NATO STANDARD

AOP-4023

ENERGETIC MATERIALS, SPECIFICATION FOR PENTHRITE (PETN)

Edition A, Version 1

JULY 2022

NORTH ATLANTIC TREATY ORGANIZATION

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NORTH ATLANTIC TREATY ORGANIZATION (NATO)

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NATO LETTER OF PROMULGATION

27 July 2022

1. The enclosed Allied Ordnance Publication AOP-4023, Edition A, Version 1, ENERGETIC MATERIALS, SPECIFICATION FOR PENTHRITE (PETN), which has been approved by the nations in the CNAD AMMUNITION SAFETY GROUPE (CASG - AC/326), is promulgated herewith. The agreement of nations to use this publication is recorded in STANAG 4023.

2. AOP-4023, 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 complete. 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 aim of this agreement is to ensure that pentaerythritol tetranitrate (PETN, penthrite) shall possess properties which make it suitable for military use and to provide, within NATO, an acceptable basis for the procurement and certification of PETN.

1.2. AGREEMENT

Participating nations agree that PETN proposed for military use, except when ordered for particular uses, shall meet all the requirements of Table A-1 of this document. The test procedures used to verify the requirements of Table A-1 are described in Annex B. The methods used and the results obtained shall be quoted on the test certificate of Annex C.

1.3. GENERAL

1.3.1. Composition

The PETN shall consist of pentaerythritol tetranitrate corresponding to the chemical formula $C(CH_2NO_3)_4$ and to the structural formula given in Figure 1 below.

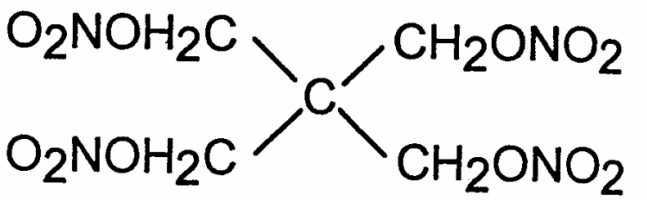

Figure1: PETN structural formula

1.3.2. Manufacturing process

Any data or information concerning the proposed manufacturing process must be provided in confidence at the request of the purchaser. Any deviation from this accepted process must be noted and the product thus manufactured put aside until the purchaser has determined its approval or rejection.

1.3.3. Appearance and granulation

1. The material shall be in the form of white crystals and shall conform to the granulation requirements specified in the contract between manufacturer and purchaser. In his order, the purchaser must clearly specify the granulation he requires. Example of PETN granulation classes and their typical use are provided in Table A-2. The purchaser is however free to require different granulation specification of PETN according to his needs.

2. At the purchaser's request, the manufacturer shall provide microphotography of PETN crystals. Magnification of the microphotography shall permit clear viewing of individual particle shape (needles, spheres, irregular crystals etc.).

1.3.4. Definition of lot

For material manufactured by a continuous process, a lot is defined as the total quantity that is offered for acceptance at one time. For material manufactured by a batch process, a lot may be either the output of a single batch or a blend of several batches that have been combined to give a material of uniform properties throughout the lot.

1.3.5. Sampling

The sample size taken from each lot should be at least 200 g. The sampling technique must lead to a representative sample of each lot and has to be agreed to by the purchaser.

1.3.6. Drying procedure

It will be necessary to dry samples before testing if taken from a water-wetted supply. The sample is dried in a thin layer in an oven at 60 °C to constant mass.

1.3.7. Rejection criteria

Failure of a representative sample of PETN to meet the requirements specified in Table A-1 shall cause rejection of the lot of PETN from which the sample was taken.

1.3.8. Warning

This AOP 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 the statutory obligations relating to health and safety at any stage during use.

ANNEX A PHYSICAL AND CHEMICAL PROPERTIES

A.1. MINIMUM REQUIREMENTS

Table A-1 shows the minimum requirements for the properties of PETN.

