METRIC

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MILITARY SPECIFICATION

TRIETHYL CITRATE

This specification is approved for use by the U.S. Army Missile Command, Department of the Army, and is available for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 Scope. This specification covers one grade of triethyl citrate.

2. APPLICABLE DOCUMENTS

2.1 Government documents.

Beneficial comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: Commander, U.S. Army Missile Command, ATTN: AMSMI-RD-SE-TD-ST, Redstone Arsenal, AL 35898-5270 by using the Standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document or by letter.

AMSC N/A FSC 6810

2.1.1 Specifications, standards, and handbooks. The following specifications, standards, and handbooks form a part of this document to the extent specified herein. Unless otherwise specified, the issues of these documents are those listed in the issue of the Department of Defense Index of Specifications and Standards (DODISS) and supplement thereto, cited in the solicitation (see 6.2).

STANDARDS

FEDERAL

FED-STD-313	-	Material Safety Data, Transportation Data and Disposal Data for Hazardous Material Furnished to Government Activities

MILITARY

MIL-STD-129	-	Marking for Shipment and Storage
MIL-STD-1190	-	Minimum Guidelines for Level C Preservation, Packing and Marking

(Unless otherwise indicated, copies of the federal and military specifications, standards, and handbooks are available from the Standardization Documents Order Desk, Bldg. 4D, 700 Robbins Ave., Philadelphia, PA 19111-5094.)

2.2 Non-Government publications. The following documents form a part of this document to the extent specified herein. Unless otherwise specified, the issues of the documents which are DoD adopted are those listed in the issue of the DODISS cited in the solicitation. Unless otherwise specified, the issues of documents not listed in the DODISS are the issues of the documents cited in the solicitation (see 6.2).

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM)

ASTM D 1193	-	Standard Specification for Reagent Water
ASTM D 1209	-	Color of Clean Liquids (Platinum-Cobalt Scale)

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

AMERICAN CHEMICAL SOCIETY (ACS)

Reagent Chemicals, American Chemical Society Specifications

(Application for copies of ACS publications should be addressed to the American Chemical Society, 1155 16th Street NW, Washington, DC 20036.)

(Non-Government standards and other publications are normally available from the organizations that prepare or distribute the documents. These documents also may be available in or through libraries or other informational services.)

2.3 Order of precedence. In the event of a conflict between the text of this document and the references cited herein, the text of this document takes precedence. Nothing in this document, however, supersedes applicable laws and regulations unless a specific exemption has been obtained.

3. REQUIREMENTS

3.1 First article sample. When specified (see 6.2), a first article sample shall be subjected to first article inspection (see 6.3) in accordance with 4.3 and 4.4.

3.2 Chemical and physical properties. Chemical and physical properties of the triethyl citrate shall be specified in table I.

3.3 Material safety data sheets. A material safety data sheet shall be prepared in accordance with the requirements of FED-STD-313 (see 6.4)

TABLE I. Chemical and physical properties.

Characteristic	Minimum	Maximum
Assay (as total ester), percent	99.0	-----
Moisture, percent	-----	0.3
Color, APHA number	-----	50
Acidity (as citric acid), percent	-----	0.02
Saponification number	607.0	611.0

3.4 Workmanship. The triethyl citrate shall be uniform in quality, free from foreign materials, and shall be manufactured under conditions and procedures standard to the industry.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order, the contractor is responsible for the performance of all inspection requirements (examinations and tests) as specified herein. Except as otherwise specified in the contract or purchase order, the contractor 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 this specification where such inspections are deemed necessary to ensure supplies and services conform to prescribed requirements.

4.1.1 Responsibility for compliance. All items shall meet all requirements of sections 3 and 5. The inspection set forth in this specification shall become a part of the contractor's overall inspection system or quality program. The absence of any inspection requirements in the specification shall not relieve the contractor of the responsibility of ensuring that all products or supplies submitted to the Government for acceptance comply with all requirements of the contract. Sampling inspection, as part of manufacturing operations, is an acceptable practice to ascertain conformance to requirements, however, this does not authorize submission of known defective material, either indicated or actual, nor does it commit the Government to accept defective material.

4.2 Classification of inspections. The inspection requirements specified herein are classified as follows:

a. First article inspection (see 4.4)

b. Quality conformance inspection (see 4.5).

4.3 Inspection conditions. Unless otherwise specified, all inspections shall be performed in accordance with the test conditions specified herein.

4.4 First article inspection. When specified in the contract or order (see 6.2) a first article sample shall be subjected to first article inspection. The quality shall be as specified in the contract or order. First article inspection shall consist of all examinations and tests specified herein. The government shall witness the examinations and tests for the first article sample acceptance at the contractor's plant. Subsequent units shall not be considered for acceptance until Government approval of the first article has been obtained.

