INCH-POUND

MIL-DTL-98B
25 February 2013
SUPERSEDING
MIL-D-98A
14 May 1962

DETAIL SPECIFICATION

DIPHENYLAMINE, TECHNICAL

Reactivated after 12 February 2013 and may be used for new and existing designs and acquisitions.

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

1. SCOPE

1.1 Scope. This specification covers technical diphenylamine (DPA) for use in the manufacture of smokeless powder.

2. APPLICABLE DOCUMENTS

2.1 General. The documents listed in this section are specified in sections 3 and 4 of this specification. This section does not include documents in other sections of this specification or recommended for additional information or as examples. While every effort has been made to ensure the completeness of this list, document users are cautioned that they must meet all requirements cited in sections 3 and 4 of this specification, whether or not they are listed.

Comments, suggestions, or questions on this document should be addressed to the Commander, U.S. Army ARDEC, ATTN: RDAR-QES-E, Picatinny, NJ 07806-5000 or emailed to usarmy.picatinny.ardec.list.ardec-stdzn-branch@mail.mil. Since contact information can change, you may want to verify the currency of this address information using the ASSIST Online database at https://assist.dla.mil.

AMSC N/A FSC 6810

DISTRIBUTION STATEMENT A. Approved for public release; distribution is unlimited.

2.2 Government documents.

2.2.1 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 solicitation or contract.

DEPARTMENT OF DEFENSE STANDARDS

MIL-STD-1916 - DOD Preferred Methods for Acceptance of Product

(Copies of these documents are available online at https://assist.dla.mil from the Standardization Documents Order Desk, 700 Robbins Avenue, Bldg. 4D, Philadelphia, PA 19111-5094.)

2.3 Order of precedence. Unless otherwise noted herein or in the contract, 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 Conformance. A sample shall be subjected to conformance inspection in accordance with 4.1.2.

3.2 Properties of diphenylamine. The properties of diphenylamine shall be in accordance with the following:

a. Setting point shall have degree centigrade not less than 51.7^0C and not greater than 53.0^0 C.

b. Purity (alternate for setting point) shall have percent minimum of 99.5%.

c. Insoluble material (residue) shall have percent maximum of 0.02%.

d. Moisture shall have percent maximum of 0.2%.

e. Acidity (as hydrochloric acid) shall have percent maximum of 0.005%

f. Alkalinity (as sodium hydroxide) shall have percent maximum of 0.005%.

g. Oxidizable material (as aniline) shall have percent maximum of 0.1%.

3.3 Workmanship. The diphenylamine shall be free of extraneous material, such as iron rust, wood particles, dirt, colored salts and other visible impurities. The color of diphenylamine shall be no darker than a light brown.

4. VERIFICATION

TABLE I. Requirements/verification cross reference.

Method of Verification		Classes of Verification						
1- Analysis 2- Demonstration 3- Examination 4- Test		A – First article B - Conformance						
Section 3 Requirements	Description	Verification Method				Verification Class		Section 4
		1	2	3	4	A	B	
3.1	Conformance			X	X		X	4.1
3.2.a	Setting point				X		X	4.2.1
3.2.b	Purity (alternate for setting point)				X		X	4.2.2
3.2.c	Insoluble material (residue)				X		X	4.2.3
3.2.d	Moisture				X		X	4.2.4
3.2.e	Acidity (as hydrochloric acid)				X		X	4.2.5
3.2.f	Alkalinity (as sodium hydroxide)				X		X	4.2.5
3.2.g	Oxidizable material (as aniline)				X		X	4.2.6
3.3	Workmanship			X			X	4.2.7

4.1 Conformance inspection.

4.1.1 Lot formation. Lot formation shall be in accordance with the lot formation requirements of MIL-STD-1916, paragraph “Formation and identification of lots and batches” In addition, a lot shall consist of one or more batches of diphenylamine produced by one manufacturer, in accordance with the same specification, or same specification revision, under one continuous set of operating conditions. Each batch shall consist of the quantity of diphenylamine that has been subjected to the same unit chemical or physical process intended to make the final product homogeneous.

4.1.2. Sampling.

4.1.2.1 Packed by lot. A random sample of 8 containers shall be selected from each lot. When lots comprise 8 containers or less, each container shall be selected.