Characteristics	Required value	Test method See Annex B
Purity	min 98 % PETN	1
Melting point	141.0 ± 1.0 °C	2 or 3, Note 1
Acidity (as HNO_3)	max 0.01 %	4
Alkalinity (as Na_2CO_3)	max 0.01 %	4
Acetone insoluble	max 0.10 %	5
Gritty particles	No more than 3 gritty particles per 50 g sample retained on a 0.25 mm aperture sieve; no gritty particles retained on a 0.42 mm aperture sieve	6
Vacuum stability test	max 0.2 cm^3/g after 48 hours at 100 °C	7
Granulation	according to purchaser's specification	8, 9 or 10, Note 1

Table A-1: Minimum requirements for properties of PETN

NOTE:

1. Only one of these tests, which are deemed to be equivalent, should be followed.

A.2. TYPICAL GRANULATION

Table A-2 shows the typical granulation classes of PETN.

	Percent passing specified sieve				
Aperture sieve (mm)	**Class 1**	**Class 2**	**Class 3**	**Class 4**	**Class 5**
0.800	-	-	-	-	min 99.5
0.600	-	-	min 95	min 100	-
0.500	-	-	-	-	min 65
0.315	-	-	-	-	min 15 – max 45
0.200	-	-	-	-	max 10
0.180	min 100	-	-	-	-
0.150	min 85	min 95	-	min 5 – max 20	-
0.106	max 55	-	-	-	-
0.075	max 30	min 65 – max 80	max 30	-	-
Typical use	Detonating cord	Primers for small arms ammunition	Pentolite	Blasting caps and detonators	General purposes

Table A-2: Minimum requirements for properties of PETN

ANNEX B TEST PROCEDURES

B.1. DETERMINATION OF PETN PURITY BY HPLC ANALYSIS

1. Principle. The chemical purity of PETN sample shall be determined by high performance liquid chromatography (HPLC) using a standard instrument.

2. Equipment. A high performance liquid chromatograph equipped with an ultraviolet (UV) or diode array detector (DAD) and an integrator or computer link to a data acquisition system; a HPLC reverse-phase column (e.g. RP-8 or RP-18); 0.45 µm syringe filters; 100 ml volumetric flasks; pipette.

3. Reagents. Acetonitrile (HPLC grade); acetone (analytical reagent grade), water (HPLC grade); PETN standard (purity > 99.5 %); appropriate internal standard (e.g. ethyl centralite) (analytical reagent quality).

4. Example HPLC conditions. Table B-1 shows example HPLC conditions which are given for information only since each instrument and column will require conditions specific to the instrument used. Baseline separation of PETN peak from peaks of its major impurities (e.g. dipentaerythritol hexanitrate - DPEHN, tripentaerythritol octanitrate - TPEON) and that of internal standard must be achieved with the HPLC conditions chosen.

Eluent	Acetonitrile / water (60 / 40)
Flow rate	1.0 ml per minute
Injection volume	5 µl
UV detector wavelength	230 nm
UV detector bandwidth	4 nm
Temperature	35 °C
Time of analysis	5 minutes

Table B-1: Example HPLC conditions

5. PETN calibration standard preparation. As a calibration standard, PETN with purity higher than 99.5 % PETN is required. PETN with the required purity can be prepared by fractional recrystallization of industrial grade PETN sample from acetone or acetone-water mix. Impurities such as DPEHN and TPEON are more soluble in

these solvents than PETN. UV absorbing impurities in such a standard shall represent less than 0.5 % of total chromatogram peak area (solvent peak excluded).

6. Sample preparation. Weigh approximately 40 mg of dry PETN sample and 40 mg of an internal standard (both weighed to 0.1 mg) and add them to a 100 ml volumetric flask. Add acetone to dissolve the sample and then fill the volumetric flask with acetone to mark. Filter the sample solution through a 0.45 micron syringe filter. This solution is used for injection on the column. These weights and volumes are suggested ones - they may be modified depending on the specific conditions used.

7. Standard preparation. Prepare solution of PETN calibration standard with an internal standard by the same procedure as described in the previous paragraph.

8. Analytical procedure. Perform calibration and analysis of the sample when the chromatographic conditions and the detector reading are stable. Three injections of the PETN standards should be run before the sample is analyzed. The injections shall be performed using a syringe or autosampler and sampling loop of appropriate volume as required for the conditions being used. Run analysis of the sample(s) (three injections per sample) and perform measurement of standards again as stated above. No more than five samples should be run between standards. All the injections must be done under the same operating conditions.

