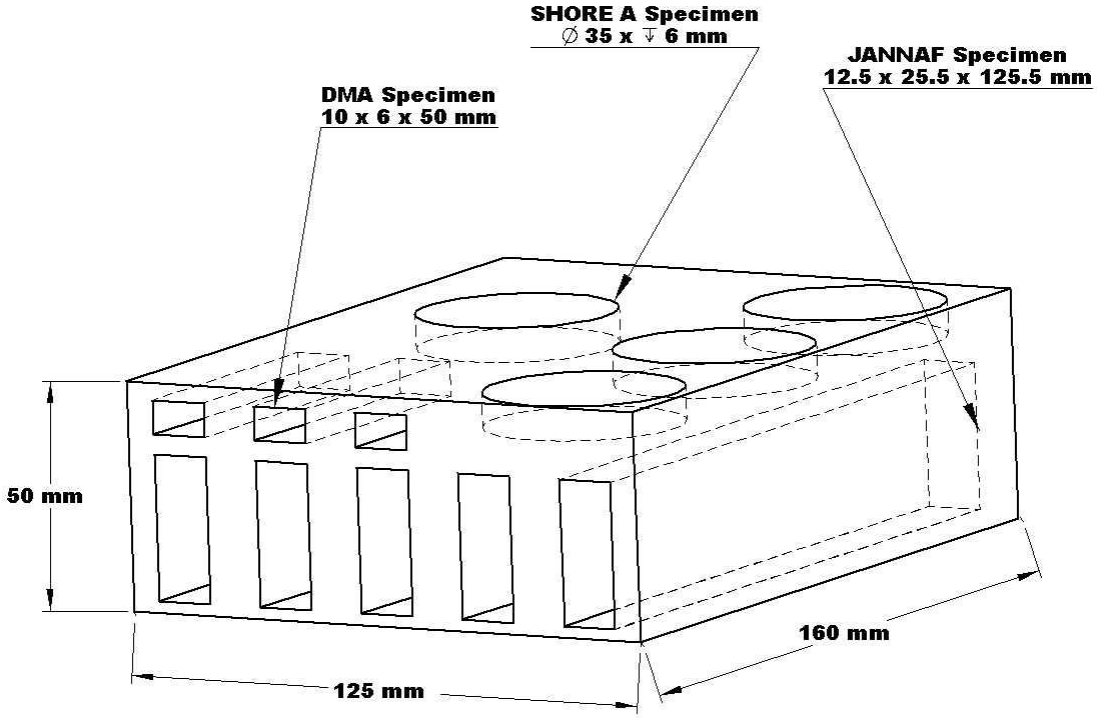

FIGURE 1
Typical example of the propellant block to be used for cutting the various samples needed.

NOTE: The actual block used for artificial ageing will have, in comparison to the one illustrated above, an increase of at least 40 mm for each dimension since after the ageing period, a minimum depth of 20 mm should be removed from all surfaces. Larger blocks and/or multiple blocks described above may be used in cases requiring additional propellant.

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ANNEX C TO
AOP-4581

ANNEX C TEST PROCEDURES

LIST OF TESTS

1. CHEMICAL TESTS

1A	Measurement of the soluble fraction
1B	Measurement of crosslink density
1C	Measurement of antioxidant content
1D	Measurement of plasticizer content

2. MECHANICAL TESTS

2A	Uniaxial tensile test
2B	Dynamic mechanical analysis
2C	Measurement of Shore A hardness

ANNEX C TO
AOP-4581

C.1. CHEMICAL TESTS

C.1.1 TEST 1A: MEASUREMENT OF THE SOLUBLE FRACTION

1. INTRODUCTION

The soluble (sol) content of a crosslinked polymer is a useful measurement of the extent of crosslinking within the polymer network. The greater the fraction of uncross linked polymer, the higher the sol content.
Previous work on propellants has shown that the mechanical strain at maximum stress (ε_{max}) is also a function of the sol content.
The sol fraction can be determined by extraction at ambient temperature or by refluxing with solvent. It can be used in the modified Charlesby-Pinner equation to evaluate the crosslink density.

NOTE C-1: The methods described in this section may lead to incorrect results if applied to composite propellants containing significant amounts of soluble fillers. In that case, it is advisable to use test 1B to determine crosslink density.

2. EXTRACTION AT AMBIENT TEMPERATURE

A. Outline of the method

A known weight of composite propellant is swollen in toluene or dichloromethane for several days at ambient temperature until a stable state of swelling is achieved. After that, the gel fraction and solvent phase are separated and the soluble fraction evaluated. For some concerns about the toxicity of toluene (polarity index is 2.4) or dichloromethane (polarity index is 3.0), it is worthy to change these solvents for others that are less toxic such as ethyl acetate (polarity index is 4.4) or others. However, an attention should be given in using with a polarity index close to dichloromethane.

B. Apparatus and reagents

- Toluene or dichloromethane (Analytical grade)
- Oven at 50°C

C. Extraction

- Introduce a weighed portion (W_i) of 1 to 2 g of composite propellant in a beaker
- Add approximately 100 ml of toluene or dichloromethane
- Change the solvent after 24, 48 and 72 hours at ambient temperature
- After 4 days, separate gel fraction and solvent phase
- Dry the gel fraction in an oven at 50°C to remove the solvent until a constant weight is obtained (W_s).
- It might be required to retain the soluble fraction for plasticizer content as described in test 1D.

D. Calculation of soluble fraction (S)

Calculate the soluble fraction (S) from the equation:

$$S = \frac{W_i - W_S}{W_i}$$

where:
W_i = weight of unswollen sample in gram
W_S = weight of dry sample after extraction in gram
The soluble fraction is expressed as a fraction of 1.

3. SOXLET EXTRACTION

A. Outline of method

A known weight of propellant is added to a weighed Soxhlet extraction thimble. The sample is extracted for at least 16 hours in a Soxhlet extraction apparatus using dichloromethane as solvent. The thimble is dried and reweighed. The sol fraction of the sample is equal to the loss in weight of the thimble divided by the weight of propellant taken initially.

B. Apparatus

- Soxhlet extraction apparatus
- Ceramic or alumina Soxhlet extraction thimbles

Extractions are conveniently heated using a thermostatically controlled electrothermal unit.

