MILITARY SPECIFICATION

PROPELLANT, MIXED HYDRAZINE FUEL, MHF-3

This specification has been approved by the Bureau of Naval Weapons, Department of the Navy.

1. SCOPE

1.1 This specification covers the requirements for mixed hydrazine fuel, MHF-3 (monomethylhydrazine-hydrazine, MMH-N_2H_4) propellant.

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 this specification to the extent specified herein:

SPECIFICATIONS

Military

MIL-P-26536	Propellant, Hydrazine
MIL-P-27401	Propellant Pressurizing Agent, Nitrogen
MIL-P-27404	Propellant, Monomethylhydrazine

STANDARDS

Federal

FED-STD-791	Lubricants, Liquid Fuels, and Related Products; Methods of Testing

Military

MIL-STD-105	Sampling Procedures and Tables for Inspection by Attributes
MIL-STD-129	Marking for Shipment and Storage
MIL-STD-172	Color Code for Containers of Liquid Propellants

PUBLICATIONS

Bureau of Naval Weapons

OP 2165	The Navy Transportation Safety Handbook
OP 3199	The Handling and Storage of Liquid Propellants

(When requesting applicable documents, refer to both title and number. Copies of unclassified documents may be obtained from the Commanding Officer, Naval Supply Depot (Code 1051), 5801 Tabor Avenue, Philadelphia, Pennsylvania 19120. Requests for copies of classified documents should be addressed to the Naval Supply Depot via the cognizant Government inspector.)

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.

American Society for Testing and Materials

ASTM Standards, Part 17	Petroleum Products
ASTM Standards, Part 18	Measurement and Sampling of Petroleum Products
ASTM Standards, Part 22	Antifreezes

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

Chemical Propulsion Information Agency

The Liquid Propellant Manual

(Application for copies should be addressed to the Chemical Propulsion Information Agency, The Johns Hopkins University Applied Physics Laboratory, 8621 Georgia Avenue, Silver Spring, Maryland.)

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.

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 (1949 Edition - Revised 1956) available from the Superintendent of Documents, Government Printing Office, Washington, D. C. 20402. Orders for the above publication should cite "49 CFR 71-90 (Rev. 1956).")

3. REQUIREMENTS

3.1 Material - The MHF-3 propellant shall be a product of high quality, suitable for the purpose intended, and so formulated as to meet the requirements specified herein (see 4.4.1).

3.2 No data is required by this specification, or by applicable documents referenced in Section 2, unless specified in the contract or order, (see 6.2).

3.3 Requirements - The MHF-3 propellant shall conform to the requirements specified in Table I when tested as specified in 4.4.

Table 1 - Chemical and Physical Requirements

Requirements	Limits
MHF-3 assay:	
Hydrazine (N_2H_4) MIL-P-26536, percent by weight	14.0±2.0
Monomethylhydrazine, MMH (CH_6N_2), MIL-P-27404, percent by weight	86.0±2.0
1/ Water, plus soluble impurities, max., percent by weight	2.0
Particulate, max., milligrams per liter	10.0
Density, g/ml at 25°C (77°F)	0.892-0.896
Freezing point, max., °F	-65

1/ Water content shall be 1 percent maximum in slurry fuel applications.

3.4 Filter - A filter with a 10 micron nominal and 40 absolute rating shall be installed between the manufacturer's plant system and the container to be filled for delivery.

3.5 Qualitative - The propellant shall be a homogeneous liquid when examined visually by transmitted light.

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, the supplier may utilize his own facilities or any commercial laboratory acceptable to 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.

4.2 Acceptance inspection - Conformance of the MHF-3 propellant to the requirements of this specification shall be determined entirely by means of acceptance inspection. Acceptance inspection shall consist of an examination for acceptability of the quality control methods used by the manufacturer, an examination of the sample of filled containers for conformance to the packaging and marking requirements, and examining and testing the sample for tests for all the requirements specified in Section 3.

4.3 Sampling -

4.3.1 Inspection lot - An inspection lot shall consist of the MHF-3 propellant blended by one manufacturer, with no change in process or materials, in not more than 24 consecutive hours, provided the operation is continuous. In the event the process is a batch process, each batch shall constitute a lot (see 6.3.2).

4.3.2 Sample for tests - The sample for tests shall consist of not less than 1000 ml of MHF-3 propellant prepared from random samples selected from each lot in accordance with Method 8001 of FED-STD-791 (ASTM D270). This sample shall be tested for all the requirements of this specification. A lot shall be unacceptable if a sample fails any of the test requirements.

4.3.3 Sample for examination of filled containers - A random sample of filled containers shall be selected from each lot of MHF-3 propellant offered for acceptance under contract in accordance with MIL-STD-105 at inspection level II and acceptable quality level (AQL) = 2.5 percent defective.