9. Expression of the results. As a method of qualitative analysis, retention times of PETN peaks of standards and samples are compared. Retention times of standards shall correspond to those of the samples. Verification of the UV spectrum using a DAD detector can also be used for an identity check of the PETN peak. Peak areas of PETN and internal standard are calculated for the three injections of the calibration standard and sample. The results of the three injections are averaged for the sample and the standard. The areas of the three injections of the same sample should agree within 1% relative to each other. The response factor (RF) for PETN calibration standard is calculated as follows:

$$\mathrm{RF} = \frac{\mathrm{m_{P-C}} \times \mathrm{A_{IS-C}}}{\mathrm{m_{IS-C}} \times \mathrm{A_{P-C}}}$$

where $m_{P\text{-}C}$ is the mass of pure PETN (g) in calibration standard, $m_{IS\text{-}C}$ is the mass of internal standard (g) in calibration standard, $A_{P\text{-}C}$ is the average area of PETN peak (mAU.s) from three runs of the calibration standard solution and $A_{IS\text{-}C}$ is the average area of internal peak standard (mAU.s) from three runs of the calibration standard solution. PETN content in the sample being analyzed is calculated as follows:

$$\%\ \mathrm{PETN} = \frac{\mathrm{A_P} \times \mathrm{m_{IS}} \times \mathrm{RF}\ \times 100}{\mathrm{A_{IS}} \times \mathrm{m}}$$

where RF is the response factor for PETN calibration standard, A_P is the average area of PETN peak (mAU.s) from three runs of the sample solution, A_{IS} is the average area of internal standard peak (mAU.s) from three runs of the sample solution, m_{IS} is the mass of internal standard (g) and m is the mass of the sample (g).

10. Example of chromatogram. Figure B-1 shows an example of a HPLC chromatogram of a PETN sample, measured with an instrument equipped with a Hypersil BDS 100 x 4 mm, 3 µm grain column. The other conditions are these described in Table B-1. For clarity, the chromatogram shows results of a PETN sample with an unacceptably high content of impurities (6 % of DPEHN).

