

MIL-S-10699B
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 SUPERSEDING
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MILITARY SPECIFICATION

SALTS, HEAT-TREATING (FOR METALS)

This specification is approved for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 Scope. This specification covers crystalline heat-treating salts suitable for use in the molten state for normalizing, annealing, hardening and tempering, cyclic annealing, process annealing, martempering and austempering of carbon and alloy steels, hardening of high speed steel, heat-treatment of light alloys, annealing and stress-relieving of cold-worked copper and copper-base alloys (see 6.1).

1.2 Classification. The salts shall be of the following classes as specified in the contract or order (see 3.5 and 6.1).

<u>Class</u>	<u>Working Range (°C)</u>
1	163-593
2	288-593
3	621-927
4	593-899
4A	552-760
5	704-899
6	899-1093
7 (see table I)	1038-1316
8	899-1288

Beneficial comments (recommendations, additions, deletions), and any pertinent data which may be of use in improving this document, should be addressed to: Commander, US Army Armament Research and Development Command, ATTN: DRDAR-TST-S, Dover, New Jersey 07801, by using the self-addressed Standardization Document Improvement Proposal (DD Form 1426), appearing at the end of this document, or by letter.

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2. APPLICABLE DOCUMENTS

2.1 Issues of documents. The following documents, of the issue in effect on date of invitation for bids, form a part of this specification.

SPECIFICATIONS

FEDERAL

PPP-C-301 - Chemicals, Dry and Paste: Packaging and Packing of

STANDARDS

FEDERAL

Fed. Test Method Std. No. 151 - Metals; Test Methods.

MILITARY

MIL-STD-105 - Sampling Procedures and Tables for Inspection by Attributes.

MIL-STD-109 - Quality Assurance Terms and Definitions.

MIL-STD-129 - Marking for Shipment and Storage.

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

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) STANDARDS

D 1193 - Reagent Water

(The ASTM test methods listed above are included in Part 20, 21, 22, 29, 31, 37, 40 of the Annual Book of ASTM Standards and are also available separately. Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.)

DEPARTMENT OF TRANSPORTATION

49 CFR 171-178 - Department of Transportation rules and regulations for the transportation of hazardous materials.

(These regulations may be purchased from the Superintendent of Documents, Government Printing Office, Washington, D.C. 20402.)

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Table 1. Composition

Class	Percent by Weight								
	Sodium Nitrite Nitrate (NaNO_2)	Sodium Nitrate (KNO_3)	Potassium Nitrate (KNO_3)	Sodium Carbonate (Na_2CO_3)	Sodium Chloride (NaCl)	Potassium Chloride (KCl)	Barium Chloride (BaCl_2)	Barium Chloride plus Silica (BaCl_2) ₂ (SiO_2)	Calcium Chloride (CaCl_2)
1	37-50	0-10	50-60						
2	45-57		45-57						
3				45-55		45-55			
4					15-25	20-32	50-60		
6A					10-15	25-30	40-45		15-20
5					40-60	40-60			
6						5-15	85-95		
7									98 min (1)
8					3-7		93-97		

(1) Class 7 salt shall be supplied in four forms containing the following amounts of rectifier, as specified (see 6.2):

- 7A - No Silica
- 7B - 0.25 to 1.25 Silica
- 7C - 1.5 to 2.5 Silica
- 7D - 4.0 to 5.0 Silica

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Table II. Impurities

Impurity	Percent by Weight								
	Class 1	Class 2	Class 3	Class 4	Class 4A	Class 5	Class 6	Class 7	Class 8
Moisture (max)	0.50	0.50	0.50	0.50	1.00	0.50	1.00	1.00	1.00
Water-insoluble (max)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	--	0.10
Chloride (max) (as Cl)	0.30	0.30	--	--	--	--	--	--	--
Sulfate (max) (as SO ₄)	0.10	0.18	0.18	0.10	0.10	0.10	0.10	0.10	0.10
Total Nitrogen (max) (as NO ₃)	--	--	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Nitrite (as NO ₂)	--	0.05	--	--	--	--	--	--	--
Carbonate (max) (as CO ₃)	0.50	0.05	--	0.05	--	0.05	--	--	--
Fluoride (max) (as F)	None(1)	None(1)	None(1)	None(1)	None(1)	None(1)	None(1)	None(1)	None(1)
Silica (max) (as SiO ₂)	--	--	--	--	--	--	--	(2)	0.05
Total Alkaline Earths (max) (Mg, Ca, Sr, Ba) (as Oxides)	0.10	0.10	0.05	--	--	0.05	--	--	--
Neutrality (pH of 1% Solution)	6.5-8.5	6.0-8.5	--	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-7.5	6.5-7.5
(1) Qualitatively	Silica added intentionally as rectifier (see Table I).								
(2) Silica added intentionally as rectifier (see Table I).									

3. REQUIREMENTS

3.1 Chemical composition. The compositional range of the salts shall be as specified in table I.

3.2 Impurities. The amount of impurities in the salts shall be within the limits specified in table II.

3.3 Physical requirements. The salts shall conform to the physical requirements specified in table III.

Table III - Physical requirements

Class	Working Range °C	Melting Range °C	Temperature at which salt shall be a clear liquid, °C
1	163-593	135-143	146
2*	288-593	221-236	232
3	621-927	560-588	621
4	593-899	560-577	593
4A	552-760	496-524	538
5	704-899	649-677	677
6	899-1093	760-843	871
7	1038-1316	954-982	982
8	899-1288	830-857	871

*See 6.3 for care in use of nitrate salt baths.

3.4 Certified test report. The contractor shall furnish at the time of delivery a report of detailed test results certifying that the material supplied conforms to the chemical and physical properties specified in tables I, II and III.

