MILITARY SPECIFICATION

PROPELLANT, MIXED HYDRAZINE FUEL, MHF-6

This specification has been approved by the Naval Air Systems Command, Department of the Navy.

1. SCOPE

1.1 This specification covers the requirements for mixed hydrazine fuel, MHF-6 (monomethylhydrazine, hydrazine, water, MMH-N_2H_4-H_2O) 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

NAVAL ORDNANCE SYSTEMS COMMAND

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 Publications and Forms Center (Code 1051), 5801 Tabor Avenue, Philadelphia, Pennsylvania 19120. Requests for copies of classified documents should be addressed to the Naval Publications and Forms Center 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

D 270-65	Sampling Petroleum and Petroleum Products
D 941-55	Method of Test for Density and Specific Gravity of Liquids by the Lipkin Pycnometer
D 1177-65	Method of Test for Freezing Point of Aqueous Antifreeze Solution

(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.

DEPARTMENT OF TRANSPORTATION

49 CFR 171-190 Hazardous Materials Regulation of the Department of Transportation

(Application for copies should be addressed to the Superintendent of Documents, Government Printing Office, Washington, D. C. 20402.)

3. REQUIREMENTS

3.1 Material - The MHF-6 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-6 propellant shall conform to the requirements specified in Table I when tested as specified in 4.4.

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 in the contract or order, the supplier may use his own or any other facilities suitable for the performance of the inspection requirements specifield 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.

TABLE I - Chemical and Physical Requirements

REQUIREMENTS	LIMITS
MHF-6 assay:	
Hydrazine (N_2H_4) MIL-P-26536, percent by weight	17.0 ± 1
Monomethylhydrazine, MMH (CH_6N_2) MIL-P-27404, percent by weight	72.5 ± 0.5
Water (H_2O), (99.99 percent min. purity) deionized, percent by weight	10.5 ± 0.5
Soluble impurities, max. percent by weight	0.5
Particulate, max. milligrams per liter	10.0
Density, g/ml at 25°C (77°F)	0.922
Freezing Point	-70 ± 3°F

4.2 Quality conformance inspection - Conformance of the MHF-6 propellant to the requirements of this specification shall be determined by means of the examinations and tests of 4.3 and 4.4. Quality conformance inspection shall consist of examinations and tests of both the filled containers and a sample of the propellant to determine conformance to all requirements specified in Section 3 and the packaging and marking requirements of Section 5.

4.3 Sampling -

4.3.1 Inspection lot - An inspection lot shall consist of the MHF-6 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 examination of filled containers - A random sample of filled containers shall be selected from each lot of MHF-6 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.

4.3.2.1 Examination of filled containers - Each filled container selected in accordance with 4.3.2 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.

4.3.3 Sample for tests - The sample for tests shall consist of not less than 1000 ml of MHF-6 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.

4.4 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-6 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-6 assay

4.4.2.1 Mixed hydrazine fuel (MHF-6) is composed of monomethylhydrazine (CH_3NHNH_2), hydrazine (N_2H_4) and water (H_2O). Gas chromatography is used to determine the percentages of hydrazine, monomethylhydrazine, water and amine impurities in the mixture.

4.4.2.2 Reagents and apparatus (or equivalent)

a. Varian Aerograph Model A-90-P Gas Chromatograph and recorder.

b. Cole Parmer "Samplejector" syringe, 5 microliter.

c. Cylinder of compressed helium (Matheson Company, Rutherford, New Jersey).

d. Five feet of copper tubing 1/4 inch O.D.

e. Perkin-Elmer No. 154-1158 stainless steel sintered metal discs.

f. Chromosorb W, HMDS (hexamethyldisilazane) treated, 30-60 mesh (Johns-Manville).

g. Carbowax 1500 (Analabs, Inc.).

h. Methylene chloride - reagent grade.

i. Hi-Eff Fluidizer (Applied Science Labs).

