MIL-T-47063(MI)
10 May 1974
SUPERSEDING
MIS 14161A
23 December 1965

MILITARY SPECIFICATION

TRIETHYL CITRATE

This specification is approved 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 The following documents, of the issue in effect on date of invitation for bids or request for proposal, form a part of the document to the extent specified herein.

STANDARDS

Military

MIL-STD-129 Marking for Shipment and Storage

(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 Other publications. 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.

FSC 6810

American Society for Testing and Materials

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, Pennsylvania 19103.)

Uniform Classification Committee

Uniform Freight Classification Rules

(Application for copies should be addressed to Uniform Classification Committee, 202 Chicago Union Station, Chicago, Illinois, 60606.)

American Trucking Association Publication

National Motor Freight Classification Rules and Container Regulations

(Application for copies should be addressed to the National Classification Board, 1424 Sixteenth Street, N.W., Washington, D.C. 20013.)

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.

3. REQUIREMENTS

3.1 Preproduction sample. Unless otherwise specified (See 6.2), a preproduction sample shall meet all the requirements of this specification.

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

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

3.3 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 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 prescribed requirements.

4.1.1 Acceptance inspection. Acceptance inspection shall, at the option of the Government, be performed either by the supplier or by a Government representative. In either case, responsibility for final acceptance rests with the Government representative.

4.2 Preproduction sample. The preproduction sample shall be prepared using the same methods proposed for the preparation of subsequent production lots of triethyl citrate. The preproduction sample shall be subjected to all examinations and tests specified herein. Unless otherwise

specified, the Government will perform the examinations and tests for preproduction sample acceptance at the contractor's plant. Preproduction samples which do not meet all the requirements of this specification shall be rejected and returned to the contractor. Subsequent quantities will not be considered for acceptance until approval of the pre-production sample has been obtained.

4.3 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. A batch shall be defined as in 6.3.

4.4 Acceptance 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).

4.4.1 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.

4.4.2 Composite sample. Each primary sample shall be subdivided to prepare a composite sample (not in excess of 500 g). Primary material not used 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.

4.5 Classification of tests. Inspection and testing of the triethyl citrate shall be classified as follows:

a. Preproduction tests.

b. Quality conformance tests.

4.6 Preproduction tests. Preproduction tests shall be conducted only on the preproduction sample and shall consist of all the examinations and tests specified herein.

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

Characteristics	Tests
Assay (total ester)	4.8.1
Moisture	4.8.2
Color, APHA number	4.8.3
Acidity (as citric acid)	4.8.4
Saponification number	4.8.5

4.8 Acceptance tests. The following procedures shall be used to determine that the requirements of this specification have been met. 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.

4.8.1 Assay (as total ester).

4.8.1.1 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.

4.8.1.2 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 1-1/2 hours. Cool and wash down condenser with distilled water. Add five drops of phenolphthalein indicator and titrate with 0.5 N 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 needed to titrate sample, ml

C = weight of sample, g

N = normality of sulfuric acid.

4.8.1.3 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 3.2.

4.8.2 Moisture.

4.8.2.1 Apparatus. The apparatus used for determination of moisture content of the sample shall be an Aquameter, Model KF-2 or KF-3, or an approved equivalent. The Aquameter shall be prepared for operation as described in the technical manual furnished by the manufacturer. Use of an alternate equivalent item of equipment approved by the procuring activity will necessitate use of the specific technical manual prepared by the manufacturer.

4.8.2.2 Reagents.

a. Karl Fischer reagent. Karl Fischer reagent must have a strength such that each milliliter of Karl Fischer 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 (0.1 percent water, maximum). Mix well and allow to stand overnight before use. Determine the water equivalent (A) of this solution as follows:

1. Use sodium tartrate dihydrate ($Na_2C_4O_6 2H_2O$) as a primary standard (with a 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 degrees Celsius (C) (302 degrees Fahrenheit (F)) 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 10P, where P is percentage moisture (as determined). Rapidly transfer 0.090-0.110 g (weighed to the nearest 0.0001 g) of 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 4.8.2.3.)

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.

Water equivalent (A) equals $\frac{156.6\ W}{V}$

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

W equals weight of $Na_2C_4O_62H_2O$ taken, g

V equals 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:

1. Put about 50 ml of the anhydrous methanol used in 4.8.2.2a into the titration beaker of the Aquameter. Add a slight excess of Karl Fischer reagent (4.8.2.2a), then back-titrate with water-methanol solution (4.8.2.2b). 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 three titrations should not be greater than 0.04. If the range exceeds 0.04, continue making titrations until three ratios are obtained whose range does not exceed 0.04. Then determine the average ratio from all the ratios which have been obtained.