3.5 Black stain. Salts of class 1 and 2 shall not produce black stain on cartridge brass when heated to 566°C for five minutes, when tested as specified in 4.6.2.2.

3.6 Decarburization, scaling and pitting. Salts of classes 4, 5, 6 and 7 shall not cause decarburizing, scaling or pitting of the work being treated in the salts during heat treatment, when tested as specified in 4.6.2.3.

3.7 Water solubility. The salts with the exception of classes 7 and 8 shall be water soluble.

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3.8 Appearance. Class 1 and 2 salts shall have a yellow, pink or red color for precautionary purposes (see 6.3). All other classes of salts shall be characteristic white crystals.

3.9 Granulation. The salts shall be granular and free from lumps. Class 4A salt may contain anhydrous calcium chloride in pellet form.

3.10 Workmanship. The salts shall be uniform mixture, free from dirt, grit and foreign matter. Class 1 and 2 salts shall be free from carbonaceous materials. Salts shall be free flowing and shall show no evidence of caking or hardening.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified in the contract or order, the supplier may use his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by 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 the specified requirements.

4.2 Terms and definitions. Quality assurance terms and definitions shall be in accordance with MIL-STD-109.

4.3 Classes of Inspection.

4.3.1 Acceptance testing. All examination and testing shall be to determine conformance to the requirements of this specification to serve as a basis for acceptance.

4.4 Lot. Unless otherwise specified, an inspection lot shall consist of all salt of the same class submitted at one time by a supplier, except that the lot shall not exceed 15,000 pounds.

4.5 Sampling.

4.5.1 End item inspection. Each lot shall be sampled in accordance with MIL-STD-105, inspector level I, acceptance quality level (AQL) 2.5 percent defective, and examined for weight, closure and visual requirements (see 4.5.2) and shall meet all the requirements cited in section 3 of this specification.

4.5.2 Examination.

4.5.2.1 Visual. Examination shall be made for compliance with the appearance (see 3.8), granulation (see 3.9) and workmanship (see 3.10) requirements.

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4.6 Tests.

4.6.1 Chemical tests. The samples shall be mixed thoroughly before conducting the chemical tests. Water in accordance with ASTM D1193 (Type III) and reagent grade chemicals shall be used. Blank determinations shall be run and corrections applied where significant. The tests shall be conducted as follows: If other methods of analysis are desired, they shall be as agreed upon by the contractor and the procuring activity. In case of dispute the chemical methods specified herein shall be used.

4.6.1.1 Major constituents.4.6.1.1.1 Major constituents of class 1.4.6.1.1.1.1 Potassium nitrate.4.6.1.1.1.1.1 Reagents.

4.6.1.1.1.1.1.1 Aluminum chloride solution (5%). Dissolve 5 g of $AlCl_3$ in 100 ml of water.

4.6.1.1.1.1.1.2 Sodium tetraphenylboron solution (3%). Dissolve 9 g of sodium tetraphenylboron in 300 ml of water, add 2 ml of aluminum chloride solution (5%), stir, allow to stand 30 minutes, and filter into a polyethylene or Pyrex container. On prolonged standing, the solution may become turbid. If it does, refilter before using.

4.6.1.1.1.1.2 Procedure. Transfer a 10-g sample, weighed to 0.3 mg, to a 400-ml beaker. Add about 200 ml of water, stir to dissolve, and dilute to 1 liter in a volumetric flask. Pipet a 10-ml aliquot into a 250-ml beaker. (Save the solution in the volumetric flask for the determination of sodium nitrite (4.6.1.1.2).) Dilute to 150 ml and add 5 drops of aluminum chloride solution (5%) and 20 ml of tetraphenylboron solution while stirring vigorously. Allow to stand 5-10 minutes. Filter through a tared sintered glass crucible of medium porosity, being careful that the crucible does not run dry during the filtration. Transfer the precipitate to the crucible and wash with water. Dry at 120°C for 45 minutes, cool in a desiccator, and weigh. Calculate the percent potassium nitrate as follows:

$$\% KNO_3 = \frac{28.22P}{Q}$$

Where: P = g of precipitate.
Q = g of sample in aliquot.

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4.6.1.1.1.2 Sodium nitrate.4.6.1.1.1.2.1 Reagents.4.6.1.1.1.2.1.1 Standard 0.1N potassium permanganate solution.

4.6.1.1.1.2.1.2 0.1N ferrous ammonium sulfate solution. Dissolve 39.2 g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in about 500 ml of dilute sulfuric acid (5 to 95) at room temperature and dilute to 1 liter with dilute sulfuric acid (5 to 95).

4.6.1.1.1.2.2.1 Procedure. To 300 ml of water in a 600-ml beaker add 10 ml of sulfuric acid (1 to 1). Carefully add standard 0.1N potassium permanganate solution dropwise until a pink color just appears and then add 40.00 ml of the permanganate. Transfer a 25-ml aliquot of the solution from the volumetric flask from the potassium nitrate determination (4.6.1.1.1.2), allowing the pipet to dip just below the surface (the solution should remain pink; if it does not remain pink, start anew and take a smaller aliquot). Add 20.00 ml of 0.1N ferrous ammonium sulfate solution while stirring and allow to stand 5 minutes (the solution should turn colorless; if it does not, add an additional measured amount of ferrous ammonium sulfate solution). Titrate with standard 0.1N potassium permanganate solution to a pink color. Determine the equivalent strengths of the ferrous ammonium sulfate and potassium permanganate solutions by adding 20.00 ml of ferrous ammonium sulfate solution to 300 ml of water and 10 ml of sulfuric acid (1 to 1) and titrating with potassium permanganate solution. Calculate the percent sodium nitrate as follows:

$$\% \text{NaNO}_2 = \frac{3.450 (A-B)N}{Q}$$

where: A = total ml of potassium permanganate solution required.

