

MIL-A-82667/2 (OS)

31 January 1977

MILITARY SPECIFICATION

AMMONIUM PERCHLORATE, CONDITIONED

This detail specification is approved for use by the Naval Sea Systems Command, Department of the Navy, and is available for use by all Departments and Agencies of the Department of Defense.

The complete requirements for procuring the ammonium perchlorate described herein shall consist of this document and the latest issue of MIL-A-82667.

1. SCOPE

1.1 Scope. This specification gives the detailed requirements for two types of ammonium perchlorate with an anticaking agent added.

1.2 Classification. The material shall be classified as follows:

Type I	Class 1 - Whole crystals (200 μ m)
	Class 2 - Ground crystals (8 to 13 μ m)
Type II	Whole crystals (80 μ m)

2. APPLICABLE DOCUMENTS

2.1 Government documents. The following documents of the issue in effect on date of invitation for bids or request for proposals, form a part of this specification to the extent specified herein:

SPECIFICATIONS

Military

MIL-D-3464	Desiccants, Activated, Bagged, Packaging Use and Static Dehumidification
MIL-A-82667	Ammonium Perchlorate, General Specification for

STANDARDS

Military

MIL-STD-105	Sampling Procedures and Tables for Inspection by Attributes
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Beneficial comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: Commanding Officer, Naval Ordnance Station, Standardization Division (611), Indian Head, Maryland 20640, by using the self-addressed Standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document or by letter.

FSC 6810

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MIL-STD-129	Marking for Shipment and Storage
MIL-STD-1218	ACS Chemicals
MIL-STD-1234	Pyrotechnics: Sampling, Inspection and Testing

(Copies of specifications, standards, drawings and publications required by suppliers in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Non-Government documents. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated the issue in effect on date of invitation for bids or request for proposal shall apply.

AMERICAN SOCIETY FOR TESTING AND MATERIALS

ASTM B 330-65(1970)	Average Partical Size of Refractory Metals and Compounds by Fisher Subsieve Tester
ASTM D 1348-61(1974)	Moisture in Cellulose
ASTM E 11-70	Wire Cloth Sieves for Testing Purposes
ASTM E 203-75	Water Using Karl Fischer Reagent

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.)

CODE OF FEDERAL REGULATIONS

49 CFR 100-199	Transportation
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(The Interstate Commerce Commission Regulations are now a part of the Code of Federal Regulations, available from the Superintendent of Documents, Government Printing Office, Washington, DC 20402. Orders should cite "49 CFR 100-199" The latest issue and supplements thereto.)

(Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.)

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3. REQUIREMENTS

3.1 Material. The material shall meet the general requirements of MIL-A-82667 and the detailed requirements given herein. The material shall be solid white crystalline ammonium perchlorate (NH_4ClO_4) containing Tricalcium Phosphate (TCP) as a conditioner. Type I Class 1 shall be solid white crystalline ammonium perchlorate consisting essentially of whole crystals with rounded corners and edges. Type I Class 2 shall be Type I ground to a particle size of 8 μm to 13 μm . Type II shall be whole crystals.

3.2 Chemical and physical properties. The chemical and physical properties shall conform to Table I.

3.3 Workmanship. The material shall be uniform, free from contamination, foreign material or any other defect that would prevent its use for the purpose intended.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified, the supplier may utilize his own facilities or any commercial laboratory acceptable to the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to prescribed requirements.

4.2 Lot.

4.2.1 Whole crystals. A lot shall consist of the total quantity of cross-blended material. For non-cross-blended material, a lot shall consist of the quantity produced in a single batch; or when manufactured by a continuous process, a lot shall consist of the total quantity offered for acceptance at one time.

4.2.2 Ground crystals. A lot shall consist of the amount of ammonium perchlorate ground in a single day in the same grinding mill under the same operating parameters and offered for acceptance at one time.

4.3 Sampling. Representative samples of each lot shall be selected for testing in accordance with MIL-A-82667.

4.4 Visual inspection. All samples shall be visually inspected to determine conformance to the workmanship requirements.

4.5 Quality conformance tests. The Type I quality conformance tests shall consist of all the tests in 4.6 and those for Type II shall consist of all the tests in 4.7. All tests shall be in accordance with MIL-A-82667. When specified in the contract or order (see 6.2), the contractor shall submit a report giving the results obtained for all inspections performed and a certified statement that the lot meets all the requirements of this specification. Unless otherwise specified, all chemicals shall be ACS grade in accordance with MIL-STD-1218.

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TABLE I - Chemical and Physical Requirements.

Requirements	Type I			Type II		
	Minimum	Maximum	Test Method	Minimum	Maximum	Test Method
Composition requirements (wt%)						
Purity	98.3	-	4.6.1	98.8	-	4.7.1
Chloride, as NH_4Cl	-	0.155	4.6.2	-	0.15	4.7.2
Chlorate, as NH_4ClO_3	-	0.020	4.6.3	-	0.02	4.7.3
Bromate, as NH_4BrO_3	-	0.004	4.6.4	-	-	-
Sulfated ash, H_2SO_4	-	-	-	-	0.45	4.7.4
Sulfated ash, calculated as NaClO_4	-	0.9	4.6.5	-	-	-
Iron, as Fe_2O_3	-	0.0036	4.6.6	-	0.0036	4.7.5
Sodium and potassium tricalcium phosphate, as $\text{Ca}_3(\text{PO}_4)_2$	-	-	-	-	0.08	4.7.6
Moisture, total	0.10	0.25	4.6.7	0.15	0.22	4.7.7
Moisture, surface	-	0.06	4.6.8	-	0.08	4.7.8
Water insolubles	-	0.02	4.6.9	-	0.020	4.7.9
Acid insolubles	-	-	-	-	0.25	4.7.10
pH	-	0.04	4.6.10	-	-	-
Granulation	5.0	6.5	4.6.11	5.5	6.5	4.7.11
		TABLE II	4.6.12		TABLE III	4.7.12

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TABLE II - Type I Class 1 Particle Size.