4.4.2.3 Preparation of column

a. Weigh out 85.0 grams of the HMDS treated Chromosorb W and place in a crystallizing dish.

b. Fifteen (15.0) grams of Carobwax 1500 are weighed into a 250 ml beaker and dissolved in methylene chloride.

c. The methylene chloride mixture is poured over the HMDS treated Chromosorb W which is contained in the crystallizing dish. Wash the beaker thoroughly using methylene chloride, and pour the washings over the solid support. This process is continued until the solid support is totally submerged.

d. Evaporate the methylene chloride using a steam bath while constantly stirring the mixture.

e. Complete drying of coated support by pouring it into Hi-Eff Fluidizer and drying with low flow (approximately 1 psig) of nitrogen for thirty minutes.

f. Clean the copper tubing with methylene chloride and blow dry with nitrogen.

g. Seal one end of the copper tubing with a sintered metal disc and attach to a vacuum line. Fill the copper tubing with the dry coated support by adding small amounts and tapping while vacuum is applied. (The vacuuum filling is used to prevent channeling of the coated support in the copper tubing.)

h. When the column has been filled, fit the other sintered metal disc into the copper tubing.

i. The copper tubing is then coiled to a 4 inch O.D. coil leaving 1 1/2 inches of uncoiled tubing at a right angle to each other at each end of the tubing.

j. The column is then placed into the chromatograph.

4.4.2.4 Instrumental conditions

a.	Column	5 foot copper tubing 1/4 inch O.D., 20 percent Carbowax 1500 on HMDS treated Chromosorb W, 30-60 mesh.
b.	Temperature, column	84° C
c.	Temperature, detector	120° C
d.	Temperature, injector	110° C
e.	Filament current	250 ma with tungsten filaments
f.	Carrier gas	helium
g.	Helium flowrate	50 ml/min
h.	Sample size	1.8 microliters
i.	Sensitivity	2X, amine impurities; 2X, water; 16X, monomethylhydrazine, 2X hydrazine
j.	Retention time	H_2O, 5.8 minutes; CH_3NHNH_2, 7.3 minutes; N_2H_4, 16.6 minutes

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

4.4.2.5 Procedure

a. Remove knurled end plug from top of syringe and pull graduated barrel away from metal body section until piston is no longer visible in glass. Insert filler syringe where knurled end plug was removed, and dip needle into sample solution. Slowly pull sample through syringe, and remove filler syringe with needle in liquid. Immediately replace knurled plug; and holding metal body firmly, bring graduated pipette onto tube until tube is at desired graduation (1.8 microliters).

b. Pass this 1.8-microliter sample into the chromatograph which has an initial sensitivity setting of 2X.

c. 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 are initially chromatographed to determine their purity and water content.

b. A screw cap bottle is tared and each component is placed in the bottle and individually weighed. The mixture is made up of 73.0 percent monoethylhydrazine, 16.5 percent hydrazine and 10.5 percent water. The exact composition of the standard is obtained from the weights and purity of the individual components.

4.4.2.7 Measurements and calculations - The method of measurement and calculation employed for this analysis is similar to that described in A. Keuleman's text (Ref 1). The internal normalization method used assumes monomethylhydrazine (MMH) to have a sensitivity of 1.00. The sensitivity of N_2H_4 and H_2O are calculated by the following formula:

$$Kc = \frac{(\text{percent C})\ (A_{MMH})}{(\text{percent MMH})\ (Ac)}$$

where A_{MMH} = Area MMH

Ac = area of component

Kc = sensitivity of component

percent C = percent of component in blend

The analyzed composition of unknown samples is calculated by the following formula:

$$\text{percent C} = \frac{Ac\ Kc}{\sum (Ac_i\ Kc_i)} \times 100$$

The areas of the peaks are obtained by multiplying the peak height by the peak width at the half peak height.

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.

Reference

1. Keuleman, A.I. M., "Gas Chromatography," Reinhold Publishing Corporation, New York, 1957.

4.4.3 Density - The density of the MHF-6 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-6 propellant shall be determined in accordance with ASTM D1177.

4.4.5 Particulate - The MHF-6 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-6 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 and thoroughly 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 the 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-6 propellant shall be packaged in DOT5, 5A, 5C, or 17E drums, tank trucks, and tank cars conforming to Department of Transportation regulations as contained in the Code of Federal Regulations 49 CFR171-190. 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 conttrol number. The nomenclature shall be as follows: PROPELLANT, MIXED HYDRAZINE FUEL-6 (MHF-6).

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-6 propellant.

6. NOTES

6.1 Intended use - The MHF-6 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 Toxicity

a. Industrial exposure - For exposures of 40 hours per week continuously, the threshold limit value (T.L.V.) of MHF-6 is 0.2 ppm.

b. Short term exposure - However, the T.L.V. for shorter terms are as follows:

60 minutes	3 ppm
30 minutes	7 ppm
10 minutes	10 ppm