B = ml of potassium permanganate solution equivalent to 20.00 ml of ferrous ammonium sulfate solution (for a larger amount of ferrous ammonium sulfate solution use the appropriate equivalency).

N = normality of potassium permanganate solution.

Q = g of sample in aliquot.

4.6.1.1.1.3 Sodium nitrate. Calculate the percent sodium nitrate by difference as follows:

$$\% \text{NaNO}_3 = 100 - \% \text{KNO}_3 - \% \text{NaNO}_2 - \% \text{moisture (as determined 4.6.1.2.1)}$$

4.6.1.1.2 Major constituents of class 3.

4.6.1.1.2.1 Potassium nitrate. Proceed as for potassium nitrate in class 1 (4.6.1.1.1.1).

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4.6.1.1.2.2 Sodium nitrate. Calculate the percent sodium nitrate by difference as follows:

$$\% \text{ NaNO}_3 = 100 - \% \text{ KNO}_3 - \% \text{ moisture (as determined in 4.6.1.2.1)}$$

4.6.1.1.2 Major constituents of class 2.

4.6.1.1.2.1 Potassium nitrate. Proceed as for potassium nitrate in class 1 (4.6.1.1.1.1).

4.6.1.1.2.2 Sodium nitrate. Calculate the percent sodium nitrate by difference as follows:

$$\% \text{ NaNO}_3 = 100 - \% \text{ KNO}_3 - \% \text{ moisture (as determined in 4.6.1.2.1)}$$

4.6.1.1.3 Major constituents of class 3.

4.6.1.1.3.1 Potassium chloride. Proceed as for potassium nitrate in class 1 (4.6.1.1.1.1) and calculate the percent potassium chloride as follows:

$$\% \text{ KCl} = \frac{20.81P}{Q}$$

where: P - g of precipitate.

Q - g of sample in aliquot.

4.6.1.1.3.2 Sodium carbonate.

4.6.1.1.3.2.1 Reagents.

4.6.1.1.3.2.1.1 Perchloric acid (approximately 1.2N). Add 400 ml of perchloric acid (70%) to 3600 ml of water and cool to room temperature. Store in a glass-stoppered Pyrex bottle.

4.6.1.1.3.2.1.2 Standard 1N sodium hydroxide solution. Standardize against potassium acid phthalate.

4.6.1.1.3.2.2 Procedure. Transfer a 10-g sample, weighed to 0.3 mg, to a 500-ml wide-mouth Erlenmeyer flask. Add 100.00 ml of perchloric acid (approximately 1.2N) and allow to stand for several minutes until most of the sample has dissolved. Carry along a blank determination, using 100.00 ml of the perchloric acid. Cover with a Speedyvap watch glass, heat to boiling, and boil moderately for 5 minutes. Cool to room temperature and wash down the watch glass and sides of the flask with water. Add 5 drops of methyl orange indicator (0.1%) and titrate with standard 1N sodium hydroxide solution to a yellow end point. In the titration of the blank determination, first add the 100.00 ml of the sodium hydroxide solution with a pipet and finish the determination by titrating from a buret. Calculate the percent sodium carbonate as follows:

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$$\% \text{ Na}_2\text{CO}_3 = \frac{5.300(\text{AB}-\text{C})\text{N}}{\text{W}}$$

where: A = ml of perchloric acid for the titration.
 B = ml of sodium hydroxide solution equivalent to
 1.00 ml of perchloric acid.
 C = ml of sodium hydroxide solution for the titration.
 N = normality of sodium hydroxide solution.
 W = g of sample

4.6.1.1.4 Major constituents of class 4.

4.6.1.1.4.1 Potassium chloride. Proceed as for potassium chloride in class 3 (4.6.1.1.3.1).

4.6.1.1.4.2 Barium chloride. Transfer a 10-g sample, weighed to 0.3 mg to a 400-ml beaker, dissolve in 200 ml of water, and dilute to 1 liter in a volumetric flask. Pipet a 50-ml aliquot into a 400-ml beaker and dilute to about 200 ml with water. Add 2 ml of hydrochloric acid and heat to boiling. Add 100 ml of sulfuric acid (3 to 97) from a graduate slowly while stirring. Immediately remove the beaker from the hot plate and allow to stand 3 or more hours at room temperature. Filter through a Whatman No. 42 filter paper and transfer and wash with water. Place the filter paper and precipitate into a tared platinum crucible. Char and burn off the filter paper while gradually increasing the temperature, then ignite at 900°C for 45 minutes. Cool in a desiccator and weigh. Calculate the percent barium chloride as follows:

$$\% \text{ BaCl}_2 = \frac{89.22\text{P}}{\text{Q}}$$

where: P = g of precipitate.
 Q = g of sample in aliquot.

4.6.1.1.4.3 Sodium chloride. Calculate the percent sodium chloride by difference as follows:

$$\% \text{ NaCl} = 100 - \% \text{ BaCl}_2 - \% \text{ KCl} - \% \text{ moisture (as determined in 4.6.1.2.1)}$$

4.6.1.1.5 Major constituents of class 4A.

4.6.1.1.5.1 Potassium chloride. Proceed as for potassium chloride in class 3 (4.6.1.1.3.1) but use a 15-ml aliquot. Save the solution in the 1-liter volumetric flask for the determination of barium chloride and calcium chloride (4.6.1.1.5.2).