U.S. Standard Sieve No.	Percent passed by the size sieve shown	
	Minimum	Maximum
40	96	-
50	89	97
70	57	87
100	14	50
140	2	15
200	-	3

TABLE III - Type II Particle Size.

U.S. Standard Sieve No.	Percent passed by the size sieve shown	
	Minimum	Maximum
100	96	-
140	92	-
230	-	45

4.6 Type I quality conformance tests.

4.6.1 Purity. Perchlorate shall be determined in accordance with the following:

Procedure: Weigh about 0.45 to 0.55 gram (g) of finely ground (carefully with a mortar and pestle) sample, to the nearest 0.1 mg, into a platinum crucible, and mix carefully with 4.0 g of anhydrous sodium carbonate weighed to the nearest 0.1 mg. Overlay the mixture with 1.0 g of sodium carbonate. Cover the crucible, and slowly raise the temperature with a Bunsen burner until the contents are completely fused, and hold the temperature just above the fusion point for a minimum of 10 minutes. Allow the crucible to cool. Transfer the melt quantitatively to a 250 ml wide-mouth Erlenmeyer flask with a minimum quantity of distilled water. Cover with a watch glass and make the solution slightly acid by adding concentrated nitric acid slowly from a dropping bottle, using litmus paper as an indicator. When all the melt is in solution and the solution is barely acid, add solid sodium bicarbonate in small portions until the solution is barely alkaline. Add 0.5 ml of 5 percent potassium chromate

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indicator, and titrate with standard 0.1 N silver nitrate solution to first indication of an orange color. Prepare and titrate a blank containing the same quantities of sodium carbonate, nitric acid and sodium bicarbonate in the same volume of solution as the sample.

Calculation: Ammonium perchlorate, as NH_4ClO_4 (percent) =

$$\frac{11.75 (A-B) N}{W} - (2.206C + 1.16D)$$

where: A = volume of standard silver nitrate required for sample, ml
 B = volume of standard silver nitrate required for blank, ml
 C = percent ammonium chloride in sample from the chloride test (4.6.2)
 D = percent ammonium chlorate in sample from the chlorate test (4.6.3)
 W = weight of sample, gram
 1.16 = factor for chlorate interference
 11.75 = factor for ammonium perchlorate times 100
 2.206 = factor for chloride interference

4.6.2 Chloride. Chloride shall be determined in accordance with the following:

Preparation of sample solution: Dissolve 49.9 to 50.1 g of sample, weighed to the nearest 0.01 g, in about 300 ml of hot distilled water. Cool the solution to room temperature. Quantitatively transfer to a 500 ml volumetric flask and dilute to volume. (Hold this sample solution for subsequent tests.)

Procedure: Pipet 10 ml of the sample solution into a 100 ml volumetric flask, dilute to volume with distilled water and mix thoroughly. Pipet 10 ml of this diluted aliquot into a Nessler tube and 20 ml of distilled water by pipet. Add 30 ml of distilled water by pipet to each of 2 other Nessler tubes. Pipet 1 ml concentrated nitric acid and 1 ml of approximately 0.1 N silver nitrate solution to sample and blanks. To one of the blanks, add 1 ml by pipet of sufficient standard chloride solution (0.022 g sodium chloride or 0.028 g potassium chloride/liter, equivalent to 0.020 g ammonium chloride per liter) to match approximately the turbidity of the sample. To one of the blank solutions, pipet 1 ml more of standard chloride solution, and to the other add 1 ml less of standard chloride than was added to the first blank. Allow the solutions to stand a minimum of 15 minutes, then visually compare the sample with the standards. Select the standard that most nearly matches the sample. If more than 4 ml of standard chloride solution are used to match the sample, use 5 ml of diluted aliquot, and repeat the procedure.

Calculation: Chloride, as NH_4Cl (percent) = $0.20 \frac{V}{S}$

where: V = volume of standard chloride solution required to match or exceed the turbidity of the sample, ml
 S = volume of dilute aliquot used, ml
 0.20 = dilution factor times 100

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4.6.3 Chlorate. Chlorate shall be determined in accordance with the following:

Reagents:

- (a) Hydrochloric acid, diluted 1:1 by volume.
- (b) Standard chlorate solution, 0.06 g potassium chlorate (ACS) per liter (equivalent to 0.05 g ammonium chlorate/liter).
- (c) o-Tolidine (Fisher certified reagent grade) reagent, one gram/liter in 10 percent hydrochloric acid.

Procedure: Pipet a 10 ml aliquot of the sample solution from the chloride test into a 125 ml glass-stoppered Erlenmeyer flask. Then pipet 1 to 4 ml, in increments of 1 ml, of the standard chlorate solution into four similar flasks. Dilute the contents of each flask to approximately 40 ml with distilled water, and then add 40 ml of 1:1 hydrochloric acid to each. Warm the flasks to approximately 40°C and hold for a minimum of 30 minutes. Add 1 ml of o-Tolidine reagent to each flask and allow to stand for a minimum of 5 minutes. Compare colors of sample and standard after transferring to Nessler tubes.