C. Extraction

Carry out the extraction and measurement in triplicate. Dry an extraction thimble by heating in a vacuum oven for 3 hours at 60°C. Leave it to cool for one hour in a vacuum desiccator and then weigh accurately (W_1 g). Add 3.0 ± 0.1 g of sliced propellant (roughly 1 mm x 2 mm x 2 mm) and reweigh accurately (W_2 g). Extract for at least 16 hours with 200 ml of dichloromethane in a Soxhlet extraction apparatus. Remove the extraction thimble and place in a fume cupboard. Allow the excess solvent to evaporate off by air drying for two hours. Then place the sample in a vacuum oven at a pressure of less than 133 Pa at ambient temperature and leave overnight to remove traces of dichloromethane. Transfer it to a vacuum desiccator containing dry silica gel and leave it to cool for an hour. Reweigh the thimble and sample (W_3 g). Retain the soluble fraction for the measurement of plasticizer content (test 1D).

D. Calculation of the soluble fraction (S)

Calculate the sol fraction from the equation:

$$S = \frac{(W_2 - W_3)}{(W_2 - W_1)}$$

where

W_1 = Weight of dry thimble
W_2 = Weight of thimble + sample before extraction
W_3 = Weight of thimble + sample after extraction

The soluble fraction is expressed as a fraction of 1.

4. CROSSLINK DENSITY CALCULATION

The crosslink density can be calculated by the modified Charlesby-Pinner equation:

$$\text{Crosslink density} = \frac{(1-S)[2-(S+\sqrt{S})]}{(S+\sqrt{S})},$$

where S is the soluble fraction.

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TEST 1A: MEASUREMENT OF THE SOLUBLE FRACTION

Report Reference Number: (Unique Reference Number) **Page 1 of 1 Page**

TEST SITE INFORMATION	**CONDITIONS OF AGEING**
Laboratory: (Name of laboratory) **Date:** (Date that form was completed) **Test Procedure:** (Name of test procedure used) **Date Tested:** (Date of test period) **POC:** (Point of contact)	**Temperature of ageing (°C):** **Test time (months):** **CONDITIONS OF ANALYSIS:** **Divergences from standard procedure:**
SPECIMEN INFORMATION	**TESTS RESULTS**
Identification of Test Material: (Trade name and/or Identify code) **Manufacturer:** (Name of manufacturer) **Test Material, Specification:** (state if specification controls chemical composition of product) **Lot, Batch or Consignment Number:** **Date of Manufacture or Receipt:** **Special Storage Conditions:** (If applicable)	**Sol fraction before ageing:** **Sol fraction after 3 months ageing:** **Sol fraction after 6 months ageing:** **Crosslink density before ageing:** **Crosslink density after 3 months ageing:** **Crosslink density after 6 months ageing:** **Comments:** **Data Sent to:**

C.1.2 TEST 1B: MEASUREMENT OF CROSSLINK DENSITY

1. INTRODUCTION

The crosslink density is a useful parameter for the physical property of a composite propellant. It is known that this parameter will be affected by the ageing of the material. Consequently it may be used to evaluate the degradation state.

2. SCOPE AND PRINCIPLES OF METHOD

A sample of composite propellant with a known volume is swollen in toluene for several days at a stable and known temperature (ideally room temperature). The compression measurements are only performed after a stable state of swelling is reached (typically one week). The compression modulus of the swollen material is determined graphically and used for the calculation of the crosslink density.

3. APPARATUS

3.1 Balance accurate to 0.1 mg
3.2 Glassware and standard laboratory equipment
3.3 Beaker with a cover to avoid solvent evaporation
3.4 Modulus apparatus (see Figure 2). It consists of a dial micrometer to measure the displacement of the swollen sample compressed by known weights.

4. REAGENTS

4.1 Toluene - Analytical grade

5. ANALYTICAL PROCEDURE

5.1 Sample preparation

Propellant samples are finely cut in disc forms. Their heights and diameters are precisely measured with a micrometer device (typically a height of 1.5 cm and a diameter of 2.5 cm).

Each sample is put in a beaker and approximately 60-100 ml of toluene is added. The sample must always be completely submerged in toluene during the experiments to keep the swelling state undisturbed.

The sample is kept in toluene until a steady state of equilibrium is reached. One way to evaluate if a steady state has been reached is by weighing the sample at every 30 s during 5 minutes. The time zero is the time at which the sample has been removed from the solvent. A graph of time as a function of weight measured is plotted. This will give a straight line and by extrapolation, the weight at time zero is evaluated. The steady state is reached when this weight at time zero of the swollen sample is constant (typically of the order of one week).

5.2 Measurement

Each swollen sample is put under the tray of the modulus apparatus to be compressed.

NOTE C-2: The measurements are performed on the swollen sample immersed in toluene.

The dial of the modulus apparatus is adjusted to zero.

Compression measurements are then performed by adding various incremented known weights (from 40 up to 400 g). The displacement is recorded for each weight added.

After each measurement of displacement, the weight is removed for 2-5 minutes to relax the sample at the original equilibrium state in the solvent. It might be necessary to adjust the zero especially for the higher weight near the end of the experiment.

The measurements are stopped when an acceptable plot is obtained (typically after 10 measurements).

The graph of the weight (kg) as a function of the deflexion (m) is plotted and the slope is determined.

5.3 Calculation of the crosslink density (C)

The crosslink density is calculated according to the following formula:

$C = h_o S/3A_o RT$

Where

h_o : Height of the sample (m)
A_o : Area of the cross section (i.e. circular face) (m^2)
R : Gas constant (8.315 J/mole·K)
T : Temperature (K)
S : Slope x 9.807 m/s^2 (N/m)
C : Crosslink density ($mole/m^3$)