4.5 Quality conformance inspection. Quality conformance tests for acceptance of the triethyl citrate shall consist of the following examinations and tests:

TABLE III. Quality conformance inspection.

Examination and test	Requirement paragraph	Test paragraph
Assay (total ester)	3.2	4.11.1
Moisture	3.2	4.11.2
Color, APHA number	3.2	4.11.3
Acidity (as citric acid)	3.2	4.11.4
Saponification number	3.2	4.11.5

4.6 Lot. A lot shall consist of triethyl citrate produced at one plant with no change in formulation or process. If manufacture is by batch process, each batch shall constitute a lot.

4.7 Batch. A batch is that quantity of material which has been subjected to one or more chemical or physical processes (or combination thereof) intended to produce a desired product having substantially uniform characteristics.

4.8 Sampling. The number of containers to be chosen at random for acceptance sampling shall be equal to the square root of the total number of containers in the lot. If the number thus obtained is not a whole number, the number of containers to be sampled shall be increased to the next higher whole number. In no case, however, shall the number of containers to be sampled be less than seven (unless there are less than seven containers in the lot, in which case each container shall be sampled).

4.9 Primary Sample. From each selected container, a sample shall be taken from three or more places throughout the container. The total weight of the sample from each container shall weigh at least 50 grams (g). Each sample thus taken shall be mixed thoroughly, placed in a clean, dry container and labeled to identify the material name, original container designation, contract number, and lot number.

4.10 Composite sample. Each primary sample shall be subdivided to prepare a composite sample (not greater than 500 g). Unused primary material shall be returned to the primary sample container. After mixing the composite sample thoroughly, place the composite sample in a clean, dry container, seal and identify the composite sample with material name, container designations, contract number, and lot number. All specified chemical and physical tests shall be made on this composite sample representing the lot. Failure of the composite sample to pass all the tests herein shall result in rejection of the lot represented.

4.11 Testing. The following procedures shall be used to determine that the requirements of this specification have been met. Chemical reagents are to be specified in accordance with American Chemical Society reagent grade standards where appropriate. Reagent water is to be specified by the appropriate grade of ASTM D 1193. Any changes in the test procedures employed shall be subject to prior approval of the procuring activity. Unless otherwise specified, all tests shall be run in duplicate. The average of the two results shall be taken as the test result.

4.11.1 Assay (as total ester).

4.11.1.1 Reagents.

a. Isopropyl alcohol, chemically pure (CP).

b. Sodium hydroxide, 0.5 normal (N).

c. Standardized sulfuric acid, 0.5N.

d. Phenolphthalein indicator, USP XVI test solution.

4.11.1.2 Procedure. Accurately weigh 1.5 g of sample into a 500-milliliter (ml) flask with a 24/40 standard taper ground-glass neck. Add 25 ml of isopropyl alcohol and 25 ml of distilled water. Pipet exactly 50 ml of 0.5N sodium hydroxide into the reaction mixture. Add boiling chips and attach to a water-cooled condenser with 24/40 standard taper joint. Reflux for 1.5 hours. Cool and wash down condenser with distilled water. Add 5 drops of phenolphthalein indicator and titrate with 0.5N sulfuric acid to a colorless end point. A blank using identical quantities of reagents is run simultaneously with the sample.

$$\text{Percent assay (total ester)} = \frac{(A - B)\ N \times 0.092 \times 100}{C}$$

where: A = volume of sulfuric acid needed to titrate blank, ml

B = volume of sulfuric acid need to titrate sample, ml

C = weight of sample, g

N = normality of sulfuric acid

4.11.1.3 Acceptance criteria. For the lot represented to pass the assay (as total ester) test, the value obtained for the percent assay (as total ester) shall be not less than the value specified in table I.

4.11.2 Moisture.

4.11.2.1 Apparatus. The apparatus used for determination of moisture content of the sample shall be an Aquameter, Model KF-4B, or an approved equivalent.