4.3.3.1 Examination of filled containers - Each filled container selected in accordance with 4.3.3 shall be examined for defects of the container and the closure, for evidence of leakage, for unsatisfactory marking, and content. Any container in the sample having one or more defects shall be rejected. When the number of defective containers in any sample exceeds the acceptance number for the appropriate sampling plan of MIL-STD-105, the lot represented by the samples shall be rejected.

4.4 Inspection methods - Unless otherwise specified, the physical and chemical values designated in Section 3 shall apply to the average of the determinations made on the sample for tests. Inspection conditions shall be described under the individual tests to which they apply.

4.4.1 Conformance of the MHF-3 propellant to the requirements for material (3.1) and qualitative (3.5) shall be determined by appropriate examination and testing in accordance with Section 3.

4.4.2 MHF-3 assay -

4.4.2.1 MHF-3 shall be analyzed by a gas chromatographic method. This method permits the major components, monomethylhydrazine and hydrazine, as well as the impurities, water and amines, to be simultaneously determined in a single analysis. The instrument used for this analysis is the Perkin-Elmer 154C Vapor Fractometer, however any equivalent chromatograph may be employed.

4.4.2.2 Reagents and apparatus -

(a) Perkin-Elmer 154-C Vapor Fractometer and recorder

(b) Hamilton syringe, 50 microliter

(c) Cylinder of compressed helium

(d) 6 feet of annealed copper tubing 1/4 inch O.D.

(e) Perkin-Elmer #154-1158 stainless steel sintered metal discs

(f) Chromatographic grade firebrick 30-60 mesh

(g) Quadrol-N, N, N', N',-tetrakis(2-hydroxypropyl) ethylenediamine - Wyandotte Chemicals Corporation

(h) Methanol - reagent grade

(i) 25-ml weighing bottle

(j) 25-ml syringe with 2 inch needle

4.4.2.3 Preparation of column -

(a) Weigh out 50.0 grams of firebrick (30-60 mesh) and place in a crystallizing dish.

(b) Fifteen (15.0) grams of Quadrol are weighed into a 250-ml beaker and dissolved using methanol.

(c) The methanol mixture is poured over the firebrick which is contained in the crystallizing dish. Wash the beaker thoroughly using methanol and pour the washings over the firebrick. This process is continued until the firebrick is totally submerged.

(d) Evaporate the methanol using a steam bath while constantly stirring the mixture.

(e) After evaporation of methanol, place the crystallizing dish containing the chromatographic support into a vacuum oven and dry the support at approximately 80°C(176°F) for two hours.

(f) After drying the support, allow it to cool. With one end of the copper tubing fitted with a sintered disc fill the column with the chromatographic support using a vibrator. (Vibration is used to eliminate channeling of the support in the copper tubing.)

(g) When the column has been filled fit the other sintered disc into the copper tubing.

(h) The copper tubing is then coiled to a 2 1/2 inch O.D. coil leaving about 6 inches of uncoiled tubing at each end of the column.

(i) The column is then placed into the chromatograph.

4.4.2.4 Instrumental conditions -

(a) Column	- 6-foot copper tubing 1/4 inch O.D. 30% Quadrol on firebrick.
(b) Temperature	- 100°C
(c) Variac setting	- 60 (dial setting)
(d) Detector voltage	- 8 volts
(e) Gas	- Helium
(f) Flowrate	- 60 mls/min.
(g) Pressure	- 5 lbs/sq. in.

(h) Sample size - 15 microliters

(i) Sensitivity - 32x, amine impurities; 4x, water; 16x, monomethylhydrazine; 2x, hydrazine

(j) Retention time - Amine impurities, 0.3 minutes, H_2O, 8 minutes; $CH_3N_2H_3$, 13 minutes; N_2H_4, 22 minutes

(k) Before using all of the above conditions the column should be allowed to normalize under the conditions of temperature and flowrate which have been stated.

4.4.2.5 Procedure -

(a) Using a 50-microliter syringe draw up 30 microliters of the mixed hydrazine sample and discharge into a beaker.

(b) Draw up another 30-microliter sample and invert the syringe. This procedure will allow the trapped air to be released. If this method is not effective, tap the syringe containing sample to permit the air to be discharged.

(c) Discharge the sample slowly until the plunger registers 15 microliters.

(d) Pass this 15-microliter sample into the chromatograph which has an initial sensitivity setting of 32x. After the desired component peak is eluted on the chromatogram, the proper sensitivity is selected for the next component.

(e) All samples should be chromatographed in duplicate. (See Note 2).

4.4.2.6 Preparation of standard samples -

(a) The hydrazine and monomethylhydrazine used in the preparation of the standards must be of known purity and water content.