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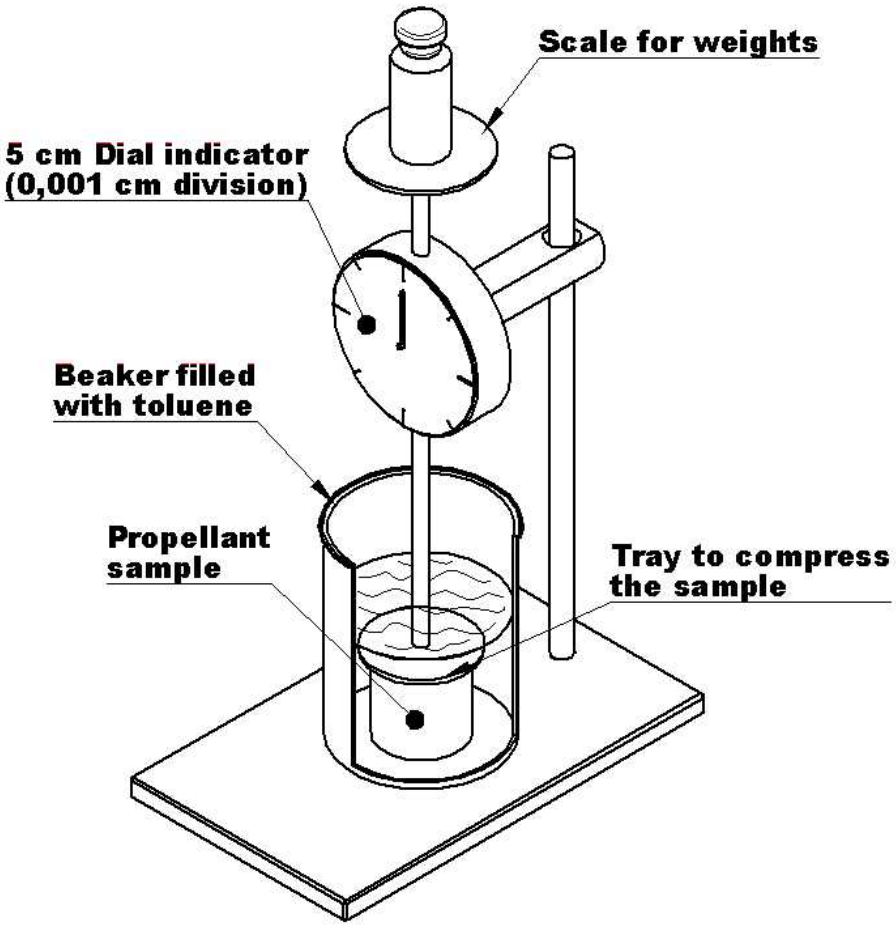

FIGURE 2

Modulus apparatus used for measurement of crosslink density.

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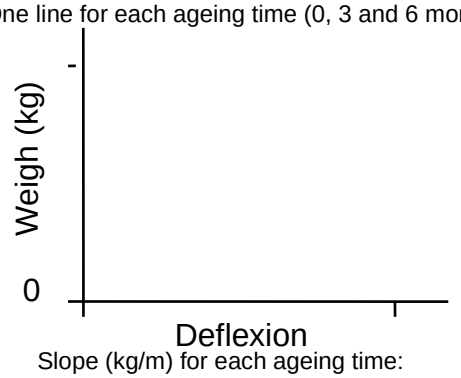
TEST 1B: MEASUREMENT OF CROSSLINK DENSITY

Report Reference Number: (Unique Reference Number) **Page 1 of 1 Page**

TEST SITE INFORMATION	**CONDITIONS OF AGEING**
Laboratory:	**Temperature of ageing (°C):**
Date:	**Test time (months):**
Test Procedure:	
Date Tested:	**TEST CONDITIONS**
POC:	**Temperature (°C):**
	Relative humidity (%):
	Solvent used:

SPECIMEN INFORMATION	**TYPICAL RESULTS**
Dimensions: Height (h_o) in m: **Diameter in m:** **Area of the cross section (A_0) in m^2:** **Form:** **Preparation Method:** **Manufacturing Method:** **Source:** **Lot or ID Number:** **Conditioning Period:** **Composition:** Component — Percent — — — — — —	One line for each ageing time (0, 3 and 6 months)  Slope (kg/m) for each ageing time:

Calculation of the crosslink density: $C = h_0S/3A_0RT$

Where

h_o	: Height of the sample (m)	A_o	: Area of the sample (m^2)
T	: Temperature (K)	R	: Gas constant (8.315 J/mole·K)
C	: Crosslink density (mole/m^3)	S	: Slope x 9.807 m/s^2 (N/m)

Crosslink density result before ageing =
Crosslink density result after 3 months ageing =
Crosslink density result after 6 months ageing =

Data Send to	**Comments**

C.1.3 TEST 1C: MEASUREMENT OF ANTIOXIDANT CONTENT

1. INTRODUCTION

This type of measurement depends on the nature of the antioxidant used. The method described below is suitable for:

- 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) for which the commercial names are CALCO, AO-2246 or MBP5
- 2,6-di-tert-butyl-p-cresol for which the commercial name is IONOL

However, it can be used for other types of antioxidants.

NOTE C-3: Some antioxidants may be very reactive toward all types of isocyanates. As a consequence, such antioxidants are attached to the molecular chain end of the HTPB network by a covalent bond and therefore are not extractable by any procedure. Therefore the method described here will not be suitable for such antioxidants. An example of such an antioxidant is N-phenyl-N'-cyclohexyl-p-phenylene diamine (Flexzone 6H) for which an amino group attached to an aliphatic group is very reactive toward isocyanates. A phenolic type antioxidant such as 2,5-di-tert-butyl-hydroquinone (DTBHQ) has also shown some covalent bonding with the polymeric network depending on the NCO/OH ratio used during the manufacturing process of the propellant.

2. SCOPE AND PRINCIPLES OF METHOD

The method utilizes solutions obtained after maceration of the composite propellant in any suitable solvent according to the formulation. The determination of antioxidant content is made by high performance liquid chromatography (HPLC) using an internal standard procedure.

3. APPARATUS

3.1 Balance accurate to 0.1 mg
3.2 Glassware and standard laboratory equipment
3.3 Centrifuge machine
3.4 Sample filtration system
3.5 Liquid chromatograph with UV detector, integrator and appropriate HPLC column

4. REAGENTS

4.1 Appropriate antioxidant standard - Analytical grade
4.2 Appropriate internal standard (e.g. triphenylamine)
4.3 Methanol or any suitable solvent - HPLC grade

5. ANALYTICAL PROCEDURE

5.1 Preparation of standard solution

In a flask, dissolve in 50 ml of methanol, or any suitable solvent, the following masses accurately weighed to 0.1 mg
- Approximately 10 mg of antioxidant
- Approximately 10 mg of internal standard
Dilution to a larger volume is acceptable as long as the mass to volume ratio is kept constant.

NOTE C-4: The internal standard can be introduced by weighing or by pipetting of a stock solution. The standard solution should be stored *in cool dark conditions* for no more than two weeks.