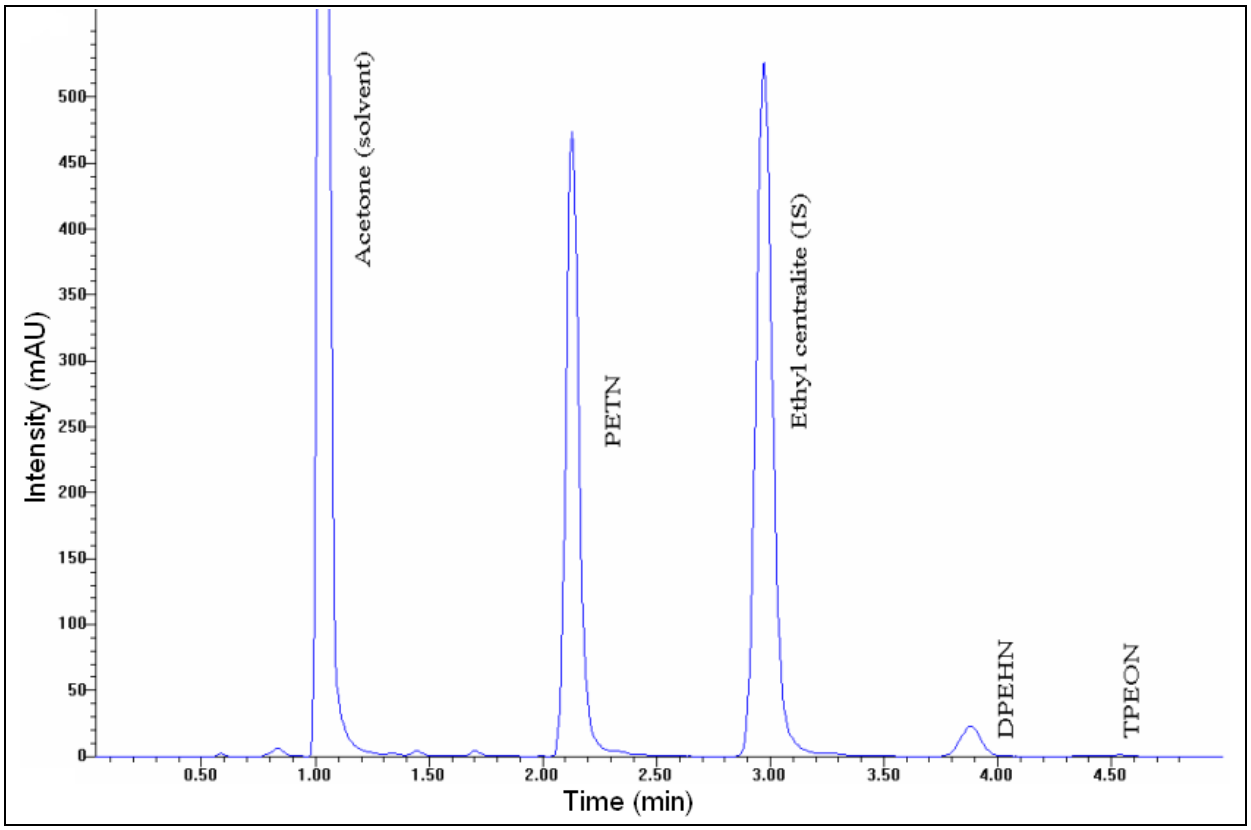

Figure B-1: HPLC chromatogram of PETN sample

B.2. DETERMINATION OF MELTING POINT BY THE CAPILLARY TUBE METHOD

1. Principle. The melting point is determined by the capillary tube method, in accordance with the procedures specified in AOP-4682 “Energetic materials, test methods for ingredients”.

2. Equipment. According to AOP-4682.

3. Procedure. Equipment preparation, calibration and test shall be carried out according to procedures described in AOP-4682.

4. Expression of the results. The melting point shall be calculated according to procedures described in AOP-4682.

B.3. DETERMINATION OF MELTING POINT BY DIFFERENTIAL SCANNING CALORIMETRY

1. Principle. Differential scanning calorimetry (DSC) is a thermal analysis technique described in STANAG 4515 “Explosives, thermal analysis using differential thermal analysis (DTA), differential scanning calorimetry (DSC), heat flow calorimetry (HFC), and thermogravimetric analysis (TGA)”.

2. Equipment. According to STANAG 4515.

3. Procedure. Approximately 0.5 - 1.0 mg of a representative portion of dry sample shall be weighted into the sample container, which shall be sealed with a lid. The sample shall be heated at 5 °C.min^{-1} from the ambient temperature to 150 °C. The test shall be repeated using a further representative proportion of the sample. Equipment preparation, calibration and test shall be carried out according to procedures described in STANAG 4515. Indium (melting point 156.6 °C) is recommended as a material for temperature calibration.

4. Expression of the results. The melting point shall be calculated according to procedures described in STANAG 4515. Figure B-2 shows an example of a PETN thermogram measured by DSC following this procedure.

