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MILITARY SPECIFICATION

CHEMICAL AGENT, TITANIUM TETRACHLORIDE

This specification has been approved by the Department of Defense and is mandatory for use by the Departments of the Army, the Navy, and the Air Force.

1. SCOPE

1.1 This specification covers one grade of titanium tetrachloride ($TiCl_4$).

2. APPLICABLE DOCUMENTS

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

SPECIFICATIONS

FEDERAL

PPP-D-700 — Drums: Metal, 55-Gallon (For Acid and Corrosive Liquids).

STANDARDS

MILITARY

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

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 shall apply:

UNIFORM CLASSIFICATION COMMITTEE

Uniform Freight Classification Rules.

(Application for copies of these freight classification rules should be addressed to the Uniform Classification Committee, 202 Union Station, Chicago 6, Illinois.)

INTERSTATE COMMERCE COMMISSION

49 CFR 71–90 — Interstate Commerce Commission Rules and Regulations for the Transportation of Explosives and Other Dangerous Articles.

(The Interstate Commerce Commission regulations are now a part of the Code of Federal Regulations (Revised 1956) and are available from the Superintendent of Documents, Government Printing Office, Washington 25, D. C. Orders for the above publication should cite "49 CFR 71-90 (Rev. 1956).")

FSC 1365

3. REQUIREMENTS

3.1 Appearance. The material shall be a colorless to reddish-brown liquid, free from sediment, when examined as specified in 4.5.1.

3.2 Purity. The material shall contain not less than 95 percent titanium tetrachloride when tested according to 4.5.2.

3.3 Specific gravity. The specific gravity shall not be less than 1.71 or more than 1.74 at 20°/4°C. when tested according to 4.5.3.

4. QUALITY ASSURANCE PROVISIONS

4.1 The supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified, the supplier may utilize his own or any other inspection facilities and services acceptable to the Government. Inspection records of the examination and tests shall be kept complete and available to the Government as specified in the contract or order. 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 Objective evidence. The supplier shall present objective evidence, as required by the Government representative, that all packing materials and that the level C preparation for delivery requirements are in accordance with section 5 (see 6.3).

4.3 Substitute inspection (including testing) procedures. The supplier may utilize any substitute inspection procedure which will insure equal or better quality by submitting a written proposal with justification and obtaining written approval from the Government prior to instituting the change. In case of dispute, the procedures of this specification will govern.

4.4 Inspection provisions.

4.4.1 *Lotting.* A lot shall consist of the titanium tetrachloride produced by one manufacturer in not more than 24 consecutive hours under essentially the same manufacturing conditions and with no change in materials, providing the operation is continuous. In the event that the process is a batch operation, each batch shall constitute a lot (see 6.4).

4.4.2 *Sampling.*

4.4.2.1 *Nondestructive examination.* Sampling shall be conducted in accordance with Standard MIL–STD–105.

4.4.2.2 *Destructive tests.* The number of containers to be used as a sample for destructive tests shall be calculated as one-tenth ($\frac{1}{10}$) of the square root of the number of containers in the lot raised to the next whole number; however, no fewer than 3 containers shall be used unless the entire lot consists of only 1 or 2 containers, in which case the entire lot shall be used as the sample. A 1-pound specimen shall be removed from each container in the sample and placed in a clean, dry container labeled to identify the lot and the container from which it was taken. A composite specimen shall be made with equal portions from each specimen except one, and the composite and the individual specimen shall be tested as specified in 4.5. Where there are only 1 or 2 specimens, each one shall be tested.

4.4.3 *Examination.* Sample containers of titanium tetrachloride shall be examined for level A preparation for delivery requirements in accordance with the classification of defects and with Standard MIL–STD–105.

4.4.4 *Classification of defects.*

4.4.4.1 *Preparation for delivery* (section 5).

Categories and defects

Critical—None

Major—AQL 4.0 percent defective

101. Container damaged, leaking, or incorrect
102. Container closure incorrect
103. Marking missing, illegible, or incorrect
104. Quantity packed incorrect

4.5 **Tests.** Distilled water and analytical reagent grade chemicals shall be used throughout the tests where appliable, blank determinations shall be run and corrections applied where significant. Tests shall be conducted as follows:

4.5.1 *Appearance.* Examine the composite and the individual specimen visually for color and for freedom from sediment (see 3.1).

4.5.2 *Purity.*

4.5.2.1 *Sodium bicarbonate solution.* Stir 10 grams (gm.) of sodium bicarbonate in 100 milliliters (ml.) of water. Allow to settle and use the supernatant liquid.

4.5.2.2 *Potassium thiocyanate solution.* Dissolve 40 gm. of potassium thiocyanane in 60 ml. of water.