4.6.1.1.5.2 Barium chloride and calcium chloride.4.6.1.1.5.2.1 Reagents.

4.6.1.1.5.2.1.1 Ammonium acetate solution (40%). Dissolve 200 g of ammonium acetate in about 300 ml of water and dilute to 500 ml.

4.6.1.1.5.2.1.2 Potassium dichromate solution (10%). Dissolve 100 g of potassium dichromate in about 900 ml of warm water, cool, and dilute to 1 liter.

4.6.1.1.5.2.1.3 Potassium dichromate wash solution. Dilute 50 ml of potassium dichromate solution (10%) to 1 liter.

4.6.1.1.5.2.1.4 Ammonium oxalate solution (6%). Dissolve 60 g of ammonium oxalate in 900 ml of warm water, cool, and dilute to 1 liter.

4.6.1.1.5.2.1.5 Ammonium oxalate wash solution. Dilute 80 ml of ammonium oxalate solution (6%) to 500 ml.

4.6.1.1.5.2.2 Procedure. Pipet a 50-ml aliquot from the solution left in the volumetric flask from the potassium chloride determination (4.7.1.1.5.1) into a 400-ml beaker and dilute to about 225-250 ml. Add 5 ml of hydrochloric acid and 25 ml of potassium dichromate solution (10%). Heat to 80°-90°C and then add 10 ml of ammonium acetate solution (40% while stirring. Add 10 g of urea. Heat to boiling, boil until a definite precipitate appears on the bottom of the beaker and then boil for 5 minutes more. Move the beaker to the edge of the hot plate and digest at about 95°C for 1-3/4 - 2-1/4 hours (do not boil during this stage). Filter through a tared sintered glass crucible of medium porosity. Transfer the precipitate to the crucible with potassium dichromate wash solution and then wash four times with water. Save the filtrate for the determination of calcium as described in the next paragraph. Dry at 110°C for an hour, cool in a desiccator, and weigh. Calculate the percent barium chloride as follows:

$$\% \text{ BaCl}_2 = \frac{88.21P}{Q}$$

where: P = g of precipitate.
Q = g of sample in aliquot.

For the determination of calcium, transfer the filtrate from the barium determination to a 400-ml beaker. Add 50 ml of ammonium oxalate solution (6%) while stirring. Allow to stand 3 hours or more. Filter through a Whatman No. 40 filter paper and transfer and wash with ammonium oxalate wash solution. Place the filter paper and precipitate into a tared platinum crucible. Char and burn off the filter paper while gradually increasing the temperature, then ignite over a blast burner for 30 minutes. Cover, place in a desiccator, and weigh as soon as cool (the precipitate is hygroscopic). Calculate the percent calcium chloride as follows:

$$\% \text{ CaCl}_2 = \frac{197.9P}{Q}$$

where: P = g of precipitate
Q = g of sample in aliquot.

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4.6.1.1.5.3 Sodium chloride. Calculate the percent sodium chloride by difference as follows:

$$\% \text{ NaCl} = 100 - \% \text{ KCl} - \% \text{ BaCl}_2 - \% \text{ CaCl}_2 - \% \text{ moisture (as determined in 4.6.1.2.1)}$$

4.6.1.1.6 Major constituents of class 5.

4.6.1.1.6.1 Potassium chloride. Proceed as for potassium chloride in class 3 (4.6.1.1.3.1) but use a 10-ml aliquot.

4.6.1.1.6.2 Sodium chloride. Calculate the percent sodium chloride by difference as follows:

$$\% \text{ NaCl} = 100 - \% \text{ KCl} - \% \text{ moisture (as determined in 4.6.1.2.1)}$$

4.6.1.1.7 Major constituents of class 6.

4.6.1.1.7.1 Potassium chloride. Proceed as for potassium chloride in class 3 (4.6.1.1.3.1) but use a 40-ml aliquot.

4.6.1.1.7.2 Barium chloride. Proceed as for barium chloride in class 4 (4.6.1.1.4.2) but use a 25-ml aliquot.

4.6.1.1.8 Major constituents of class 7.

4.6.1.1.8.1 Barium chloride. Proceed as for barium chloride in class 4 (4.6.1.1.4.2) but filter the solution through a Whatman No. 40 filter paper (to remove the silica) and wash with water, prior to dilution in the 1-liter volumetric flask.

4.6.1.1.8.2 Silica. Transfer a 5-g sample, weighed to 1 mg, to a 400-ml beaker. Add 50 ml of water, 5 ml of nitric acid, and 50 ml of perchloric acid. Cover with a watch glass and warm on the hot plate to dissolve. Evaporate to fumes of perchloric acid and heat so that the perchloric acid refluxes for 20 minutes. Allow to cool, add about 200 ml of water, and stir to dissolve the salts. Filter through a Whatman No. 40 filter paper and transfer and wash well with water. Place the filter paper and precipitate into a platinum crucible. Char and burn off the filter paper while gradually increasing the temperature, then ignite at about 1000°C for 30 minutes. Cool in a desiccator and weigh. Add 2 ml of hydrofluoric acid and 2 drops of sulfuric acid. Evaporate to dryness of the hot plate and ignite at almost 900°C for 10 minutes. Cool in a desiccator and weigh. Calculate the percent silica as follows:

$$\% \text{ SiO}_2 = \frac{46.76L}{W}$$

where: L = g loss in weight.
W = g of sample.

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4.6.1.1.9 Major constituents of class 8.