Calculation: Chlorate, as NH_4ClO_3 (percent) = $\frac{0.05V}{S} - 0.69B$

where: V = volume of standard chlorate solution required to match or exceed the color developed by sample, ml
 S = volume of aliquot of sample solution, ml
 B = percent bromate, as NH_4BrO_3 from the bromate test
 0.05 = dilution factor times 100
 0.69 = conversion factor, ammonium bromate to ammonium chlorate

4.6.4 Bromate. Bromate shall be determined in accordance with the following:

Procedure: Pipet 100 ml of the sample solution from the chloride test into a 500 ml glass-stoppered Erlenmeter flask and add 100 ml of freshly boiled and cooled distilled water. Weigh 0.49 to 0.51 g of potassium iodide, to the nearest 0.01 g, pipet 5 ml of 1:9 hydrochloric acid and pipet 5 ml of 0.2 percent starch indicator solution into the flask. Mix well and allow to stand in a dark place for about 1 hour. Titrate with standard 0.02 N sodium thio-sulfate solution until the blue color disappears. Perform a blank determination on the reagents using the same volumes as during the determination.

Calculation: Bromate, as NH_4BrO_3 (percent) =

$$\frac{24.3N (V - B)}{S}$$

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where: V = volume of standard sodium thiosulfate required by sample, ml
 B = volume of standard sodium thiosulfate required by blank, ml
 N = normality of standard sodium thiosulfate
 S = volume of composite solution, ml
 24.3 = combined ammonium bromate and dilution factor times 100

4.6.5 Sulfated ash. Sulfated ash shall be determined in accordance with the following:

Procedure: (Weighed as sodium sulfate and calculated as sodium perchlorate.) Grind a minimum of 5 grams of sample with mortar and pestle to a fine powder. Weigh 4.5 to 5.5 g of the ground sample to the nearest 0.1 mg. Add about 1/5 to 1/6 of the weighed sample to a previously ignited and tared silica crucible and cover. Add 1 to 2 drops of sulfuric acid onto the sample. Cover, and heat carefully with a Bunsen flame until the portion has decomposed. Continue the ignition of small increments with sulfuric acid until the entire sample has been decomposed and the volatile matter driven off. Continue to heat and complete the volatilization of sulfuric acid at a dull red heat. Cool in a desiccator and reweigh. Save the residue for the iron determination.

Calculation: Sulfated ash, as NaClO_4 (percent) = $\frac{172 A}{B}$

where: A = weight of residue, g
 B = weight of sample, g
 172 = conversion factor from sodium sulfate to sodium perchlorate times 100

4.6.6 Iron. Iron shall be determined in accordance with the following:

Reagents:

- (a) Hydrochloric acid
- (b) Nitric acid
- (c) Hydroxylamine hydrochloride, 10 percent
- (d) o-Phenanthroline, 0.25 percent
- (e) Sodium citrate (Fisher certified reagent grade), 25 percent
- (f) Iron wire

Apparatus:

- (a) Beckman DU spectrophotometer.

Procedure: Add 1 ml concentrated hydrochloric acid and 1 ml concentrated nitric acid to the ash from the sulfated ash determination. Transfer to a 50 ml beaker with a minimum of distilled water, and boil to dryness on a hot plate. Moisten the cooled residue with 2 drops of concentrated hydrochloric acid using a dropping pipet, or equal, and wash with distilled water into a 100 ml glass-stoppered volumetric flask. Dilute to about 70 ml. Prepare a blank in the same manner with 70 ml of distilled water and 2 drops of concentrated

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hydrochloric acid. The balance of the procedure applies to both the sample and blank. Add 1 ml of freshly made 10 percent hydroxylamine hydrochloride solution, mix well and let the mixture stand a minimum of 15 minutes. Add 10 ml of 0.25 percent o-Phenanthroline solution, and mix well. Add 1 ml of 25 percent sodium citrate solution, and dilute to volume. Mix well, and allow to stand a minimum of 30 minutes at not less than 20°C. Using the blank for comparison, determine the absorbance (A) of the sample solution with the Beckman spectrophotometer at a wave length of 510 nanometres (nm) and a slit width of 0.18 mm.

$$\text{Calculation: Iron, as Fe}_2\text{O}_3 \text{ (percent)} = \frac{(14.3)(10^5)A}{(a)(b)(V)(W)}$$

where: A = absorbance of sample solution
 a = absorbtivity, ml/g-cm from calibration
 b = cell length, cm
 V = volume of aliquot, ml
 W = sample weight, from sulfated ash test, g
 14.3 = factor for Fe₂O₃ times 100
 10⁵ = concentration factor

Calibration: (Determination of the absorptivity.) Weigh 0.05 g of bright iron wire to the nearest 0.1 mg, and place it in a 1 liter volumetric flask. Add 2 ml of concentrated hydrochloric acid and a few ml of hot distilled water. When all the iron is dissolved, dilute to volume and mix. Transfer by pipet 1, 3, 5, 7, and 9 ml portions of the standard iron solution to a series of 100 ml volumetric flasks, and prepare a blank. Dilute each to about 70 ml and determine absorptivity (a) by the procedure described for analysis of the sample.

$$\text{Calculation: Absorptivity (ml/g-cm)} = (A)(l)(C)$$

where: C = concentration of iron in diluted aliquot, g/ml
 l = length of light path through the cell, cm
 A = absorbance

4.6.7 Phosphate. Phosphate shall be determined in accordance with the following:

Reagents:

- (a) Ammonium vanadate, purified (Fisher certified reagent grade)
- (b) Perchloric acid, 70 percent
- (c) Molybdic acid, 85 percent
- (d) Ammonium hydroxide
- (e) Tricalcium phosphate (TCP), precipitated (Fisher certified)

Apparatus:

- (a) Volumetric flask - 100 ml, 250 ml and one liter
- (b) Graduated cylinder, 100 ml

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- (c) Pipet, 10 and 100 ml
- (d) Pipet, Mohr measuring, 10 ml
- (e) Beckman DU spectrophotometer

Preparation of reagents:

(a) Prepare 0.25 percent ammonium vanadate solution by dissolving 2.350 g of ammonium vanadate in approximately 400 ml of hot distilled water. Add 14 ml of perchloric acid and cool. Transfer to a one liter volumetric flask and dilute to volume.