4.5.2.3 *Ferric chloride solution.* Dissolve 27.0 gm. of ferric chloride ($FeCl_3 . 6H_2O$) in 800 ml. of water containing 15 ml. of concentrated sulfuric acid. Dilute to 1 liter. Weigh approximately 0.3 gm. of pure titanium dioxide (see 6.5) to the nearest 0.1 milligram (mg.), and transfer to the flask of titration assembly (see 6.6), and add 25 ml. of concentrated sulfuric acid and 25 gm. of ammonium sulfate. Mix well and heat on a hot plate until fumes of sulfur trioxide appear. Continue heating over a strong flame until solution is complete, or it is apparent that the residue is siliceous matter (usually not more than 5 minutes of boiling is required). Cool to room temperature. Cautiously add 130 ml. of water and 20 ml. of concentrated hydrochloric acid. Reheat to boiling and remove the flask from the vicinity of any open flame since hydrogen gas will be evolved in the next operation. Swirl the flask gently to release any steam and then add 1 gm. of aluminum foil having a minimum purity of 99.8 percent. Insert the stopper and delivery tube in the neck of the flask and place the outlet of the delivery tube below the level of sodium carbonate solution in an adjoining beaker. After all the aluminum has dissolved and no more hydrogen gas is evolved, cool the reduced solution to less than 60°C. (see 6.7), remove the delivery tube, and add 2 ml. of potassium thyiocyanate solution (see 4.5.2.2). Titrate with the ferric chloride solution to a light orange end point. Calculate the normality of the ferric chloride solution as follows:

$$\text{Normality of ferric chloride solution} = \frac{T\,W}{7.99\,V}$$

where: T = purity of titanium oxide.

W = weight of titanium dioxide used, in gm.

V = volume of ferric chloride solution used to titrate titanium dioxide, in ml.

4.5.2.4 *Procedure.* Dry a thin-walled glass sample bulb in an oven at 110°C., cool in a desiccator, and weigh to the nearest 0.1 mg. Store in the desiccator until needed. Pass dried air from a phosphorus pentoxide tube through the sample apparatus (see figure 1) to remove all moisture. Unstopper the bottle containing the specimen, cover the opening immediately with a piece of cardboard having a ¼-inch hole in the center, and push the stem of the glass sampling tube through the cardboard until the end is well immersed in the specimen. Apply gentle suction to the neck of the apparatus until the spherical portion is nearly filled. Place the weighed bulb in the neck of the apparatus so that the capillary tube extends almost to the bottom

of the spherical portion of the apparatus. Warm the bulb gently and allow to cool until 0.40 to 0.55 gm. of the specimen is drawn into the bulb. Seal the tip of the capillary in a flame, allow to cool, and weigh to the nearest 0.1 mg. Cautiously add 25 ml. of concentrated sulfuric acid to 125 ml. of water in the titration flask (see 6.6). Place the sample bulb in the flask, stopper, and break the bulb by shaking. Continue shaking until fumes disappear and heat if necessary to effect solution. Add 20 ml. of concentrated hydrochloric acid. Reheat to boiling and remove the flask from the vicinity of any open flame since hydrogen gas will be evolved in the next operation. Swirl the flask gently to release any steam and then add 1 gm. of aluminum foil having a minimum purity of 99.8 percent. Insert the stopper and delivery tube in the neck of the flask and place the outlet of the delivery tube below the level of sodium bicarbonate solution (see 4.5.2.1) in an adjoining beaker.

After all the aluminnum has been dissolved and no more hydrogen gas is evolved, cool the reduced solution to less than 60°C. (see 6.7), remove the delivery tube, and add 2 ml. of potassium thiocyanate solution (see 4.5.2.2). Titrate with standard ferric chloride solution (see 4.5.2.3) to a light orange end point. Calculate the percent of titanium tetrachloride as follows:

$$\text{Percent titanium tetrachloride} = \frac{18.97\ N\ V}{W}$$

N = normality of ferric chloride solution (see 4.5.2.3).

V = volume of ferric chloride solution used to titrate specimen, in ml.

W = weight of specimen used, in gm.

4.5.3 *Specific gravity.* Determine the specific gravity of the material by means of a calibrated hydrometer at 15° to 16°C. Reduce the reading obtained to its equivalent at 20°/4°C. by multiplying the reading by 0.9945.

4.6 Acceptance/rejection criteria. If the composite or individual specimen fail to meet the requirements of this specification, the lot represented shall be rejected.

5. PREPARATION FOR DELIVERY

5.1 Packing.

5.1.1 *Level A.* Titanium tetrachloride shall be packed in a 5-gallon drum conforming to Interstate Commerce Commission Specification 17C or in type I, 55-gallon drums conforming to Specification PPP–D–700.

5.1.2 *Level C.* The titanium tetrachloride shall be furnished in containers packed in such a manner as to insure carrier acceptance and safe delivery to the first receiving activity for immediate use. Containers used shall comply with Interstate Commerce Commission Regulations, Uniform Freight Classification Regulations, or other carrier regulations applicable to the mode of transportation.

5.2 Marking. In addition to any special marking required by the contract or order, all shipping containers shall be marked in accordance with Standard MIL–STD–129.