(b) Clean, dry and weigh to the nearest 0.2 mg a 25-ml stoppered weighing bottle.

(c) Weigh to the nearest 0.2 mg into the tared weighing bottle 8.4 to 8.6 g of MMH and 1.3-1.5 g of N_2H_4.

(d) Calculate the weight percentage of each component in the standard sample

$$\%MMH = \frac{\text{wt. of MMH} \times \text{purity factor}}{\text{total wt. of sample}} \times 100$$

$$\%N_2H_4 = \frac{\text{wt. of } N_2H_4 \times \text{purity factor}}{\text{total wt. of sample}} \times 100$$

$$\%H_2O = \frac{(\text{wt. of MMH})(\text{MMH water factor}) + (\text{wt. of } N_2H_4)(N_2H_4 \text{ water factor})}{\text{total wt. of sample}} \times 100$$

(e) Chromatograph the standard mixture as described in 4.4.2.5.

4.4.2.7 Calculations and Measurements -

(a) Measure to the nearest 0.1 mm the peak heights of the components for the chromatogram of the standard sample. Repeat for the unknown sample being analyzed.

(b) Calculate the percentage of each component as follows:

$$\%MMH = \frac{\%MMH \text{ in standard sample} \times \text{MMH peak height in unknown}}{\text{MMH peak height in standard}}$$

$$\%N_2H_4 = \frac{\%N_2H_4 \text{ in standard sample} \times N_2H_4 \text{ peak height in unknown}}{N_2H_4 \text{ peak height in standard}}$$

$$\%H_2O = \frac{\%H_2O \text{ in standard sample} \times H_2O \text{ peak height in unknown}}{H_2O \text{ peak height in standard}}$$

NOTES

1. The passivation of all glassware is essential when storing the mixed hydrazine fuels for analysis.

2. The column must be passivated in order to achieve reproducible results. After passing several samples of the hydrazine mixture through the column, passivation is achieved.

3. The sampling process should be carried out as rapidly as possible.

4. After the completion of the analysis the column should be removed and the detectors rinsed with warm water. The water is then removed using acetone.

4.4.3 Density - The density of the MHF-3 propellant shall be determined in accordance with Method 402.2 of FED-STD-791 (ASTM D941).

4.4.4 Freezing point - The freezing point of the MHF-3 propellant shall be determined in accordance with ASTM D1177.

4.4.5 Particulate - The MHF-3 propellant sample shall be tested for solid particle contamination in a clean dust-free area in accordance with the following method (see 6.3.1).

4.4.5.1 Reagent preparation - The complete filter apparatus shall be washed with detergent and water. Rinse the apparatus twice with warm, distilled water. Assemble the 47-mm filter apparatus using an 0.80 micron filter disc and connect to a vacuum system. Turn on the vacuum system and filter separately a desired volume of isopropyl alcohol, petroleum ether, and distilled water. Each reagent shall be filtered three times.

4.4.5.2 Apparatus and bottle preparation - Prior to each sample test all items of the filtration apparatus and sample bottle, including cap, shall be cleaned. Remove all sample tags from bottles and flasks. Wash with detergent and water. Rinse twice with warm, filtered distilled water. Rinse twice with filtered isopropyl alcohol and allow to dry thoroughly. Finally, rinse twice with the filtered petroleum ether and allow to dry thoroughly until the petroleum ether vapors completely disappear. Immediately cap the sample bottles after cleaning. Reassemble the filter apparatus.

4.4.5.3 Procedure - Weigh one 10-micron solvent resistant filter disc to the nearest 0.1 mg. Using forceps, place the filter disc in a covered petri dish and identify suitably. Using an additional filter disc, repeat the above procedure and set aside as the control filter. Using forceps, remove the identified tared filter disc from the petri dish and place on the filter holder base. Clamp the filter holder funnel to the base. Thoroughly agitate the sample for tests and collect a 500 ± 5 ml sample of MHF-3 propellant in the cleaned sample bottle. Using vacuum, filter the entire contents of the sample bottle by pouring into the filter funnel in approximately 250-ml portions. Rinse the sample bottle with filtered distilled water. Thoroughly rinse the sides of the filter funnel and the filter disc by pouring the sample bottle rinsing into the funnel. Disconnect the funnel from the base and rinse the filter disc surface carefully with a jet of filtered distilled water to accumulate residue toward the center of the disc while vacuum continues. Release vacuum. Using forceps, immediately place the filter disc in the covered petri dish. In at least one filtration process of each group of samples to be tested, a control filter disc shall be placed on the filter funnel holder directly below but apart from the test filter disc. Weight increase greater than 0.2 mg of the control filter disc indicates inadequate flushing of sample residue and shall not be permitted. When a control filter disc is used during filtration, immediately place the disc in an additional covered petri dish. Place the dishes in a vacuum oven at approximately 70°C(158°F) for 30 minutes. Remove the dish(es) from the oven and allow to cool to ambient temperature. Reweigh the filter disc(s) to the nearest 0.1 mg and record. By difference, obtain the increase weight of the test filter disc. By difference, determine gain or loss in tare weight of the control filter disc. Apply the weight change of the control filter disc as a correction factor for each test result. Calculate the particulate using the following formula:

Particulate, mg/L = (Corrected weight of residue in milligrams) X 2.