4.1.2.1.1 Preparation of composite sample (after packing). A primary sample of approximately 2 ounces of diphenylamine shall be removed from each of the 8 containers in order to equal 16 ounces. If there are less than 8 containers, a primary sample in sufficient quantity to equal 16 ounces shall be removed from each container. The individual primary samples shall then be combined in order to form a homogeneous sample of 16 ounces. The determination shall be performed as specified in 4.2. If the composite sample fails to comply with any of the requirements specified the lot shall be rejected.

4.1.2.1.2 Prior to packing. Equal primary samples shall be taken from different places and depths so as to form a representative sample of the lot. The individual primary samples shall then be combined in order to form a homogeneous composite sample of 16 ounces. The determination shall be performed as specified in 4.2. If the composite sample fails to comply with any of the requirements specified, the lot shall be rejected.

4.1.2.2 Molten DPA in bulk storage container. A sample of 2 ounces shall be taken in duplicate from a closed-out bulk storage tank. The closed-out bulk storage tank shall be circulated for one hour minimum prior to sampling to assure a representative sample. The bulk storage tank shall be assigned a lot number. No new molten DPA shall be transferred into the closed-out bulk storage tank. If the sample fails to comply with any of the requirements specified, the lot shall be rejected.

4.2 Methods of inspection**.** Test methods and procedures shall be performed as specified in paragraph 4.2.1 to 4.2.6.

4.2.1 Determination of setting point.

4.2.1.1 Drying the sample. Grind 80 to 100 grams (gm) of the sample fine enough to pass through 1680 micron screen in American Standard Testing and Material E11 and dry for four hours at 40 degrees C., or melt the sample then add 20 gm. of anhydrous calcium chloride or sodium sulfate, and stir the mixture for 15 minutes at a temperature of 80 degrees C., allow the mineral salts to settle and pour off the molten diphenylamine.

4.2.1.2 Apparatus. A solidification point apparatus shown in Figure 1 shall be used with a 76 millimeter partial immersion number American Standard Testing and Material E1 type 92 C or equivalent thermometer with a range of 40 to 70 degrees C.