4.6.1.1.9.1 Barium chloride. Proceed as barium chloride in class 6 (4.6.1.1.3.1).

4.6.1.1.9.2 Sodium chloride. Calculate the percent sodium chloride by difference as follows:

$$\% \text{ NaCl} = 100 - \% \text{ BaCl}_2 - \% \text{ moisture (as determined in 4.6.1.2.1)}$$

4.6.1.2 Determination of impurities.

4.6.1.2.1 Moisture.

4.6.1.2.1.1 Moisture, class 1. Transfer approximately a 10-g sample to a tared weighing dish (60 mm in diameter and 30 mm deep) and weigh the dish and contents to 0.2 mg. Heat at 120°C for 2 hours, cool in a desiccator, and weigh. Calculate the percent moisture as follows:

$$\% \text{ moisture} = \frac{100L}{W}$$

where: L = g loss in weight.
W = g of sample.

4.6.1.2.1.2 Moisture, class 2, 3, 4, 4A, 5, 6, 7, and 8. Proceed as for moisture in class 1 (4.6.1.2.1.1) but use a temperature of 180°C.

4.6.1.2.2 Water-insoluble matter, all classes except class 7. Transfer a 25-g sample, weighed to 5 mg, to a 400-ml beaker, add 200 ml of water, and stir to dissolve. Heat to boiling and boil for 2 minutes. Filter while hot through a tared sintered glass crucible of medium porosity. Transfer and wash with hot water. Save the filtrate for the determination of chloride for classes 1 and 2 (4.6.1.2.3). Dry at 120°C for 1 hour, cool in a desiccator, and weigh. Calculate the percent water-insoluble matter as follows:

$$\% \text{ water-insoluble matter} = \frac{100P}{W}$$

where: P = g of residue.
W = g of sample.

4.6.1.2.3 Chloride, classes 1 and 2. Transfer the filtrate from water-insoluble matter (4.6.1.2.2) to a 600-ml beaker. Add 3 ml of nitric acid and boil several minutes. Add 5 ml of silver nitrate solution (1%) and boil for 2 minutes. Allow to stand overnight in a dark place. Filter

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through a tared sintered glass crucible of fine porosity and transfer and wash with water. Heat at 180°C for 1 hour, cool in a desiccator, and weigh. Calculate the percent chloride as follows:

where: P = g of precipitate.
W = g of sample.

4.6.1.2.4 Sulfate.

4.6.1.2.4.1 Sulfate, classes 1, 2, and 5. Transfer a 25-g sample, weighed to 5 mg, to a 400-ml beaker, add about 300ml of water, and stir to dissolve. Add 5 ml of hydrochloric acid (1 to 1) heat to boiling and boil 5 minutes. Carry along a blank determination. Add 10ml of barium chloride solution (10%) and boil for 2 minutes. Allow to stand overnight. Filter through a Whatman No. 42 filter paper and transfer and wash with water. Place the filter paper and precipitate into a tared platinum crucible. Char and burn off the filter paper while gradually increasing the temperature, then ignite at 900°C for 30 minutes. Allow to cool, add 3 drops of sulfuric acid and 5 ml of hydrofluoric acid, and evaporate to dryness by heating at the edge of the hot plate. Ignite at 900°C for 30 minutes, cool in a desiccator, and weigh. Calculate the percent sulfate as follows:

$$\% \text{SO}_4 = \frac{41.2P}{W}$$

where: P = g of precipitate.
W = g of sample.

4.6.1.2.4.2 Sulfate, class 3. Transfer a 25-g sample, weighed to 5mg, to a 400-ml beaker, add about 300 ml of water, and stir. Add hydrochloric acid (1 to 1) slowly with stirring until the solution is acid to litmus paper and then add about 5 ml hydrochloric acid (1 to 1) in excess. Heat to boiling and boil for 5 minutes. Proceed with the addition of barium chloride as for sulfate in classes 1, 2, and 5 (4.6.1.2.4.1).

4.6.1.2.4.3 Sulfate, classes 4, 4A, 6 and 8. Proceed as for sulfate in classes 1, 2, and 5 (4.6.1.2.4.1), but omit the addition of the barium chloride since barium is contained in the sample.

4.6.1.2.4.4 Sulfate, class 7. Proceed as for sulfate in classes 1, 2, and 5 (4.6.1.2.4.1), but use a 10-g sample.

4.6.1.2.5 Total nitrogen as nitrate, classes 3, 4, 4A, 5, 6, 7, and 8. Use a nitrogen distillation apparatus consisting of a 500-ml long necked Kjeldahl digestion flask connected by means of a suitable scrubbing bulb

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to a condenser, the end of which extends into a 500-ml Erlenmeyer flask. Add 70 ml of water and 30.00 ml of standard 0.1N hydrochloric acid to the Erlenmeyer flask and adjust the apparatus so that the tip of the condenser dips just below the surface of the liquid. Transfer a 10-g sample, weighed to 5mg, to the Kjeldahl flask. Add 300 ml of water, 1 g of 20-mesh Devarda alloy, 5 drops of white USP paraffin oil (to minimize frothing), and 5 ml of 50% sodium hydroxide solution (made of dissolving 100 g NaOH in 200 ml of water), pouring the latter solution slowly down the sides of the flask so that it does not mix at once with the contents. Carry along a blank determination. Connect the flask and mix the contents by gentle swirling. Heat slowly at first and then at such a rate that 250 ml of the required distillate will pass over in 1 hour. Add 3 drops of methyl red indicator (0.1%) and titrate with standard 0.1N sodium hydroxide solution to a yellow end point. Calculate total nitrogen (as NO_3) as follows:

$$\% \text{ total nitrogen (as NO}_3\text{)} = \frac{6.20(AB-C)N}{W}$$

where: A = ml of hydrochloric acid.
 B = ml of sodium hydroxide solution equivalent to 1.00 ml of hydrochloric acid.
 C = ml of sodium hydroxide solution for titration.
 N = normality of sodium hydroxide solution.
 W = g of sample.