5.2 Preparation of the solution to be measured to:

Extract in 50 ml of methanol, or any suitable solvent, under agitation, approximately 5 g of propellant (cut into 2 to 3 mm pieces) and approximately 10 mg of internal standard.
Agitate for at least 6 hours.
Allow to settle for a few minutes and take 10 ml to 15 ml of the supernatant solution.
Centrifuge to obtaining a perfectly clear solution or filter (3 µm) before injecting.

5.3 Analysis of standards and samples

Inject 3 µl of the solution to be analyzed into the HPLC.
The injections of standard solutions and solutions to be analyzed must be done under the same operating conditions.

The determination is performed by calculating peak areas.

6. EXPRESSION OF RESULTS

Results shall be expressed as percentage of antioxidant present in the material using internal standard procedure.

7. EXAMPLE OF CHROMATOGRAM

This example illustrates an HPLC method based on a methanol/water mobile phase but any other equivalent method using a different mobile phase can be used.

7.1 Column: Lichrosorb RP 18 (5 µm) 25 cm x 4 mm

7.2 Instrument conditions

Eluent composition: methanol / water (80/20 by volume)
Eluent flow: 1.3 ml/min
Column head pressure: approximately 130 bars
Temperature: 35°C
Injection volume: 3 µl
UV detector, wavelength: 205 nm

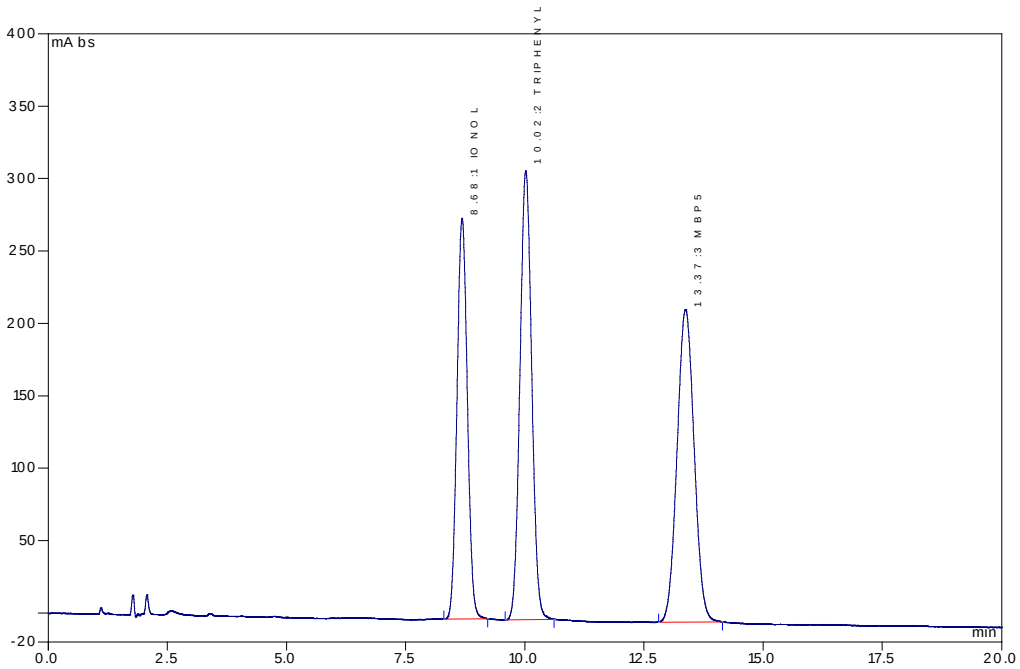


FIGURE 3

CHROMATOGRAM OF ANTIOXIDANTS IN PROPELLANT

Components are:

- IONOL: 2,6-di-tert-butyl-p-cresol (antioxidant)
- MBP5: 2,2'-methylene-bis- (4-methyl-6-tert-butylphenol) (antioxidant)
- Triphenylamine (internal standard)

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TEST 1C: MEASUREMENT OF ANTIOXIDANT CONTENT

Report Reference Number: (Unique Reference Number) **Page 1 of 1 Page**

TEST SITE INFORMATION	**CONDITIONS OF AGEING**
Laboratory: (Name of laboratory) **Date:** (Date that form was completed) **Test Procedure:** (Name of test procedure used) **Date Tested:** (Date of test period) **POC:** (Point of contact)	**Temperature of ageing (°C):** **Test time (months):** **CONDITIONS OF ANALYSIS BY HPLC** **Name of antioxidant:** **Column:** **Name and flow of eluent:** **Name of internal standard**: **Divergences from standard procedure:**
SPECIMEN INFORMATION	**TEST RESULTS**
Identification of Test Material: (Trade name and/or Identify code) **Manufacturer:** (Name of manufacturer) **Test Material, Specification:** (state if specification controls chemical composition of product) **Lot, Batch or Consignment Number:** **Date of Manufacture or Receipt:** **Special Storage Conditions:** (If applicable)	**Antioxidant before ageing:** **Antioxidant after 3 months ageing:** **Antioxidant after 6 months ageing:** **Difference:** **after 3 months:** **after 6 months:** **Comments:** **Data Sent to:**

C.1.4 TEST 1D: MEASUREMENT OF THE PLASTIZER CONTENT

1. INTRODUCTION

The methods for the measurement of plasticizer content in composite propellants described in this section were specifically developed for nonanoic acid 8-methylnonyl ester, better known as isodecyl pelargonate (IDP) and commercially sold under the name Emery® 2911 synthetic lubricant basestock by Cognis Corporation (formerly Henkel Corporation Chemicals Group). Similar methods could be developed for other plasticizers, such as bis (2-ethyl hexyl) adipate (BEHA) and nonanedioic acid di-octyl ester (better known as di-octyl azelate or DOZ).

2. SCOPE AND PRINCIPLES OF METHOD

The determination of the plasticizer content is performed by using the gas chromatography (GC) technique. Two different detectors could be used: the flame ionization detector (FID) or a mass spectrometer (MS).

The Soxhlet extractions in dichloromethane conducted to determine the sol fraction of composite propellants is outlined in Paragraph 3 of Method 1A. However, various modifications can be made to this procedure. These modifications are reported in Paragraph 5.1 of the present section.