4.8.2.3 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 (4.8.2.2a). When the indicator light glows, read the Karl Fischer buret to the nearest 0.01 ml. Where necessary, water methanol solution (4.8.2.2b) may be used to back-titrate.

$$\text{Percent moisture equals } \frac{100A\ (V_{KF} \text{ minus } {}^{B}V_{WM})}{W}$$

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

V_{KF} equals volume of Karl Fischer reagent titrant used, ml

V_{WM} equals volume of water-methanol solution titrant used, ml

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

W equals weight of sample taken, g

4.8.2.4 Acceptance criteria. For the lot represented to pass the moisture test, the value obtained for the percent moisture shall be no greater than the value specified in 3.2.

4.8.3 Determination of color. Reference: ASTM D 1209.

4.8.3.1 Reagents and equipment.

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.

4.8.3.2 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)
0.30	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

4.8.3.3 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.

4.8.3.4 Acceptance criteria. For the lot represented to pass the color test, the value obtained for the APHA color standard shall be no greater than the value specified in 3.2.

4.8.4 Determination of free acidity (as citric acid).

4.8.4.1 Reagents.

a. Isopropyl alcohol, neutralized.

b. Standardized sodium hydroxide, 0.1N.

c. Bromothymol blue indicator, 0.04 percent aqueous solution.

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

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

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

N equals normality of sodium hydroxide.

0.064 equals milli-equivalent for citric acid

B equals weight of the sample, g

4.8.4.3 Acceptance criteria. For the lot represented to pass the free acidity test, the value obtained for the percent free acidity shall be no greater than the value specified in 3.2.

4.8.5 Saponification number.

4.8.5.1 Procedure. The saponification number can be calculated from the assay procedure 4.8.1 using the following equation:

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

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

B equals volume of sulfuric acid needed to titrate sample, ml.

C equals weight of sample, g.

N equals normality of sulfuric acid.

4.8.5.2 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 3.2.

5. PREPARATION FOR DELIVERY

5.1 Packing.

5.1.1 Packaging. packaging shall be Level C as follows: The material shall be packaged to afford adequate protection against deterioration and damage during shipment from supply source to first receiving activity (See 6.2).

5.1.2 Packing. Material packaged as specified in 5.1.1, shall be packed Level C as follows: Packages shall be secured and packed in shipping containers in a manner to insure carrier acceptance and safe delivery at destination at the lowest transportation rate. Containers shall comply with the Uniform Freight Classification Rules or National Motor Freight Rules as applicable.

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

6. NOTES

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

6.2 Ordering data. Procurement documents should specify, but not be limited to, the following information:

a. Title, number and date of specification.

b. Whether a preproduction sample is required (see 3.1).

c. Type and size of shipping container (see 5.1.1).

6.3 Definitions.

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

6.4 Supersession data. This specification includes the requirements of MIS-14161A, dated 23 December 1965.

Custodian:
ARMY-MI

Preparing Activity:
ARMY - MI
Project No. 6810-AA10

STANDARDIZATION DOCUMENT IMPROVEMENT PROPOSAL

OMB Approval
No. 22-R255

INSTRUCTIONS: The purpose of this form is to solicit beneficial comments which will help achieve procurement of suitable products at reasonable cost and minimum delay, or will otherwise enhance use of the document. DoD contractors, government activities, or manufacturers/ vendors who are prospective suppliers of the product are invited to submit comments to the government. Fold on lines on reverse side, staple in corner, and send to preparing activity. Comments submitted on this form do not constitute or imply authorization to waive any portion of the referenced document(s) or to amend contractual requirements. Attach any pertinent data which may be of use in improving this document. If there are additional papers, attach to form and place both in an envelope addressed to preparing activity.

DOCUMENT IDENTIFIER AND TITLE

NAME OF ORGANIZATION AND ADDRESS

CONTRACT NUMBER

MATERIAL PROCURED UNDER A

☐ DIRECT GOVERNMENT CONTRACT ☐ SUBCONTRACT

1. HAS ANY PART OF THE DOCUMENT CREATED PROBLEMS OR REQUIRED INTERPRETATION IN PROCUREMENT USE?
   A. GIVE PARAGRAPH NUMBER AND WORDING.

   B. RECOMMENDATIONS FOR CORRECTING THE DEFICIENCIES

2. COMMENTS ON ANY DOCUMENT REQUIREMENT CONSIDERED TOO RIGID

3. IS THE DOCUMENT RESTRICTIVE?

   ☐ YES ☐ NO *(If "Yes", in what way?)*

4. REMARKS

SUBMITTED BY *(Printed or typed name and address - Optional)*

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