4.6.1.2.6 Nitrite class 2. Transfer a 5-g sample, weighed to 5 mg, to a 400-ml beaker, add 300 ml of water, and stir to dissolve. Add 10 ml of sulfuric acid (1 to 1) and 10.00 ml of standard 0.1N potassium permanganate solution. Add 15.00 ml of 0.1N ferrous ammonium sulfate solution while stirring and immediately titrate with the standard 0.1N potassium permanganate solution to a pink color. Determine the equivalent strengths of the ferrous ammonium sulfate and potassium permanganate solutions by adding 15.00 ml of ferrous ammonium sulfate solution to 300 ml of water and 10ml of sulfuric acid (1 to 1) and titrating with potassium permanganate solution. Calculate the percent nitrate (NO_2) as follows:

$$\% \text{ nitrate (as NO}_2\text{)} = \frac{2.30(A-B)N}{W}$$

where: A = total ml of potassium permanganate solution required for the sample
 B = ml of potassium permanganate solution equivalent to 15.00 ml of ferrous ammonium sulfate solution.
 N = normality of potassium permanganate solution.
 W = g of sample.

4.6.1.2.7 Carbonate, classes 1, 2, 4, and 5. Transfer a 10-g sample, weighed to 5 mg, to a 250-ml Erlenmeyer flask fitted with a rubber stopper. Add 50 ml of water and shake for 1 or 2 minutes to dissolve the salts. Add

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10 ml of barium chloride solution (10%)(this can be omitted for class 4) and swirl. Add 2 drops of ammonium hydroxide and swirl. Allow to stand for 3 hours or more. Filter through a sintered glass crucible of fine porosity and transfer and wash with water. Place the crucible upright in a 250-ml beaker, add 20.00 ml standard 0.1N hydrochloric acid to the crucible with a pipet and stir. Carry along a blank determination by adding 20.00 ml of 0.1N hydrochloric acid to a clean crucible in a 250-ml beaker. Wash down and remove the crucible. Cover with a watch glass and boil for 1 minute. Disregard any siliceous residue. Add 3 drops of methyl orange indicator (0.1%) and titrate with standard 0.1N sodium hydroxide to a pink end point. Calculate the percent carbonate (as CO_3) as follows:

$$\% \text{ carbonate (as } \text{CO}_3) = \frac{3.00(\text{A}-\text{C})\text{N}}{\text{W}}$$

where: A = ml of 0.1N hydrochloric acid for the titration.
 B = ml of sodium hydroxide solution equivalent to 1.00 ml of hydrochloric acid.
 C = ml of 0.1N sodium hydroxide solution for the titration.
 N = Normality of sodium hydroxide solution.
 W = g of sample.

4.6.1.2.8 Fluoride, all classes. Transfer a 20-g sample, weighed to 5 mg, to 250-ml beaker. Add 100 ml of water, and warm on the hot plate to dissolve. Filter through a Whatman No. 40 filter paper and wash with water. If the water-insoluble matter (as determined in 4.6.1.2.2) is less than 0.10%, discard the filter paper and precipitate; if the water-insoluble matter is greater than 0.10%, save the filter paper and test the precipitate for fluoride as described in the next paragraph. Adjust the solution to pH of 4 by adding hydrochloric acid (1 to 1), using pH paper. Remove the pH paper and boil 1 minute to drive off the carbon dioxide (otherwise calcium carbonate will precipitate with the calcium fluoride). Cool, adjust to pH 10 by adding sodium hydroxide solution (10%), using pH paper. Adjust to pH 5 by adding acetic acid (1 to 1). Remove the pH paper, add 5 ml of calcium chloride solution (10%), and allow to stand overnight. Observe the solution for the appearance of a white precipitate of calcium fluoride while comparing with a blank run simultaneously. In the absence of a precipitate report the fluoride as "none".

If necessary, test for fluoride in the filtered precipitate (see previous paragraph as follows: Transfer the filter paper and precipitate to a platinum crucible, and char and burn off the filter paper at dull red heat. Fuse with 1g of sodium carbonate. Allow to cool, place the crucible in a 250-ml beaker, add 50 ml of water, and boil to dissolve the soluble salts. Wash down and remove the crucible. Filter through a Whatman No. 40 filter paper and wash with water. Discard the filter paper and precipitate. Adjust to pH 4 by adding hydrochloric acid (1 to 1), using

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pH paper. Remove the pH paper and boil for 1 minute. Cool and adjust to pH 10 by adding sodium hydroxide solution (10%) and then adjust to pH 5 by adding acetic acid (1 to 1). Remove the pH paper, add 5 ml of calcium chloride solution (10%), and observe whether a precipitate is formed as described above.

NOTE: pH paper must be used, since the identifying dyes frequently present in the heat treating salts prevent the use of indicators.