3. APPARATUS

3.1 Balance accurate to 0.1 mg
3.2 Glassware and standard laboratory equipment
3.3 Sample filtration system
3.4 Syringe
3.5 GC with FID or GC/MS
3.6 Appropriate GC column and other relevant GC accessories

4. REAGENTS

4.1 Isodecyl pelargonate (IDP) from Cognis Corporation or appropriate plasticizer standard
4.2 Dichloromethane
4.3 Acetonitrile
4.4 Acetone

5. ANALYTICAL PROCEDURE

5.1 Extraction procedures

The sample solution can be taken directly from the dichloromethane extract of the soluble fraction (test 1A). However, the sample solution can be prepared according to one of these three Soxhlet extraction procedures:

5.1.1 Standard Soxhlet extraction procedure

Weight of sample: 3.0 g
Volume of dichloromethane solvent: 200 ml
Extraction time: at least 16 hours
Container: alumina or ceramic extraction thimble

5.1.2 Soxhlet extraction procedure I

Weight of sample: 0.3 g
Volume of dichloromethane solvent: 30 ml
Extraction time: 4 hours
Container: glass filter extraction tube (porosity 3)

5.1.3 Soxhlet extraction procedure II

Weight of sample: 10 g
Volume of dichloromethane solvent: 100 ml
Extraction time: 17 hours
Container: cellulose extraction thimble

5.2 Preparation of standard solutions

Four plasticizer standard solutions ranging from 1 to 4 mg/ml are prepared in an 80/20 v/v mixture of acetonitrile/acetone.

5.3 Preparation of sample solutions

The dichloromethane extract of the sol fraction mainly consists of the plasticizer, the antioxidants and the free polymer chains that are not or that are no longer attached to the crosslinked network. To prepare the sample solutions, the dichloromethane extract of the sol fraction is evaporated in a beaker under a fume hood for at least 6 hours. The beaker is then put in a vacuum oven at 50˚C for about 2 hours. A volume of 100 ml of an 80/20 v/v mixture of acetonitrile/acetone is added to the solid residue. In the obtained solution, the polymer remains in the beaker as a solid residue whereas the other ingredients are soluble in the solvent. The upper liquid, which contains the plasticizer, is filtered through a 13 mm / 0.45 µm PTFE syringe filter prior to analysis by GC. The removal of the polymer from the sol fraction is carried out in order to prevent the plugging of both the GC liner and column.

5.4 Analysis of standards and samples

To analyze the standards and samples, a volume of 1 µl is injected into the chromatograph using FID or MS as detector. A calibration curve is built from the standards. The injections of standards and samples must be done under the same operating conditions. Since some plasticizers (e.g. IDP) consist of a mixture of isomers, the total area of all the peaks corresponding to these isomers is integrated for quantification purposes.

6. EXPRESSION OF RESULTS

The results shall be expressed in percentages of plasticizer present in the propellant sample as output by the chromatography integration system. The original weight of the propellant sample from the sol fraction extraction and the volume of the diluted extract will be required as input data for the chromatography integration system.

7. EXAMPLES OF CHROMATOGRAMS

7.1 Figure 4 shows an example of suitable conditions for a procedure using GC-FID

7.1.1 Column: DB-5, 30 m length, 0.53 mm inner diameter

7.1.2 Instrument conditions:

Instrument: Fisons Instruments HRGC Mega 2 or equivalent
Carrier gas and flow rate: helium 5 ml/min
Injected sample volume: 1 µl
Oven conditioning: 160˚C (5 min), 2˚C/min to 250˚C
Injector temperature: 220˚C
Detector temperature: 250˚C

7.2 Figure 5 shows an example of suitable conditions for a procedure using GC-MS

7.2.1 Column: DB-5, 30-m length, 0.25-mm inner diameter

7.2.2 Instrument conditions:
Instrument: HP 5890 GC / Finnigan Mat series 700 SSQ (single stage quadrupole) or equivalent
Carrier gas and flow rate: helium 1 ml/min (split ratio 1:100)
Injected sample volume: 1 µl
Oven conditioning: 160˚C (5 min), 10˚C/min to 250˚C (7 min)
Injector temperature: 220˚C (transfer line at 250˚C)
Detector temperature: 185˚C

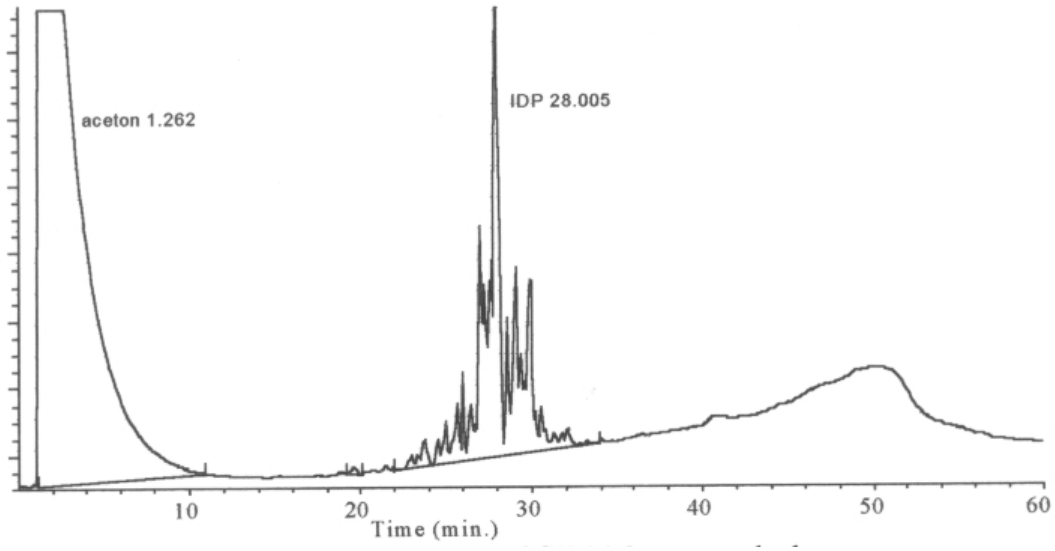


FIGURE 4

CHROMATOGRAM OF IDP PLASTICIZER IN PROPELLANT WITH THE CONDITIONS GIVEN IN 7.1 (GC/FID)