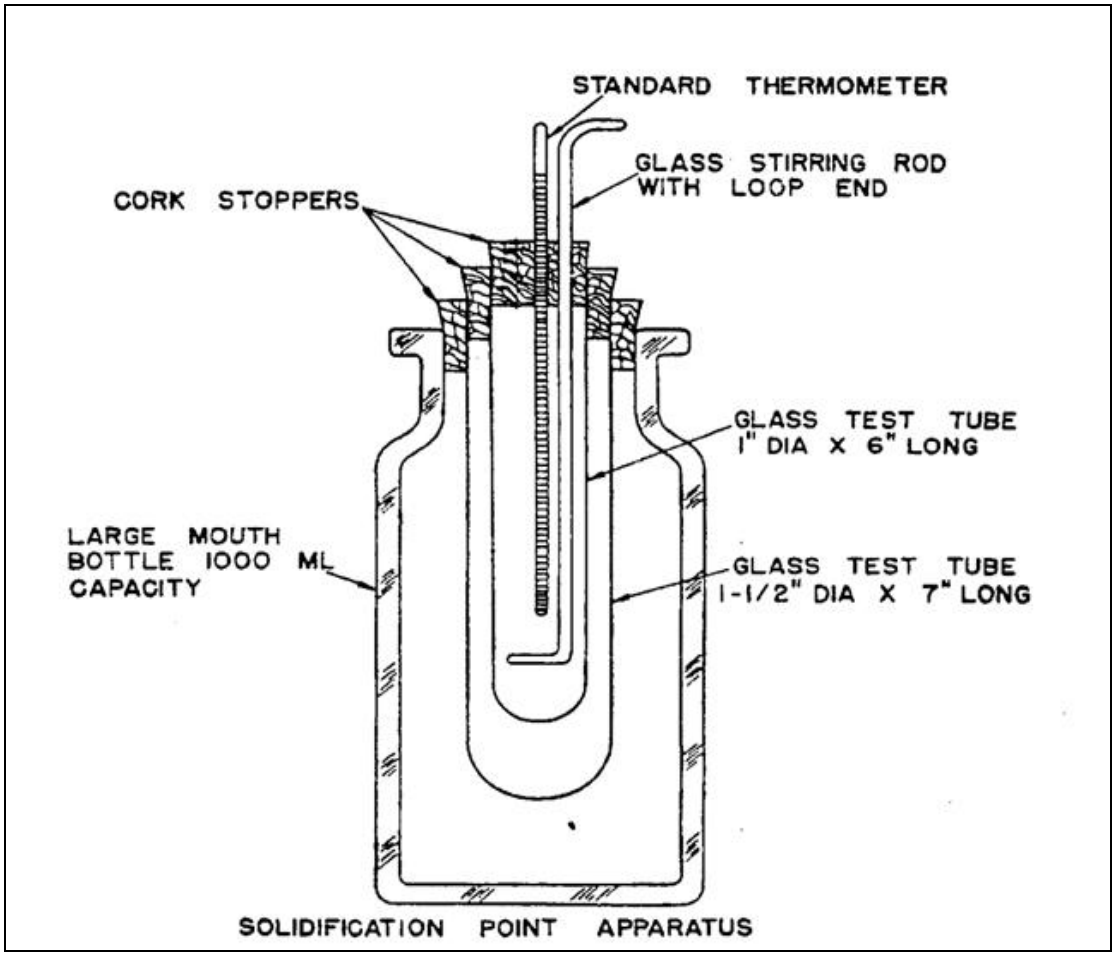

FIGURE 1. Solidification point apparatus.

4.2.1.3 Procedure. Transfer the dried sample to the inner test tube and melt it. Place the tube in the apparatus and adjust the thermometer so that the bulb is in the center of the diphenylamine. Stir the molten material vigorously by means of a hand stirrer and carefully note the point where the temperature begins to rise when solidification begins. Observe the temperature every 15 seconds until the maximum reading is obtained. Observe the maximum reading as the setting point of the diphenylamine.

4.2.2 Purity by gas chromatography (alternate for setting point). A DPA control standard is analyzed every day by gas chromatography fitted with a split/splitless capillary inlet, flame ionization detector, and a non-polar capillary column. The % Purity analysis for the DPA control standard is plotted on an individuals/range statistical process control chart. The standard analysis must be in control prior to evaluating production samples. Out-of-control conditions are indicated by any one analysis exceeding the upper or lower control limits or a sequence of eight consecutive analyses on one side of the mean. An out of control data point would invoke a corrective action plan according to established trouble shooting guidelines.

4.2.2.1 Procedure for making the DPA purity control standard. To a 25 ml volumetric flask add 0.250 grams each of reagent grade indole, acridine and quinoline. These components are used to determine detection capability of the "lights" and "heavies" used in the % Purity determination and calculation. Dilute to mark with acetonitrile (ACN) such that the stock standard is equal to approximately 10,000 ppm of each impurity. Place a 4 oz bottle on a 2-place balance and tare the balance. Add 5.00 grams of the DPA control (>99.8%). Tare the balance. Add 70.00 grams of reagent grade acetonitrile. Add 50 µl of stock standard. Shake to mix well. This standard contains approximately 0.01% of each impurity. Pour into five ½ oz. bottles. Seal and label each bottle.

4.2.2.2 Method for determination of DPA % purity. Run a control standard by injecting 0.5 µl of the control and integrating. The DPA analysis must be in statistical control prior to proceeding. Place a solid sample of the test material in an 116° C convection oven to melt. Dilute 1.0 gram of the molten sample with 14.0 grams of reagent grade ACN. Inject 0.5 µL of the diluted sample into a gas chromatograph fitted with a split/spitless capillary inlet and a flame ionization detector. Start the integrator. Report %Purity, %Lights, and %Heavies. DPA purity input parameters shall be in accordance with Figure 2.

% Purity = % Total area-(% Lights + % Heavies)

Where: %Lights = total area% between solvent and DPA peak

or

$$\frac{\text{Area counts between Solvent and DPA} \times 100}{\text{Total Area} - \text{Solvent Area}}$$

% Heavies = total area% after DPA peak

or

$$\frac{\text{Area counts after DPA peak} \times 100}{\text{Total Area} - \text{Solvent Area}}$$

DPA Purity Analysis Gas Chromatograph Parameters

HP 6890 Series Gas Chromatograph or equivalent

Oven Settings:

Temp	140 deg C
Initial Time	2.00 min
Maximum Temp	320 deg C
Equib Time	0.50 min

Oven Temperature Program:

#	Rate(deg C/min)	Final Temp (deg C)	Final Time (min)
1	20.00	240	2.00
2	25.00	260	4.00
3	0.00	Off	

Inlet parameters:

Mode	Split
Temp	250 deg C
Pressure	15.6 psi
Split ratio	75.0
Split flow	201 ml/min
Total flow	206 ml/min
Gas Type	He

Column Parameters

Restek RTX-5 – 30 M x 320 µm X 0.25 µm (or equiv.)