4.6.1.2.9 Silica, class 5. Proceed as described for the determination of silica in class 7 (4.6.1.1.7.2).

4.6.1.2.10 Total alkaline earths (Mg, Ca, Sr, and Ba), classes 1, 2, 3, and 5. Transfer a 10-g sample, weighed to 1 mg, to a 400-ml beaker and dissolve in about 200 ml of water. Add 2 ml of hydrochloric acid to class 1, 2, and 5 salts and 10 ml of hydrochloric acid to class 3 salt. Carry along a blank determination. Heat to boiling and boil for 5 minutes. (If the solution is not clear, filter through a Whatman No. 40 filter paper, wash with water, ignite in a platinum crucible, fuse with 5 g of sodium carbonate, cool, dissolve the melt by boiling with 50 ml of water contained in a 250-ml beaker, filter through a Whatman No. 40 filter paper, transfer and wash with water, dissolve the carbonates off the filter paper with hot hydrochloric acid (1 of 2), wash with water, boil off the carbon dioxide, and combine with the original solution). Add 3 drops of methyl red indicator (0.1%) and then add ammonium hydroxide until the color of the solution changes to yellow. Heat to boiling and boil for 1 minute. Filter through a Whatman No. 40 filter paper and wash with hot ammonium chloride solution (2%), made alkaline to methyl red. Discard the filter paper and precipitate. Add 5 drops of ammonium hydroxide (1 to 1) to the filtrate, heat to boiling, and add 50 ml of hot ammonium oxalate solution (4%) and 20 ml of ammonium carbonate solution (4%) while stirring. Boil 1-2 minutes and digest at about 90°C for 30 minutes. Allow to stand at room temperature for 2 hours or more. Filter through a Whatman No. 40 filter paper and transfer and wash with ammonium oxalate wash solution (0.1%). Place the filter paper and precipitate into a tared platinum crucible. Char and burn off the filter paper while gradually increasing the temperature, then ignite over a blast burner for 15 minutes. Cover, cool in a desiccator, and weigh (the precipitate is hygroscopic). Calculate the total alkaline earths (magnesium, calcium, strontium, and barium) as follows:

$$\text{Total alkaline earths (Mg, Ca, Sr, and Ba) as oxides} = \frac{100P}{W}$$

where: P = g of precipitate.
W = g of sample.

4.6.1.2.11 Neutrality (pH), all classes except class 3. Transfer a 1-g sample, weighed to 0.5 mg, to a 150-ml beaker and dissolve in 100 ml of carbon-dioxide-free water. Determine the pH by means of pH meter.

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4.6.2 Physical tests.

4.6.2.1 Determination of melting point. Weigh approximately 300 g of the salt mixture in a 400-ml crucible. Class 1, 2, and 3 salt shall be placed in a steel or iron crucible, while class 4, 4A, 5, 6, 7, and 8 salt shall be placed in a clay crucible. The crucible and its contents shall be heated in a suitable furnace, equipped with temperature control to approximately 38°C. above the probable melting point of the salt. A chromelalumel or a platinum-platinum rhodium thermocouple shall be inserted into the completely molten salt, and the furnace, crucible, and sample shall be allowed to cool sufficiently to enable the determination of the hysteresis or leveling-off temperature. The drop-of-temperature versus time-of-cooling curve shall be determined by means of either a manually-operated, or automatic recording potentiometer. The hysteresis or leveling-off temperature shown on the resulting curve shall be considered the melting point of the salt mixture.

WARNING - Extreme precautions must be taken when performing this test. Personnel handling heated parts and molten salt must be adequately protected (goggles, face shield, gloves) to prevent injury resulting from contact with heated parts, molten salt and oven. Molten salt may react violently with water.

4.6.2.2 Black stain, classes 1 and 2.

4.6.2.2.1 Test specimen. The specimen shall consist of a piece of cartridge brass (70 Cu - 30 Zn) of a size suitable for the testing equipment.

4.6.2.2.2 Procedure. The test specimen shall be pickled for 20 to 30 seconds in a 40% (by volume) solution of nitric acid at a temperature of 21 to 27°C, and washed and dried. The specimen shall be immersed for 5 minutes in the molten salt (class 1 or 2), at approximately 566°C. The specimen shall then be quenched clean water and examined for evidence of any objectional black stain.

4.6.2.3 Decarburization, scaling, and pitting, classes 4, 5, 6, and 7.

4.6.2.3.1 Test specimen. The test specimen should be approximately one inch in length and approximately one-half inch in diameter or width with two opposite flat ground surfaces free from decarburization. The composition of the steel of which the specimens shall be made are as follows:

For classes 4 and 5 salts - 0.50% carbon steel.

For class 6 salt - high carbon - high chromium steel
(1.50% carbon).

For classes 7 and 8 salts - high speed steel (18-4-1).

4.6.2.3.2 Procedure. The specimen shall be immersed in the molten salt heated to its maximum working temperature (see 1.2). The specimen shall

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be immersed for 45 minutes in class 4, 5, or 6 salts, and for 3 minutes in class 7 salt. The specimen shall then be quenched in the proper quenching medium for the steel of which it is made. Rockwell "C" scale hardness readings shall be made on the quenched specimen. The specimen shall then be surface-ground to a minimum depth of 0.025-inch in such manner that its surface will not be burned or overheated during grinding. A hardness reading shall then be made on the ground surface. Decarburization of the steel shall be suspected if a difference of more than 2 Rockwell "C" scale points is obtained between the readings made on the quenched and the ground surfaces. In such case a metallographic examination of the specimen shall be made to determine extent of decarburization. Rockwell hardness tests shall be made in accordance with method 243 of Fed. Test Method Std. No. 151.

4.6.2.3.3 Metallographic examination. The metallographic examination of the specimen shall be made as follows:

1. Heat the specimen for 30 minutes at 316° to 427°C in order to produce tempered martensite.

2. Mount the specimen in a vertical position so that its cross-sectional area is exposed for examination.

3. Prepare the specimen for metallographic examination by any suitable means.

4. Etch the polished surface with 10-percent Amyl-Nital solution.

5. Examine the etched specimen microscopically, under 100 magnification, and measure the depth of any observed partial or total decarburization.

The decarburization of the steel shall be considered excessive if a hardness reading differential of more than 2 Rockwell "C" scale points is obtained between the quenched and ground surfaces of the specimen (see 4.7.2.4) and either partial or total decarburization is observed in the subsequent metallographic examination of the specimen.