(b) Prepare 10 percent ammonium molybdate solution by dissolving 100 g of molybdic acid in a mixture of 300 ml of distilled water and 80 ml of ammonium hydroxide. When the molybdic acid has dissolved, filter the solution and boil the filtrate for a minimum of 20 minutes. Cool and transfer to a one liter volumetric flask and dilute to volume.

Procedure: Weigh a 25 g sample, to the nearest 0.1 mg, and transfer to a 250 ml volumetric flask. Add about 50 ml of distilled water and 25 ml of perchloric acid to the flask with constant swirling and cool to room temperature. Dilute to volume and mix well. Pipet 10 ml aliquot into 100 ml of perchloric acid with constant swirling and cool to room temperature. Add 10 ml of 0.25 percent ammonium vanadate, dilute to about 75 ml with distilled water and mix well. Add 10 ml of 10 percent ammonium molybdate, dilute to volume and mix well. Allow the solution to stand for a minimum of 30 minutes at room temperature. Using a blank for comparison, determine the absorbance (A) of the sample solution with the Beckman DU spectrophotometer at a wave length of 470 nm and a slit width of 0.15 mm.

$$\text{Calculation: Phosphate, as TCP (percent)} = \frac{(2.5) (10^6) A}{(a) (b) (v) (w)}$$

where: A = absorbance of sample solution
 a = absorptivity, ml/g-cm from calibration
 b = cell length, cm
 v = volume of aliquot, ml
 w = sample weight, g
 2.5 = factor for calcium phosphate
 10⁶ = concentration factor times 100

Calibration: (Determination of the absorptivity.) Weigh 5.0048 grams TCP, to the nearest 0.1 mg, into a 100 ml beaker and transfer quantitatively to a one liter volumetric flask with distilled water. Dissolve in approximately 600 ml of distilled water, add 20 ml of perchloric acid with constant swirling and dilute to volume. Pipet a 100 ml aliquot to a second one liter volumetric flask and dilute to volume. Pipet 1, 2, 3, 4, and 5 ml of this standard solution into separate 100 ml volumetric flasks and prepare a blank. Add 20 ml of distilled water to the empty blank and samples. Treat the samples and blank as described in "Procedure" from this point of the procedure and determine their absorbance (A). The initial calibration should consist of 4 complete determinations, one on each of two days, preferably by each of two analysts. Calculate the concentrations, plot them against the measured absorbances, and draw the line of best fit. A line that shows curvature indicates error and the calibration should be repeated.

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Calculation: Absorptivity (ml/g-cm) = (A) (l) (C)

where: C = concentration of TCP in diluted aliquot, g/ml

A = absorbance

l = length of light path through the cell, cm

4.6.8 Total moisture. Total moisture shall be determined in accordance with ASTM E-203-75 and the following:

Reagents:

(a) Methanol

(b) Carrier solution -- 3:1 mixture by volume of pyridine and methanol

(c) Stabilized Karl Fischer reagent, diluted to a water equivalent of 2.5 to 3.0 (mg) of water (H₂O)/ml with Karl Fischer diluent

(d) Sodium tartrate

Apparatus:

(a) Aquameter, Beckman Model KF-4, or equivalent

(b) Graduated cylinder, 100 ml

Standardization of Karl Fischer reagent: Add 100 ml of methanol to the reaction vessel. Neutralize the methanol with dilute Karl Fischer reagent by automatically titrating to a 30-second endpoint using the Aquameter. Carefully add 0.09 to 0.11 g of sodium tartrate, weighed to the nearest 0.1 mg, to the neutralized methanol. Dissolve the sodium tartrate in the methanol by setting the stirring action to the highest speed which will not cause splashing or bubble formation. Automatically titrate with dilute Karl Fischer reagent to a 30-second endpoint. Record the volume of dilute Karl Fischer reagent. Repeat the standardization procedure until 3 determinations agree within 0.05mg/ml.

Calculation: Water equivalent (mg H₂O/ml Karl Fischer reagent) =

$$\frac{0.1566 W}{V}$$

where: W = weight of sodium tartrate, mg

V = volume of dilute Karl Fischer reagent, ml

0.1566 = factor for sodium tartrate

Procedure: Add 100 ml of the carrier solution to the reaction vessel. Neutralize the carrier solution with dilute Karl Fischer reagent by automatically titrating to a 30-second endpoint using the Aquameter. Add 13 to 15 g of sample, weighed to the nearest 0.01 g, to the carrier solution in the reaction vessel. Set the stirring action the same as that used in the standardization to dissolve the sample and automatically titrate with standardized dilute Karl Fischer reagent. (Proceed with external moisture determination with this neutralized carrier solution.)

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$$\text{Calculation: Total moisture (percent)} = \frac{VE}{1000 W} \times 100$$

where: V = volume of standardized Karl Fischer reagent, ml
 E = water equivalent of Karl Fischer reagent, mg H₂O/ml
 W = weight of sample, g
 1000 = conversion factor for sample weight to mg

4.6.9 External moisture. External moisture shall be determined in accordance with the following:

Reagents: Same as for the total moisture test.