Flow	2.7 ml/min
Velocity	49 cm/sec
Mode	Constant Flow

Detector parameters (Flame Ionization)

Temp	275 deg C
H2 Flow	40.0 ml/min
Air Flow	400 ml/min
Mode	Constant Makeup
Makeup flow	30.0 ml/min
Makeup gas	N2

Figure 2. DPA purity analysis.

4.2.3 Insoluble material. Dissolve 25 gm. of the sample in 100 milliliters (mL.) of benzene (specific gravity of 0.878 at 20 degrees/20 decrees C.) or ethyl ether (specific gravity 0.717 to 0.723 at 20 degrees/20 degrees C.). Filter through a tared filtering crucible and wash thoroughly with the solvent. Dry the crucible for one hour at 100 degrees C., cool in a desiccator and weigh. Calculate the insoluble matter to percent of the weight of sample.

4.2.4 Moisture. Dry 4 to 6 gm. of the powdered material in a weighing bottle about 4 centimeters diameter. Heat for 4 hours at 40 degrees C. uncorked, and calculate the loss in weight to percent of the sample taken and observe as moisture.

4.2.4.1 Alternate moisture method by gas chromatography. Water in DPA is determined using a gas chromatograph fitted with a polymer-packed column and a thermal conductivity detector (or equivalent). The internal standard used in the analysis is 1000 ppm of methanol (MeOH) in reagent grade acetonitrile (ACN). Approximately 500 ppm of water is added to the internal standard. The water addition increases the sensitivity of the analysis. The actual

concentration of MeOH in the ACN is determined by measuring the weight of the MeOH and the weight of the total internal standard solution. The actual water content of the internal standard is determined by coulometric Karl Fischer (KF) analysis using a Brinkman 756 (KF) coulometric titroprocessor. The response factor between water and MeOH is calculated at the beginning of each shift and is determined by analyzing the internal standard solution with KF coulometric analysis and by gas chromatography. The DPA sample is solvated in the internal standard solution, analyzed by gas chromatography and total water content of solvent and sample is determined. The water content of the DPA sample is calculated by subtracting the water content of the internal standard solution from the total water content.

4.2.4.1.1 Procedure for making the methanol/water internal standard. Weigh 650.0 grams of dried acetonitrile (ACN) into a 16 oz. amber bottle using a 2-place balance. Using a- 4-place balance and appropriate weight of water to the bottle to make an approximate 500 ppm water in ACN solution(weight of water = 0.0005 * weight of ACN) Using a 4-place balance and appropriate weight of methanol (MeOH) to the bottle to make an approximate 1000 ppm MeOH in ACN solution (weight of MeOH = 0.001 * weight of ACN). Record the exact weight of MeOH in the bottle. Determine the actual concentration of MeOH in the solvent as follows:

$$\text{Actual MeOH concentration ppm} = \frac{(\text{Wt. of MeOH in grams}) * ((10^6))}{(\text{Wt. of ACN} + \text{MeOH} + \text{water in grams})}$$

4.2.4.1.2 Method for determination of moisture by gas chromatography. Place ½ oz. bottles and autoinjector vials in a 65° C heated vacuum dessicator to warm. Place the DPA sample in a 100° C convection oven to melt. Prepare an internal standard solution (ISTD) as described to be used for water calculation. Inject 5 µl of the ISTD in duplicate into a gas chromatograph fitted with a thermal conductivity detector. Duplicates shall match within 20 ppm for methanol. Record average heights of water peaks and average heights of the MeOH peaks for use in determination of response factor. Analyze the water content of the ISTD in duplicate. Pull up 1 ml of ISTD into a gas tight 1 ml syringe. Zero the syringe on a 4-place balance. Inject 1ml of the ISTD into a coulometric Karl Fisher (KF) titroprocessor. Reweigh the syringe and enter the weight into the titroprocessor. Record the average water content of the duplicate analyses for use in determination of the response factor. The response factor is determined at the beginning of every shift. DPA water analysis shall be in accordance with Figure 3.

$$\text{Response factor} = \frac{(\text{peak height of water}_{(\text{ISTD})} * (\text{ppm of MeOH}_{(\text{ISTD})})}{(\text{ppm of water from coulometric KF analysis} * (\text{peak height of MeOH}_{(\text{ISTD})})}$$