4.7 Tightened or reduced inspection. In end item inspection, tightened or reduced inspection shall be instituted, as required, in accordance with requirements of MIL-STD-105.

4.8 Reinspection.

4.8.1 Visual. A lot may be resubmitted for examination upon approval of the procuring agency if all nonconforming units in the lot are removed.

4.8.2 Filler containers. A lot may be resubmitted for examination upon approval of the procuring agency if all nonconforming units in the lot are removed.

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5. PACKAGING

5.1 Packaging and packing.

5.1.1 Level A. Salts shall be packaged level A and shall be packed in containers conforming to PPP-C-301, Type II. The salts shall be packed in air-tight and water resistant drums with open head, quick level locking type, with fully removable covers. The drums shall be DOT 17H steel drums. The net weight shall not exceed 480 pounds.

5.1.2 Level C. Unless otherwise specified, the salts shall be packaged and packed for level C protection. The salts shall be placed in air-tight and water resistant drums of the open-top type with quick level locking type of fully removable covers. The drums shall be either steel or fibre as specified in the contract or order. The drums containing class 1 and class 2 salts shall be such as to meet the requirements of the Department of Transportation rules and regulations for the transportation of hazardous materials 49 CFR 171-178.

5.2 Marking. All containers shall be marked as specified in MIL-STD-129. In addition, the words "STORE IN DRY PLACE" shall be marked in red stencil on the top and side of each container. Containers with class 1 and class 2 salts shall have a DOT label for sodium nitrite mixture-sodium nitrate, sodium nitrite and potassium nitrate-oxidizer.

5.2.1 Additional marking. In addition to the above, a special marking shall be used to ensure special handling by personnel when using nitrates and nitrites in combination with cyanides, aluminum, magnesium, or carbonaceous materials, such as; soot, carbon, oils, etc., which could cause burns or explode.

6. NOTES

6.1 Intended use. Specific uses of the salts covered by this specification are as follows:

Class 1 - Blueing and tempering of steels, quenching of carbon and low alloy steels for martempering and austempering, annealing and stress-relieving of cold-worked copper and brasses.

Class 2 - Primarily designed for the heat-treatment of aluminum alloys but can be used for the annealing of copper and brasses, and tempering of steel.

Class 3 - High temperature draw of low carbon alloys steels, process anneal of low carbon steel, brazing with silver solder and process anneal of stainless steels.

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Class 4 - Wide temperature range hardening, annealing and high temperature quenching for medium to high carbon alloy and carbon steels, reheat of carburized steels and preheating of tool steels. (Note: Not desirable for use in austempering or martempering with salt quench.)

Class 4A - Hot quenching and tempering of high speed steel.

Class 5 - General heat-treating purposes, normalizing, annealing, hardening of certain carbon and alloy steels, brazing of all silver solders, preheating of high speed steels and preparation of steels for isothermal processes.

Class 6 - Annealing of stainless steel and hardening of high carbon chromium tool steels.

Class 7 - Hardening of high speed steels and in the heat treatment of certain high alloy steels.

Class 8 - Hardening of high speed steel as well as the high carbon-high chromium tool steels. This salt is desirable where only one furnace is available for heat treating both of the above mentioned steels. Class 8 is intended for intermittent operation. For continuous operation at the upper end of the high speed steel hardening range use class 7.

6.2 Ordering data. Procurement documents should specify the following:

- (a) Title, number, and data of this specification.
- (b) Class of salt required (see 1.2).
- (c) Form of class 7 salt required (see table 1).
- (d) Level of protection if other than level C (see 5.1.1 and 5.1.2).
- (e) Type of container required (see 5.1.2).

6.3 Precautions on use of nitrate and nitrate salts. Extreme care must be taken in the use of salt baths of classes 1 and 2. This warning cannot be over emphasized. These types of molten salt baths carry with them as low temperature heating media certain fire and explosion hazards especially in the heat-treatment of aluminum alloys. These hazards are attendant with over heating of the nitrate and nitrate baths accidental admixture of cyanides, or inadvertent immersion of magnesium alloys into the nitrate bath, structural failure of the bath containers, and improper remelting of the frozen bath. Violent chemical reactions are very apt to occur between the nitrate baths and carbonaceous materials such as oils, soot, graphite, or cyanide carried over from adjacent carburizing baths, and vigorous and explosive reaction between overheated nitrate baths and aluminum alloys

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and the use of the same salt bath for alternate heating of aluminum or aluminum alloys and ferrous metals. It is advisable to issue a strong warning regarding the excessive temperature danger. This warning should be conspicuously placed at the temperature controls of nitrate salt baths. This warning should state how high the operating temperature of the nitrate bath can safely be used and the temperature that must not be exceeded (593°C). Care should be taken not to allow any drop off metal in the bottom of the heating container. This also holds true for all classes of salts covered by this specification. All furnaces should be equipped individually with reliable excess temperature devices. Great care should be taken to keep the nitrate and nitrite salts dry by having them stored in a dry place.

6.4 Decomposition points of the salts. The approximate decomposition points of the salts covered by this specification at which fuming should be expected to occur are as follows:

Class 1	635°C
Class 2	649°C
Class 3	938°C
Class 4	941°C
Class 4A	788°C
Class 5:	941°C
Class 6	1149°C
Class 7	1371°C
Class 8	1343°C

Custodian:
 Army - AR
 Navy - YD
 Air Force - 68

Preparing activity:
 Army - AR

Project No. 6850-0595

Review Activities:
 Army - MD
 Navy - AS
 Air Force - 11
 DSC-DGSC

User Activity:
 Army - MI
 Navy - SH