Apparatus: Same as for the total moisture test.

Standardization of Karl Fischer reagent: Same as for the total moisture test.

Procedure: Add 18 to 22 g of sample, weighed to the nearest gram, to the neutralized solution from the total moisture procedure, to saturate the solution. (This procedure may also be conducted by the use of 100 ml of carrier solution saturated with 35 grams of sample.) Neutralize the solution, using the same stirring action, with dilute Karl Fischer reagent by automatically titrating to a 30-second endpoint. Weigh 18 to 22 g of sample, to the nearest 0.01 g into the reaction vessel. Using the same stirring action, titrate with dilute Karl Fischer reagent to a 30-second endpoint. Record the volume of dilute Karl Fischer reagent.

$$\text{Calculation: External moisture (percent)} = \frac{VE}{1000 W} \times 100$$

where: V = volume of standardized Karl Fischer reagent, ml
 E = water equivalent of Karl Fischer reagent, mg H₂O/ml
 W = weight of sample, g
 1000 = conversion factor for sample weight to mg

4.6.10 Acid insolubles. Acid insolubles shall be determined in accordance with the following:

Procedure: Weigh 23 to 27 g of sample, to the nearest 0.1 mg, into 250 ml of distilled water and dissolve. Add 5 ml of 10 percent hydrochloric acid. Filter the solution through a tared Selas crucible. Wash the crucible and residue with distilled water, then dry for a minimum of 1.5 hours at 105° ± 5°C. Cool in a desiccator and reweigh.

$$\text{Calculation: Acid insolubles (percent)} = \frac{A}{B} \times 100$$

where: A = weight of residue, g
 B = weight of sample, g

4.6.11 pH. pH shall be determined in accordance with the following:

Reagents:

- (a) Fisher certified buffer solution, So-B-98, pH 4.00 at 25°C.
- (b) Fisher certified buffer solution, So-B-116, pH 10.00 at 25°C.

Procedure: Add 50 ml of hot freshly boiled distilled water to an 18 to 22 g sample, weighed to the nearest 0.1 g. Stir the solution well and cool to room temperature. Measure the pH with the pH meter and glass/calomel electrode pair which have been calibrated with the certified buffers immediately before use.

4.6.12 Type I Class I particle size. Particle size shall be determined in accordance with the following:

Reagent: TCP precipitated, Fisher Certified or National Formulary Grade

Apparatus:

(a) Eight inch diameter U.S. Standard sieves conforming to ASTM E 11-70: Cover, no. 40, 50, 70, 100, 140, 200 and pan

(b) Tyler "Ro-Tap", sieve shaker, with automatic timer

Procedure: Weigh a 100 g sample, to the nearest 0.1 g, into a one pint glass container. Add 1.0 g of TCP conditioner and mix by shaking for approximately 1 minute. Assemble the U.S. Standard sieves in numerical order from top to bottom, place the pan under the stack and transfer the sample to the top sieve. Place the cover on top of the stack and insert the sieve assembly into the shaker. Set the shaker to operate for 13 minutes. Remove the top sieve and brush any material adhering to the bottom into the next lower sieve. Transfer the material retained on the sieve to a tared container on a balance using a brush to ensure removal of all the material. Weigh the material retained on the sieve to the nearest 0.1 g. Similarly, transfer the material from each of the sieves in successive order, add each fraction to the preceding ones and weigh. Record the cumulative weight retained for each sieve.

Calculation: Percent passed by sieve =

$$\frac{W - \text{cumulative weight retained}}{W} \times 100$$

where: W = the weight of the sample, g

4.6.13 Type I, Class 2 particle size. The particle size shall be determined in accordance with ASTM B 330-65.

4.7 Type II quality conformance tests.

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4.7.1 Purity. Transfer an accurately weighed portion of approximately 0.5 g of the specimen to a platinum crucible containing a known weight of approximately 5 g of sodium carbonate and mix carefully. Overlay the mix with a known weight of sodium carbonate (approximately 1 g) so that a correction can be made for any chloride in the sodium carbonate. Fuse the mixture over a low flame for approximately 30 minutes and then gradually increase the flame to full heat. Dissolve the fusion in a covered beaker containing 50 ml of water and add 50 ml of 1 nitric acid: 1 water. Quantitatively transfer this solution to a 500 ml Erlenmeyer flask and dilute to about 150 ml with water. Add exactly 50 ml of 0.1 N silver nitrate solution (see 6.6.1), mix well, add 2 ml of nitrobenzene and mix again. The supernatant liquid must not be milky. Add 2 to 3 ml of ferric alum indicator solution (see 6.6.3) and back titrate with 0.1 N potassium thiocyanate solution (see 6.6.2) to the first detectable color change which persists for at least 30 seconds. Using the same quantities of reagents and equal volumes of solutions as in the determination conduct a blank determination to correct for titratable impurities. Calculate the ammonium perchlorate content as follows:

$$\text{Percent ammonium perchlorate} = \frac{11.75 N(A - B)}{W} - (2.20 C + 1.16 D)$$

where: N = normality of potassium thiocyanate
 A = Volume of potassium thiocyanate required for blank titration, ml
 B = volume of potassium thiocyanate required for sample titration, ml
 C = percent ammonium chloride (see 4. 7.2)
 D = percent ammonium chlorate (see 4. 7.3)
 W = weight of specimen, g.