For DPA moisture determination weigh 2.0 g of molten sample into a heated ½ oz. bottle. Add 2.0 g of the ISTD. Cap the bottle. Mix well and immediately fill an autoinjector vial with the same and cap the vial. Autoinject into the gas chromatograph and start the integrator. Order of elution is air, water and methanol. The integrator will print out the peak heights to be used in the calculation as follows:

$$\text{ppm } H_2O = \frac{(\text{Peak height of } H_2O_{(\text{sample})}) * (\text{ppm Methanol}_{\text{ISTD}})}{(\text{peak height of Methanol}_{(\text{sample})}) * \text{Resonse Factor}} - \text{ppm}H_2O_{(\text{ISTD coulometric KF analysis})}$$

$$\%\ H_2O = \frac{\text{ppm}H_2O}{10{,}000}$$

DPA Water Analysis Gas Chromatograph Parameters

HP 6890 Series Gas Chromatograph or equivalent

Oven Settings:

Temp	125 deg C
Initial Time	8.00 min
Maximum Temp	250 deg C
Equib Time	0.50 min

Inlet parameters		*Column Parameters*	
Mode	Splitless	8' x ¼" FEP Teflon Porapak PS 50/80 Mesh (or equiv.)	
Temp	175 deg C		
Pressure	14.7 psi	Flow	233 ml/min
Purge time	75.0	Velocity	1570 cm/sec
		Mode	Constant Flow
Gas Type	He		

Detector Parameters (Thermal conductivity)

Temp	250 deg C
Ref Flow	25.0 ml/min
Mode	Constant Makeup
Makeup flow	5.0 ml/min
Makeup Gas	He

FIGURE 3. DPA water analysis.

4.2.5 Acidity or alkalinity. Place 20 gm. of an as received sample in a 250 ml. Erlenmeyer flask and add 50 ml. of nearly boiling distilled water. Stopper immediately and shake vigorously for about ten minutes. Cool to 25 degrees C. and filter, retaining the diphenylamine in the flask. Repeat the extraction with 50 ml. of hot water exactly as above. To the combined filtrates add a few drops of phenolphthalein and titrate with 0.01 normal (N) alkali if it is acid, 0.01N acid if alkaline. Make a blank titration on the water used and correct the titration for any acidity or alkalinity found. Calculate the acidity or alkalinity to hydrochloric acid or sodium hydroxide, respectively. Reserve this solution for the determination of aniline.

4.2.6 Free aniline, aniline salts, and other oxidizable material. Use the solution from the acid or alkali determination for determining aniline, aniline salts and other oxidizable material by

the volumetric bromide-bromate method as follows. Measure accurately 25 ml. of 0.10N bromide-bromate solution with a pipette into a glass-stoppered Erlenmeyer flask containing the above filtrate and cool the contents to 15 degrees C. Add 5 ml. of concentrated hydrochloric acid and follow with the addition of 10 ml. of 10 percent potassium iodide solution after one minute. Titrate the contents with 0.10N sodium thiosulfate solution, using starch as indicator. Make blank determination on 25 ml. of 0.10N bromide-bromate solution exactly as above and calculate the aniline from the difference obtained by subtracting the number of ml. of thiosulfate solution used in titrating the sample from that used in titrating the blank. (A correction must be made for the amount of diphenylamine dissolved in 100 ml. of water at 25 degrees C. and also is shown in the formula as 0.33 ml. 0.1 normal sodium thiosulfate solution.)

Calculation:

$$\text{Percent aniline} = \frac{\left[N(\mathrm{V} - \mathrm{v}) - 0.033\right]1.551}{\mathrm{W}}$$

Where:

V= ml. sodium thiosulfate used in blank
v= ml. sodium thiosulfate used in titration
N= Normality of sodium thiosulfate
W= Weight of sample in grams

4.2.7 Workmanship. The compliance of workmanship shall be determined by visual examination.

5. PACKAGING

5.1 Packaging. For acquisition purposes, the packaging requirements shall be as specified in the contract or order (see 6.2). When packaging of materiel is to be performed by DOD or in-house personnel, these personnel need to contact the responsible packaging activity to ascertain packaging requirements. Packaging requirements are maintained by the Inventory Control Point's packaging activities within the Military Service or Defense Agency, or within the military service's system commands. Packaging data retrieval is available from the managing Military Department's or Defense Agency's automated packaging files, CD-ROM products, or by contacting the responsible packaging activity.

6. NOTES

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

6.1 Intended use. The intended use for the diphenylamine in this specification is as a stabilizer in the production of smokeless propellants.