4.11.2.2 Reagents.

A. Karl Fischer reagent. Karl Fischer reagent must have a strength such that each milliliter of reagent corresponds to 0.0014-0.0023 g of water. Dilute 750 ml of commercially available stabilized Karl Fischer reagent (with water equivalent of 0.005-0.007 g/ml) to 2000 ml with absolute methanol (not greater than 0.1 percent water). Mix well and allow to stand overnight before use. Determine the water equivalent (A) of this solution as follows:

(1) Use sodium tartrate dihydrate ($Na_2C_4O_62H_2O$) as a primary standard (with water content of 15.66 percent) for standardizing Karl Fischer reagent. If the water content value is in question, it may be determined by heating some of the salt at 150° Celsius (C) for 3 hours. Should the value (as determined) differ from the theoretical value of 15.66, then the experimental value shall be used in the determination of water equivalent (A) of the Karl Fischer reagent; instead of the 15.66 in the formula below, the factor should be 10P, where P is percentage moisture (as determined). Rapidly transfer 0.090-0.110 g (weighed to the nearest 0.0001 g) or reagent-grade $Na_2C_4O_62H_2O$ to the titration vessel.

(2) Titrate to an end point in the same manner as with the sample. (See 4.11.2.3)

(3) Repeat the standardization procedure until three successive results agree within five parts per thousand.

(4) If the indicated water equivalent (A) of the Karl Fischer reagent is less than 0.0014 g of water per milliliter of Karl Fischer reagent, it may be due to the presence of too much water in the absolute methanol used. In this case, distill the methanol from metallic calcium or calcium hydride. Passing the methanol through a column of Molecular Sieves, Type 4A, or equivalent, may also reduce the water content of the methanol sufficiently.

$$\text{Water equivalent (A)} = \frac{156.6\,W}{V}$$

where: A = water equivalent of the Karl Fischer reagent, g/ml

W = weight of $Na_2C_4O_62H_2O$ taken, g

V = volume of Karl Fischer reagent used, ml

b. Water-in-methanol solution. The water-methanol solution should contain 0.0015-0.0020 g of water per milliliter of solution. A good grade of commercial absolute methanol contains about 0.0010 g water per milliliter of methanol. Water content can be adjusted by adding 1.0 g of water to 1000 ml of the water-methanol solution to produce a change of

0.0010 g per milliliter. Determine the relative strength of the water-methanol solution in terms of Karl Fischer reagent as follows:

Put about 50 ml of the anhydrous methanol used in 4.11.2.2a into the titration beaker of the Aquameter. Add a slight excess of Karl Fischer reagent (4.11.2.2a), then back-titrate with water-methanol solution (4.11.2.2b). Then run in an additional 5 to 8 ml of Karl Fischer reagent, read to the nearest 0.01 ml, and again back-titrate with water-methanol solution (read to the nearest 0.01 ml). Repeat the addition and back-titrating steps twice more to provide triplicate determinations of the equivalency ratio. Calculate the ratio (B) of Karl Fischer reagent to that of the water-methanol solution. The range of the ratios calculated from the 3 titrations should not be greater than 0.04. If the range exceeds 0.04, continue making titrations until 3 ratios are obtained whose range does not exceed 0.04. Then determine the average ratio from all the ratios which have been obtained.

4.11.2.3 Procedure. Determine the moisture content of the sample by the Karl Fischer method using a direct-titration technique. Introduce to the titration beaker, through the opening in the diaphragm, approximately 10 g of sample weighed to the nearest 0.001 g. Close the opening, start the stirrer, and press the titrate button to titrate with Karl Fischer reagent (4.11.2.2a). When the indicator light glows, read the Karl Fischer buret to the nearest 0.01 ml. Where necessary, water methanol solution (4.11.2.2b) may be used to back-titrate.

$$\text{Percent moisture} = \frac{100A\ ({}^{V}KF - {}^{BV}WM)}{W}$$

where: A = weight of water equivalent to 1.00 ml of Karl Fischer reagent, g/ml

${}^{V}KF$ = volume of Karl Fischer reagent titrant used, ml

${}^{V}WM$ = volume of water-methanol solution titrant used, ml

B = ratio of Karl Fischer reagent to that of water-methanol solution, ml/ml

W = weight of sample taken, g

4.11.2.4 Acceptance criteria. For the lot represented to pass the moisture test, the value obtained for the percent moisture shall be not greater than the value specified in table I.

4.11.3 Determination of color. The color of the triethyl citrate shall be determined in accordance with ASTM D 1209

a. Cobalt chloride, analytical reagent.

b. Potassium chloroplatinate, chemically pure grade.

c. Hydrochloric acid, concentrated, analytical reagent grade.

d. Nessler tubes. APHA standard, high form, 50-ml capacity.

4.11.3.2 Preparation of standards. Dissolve exactly 1.245 g of potassium chloroplatinate and 1 g of cobalt chloride in a mixture of 500 ml of water and 100 ml of hydrochloric acid. Transfer to a liter volumetric flask, dilute to volume with water and mix well. This solution has a color of 500 units. Transfer the aliquots of this stock solution, listed below, to 50-ml Nessler tubes and dilute to volume with water. The resulting standards have the corresponding color values in APHA units.