Alternatively, perchlorate may be determined by a direct electrometric titration. If this method is selected, fuse the sample with sodium carbonate and dissolve in nitric acid as directed above. Then titrate with 0.1 N silver nitrate solution to a permanent end-point using a silver indicator electrode and a glass reference electrode. Conduct a blank determination. Calculate the ammonium perchlorate content as follows:

$$\text{Percentage ammonium perchlorate} = \frac{11.75 N' (A' - B')}{W} - (2.20 C + 1.16 D)$$

where: N' = normality of silver nitrate
 A' = volume of silver nitrate required for sample titration, ml
 B' = volume of silver nitrate required for blank titration, ml

4.7.2 Chloride. Dissolve 20 g of the specimen weighed to the nearest 0.05 g in 150 ml of water in an Erlenmeyer flask and add 3 to 4 ml of nitric acid. Add standardized 0.05 normal (N) silver nitrate solution (see 6.6.1) from a buret until the precipitate coagulates, mix thoroughly, allow to stand a moment and add a little more silver nitrate solution to the clear supernatant liquid. If precipitation is complete (no marked cloudiness occurs) add an additional 5 ml of the silver nitrate solution. If precipitation is incomplete, add more silver nitrate. Mix, add 1 to 2 ml of nitrobenzene and mix again. The supernatant liquid must not be milky. Add 2 to 3 ml of ferric alum indicator (see 6.6.3) solution and titrate with 0.05 N potassium thiocyanate solution (see 6.6.2) to a permanent red-brown color.

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Alternatively, chloride may be determined by direct potentiometric titration. If this method is selected, prepare the specimen as in the preceding paragraph, and titrate with 0.05 N silver nitrate solution to a permanent end point using a silver indicator electrode and a glass reference electrode.

Calculate the ammonium chloride content as follows:

	<u>Back Titration</u>	<u>Direct Titration</u>
Percent ammonium chloride =	$\frac{5.35 (aA - bB)}{W}$	$\frac{5.35 aA}{W}$

where: A = volume of silver nitrate solution, ml
 B = volume of potassium thiocyanate solution, ml
 a = normality of silver nitrate solution
 b = normality of potassium thiocyanate solution
 W = weight of sample, g

4.7.3 Chlorate.

4.7.3.1 Orthotolidine reagent. Dissolve 1.35 g of o-tolidine dihydrochloride in 500 ml of water. Add this solution, with constant stirring, to a mixture of 350 ml of water and 150 ml of concentrated hydrochloric acid. This reagent should be stored at room temperature in amber bottles or in the dark, protected from sunlight and contact with rubber. The reagent must be discarded after 6 months.

4.7.3.2 Standard solution. Dissolve 0.212 g of sodium chlorate in water and dilute to one liter.

4.7.3.3 Procedure. Transfer 2.00 g of the specimen and 1.8, 1.9, 2.0 and 2.1 ml aliquots of the standard solution to separate, glass stoppered Erlenmeyer flasks. Add 50 ml of water and 20 ml of hydrochloric acid. Maintain at 40°C for 30 minutes, cool to room temperature, and transfer to 100 ml Nessler tubes containing 5 ml of o-tolidine reagent. Dilute to 100 ml with water, mix and allow the color to develop for 5 minutes, preferably in the dark. Compare the color with the standards and calculate the ammonium chlorate content on the basis of the matching standard as follows:

$$\text{Percent NH}_4\text{ClO}_3 = 0.01A$$

where: A = volume of aliquot in matching standard, ml.

Note: Permanent standards may be prepared from copper sulfate and potassium dichromate (see 6.4).

4.7.4 Sulfated ash. Ignite a clean porcelain, silica or platinum crucible and cover for approximately 30 minutes at 800° ± 25°C. Cool in a desiccator, weigh to the nearest 0.5 mg, and add approximately 1.0 gm of sample weighed to nearest 0.01 g. Add 3 ml of concentrated sulfuric acid, place the cover on upside down and heat over a bunsen burner or hot plate until most of the sample is burned off. (Caution: Heat the sample in a hood and keep a safety shield interposed between the operator and

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the sample. Heat gently since NH_4ClO_4 may decompose violently if heated over 300°C . When volatilization of the sample is essentially complete, transfer the crucible with inverted cover to a muffle furnace, and ignite at $800 \pm 5^\circ\text{C}$ for at least 30 minutes, and transfer to a desiccator. Replace the crucible cover in an upright position, cool and weigh to the nearest 0.5 mg. Calculate the sulfated ash content as follows:

$$\text{Percent sulfated ash} = \frac{100 W'}{W}$$

where: W' = weight of residue, g
 W = weight of sample, g

4.7.5 Iron.

4.7.5.1 Preparation of standard iron solution (1 ml = 0.0001 g Fe). Dissolve 0.8635 g of ferric alum, $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ in 100 ml of sulfuric acid (H_2SO_4) solution prepared by cautious addition of 5 ml of H_2SO_4 to 95 ml of water. When solution is complete and at room temperature ($20\text{--}25^\circ\text{C}$), dilute to 1 liter in a volumetric flask.

4.7.5.2 Procedure. Dissolve 7.00 g of the specimen in 75 ml of water. Add 2.0 ml of concentrated H_2SO_4 and transfer to a 100 ml Nessler tube. Add 2 drops of 1 percent potassium permanganate solution and 10 ml of 2 percent ammonium thiocyanate. Dilute to 100 ml and mix well. Into a second Nessler tube containing the same amounts of water and reagents as above, pipette 1.75 ml of the standard iron solution. Dilute and mix well. If the unknown is no darker than the standard, the specimen meets the requirement for iron.