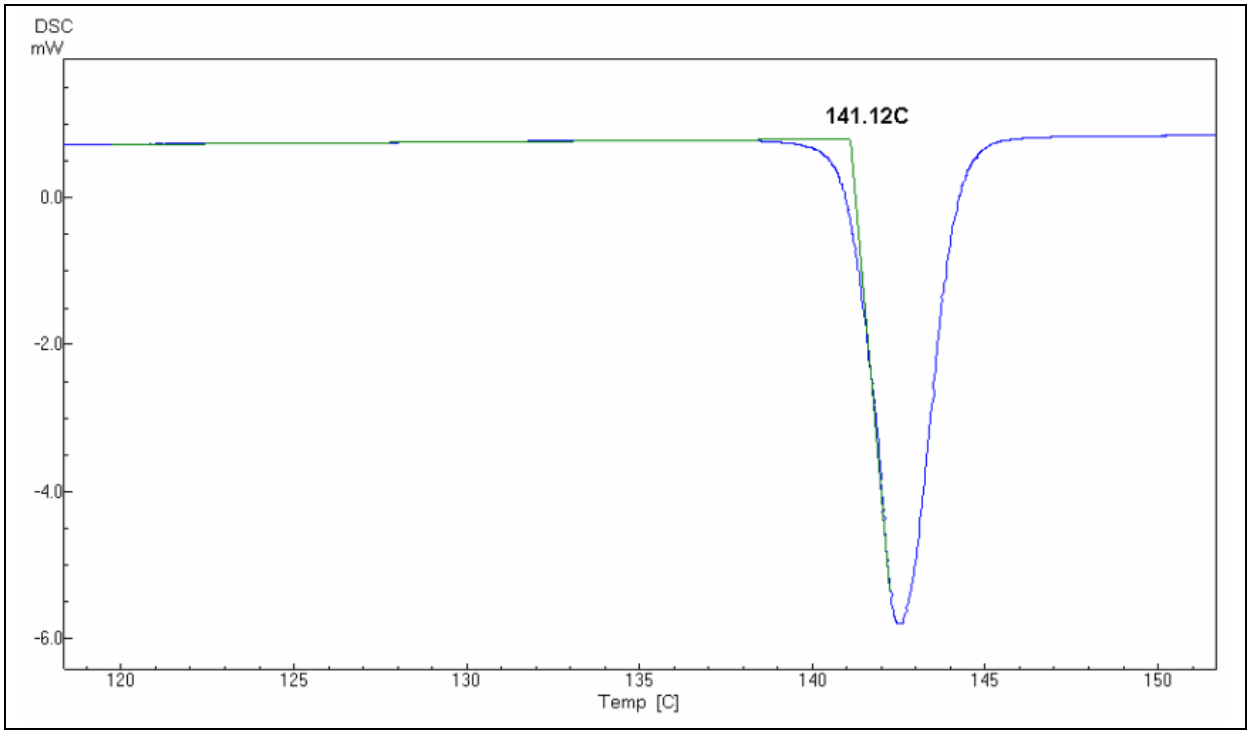

Figure B-2: Example of a PETN thermogram with PETN melting peak

B.4. DETERMINATION OF ACIDITY OR ALKALINITY

1. Principle. The acidity or the alkalinity is determined in back-titration by sodium hydroxide solution of a known quantity of excess sulfuric acid, in accordance with the procedures specified in AOP-4682 “Energetic materials, test methods for ingredients”.

2. Equipment. According to AOP-4682.

3. Procedure. Equipment preparation and test shall be carried out according to procedures described in AOP-4682.

4. Expression of the results. The acidity or alkalinity shall be calculated according to procedures described in AOP-4682.

B.5. DETERMINATION OF ACETONE INSOLUBLE

1. Principle. The quantity of acetone insoluble matter is determined in accordance with the procedures specified in AOP-4682 “Energetic materials, test methods for ingredients”.

2. Equipment. According to AOP-4682.

3. Procedure. Equipment preparation and test shall be carried out according to procedures described in AOP-4682.

4. Expression of the results. The quantity of acetone insoluble matter shall be calculated according to procedures described in AOP-4682.

B.6. DETERMINATION OF GRITTY PARTICLES

1. Principle. The number of gritty particles in PETN sample is determined in accordance with the procedures specified in AOP-4682 “Energetic materials, test methods for ingredients”.

2. Equipment. According to AOP-4682.

3. Procedure. Equipment preparation and test shall be carried out according to procedures described in AOP-4682.

4. Expression of the results. The number of gritty particles retained on 0.25 and 0.42 mm aperture sieves shall be reported according to procedures described in AOP-4682.

B.7. DETERMINATION OF STABILITY BY VACUUM STABILITY TEST

1. Principle. This method determines possible instability of the sample due to the presence of destabilizing impurities. A sample of the energetic material is heated for a specified time in an evacuated tube in a heating bath maintained at a constant specified temperature. The volume of gas evolved is determined by either a mercury manometric method or by using a pressure transducer, in accordance with the procedures specified by STANAG 4556 "Explosives: Vacuum Stability Test".

2. Equipment. According to STANAG 4556.

3. Procedure. Equipment preparation and calibration shall be carried out according to procedures described in AOP-4556. Sample of dry PETN shall be tested using the following experimental conditions: sample mass of 1 g, temperature of 100 °C and duration of heating of 48 hours.

4. Expression of the results. Amount of gases evolved from the sample at the test shall be calculated according to procedures described in STANAG 4556. The result shall be expressed as an average value from at least two trials.

B.8. DETERMINATION OF GRANULATION BY WET SIEVES METHOD

1. Principle. The granulation is determined by sieving a sample of PETN using water spray and a set of specified sieves, in accordance with the procedures specified in AOP-4682 “Energetic materials, test methods for ingredients”.