6.2 Acquisition requirements. Acquisition documents should specify the following:

a. A statement that the lot complies with all quality assurance provisions of the approved current written description of the system.

b. Quantity of product inspected.

c. Results obtained for all inspection performed.

d. Specification number and date, together with an identification and date of changes.

e. Certificates of analysis on all material procured directly by the contractor when such material is controlled by government specifications referenced in any of the contractual documents. The certificate shall be signed by a responsible agent of the certifying organization. The initial certificate submitted shall be substantiated by evidence of the agent's authority to bind his principal. Substantiation of the agent's authority will not be required with subsequent certificates unless, during the course of the contract, this authority is vested in another agent of the certifying organization.

f. Quantity of product in the lot.

g. Date submitted

h. Packaging requirements (See 5.1 and 6.5).

6.3 Alternative conformance acceptance. Unless otherwise specified herein or provided for in the contract/statement of work, alternate conformance procedures may be proposed by the contractor (See paragraph "Acceptance by contractor-proposed provisions" of MIL-STD-1916).

6.4 Request for establishment of visual standards. Submit requests to: Commander, U.S. Army ARDEC, ATTN: RDAR-QEM-C, Picatinny Arsenal, NJ 07806-5000.

6.5 Packaging examinations and tests. The acceptance criteria for sampling inspection should be in accordance with the levels provided in MIL-STD-1916 and the following conformance inspection by classification of characteristics in paragraphs 6.5.1-6.5.7.

6.5.1	Drum, prior to filling (polyethylene liner).		
Classification	Examination or Test	Conformance Criteria	Inspection Method Reference
Critical	None defined		
Major			
101	Liner cut, torn or punctured	VL-IV	Visual
Minor			
201	Evidence of poor workmanship	VL-II	Visual

6.5.2	Drum, prior to filling (alternative method).		
Classification	Examination or Test	Conformance Criteria	Inspection Method Reference
Critical	None defined		
Major			
101	Laminations or coatings incomplete	VL-IV	Visual
Minor	None defined		

6.5.3	Drum, prior to closing (polyethylene liner).		
Classification	Examination or Test	Conformance Criteria	Inspection Method Reference
Critical	None defined		
Major			
101	Liner not completely sealed	VL-IV	Visual
Minor	None defined		

6.5.4	Drum sealed (steel).		
Classification	Examination or Test	Conformance Criteria	Inspection Method Reference
Critical	None defined		
Major			
101	Closure improper	VL-IV	Visual
102	Weight of contents	VL-IV	Scale
Minor			
201	Markings misleading or unidentifiable	VL-II	Visual

6.5.5	Drum sealed (fiber).		
Classification	Examination or Test	Conformance Criteria	Inspection Method Reference
Critical	None defined		
Major			
101	Weight of contents	VL-IV	Scale
102	Closure incomplete or damaged to the extent that contents sifts out	VL-IV	Visual
Minor			
201	Markings misleading or unidentifiable	VL-II	Visual

6.5.6	Drum sealed (plywood).		
Classification	Examination or Test	Conformance Criteria	Inspection Method Reference
Critical	None defined		
Major			
101	Weight of contents	VL-IV	Scale
102	Strapping missing or broken	VL-IV	Visual
Minor			
201	Markings misleading or unidentifiable	VL-II	Visual

6.5.7	Truck tanker, prior to and after filling (molten DPA).		
Classification	Examination or Test	Conformance Criteria	Inspection Method Reference
Critical	None defined		
Major			
101	Tanker not dry, contaminated	VL-IV	Visual
102	No wash-out certificate	VL-IV	Certification
103	No nitrogen blanket (after filling)	VL-IV	Visual
Minor	None defined		

6.6 Subject term (key word) listing.
Acidity
Alkalinity
Polyethylene liner
Propellant
Stabilizer

6.7 Changes from previous issues. Marginal notations are not used in this revision to identify changes with respect to the previous issues due to the extent of the changes.

Custodian:
Army-AR
Navy – SH
Air Force - 68

Preparing activity:
Army-AR

(Project 6810-2010-003)

Review activities:
Army – EA, MR, TE
Navy – AS
Air Force – 03, 11
DLA – GS

Other agencies:
GSA – FAS

NOTE: The activities listed above were interested in this document as of the date of this document. Since organizations and responsibilities can change, you should verify the currency of the information above using the ASSIST Online database at https://assist.dla.mil.