4.7.6 Sodium (Na) and potassium (K).

4.7.6.1 Preparation of reagents. Quantitatively transfer 1.9066 g of potassium chloride and 2.5416 g of sodium chloride into separate 1 liter volumetric flasks containing approximately 250 ml of water. Swirl to dissolve the salt and dilute to volume with water. Each solution contains 1 mg/ml of cation. From these stock solutions transfer aliquots to other volumetric flasks and dilute with water so that at least four standard solutions are prepared in the range 0.005 to 0.03 mg/ml for K ion and 0.001 to 0.005 mg/ml for Na-ion.

4.7.6.2 Preparation of standard curves. Determine the net emission in terms of absorbance or percent transmittance of the standard solutions using a wavelength of 766.5 nm for K-ion and 589 nm for Na-ion. The minimum practical slit width should be used. Prepare a graph by plotting absorbance vs. concentration on linear coordinates or percent transmittance vs. concentration on semi-log coordinates. Fit a straight line to the points.

4.7.6.3 Analysis of sample. Quantitatively transfer 4.0 g of ammonium perchlorate, weighed to the nearest mg, into a 100 ml volumetric flask. Dissolve in distilled water and dilute to volume. Determine the absorbance or percent transmittance of each standard solution, a distilled water blank solution, and the sample solution, by flame photometry using the manufacturer's manual of instructions for the spectrophotometer. Read the concentration of the sample directly from the standard curve.

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Calculate the potassium and sodium content as follows:

$$\text{Potassium and sodium, percent} = \frac{10(R_K + R_{Na})}{W}$$

where: R_K = potassium concentration as read from standard curve, mg/ml
 R_{Na} = sodium concentration as read from standard curve, mg/ml
 W = Weight of sample, gm/100 ml

4.7.7 Tricalcium phosphate (TCP).

4.7.7.1 Preparation of reagents. (a) Ammonium Vanadate Solution - Add 2.350 gm of ammonium metavanadate to approximately 400 ml of warm distilled water in a 1 liter volumetric flask. Slowly and cautiously add 14 ml of 70-72 percent perchloric acid, mix to effect solution, cool to room temperature, and dilute to volume with water; (b) Ammonium Molybdate Solution - Dissolve 100 gm of molybdic acid in a mixture of 300 ml of distilled water and 80 ml of ammonium hydroxide. Filter the solution and boil the filtrate for 20 minutes. Cool, transfer to a 1 liter volumetric flask and dilute to volume with distilled water.

4.7.7.2 Preparation of calibration curve. Quantitatively transfer 5.000 gm of TCP to a 1 liter volumetric flask, add 500 ml of water and 20 ml of perchloric acid. Mix to dissolve and dilute to volume with distilled water. Transfer 1, 2, 3, 4 and 5 ml aliquots to separate 100 ml volumetric flasks. Add to each flask 25 ml of water and 1.7 ml of perchloric acid. Cool to room temperature and add 10 ml of ammonium vanadate solution. Dilute to 75 ml with water, mix and cool to room temperature, add 10 ml of ammonium molybdate solution, dilute to volume with water and let stand at room temperature for at least 30 minutes. Prepare a blank solution containing all the reagents in the specified amounts but without the TCP. Using the blank solution in the reference cell, determine the absorbance of each of the five standard solutions at 470nm. Prepare a calibration curve by plotting absorbance vs. concentration, expressed as gm TCP/100 ml of solution, and draw the calibration curve by fitting the best straight line to the points.

4.7.7.3 Procedure. Quantitatively transfer 2.50 gm of sample to a 100 ml volumetric flask and dissolve in about 50 ml of water. Add, slowly and cautiously, 20 ml of perchloric acid and, after thorough mixing, cool to room temperature. Add 10 ml of ammonium vanadate solution, dilute to 75 ml with water, mix and cool to room temperature. Add 10 ml of ammonium molybdate solution, dilute to volume with water, mix well and allow to stand at room temperature for at least 30 minutes. Determine the absorbance of the sample solution at 470 nm, using the blank solution in the reference cell. Determine the weight of the TCP by referring to the calibration curve and calculate the amount in the sample by substituting in the following equation:

$$\text{TCP, percent} = \frac{100 A}{W}$$

where: A = weight of TCP in sample, g
 W = weight of sample, g

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4.7.8 Total Moisture. This determination shall be conducted in accordance with ASTM E 203-75 for the direct titration or with ASTM D 1348-61 for a back titration method. A 3:1 anhydrous pyridine: absolute methanol solution shall be used for the carrier solution (see 6.5).

4.7.9 Surface moisture. Proceed as specified in 4.7.8 except that a 1:1 methanol/benzene shall be used in place of the methanol pyridine mixture and titrating as soon as the sample has been transferred to the flask.

4.7.10 Water insoluble. Transfer a specimen of about 50 g (weighed to the nearest 0.1 g) to a 400 ml beaker and add about 250 ml of water. Heat to $75 \pm 5^\circ\text{C}$ and stir until the salt is completely dissolved. Filter the contents of the beaker through a tared, fine porosity, sintered glass crucible and transfer any residue from the beaker to the crucible by washing thoroughly with additional water heated to the same temperature as above. Dry the crucible and contents for 2 hours at $100 \pm 5^\circ\text{C}$, cool in a desiccator and weigh. Calculate the water insoluble content of the sample as follows:

$$\text{Percent water insoluble} = \frac{100 W'}{W}$$

where: W' = weight of residue, g
 w = weight of sample, g

4.7.11 pH. Add 50 ml of hot freshly boiled distilled water to 20.0 g of specimen. Stir and cool to room temperature (20 to 25°C). Measure the pH on a suitable potentiometer having glass, calomel electrodes.

4.7.12 Granulation. The granulation shall be determined in accordance with MIL-STD-1234, Method 201.1.

4.8 Acceptance and rejection criteria. If any sample does not meet all the requirements of this specification, the lot represented shall be rejected.