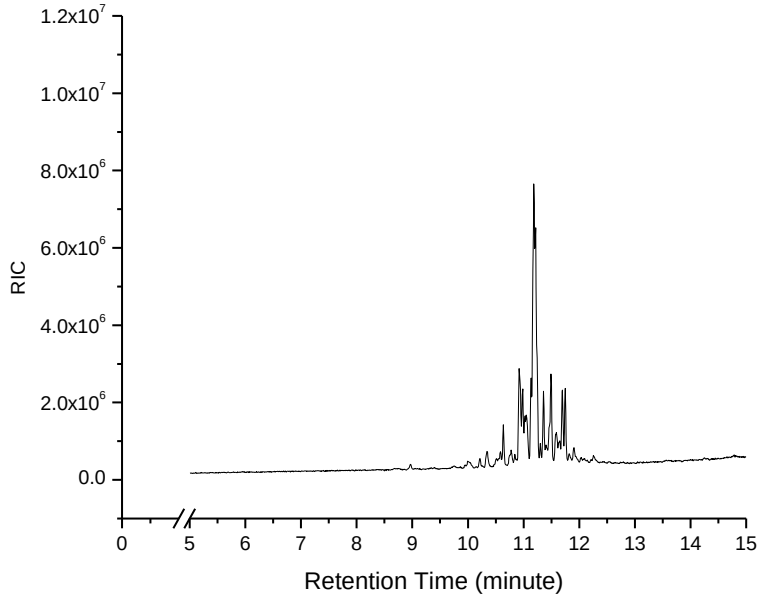


FIGURE 5

CHROMATOGRAM OF IDP PLASTICIZER IN PROPELLANT WITH THE CONDITIONS GIVEN IN 7.2 (GC/MS)

ANNEX C TO
AOP-4581

NATO AOP-4581 DATA SHEET

TEST 1D: MEASUREMENT OF PLASTICIZER CONTENT

Report Reference Number:
Page 1 of 1 Page
(Unique Reference Number)

TEST SITE INFORMATION

Laboratory:
(Name of laboratory)

Date:
(Date that form was completed)

Test Procedure:
(Name of test procedure used)

Date Tested:
(Date of test period)

POC:
(Point of contact)

CONDITIONS OF AGEING

Temperature of ageing (°C):

Test time (months):

CONDITIONS OF ANALYSIS BY GC

Name of plasticizer:

Detector type (FID or MS):

Column type and dimensions:

Carrier gas and flow rate:

Injected sample volume:

Oven temperature programming:

Injector temperature:
Detector temperature:

Divergences from standard procedure:

SPECIMEN INFORMATION

Identification of Test Material:
(Trade name and/or Identify code)

Manufacturer:
(Name of manufacturer)

Test Material Specification:
(State if specification controls chemical composition of product)

Lot, Batch or Consignment Number:

Date of Manufacture or Receipt:

Special Storage Conditions:
(If applicable)

TEST RESULTS

Plasticizer content before ageing:

Plasticizer content after 3 months ageing:

Plasticizer content after 6 months ageing:

Difference:

After 3 months ageing:

After 6 months ageing:

Comments:

Data Sent to:

C.2. MECHANICAL TESTS

C.2.1 TEST 2A: UNIAXIAL TENSILE TEST

1. INTRODUCTION

The accelerated ageing of composite propellant may lead generally to changes in the modulus of elasticity (E_o), the maximum stress (σ_m) and the deformation at maximum stress (ε_m).

2. TEST PROCEDURE

The test procedure is that described in STANAG 4506 with the following specific conditions.

2.1 Sample preparation (see paragraph 4.1 of STANAG 4506)

The samples are collected at the centre of the aged block as described in Figure 1.

2.2 Preconditioning (see paragraph 5.1 of STANAG 4506)

The samples will be preconditioned at 12% RH and 23 $\pm$ 5 ºC for 48 hours.

2.3 Test temperature (see paragraphs 3.2 B and 5.2 of STANAG 4506)

The test temperature shall be 20 $\pm$ 1ºC. Additional tests at higher or lower temperatures between -46ºC and +60ºC may be required as part of an ageing program. In this case, it is necessary to age propellant blocks of greater dimensions.

2.4 Crosshead speed (see paragraph 3.3 of STANAG 4506)

The test speed is generally 50 mm/min.

2.5 Test (see paragraph 5.6 of STANAG 4506)

Test 5 samples of unaged composite propellant and 5 samples of propellant aged under the same operating conditions.

ANNEX C TO AOP-4581

NATO AOP-4581 DATA SHEET (Side A)

TEST 2A: Uniaxial Tensile Test

Report Reference Number: **Page 1 of 2 Pages**
(Unique Reference Number)

TEST SITE INFORMATION

Laboratory:
Date:
Test Procedure:
NATO Test Procedure Number: STANAG 4506
Date Tested:

POC:

SPECIMEN INFORMATION

Dimensions: Length (Gage Length):
(mm) Width:
Thickness:
Cross-Sectional Area (mm^2):
Form:
Preparation Method:
Manufacturing Method:
Source:
Lot or ID Number:
Conditioning Period:
Composition:

Component	Percent
—	—
—	—
—	—

CONDITIONS OF AGEING

Temperature of ageing (ºC):

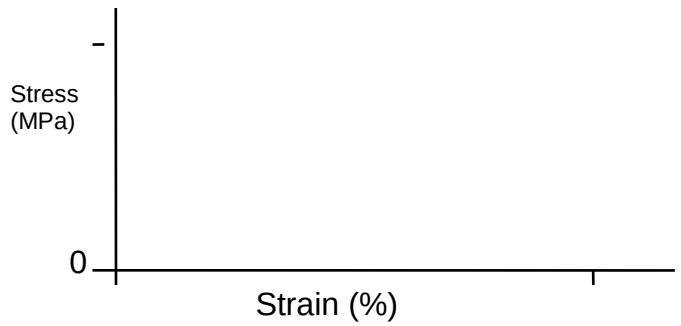
Ageing time (months):

TEST CONDITIONS

Temperature (°C): **Extensometer**
Relative humidity (%): **Yes □ No □**
Cross-head speed (mm/sec):
Machine type:
Grip type:
Machine stiffness (kN/mm):

TYPICAL RESULTS

(Plot typical results of unaged sample and aged samples together in this graph)



ANNEX C TO AOP-4581

NATO AOP-4581 DATA SHEET (Side B)

TEST 2A: Uniaxial Tensile Test

Report Reference Number: (Unique Reference Number)