4.4.5.4 Reagents and equipment - The following reagents and equipment shall apply as test conditions:

(a) Petroleum ether: boiling point 86 - 140°F(30-60°C), ACS reagent grade,

(b) Isopropyl alcohol: ACS reagent grade,

(c) Water: double distilled or deionized,

(d) Apparatus: filter, complete with fritted glass base, 300-ml glass funnel and holding clamp - to hold a 47-mm membrane filter disc,

(e) Pump: vacuum (or aspirator), capable of pulling 85 percent of the ambient pressure,

(f) Bottle: sample, small mouth, 1 liter, permanently marked, with polyethylene lined cap,

(g) Bottle: wash, 3 required,

(h) Flask: filter, 1 liter, with neoprene stopper,

(i) Disc: filter, membrane, 0.80 micron, 47-mm diameter

(j) Disc: filter, polyethylene membrane, solvent resistant, plain, white, 10±3.0 microns, 47-mm diameter,

(k) Dish: petri, glass with cover, 2 required,

(l) Balance: analytical, ±0.05 mg sensitivity, 0.1 mg accuracy,

(m) Oven: vacuum, capable of maintaining approximately 70°C(158°F) and pulling 85 percent of the ambient pressure.

5. PREPARATION FOR DELIVERY

5.1 Preservation and packaging - Unless otherwise specified, the MHF-3 propellant shall be packaged in ICC5, 5A, 5C or 17E drums, tank trucks, and tank cars conforming to Interstate Commerce Commission regulations as contained in the Code of Federal Regulations 49 CFR 71-90. The space above the liquid level shall be filled with contractor-furnished dry nitrogen gas conforming to MIL-P-27401 at atmospheric pressure for drums and 5-10 psig for tank trucks or tank cars. The contractor shall assure that gaskets which shall be made of teflon or other material approved by the procuring activity are serviceable and shall furnish new gaskets when necessary. The contractor shall perform the usual inspection and cleaning to assure that all containers are free from contamination, and are suitable for shipment and storage.

5.2 Marking - In addition to any special marking required by the contract or order, containers shall be marked in accordance with MIL-STD-129 and MIL-STD-172 including lot, batch, or control number. The nomenclature shall be as follows: PROPELLANT, MIXED HYDRAZINE FUEL-3.

5.2.1 Labeling - Each drum shall be labeled with a dangerous article caution label required by regulations or statutes without exception. The label shall contain the following information in red letters:

WARNING: HAZARDOUS LIQUID AND VAPOR FLAMMABLE.

Do not breathe vapor

Do not get in eyes, on skin or clothing.

Use with adequate ventilation.

Keep away from heat, sparks, and open flame.

Keep container closed.

In case of contact, immediately flush skin or eyes with plenty of water for 15 minutes; for eyes, obtain medical attention.

5.3 Handling, storage, and transportation - The Navy Transportation Safety Handbook (OP 2165 (3rd Revision)), the Handling and Storage of Liquid Propellants (OP 3199 dated January 1963), and the Liquid Propellant Manual prepared by the Chemical Propulsion Information Agency should be referred to in connection with the handling, storage, and transportation of MHF-3 propellant.

6. NOTES

6.1 Intended use - The MHF-3 propellant covered by this specification is intended for use as a fuel in Navy advanced packageable liquid propellant missile rocket engines.

6.2 Ordering data - Procurement documents should specify the following:

(a) Title, number, and date of this specification.
(b) Method of shipment, type and capacity of containers.
(c) Quantity by weight in pounds (avoirdupois).

6.3 Definitions -

6.3.1 Particulate - Particulate is defined as the undissolved solids retained on a 10-micron filter paper.

6.3.2 Batch - A batch is defined as the end product of all the raw materials mixed or blended in a unit operation.

6.4 Flammability - MHF-3 has a flash point of approximately 24°C(75°F). Care should be taken where this propellant is being handled.

6.5 Toxicity - MHF-3 has a maximum allowable concentration (MAC) of 0.2 ppm. Adequate provision must be made in view of the high toxicity of this liquid propellant.