2. Equipment. According to AOP-4682.

3. Procedure. Equipment preparation and test shall be carried out according to procedures described in AOP-4682.

4. Expression of the results. The granulation shall be reported according to procedures described in AOP-4682.

B.9. DETERMINATION OF GRANULATION BY SONIC SIFTER METHOD

1. Principle. The specimen is sieved either dry or wetted by an anti-static agent on a set of sieves.

2. Equipment. Sonic sifter or equivalent equipment; set of sieves according to the purchaser’s specification or Table A-2 (e.g. with 0.800 mm, 0.600 mm, 0.500 mm, 0.315 mm, 0.200 mm, 0.180 mm, 0.150 mm, 0.106 mm and 0.075 mm aperture), with diameters of at least 150 mm; dust stop/diaphragm/spacers/top cone/fines collector - assembled to form a nest; analytical balance capable of measuring to 0.1 mg; stiff bristled brush.

3. Reagents. Anti-static solution: prepare a 0.1% solution of non-ionic surfactant in purified water; anti-static clothing dryer sheets or aerosol spray for treating nest of sieves and/or inside of sonic sifter.

4. Procedure. Weigh approximately 2 - 10 g of the dry sample. Samples which retain a static charge after drying may be treated with a dilute aqueous anti-static solution. Following treatment, the specimen must be redried until constant weight is obtained. Pre-weigh each sieve and the receiving pan. Stack the sieve in size order (coarsest on top). Transfer sample to the top of the coarsest sieve. Place sieve assembly in the sonic sifter. Set the sift/pulse mode dial to a proper amplitude. Proper amplitude is determined as the minimum level which causes the granules to "dance" on the top sieve. Set timer to 4 minutes. After sifter stops, reweigh each sieve and receiving pan. For safety reasons, the sieving operations can be accomplished with pressurized water having a pressure between 0.5 and 1.5 bars.

5. Expression of the results. Calculate the percentage of the sample passed through the specified sieve. For a stack of n sieves, where sieve s_1 is on the top and s_n is the bottom sieve:

$$\% \textbf{ passing sieve } s_i = \frac{\left(m_{tot} - \sum_{k=1}^{i} m_k\right)}{m_{tot}}$$

where m_k is the mass of sample retained on the k^{th} sieve (g) and m_{tot} the total mass of the sample (g).

B.10. DETERMINATION OF GRANULATION BY LALLS METHOD

1. Principle. The granulation is determined by use of a particle size analyser based on low angle laser light scattering (LALLS), in accordance with the procedures specified in AOP-4682 “Energetic materials, test methods for ingredients”.

2. Equipment. According to AOP-4682.

3. Procedure. Equipment preparation and test shall be carried out according to procedures described in AOP-4682.

4. Expression of the results. The granulation shall be reported according to procedures described in AOP-4682.

ANNEX C TO AOP-4023

ANNEX C TEST CERTIFICATE FOR PETN

AOP-4023 – TEST CERTIFICATE FOR PETN

Report Reference Number
(Unique Reference Number)
Page

TEST SITE INFORMATION	PETN SAMPLE INFORMATION
Laboratory (Name of Laboratory) **Date:** (Date that form was completed) **Date Tested:** (Date of test period) **POC:** (Point of contact)	**Identification:** (Trade name and/or Identity code) **Manufacturer:** (Name of Manufacturer) **Lot, Batch of Consignment Number:** **Date of Manufacture or Receipt:** **Quantity:**

TEST RESULTS

PROPERTY	METHOD	VALUE FOUND	UNIT
Purity	HPLC		% PETN
Melting point	Capillary Tube or DSC		°C
Acidity	Titration by indicator or Titration by pH electrode		% HNO_3
Alkalinity			% Na_2CO_3
Acetone insoluble			%
Gritty particles	Soxhlet extraction		ea retained on 0.25 mm sieve
			ea retained on 0.42 mm sieve
Stability	Vacuum stability test		cm^3/g
Granulation	Wet sieve or Sonic sifter or LALLS		% passing 0.800 mm sieve
			% passing 0.600 mm sieve
			% passing 0.500 mm sieve
			% passing 0.315 mm sieve
			% passing 0.200 mm sieve
			% passing 0.180 mm sieve
			% passing 0.150 mm sieve
			% passing 0.106 mm sieve
			% passing 0.075 mm sieve

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