4.9 Packaging inspection. The packaging, packing and marking shall be inspected to verify conformance with the requirements of section 5. Sampling shall be in accordance with MIL-STD-105 with an AQL of 2.5% defective.

5. PACKAGING

5.1 Packaging and packing. Unless otherwise specified in the contract (see 6.2), packaging and packing shall be level C.

5.1.1 Level C. Unless otherwise specified in the contract (see 6.2), packaging and packing of ammonium perchlorate shall be in accordance with standard commercial practice applicable to the type of material. The packaging and packing shall be of such construction and materials that the contents will be adequately protected against loss or contamination. The containers shall conform to 49 CFR 171-179. Dessicant, conforming to Type I of MIL-D-3464, shall be included in containers as specified in the contract or purchase order.

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5.2 Marking. Marking of containers shall be in accordance with MIL-STD-129 and 49 CFR 171-179 and shall include, but not be limited to, the following:

- (a) Title, number, revision letter and date of this specification
- (b) Lot number
- (c) Contract or purchase order number
- (d) Net weight
- (e) Material trade name
- (f) Manufacturer's name and location

6. NOTES

6.1 Intended use. The material is intended for use as oxidizer in solid propellant manufacture. The Type I material is to be used for the CCU-22/A Cartridge Impulse Assembly. The Type II material is to be used in the CKU-5/A Aircraft Ejection Seat Assembly.

6.2 Ordering data. Procurement documents should specify the following:

6.2.1 Procurement requirements.

- (a) Title, number, revision letter and date of this specification
- (b) Quantity required
- (c) Place of inspection
- (d) Place of delivery
- (e) Amount of desiccant required (see 5.1.1)
- (f) Packaging requirements if other than as specified (see 5.1.1)

6.2.2 Contract data requirements. The items of deliverable data required by this specification are cited in the following paragraphs:

<u>Paragraph</u>	<u>Data Requirement</u>	<u>Applicable DID</u> *
4.5	Test report	-

* DID's (Data Item Descriptions/DD Form 1664) for the above data requirement are documented in the applicable ADL (Authorized Data List). Such data will be delivered as identified on completed (numbered) DID's when specified on DD Forms 1423 (Contract Data Requirements Lists) and incorporated into applicable contracts.

6.3 Batch. A batch is defined as that quantity of material which has been manufactured by some unit chemical process and subjected to some physical mixing operation intended to make the final product substantially uniform.

6.4 Chlorate test. For further information on the o-tolidine reagent and permanent standards for chlorate test (see 4.7.3), refer to the Standard Methods for the Examination of Water and Waste Water, 11th ed., p. 85-91, published by the American Public Health Association, 1790 Broadway, New York 10, N.Y.

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6.5 Total moisture determination. The solutions and standards required for the Karl Fischer tests may be prepared as follows:

6.5.1 Karl Fischer Reagent. Dilute stabilized KFR (water equivalence 5-7 mg/ml) with absolute methyl alcohol (0.01 percent water max.) or stabilized KF diluent, so that the water equivalence is 1.4-2.3 mg/ml.

6.5.2 Water-in-methanol solution. Add sufficient water to absolute methanol so that the final concentration is approximately 1 mg/ml.

6.5.3 Pyridine-methanol solution. Mix 3 volumes of anhydrous pyridine with 1 volume of anhydrous methanol. If necessary, the solvents can be made anhydrous (0.01% H₂O, max.) by the methods given below.

6.5.3.1 Pyridine. Add 1 volume of benzene to 19 volumes of pyridine and distill until 5 percent of distillate has been collected. Discard the distillate and use the dry residual 95 percent.

6.5.3.2 Methanol. Distill the methanol over magnesium.

6.5.4 Sodium tartrate dihydrate standard. The water content of the standard may be verified by drying a 2 to 3 g sample in a wide-mouth weighing bottle at 155 ± 5°C for 4 hours. The loss in weight should not be less than 15.61 percent nor more than 15.71 percent.

6.6 Standard and indicator solutions. The solutions required for the determination of chloride content (see 4.7.2) and assay (see 4.7.1) may be prepared as follows:

6.6.1 Silver nitrate solutions. The 0.1 N solution (nominal) may be prepared as described in MIL-STD-1234, method 607.1. An aliquot of this solution may be diluted with an equal volume of water to give a nominal 0.05 N solution.

6.6.2 Potassium thiocyanate solutions. The 0.1 N solution (nominal) may be prepared and standardized as described in MIL-STD-1234, method 608.1. An aliquot of this solution may be diluted with an equal volume of water to give a nominal 0.05 N solution.

6.6.3 Ferric alum indicator. This solution may be prepared from FeNH₄(SO₄) · 12 H₂O as described in MIL-STD-286 method 705-1.

6.7 Safety precautions. The safety precaution requirements of the "Contractors' Safety Manual for Ammunition, Explosives, and Related Dangerous Material" (DOD 4145.26M) are applicable and should be specified in the contract or order as required by the Armed Services Procurement Regulations (ASPR) 1-323.

NOTE: When this specification is used as part of the description of work to be accomplished by a Government activity, the safety precaution requirements of "Ammunition and Explosives Ashore" (OP 5) should be made applicable.

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6.8 Suggested source of supply. Products that have met the requirements of this specification in past procurement actions are manufactured by Kerr-McGee Chemical Corporation, Kerr-McGee Building, Oklahoma City, OK 73102. This information is for the convenience of the procuring activity and is not to be construed as a waiver of any requirement of this specification nor as any limitation of additional potential sources of supply.

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