6. NOTES

6.1 Intended use. The titanium tetrachloride covered by this specification is intended for use as a screening smoke.

6.2 Ordering data. Procurement documents should specify:

(a) Title, number, and date of this specification.

(b) Unit quantities required (see 5.1).

(c) Level of packing required.

6.3 Objective evidence. Provisions for the preparation of objective evidence and inspection records, and for the maintenance

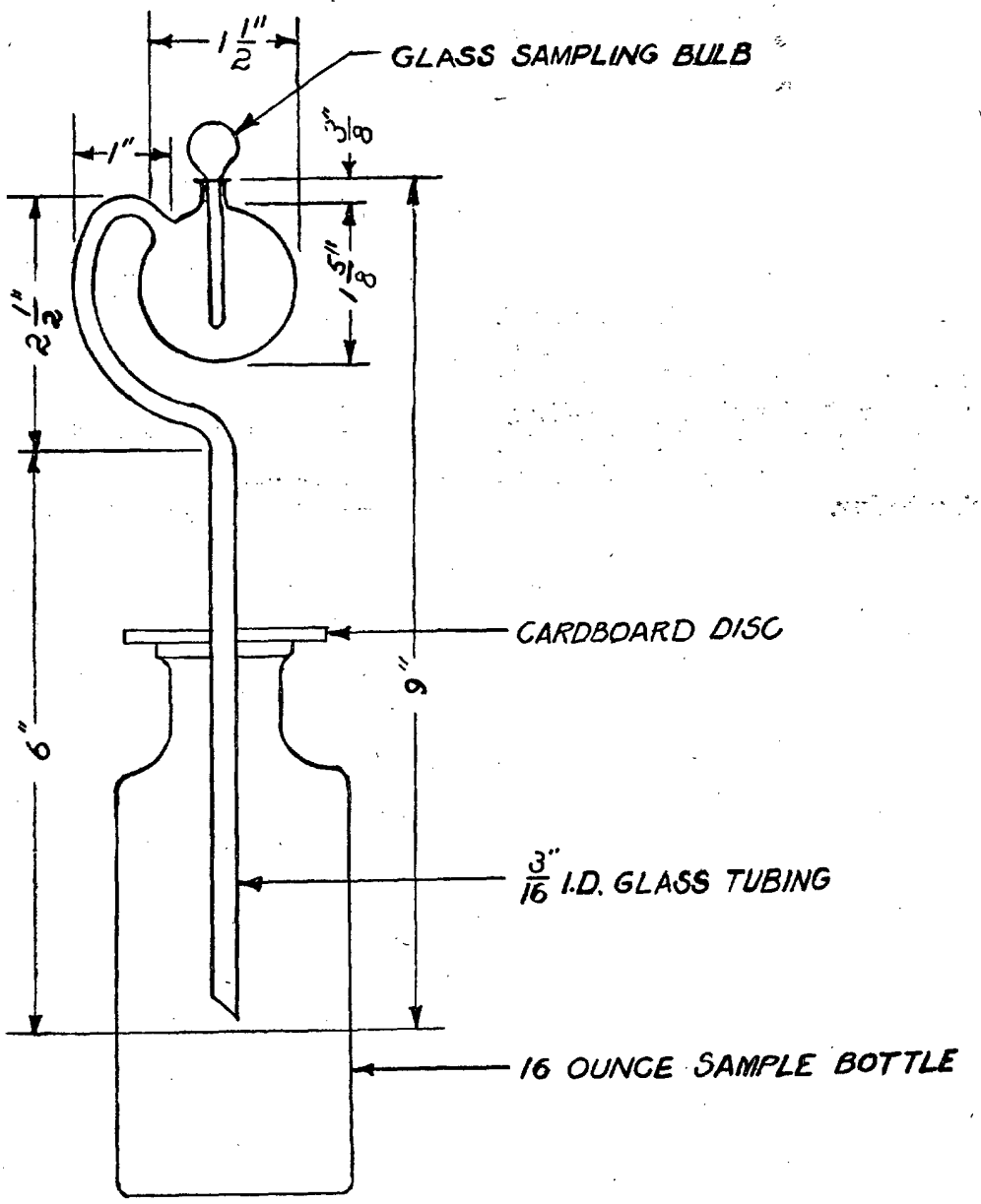

FIGURE 1.

of inspection records will be specified by the procuring activity.

6.4 **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 product substantially uniform.

6.5 **Titanium dioxide.** National Bureau of Standard Sample 154 or equivalent.

6.6 **Titration assembly.** This is described by J. A. Rahm, *Analytical Chemistry*, vol. 24, p. 1832, 1952. The assembly consists of a 500-ml. Erlenmeyer flask with a one-hole rubber stopper fitted with a glass delivery tube which leads below the surface of a saturated sodium bicarbonate solution in an adjoining beaker.

6.7 The solution must be no warmer than 60°C. when the indicator is added to avoid decomposition of the thiocyanate.

Custodians:
Army—Chemical Corps
Navy—Bureau of Naval Weapons

Preparing activity:
Army—Chemical Corps