Aliquot (ml)	Standard (APHA units)
0.50	5
1.00	10
2.00	20
3.00	30
4.00	40
5.00	50
7.50	75
10.00	100
15.00	150
20.00	200
30.00	300
40.00	400
50.00	500

4.11.3.3 Procedure. Transfer exactly 50 ml of the solution to be tested into a 50-ml Nessler tube. Compare the color of this solution to the color standards. If the color matches that of one of the standards, record the color value of that standard. If the color lies between two standards, record the color values of these standards. Additional standards may be prepared when a more accurate color estimation is desired.

4.11.3.4 Acceptance criteria. For the lot represented to pass the color test, the value obtained for the APHA color standard shall be not greater than the value specified in table I.

4.11.4 Determination of free acidity (as citric acid).

4.11.4.1 Reagents.

a. Isopropyl alcohol, neutralized.

b. Standardized sodium hydroxide, 0.1N.

c. Bromothymol blue indicator, 0.04 percent aqueous solution.

4.11.4.2 Procedure. Dissolve 30 to 50 g of the sample in 30 ml of neutralized isopropyl alcohol. Add 5 drops of bromothymol blue indicator and titrate to neutrality with 0.1N sodium hydroxide.

$$\text{Percent free acidity (as citric acid)} = \frac{A \times N \times 0.064 \times 100}{B}$$

where: A = volume of sodium hydroxide used in titration, ml.

N = normality of sodium hydroxide.

0.064 = milli-equivalent for citric acid.

B = weight of the sample, g.

4.11.4.3 Acceptance criteria. For the lot represented to pass the free acidity test, the value obtained for the percent free acidity shall be not greater than the value specified in table I.

4.11.5 Saponification number.

4.11.5.1 Procedure. The saponification number can be calculated from the assay procedure in 4.11.1 using the following equation:

$$\text{Saponification number} = \frac{(A - B)\ N \times 0.0561 \times 1000}{C}$$

where: A = volume of sulfuric acid needed to titrate blank, ml.

B	=	volume of sulfuric acid needed to titrate sample, ml.
C	=	weight of sample, g.
N	=	normality of sulfuric acid.

4.11.5.2 Acceptance criteria. For the lot represented to pass the saponification number test, the value obtained for the saponification number shall be within the range specified in table I.

4.12 Inspection of packaging. The sampling and inspection of the preservation, packaging, and container marking shall be in accordance with the requirements of MIL-STD-129.

5. PACKAGING

5.1 Packaging and packing. Unless otherwise specified (see 6.2) packaging and packing shall be level C in accordance with MIL-STD-1190.

5.2 Marking. In addition to the markings specified in the contract or order, unit packages and shipping containers shall be marked in accordance with MIL-STD-129.

6. NOTES

(This section contains information of a general or explanatory nature that may be helpful, but is not mandatory.)

6.1 Intended use. Triethyl citrate described in this specification is intended for use as a restrictor bonding agent.

6.2 Acquisition requirements. Acquisition documents must specify the following:

a. Title, number, and date of the specification

b. Issue of DODISS to be cited in the solicitation, and if required, the specific issue of individual documents referenced (see 2.1, 2.1.1 and 2.2)

c. When a first article sample is required (see 3.1, 4.4 and 6.3)

d. First article sample size (see 4.4)

e. Required packaging and packing (see 5.1).

6.3 First article. When first article inspection is required, the contracting officer should provide specific guidance to offerers whether the item(s) should be a first article sample, a first production item, or a number of items to be tested as specified in 4.4. The contracting officer should include specific instructions in acquisition documents regarding arrangements for examinations, approval of first article test results and disposition of first articles. Invitations for bids should provide that the Government reserves the right to waive the requirement for samples for first article inspection to those bidders offering a product which has been previously acquired or tested by the Government, and that bidders offering such products, who wish to rely on such production or test, must furnish evidence with the bid that prior Government approval is presently appropriate for the pending contract.

6.4 Material safety data sheets. Contracting officers will identify those activities requiring copies of completed material safety data sheets prepared in accordance with FED-STD-313. The pertinent Government mailing addresses for submission of data are listed in FED-STD-313.

6.5 Subject term (keyword) listing.

Bonding agent
Chemical agent
Restriction bonding agent

6.6 Changes from previous issue. Marginal notations are not used in this revision to identify changes with respect to the previous issue due to the extensiveness of the changes.

Custodian:
Army - MI

Review Activity:
DLA-GS

Civilian Coordinating Activity:
GSA - FSS

Preparing activity:
Army - MI

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