RESULTS BEFORE AGEING

Test ID	Specimen T (°C)	Specimen A_0 (mm^2)	$\dot{\varepsilon}$ (s^{-1})	σ_m (MPa)	ε_m (%)	σ_r (MPa)	ε_r (%)	E_0 (MPa)	ε_m (direct) (%)	ε_r (direct) (%)	E_0 (direct) (MPa)
Average before ageing											
$\sigma_{(n-1)}$											

RESULTS AFTER AGEING FOR 3 MONTHS

Test ID	Specimen T (°C)	Specimen A_0 (mm^2)	$\dot{\varepsilon}$ (s^{-1})	σ_m (MPa)	ε_m (%)	σ_r (MPa)	ε_r (%)	E_0 (MPa)	ε_m (direct) (%)	ε_r (direct) (%)	E_0 (direct) (MPa)
Average after 3 months											
$\sigma_{(n-1)}$											

RESULTS AFTER AGEING FOR 6 MONTHS

Test ID	Specimen T (°C)	Specimen A_0 (mm^2)	$\dot{\varepsilon}$ (s^{-1})	σ_m (MPa)	ε_m (%)	σ_r (MPa)	ε_r (%)	E_0 (MPa)	ε_m (direct) (%)	ε_r (direct) (%)	E_0 (direct) (MPa)
Average after 6 months											
$\sigma_{(n-1)}$											

Data Send to:	**Comments**

C.2.2 TEST 2B: DYNAMIC MECHANICAL ANALYSIS

1. INTRODUCTION

1.1 DMA provides a measurement of viscoelastic mechanical properties of a propellant in a wide range of temperatures and frequencies and gives the temperature/frequency dependencies of the storage modulus (G' or E'), the loss modulus (G'' or E'') and the loss factor (tan δ).

1.2 In a DMA plot, the storage modulus values generally tend to be highest in the low temperature region (at approximately -110 to -75°C). In this region, the specimens resemble hard, low strain to failure materials. The modulus values then tend to decrease as the temperature is increased. In a temperature sweep, the low temperature peak of the loss modulus corresponds to the glass transition temperature of the propellant, which characterizes the brittle-to-ductile transition.

1.3 Accelerated ageing of composite propellant may lead to changes in the storage modulus across the entire temperature range. These changes tend to be more obvious at the higher temperatures. There is a correlation between the extent of the degradation of the propellant and the difference in modulus. The glass transition temperature, T_g, may also be seen to shift in temperature.

1.4 This AOP refers to STANAGs 4540 and 4506.

2. TEST PROCEDURE

The test procedure used is that described in STANAG 4540 with the following conditions:

2.1 Sample preparation

For information on the specimen configuration, refer to STANAG 4540, ANNEX B, and paragraph 2.2. The specimen configuration is dependent on the instrument manufacturer's recommendations. Details on how to prepare the specimen from the bulk material are described in ANNEX C of STANAG 4540.

2.2 Preconditioning

Samples will be preconditioned as required. Preconditioning includes a number of factors:
(1) Environmental test equipment used to age the propellant,
(2) Conditions the propellant is exposed to whilst waiting to be tested and
(3) Conditioning of the propellant once loaded on the instrument, but prior to initiating the test.

2.3 Test method (see ANNEX B, paragraph 3.1 of STANAG 4540)

The mechanical properties shall be measured in the temperature region –120°C to 100°C with a single frequency (e.g. 1 Hz). This temperature range may vary depending on the chemical composition of the propellant. Where a thermal ramp is used, consideration must be given to the temperature lag in the sample.

2.4 Performance of the test

A series of tests are normally performed on both original (unaged) and artificially aged materials. Usually the mechanical changes in these materials occur gradually. Therefore, a series of tests on aged materials will show a progressive change rather than an abrupt change, reducing the need for duplication. If however, dramatic changes in properties are observed, additional tests need to be performed to determine the cause of these changes. All tests on unaged and aged propellant shall be carried out under the same conditions.

ANNEX C TO AOP-4581

NATO AOP-4581 DATA SHEET (Side A)

TEST 2B: DYNAMIC MECHANICAL ANALYSIS

Report Reference Number: **Page 1 of 2 Pages**
(Unique Reference Number)

TEST CONDITIONS	**SPECIMEN INFORMATION**
Initial/final temperature (°C): (Temperature range):	**Dimensions (mm):** (Mean specimen length, width and thickness) **Length:** **Width:** **Thickness:**
Conditioning temperature (°C):	**Length Correction:** (Effective length extension of specimen)
Conditioning time (min):	**Form:** (Specimen geometry descriptor)
Osc. amp. (°, mm or %): (Amplitude oscillation)	**Identification:** (Trade name and/or identify code)
Frequency (Hz, rad/s): (Frequency of oscillation)	**Preparation Method:** (Specimen preparation procedure)
Temperature rate (°C min^{-1}): (Rate of temperature sweep)	**Manufacturer Method:** (Material processing technique)
Machine type: (Name and model number of machine)	**Source:** (Name of manufacturer)
Grip type: (Name of grip)	**Lot, Batch or Consignment Number:** (Same as on material description sheet)
Test type: (Type of DMA test)	**Conditioning History:** (Period specimen was conditioned)
CONDITIONS OF AGEING:	
Temperature of ageing (°C):	
Test time (months):	
TEST SITE INFORMATION	**COMPOSITION**
Laboratory: (Name of laboratory)	**(Component and percentage)**
Date: (Date that form was completed)	
Date Tested: (Date of test period)	
Test Procedure: STANAG 4540 (Name of test procedure used)	
POC (Point of contact):	

ANNEX C TO AOP-4581

NATO AOP-4581 DATA SHEET (Side B)

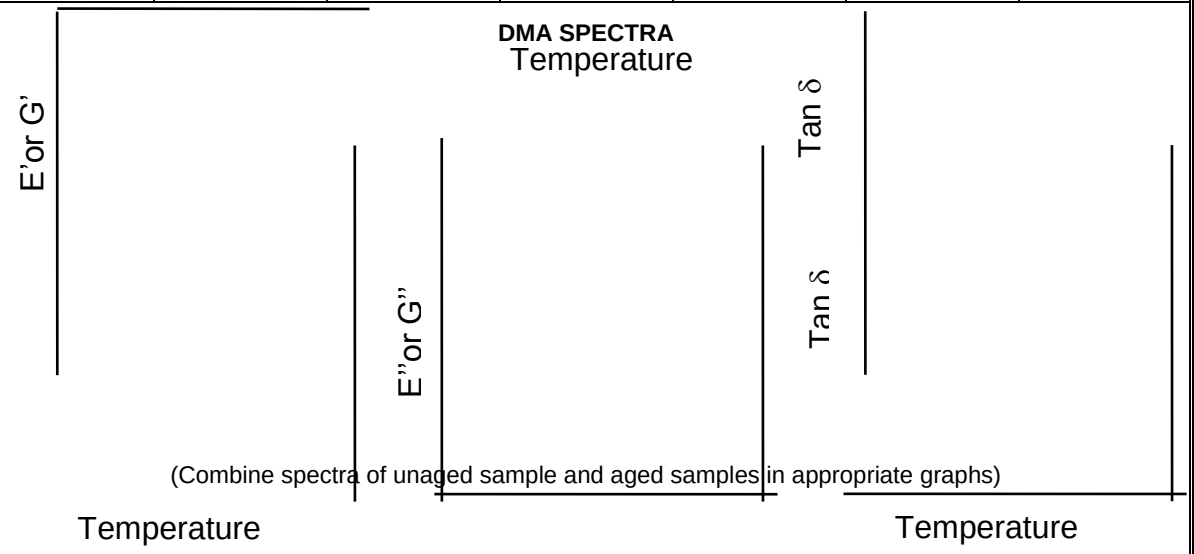
TEST 2B: DYNAMIC MECHANICAL ANALYSIS

Report Reference Number: (Unique Reference Number) **Page 2 of 2 Pages**

RESULTS

	Before ageing		**After ageing for 3 months**		**After ageing for 6 months**	
T (°C)	**E'or G' (MPa)**	**Tan δ**	**E'or G' (MPa)**	**Tan δ**	**E' or G' (MPa)**	**Tan δ**
(Specimen temperature)	(Storage tensile or shear modulus)	(E''/E' or G''/G')	(Storage tensile or shear modulus)	(E''/E' or G''/G')	(Storage tensile or shear modulus)	(E''/E' or G''/G')

DMA SPECTRA



(Combine spectra of unaged sample and aged samples in appropriate graphs)

GLASS TRANSITION TEMPERATURE T_g (°C)

Before ageing :
After ageing for 3 months:
After ageing for 6 months:

at frequency of Hz

Comments:

Data Sent to: (Name and address of person receiving this information)

C.2.3 TEST 2C: MEASUREMENT OF SHORE A HARDNESS

1. INTRODUCTION

Shore A hardness provides a measurement of the hardness of the propellant measured in Shore A. Ageing may lead to changes in hardness of the propellant.

2. TEST PROCEDURE

The test procedure used is that described in ASTM D2240-00 with the following conditions:

2.1 Sample preparation

The sample shall have a diameter of at least 35 mm with a smooth and even surface. The thickness of the sample shall be at least 6 mm.

2.2 Preconditioning

Samples shall be preconditioned for at least 30 minutes if any temperature other than (23 ± 2)°C is used.

2.3 Apparatus

An apparatus as specified in ASTM D2240-00 shall be used.

2.4 Test method

(1) The apparatus shall be carefully placed in close contact with the sample, avoiding any form of impact.
(2) At least three measurements on each sample shall be made with a distance of at least 5 mm from each other and with a distance from the edges of at least 13 mm.
(3) The Shore A hardness is read on the apparatus after 3 sec.

2.5 Performance of the test

The difference between two measurements performed by the same person with the same apparatus must not exceed 2 Shore A.

The difference between two measurements performed by two different persons with different apparatus must not exceed 3 Shore A.

ANNEX C TO
AOP-4581

NATO AOP-4581 DATA SHEET

TEST 2C: MEASUREMENT OF SHORE A HARDNESS

Report Reference Number: **Pages 1 of 2**
Pages
(Unique Reference Number)

TEST SITE INFORMATION

Laboratory:

Date:

Date Tested:

Test Procedure:

POC:

CONDITIONS OF AGEING

Temperature of ageing (°C):

Test time (months):

TEST CONDITIONS

Test temperature (°C):

Conditioning history:

Apparatus manufacturer:

Apparatus number:

SPECIMEN INFORMATION

Dimensions (mm):
(Mean specimen diameter and thickness)

Length:

Width:

Thickness:

Form:

Identification:
(Trade name and/or Identification code)

Preparation Method:

Manufacturer:

Source:

Lot, Batch or Consignment Number:

COMPOSITION

(Component and percentage)

ANNEX C TO AOP-4581

NATO AOP-4581 DATA SHEET

TEST 2C: MEASUREMENT OF SHORE A HARDNESS

Report Reference Number: **Pages 2 of 2**
Pages
(Unique Reference Number)

RESULTS
(in Shore A)

Before ageing

Sample/measurement	**1**	**2**	**3**	**Mean**	**SD**
1					
2					
3					
4					

After 3 months ageing

Sample/measurement	**1**	**2**	**3**	**Mean**	**SD**
1					
2					
3					
4					

After 6 months ageing

Sample/measurement	**1**	**2**	**3**	**Mean**	**SD**
1					
2					
3					
4					

ANNEX D TO AOP-4581

ANNEX D ASSESSMENT OF THE RESULTS

1. GUIDELINES TO ASSESS THE RESULTS

The behaviour of a propellant towards the tests described in this AOP might be different from the behaviour of another propellant containing a different binder. In addition, a clear correlation between changes in the chemical properties and changes in the mechanical properties has not been demonstrated yet. Therefore, it is impossible to give specific sentencing criteria for all types of propellants. Sentencing criteria shall thus be agreed between the purchaser and the manufacturer. The results obtained could also be used as criteria to select a propellant formulation intended for a specific application.

Propellants are designed to meet a variety of mission applications, which place increasingly severe demands on the structural capability of the propellant grain. It is generally accepted that the specific service life of a given propellant cannot be assigned without knowledge of its missile system application. When a solid rocket motor fails catastrophically, it is usually due to a structural problem such as a bore crack or case debond. Service life methodologies for composite solid propellant grains have therefore been based on mechanical behavior measurements and predictions. Mechanical property measurements from uniaxial tensile tests and dynamic mechanical analysis provide an assessment of the propellant's current condition. Coupling mechanical behavior degradation rates with finite element structural analyses generally makes predictions in motor service life.

AOP-4581(A)(1)