HYDRAZINE AND ITS DERIVATIVES

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1.0 SCOPE

This data sheet provides guidelines for the storage and use of anhydrous hydrazine (AH), monomethyl hydrazine (MMH), unsymmetrical dimethyl hydrazine (UDMH), hydrazine monohydrate and its water solutions. Monohydrate and its solutions are likely to be found at chemical and pharmaceutical plants, while the other materials are limited to use as rocket fuels, and thus not widely used.

This data sheet does not provide guidelines on the manufacture of these materials.

1.1 Changes

January 2012. Terminology related to ignitable liquids has been revised to provide increased clarity and consistency with regard to FM Global's loss prevention recommendations for ignitable liquid hazards.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Construction and Location

2.1.1 Spacing of bulk storage tanks of AH, MMH, or UDMH should be in accordance with Figure 1a or 1b based on the volume of the largest tank. Vessels with a capacity of less than 400 gal (1.5 m^3) should be treated as ordinary ignitable liquids.

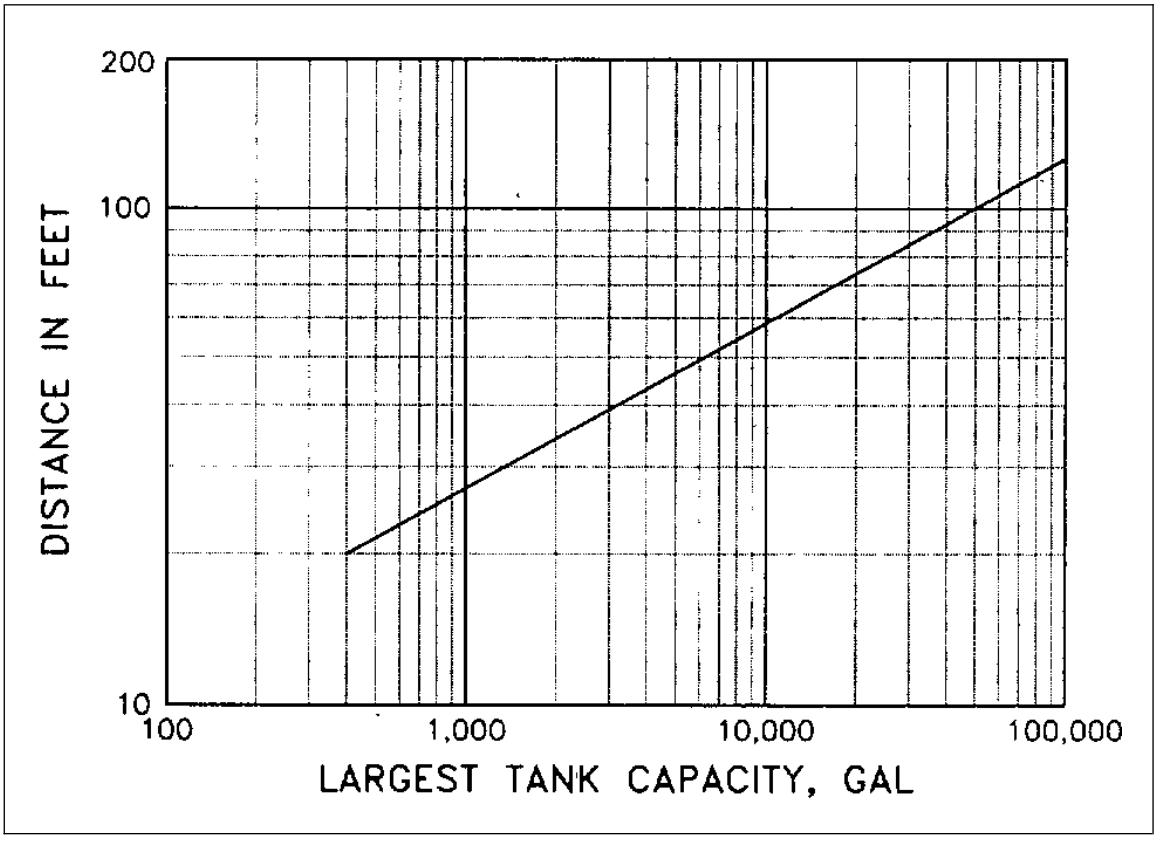

Fig. 1a. Spacing of outdoor storage tanks for AH, MMH and UDMH (English units).

2.1.2 Spacing for storage of hydrazine monohydrate and its ignitable solutions should be in accordance with requirements for ordinary ignitable liquids.

2.1.3 Dikes should be provided around all bulk storage tanks in accordance with requirements for ordinary ignitable liquids.

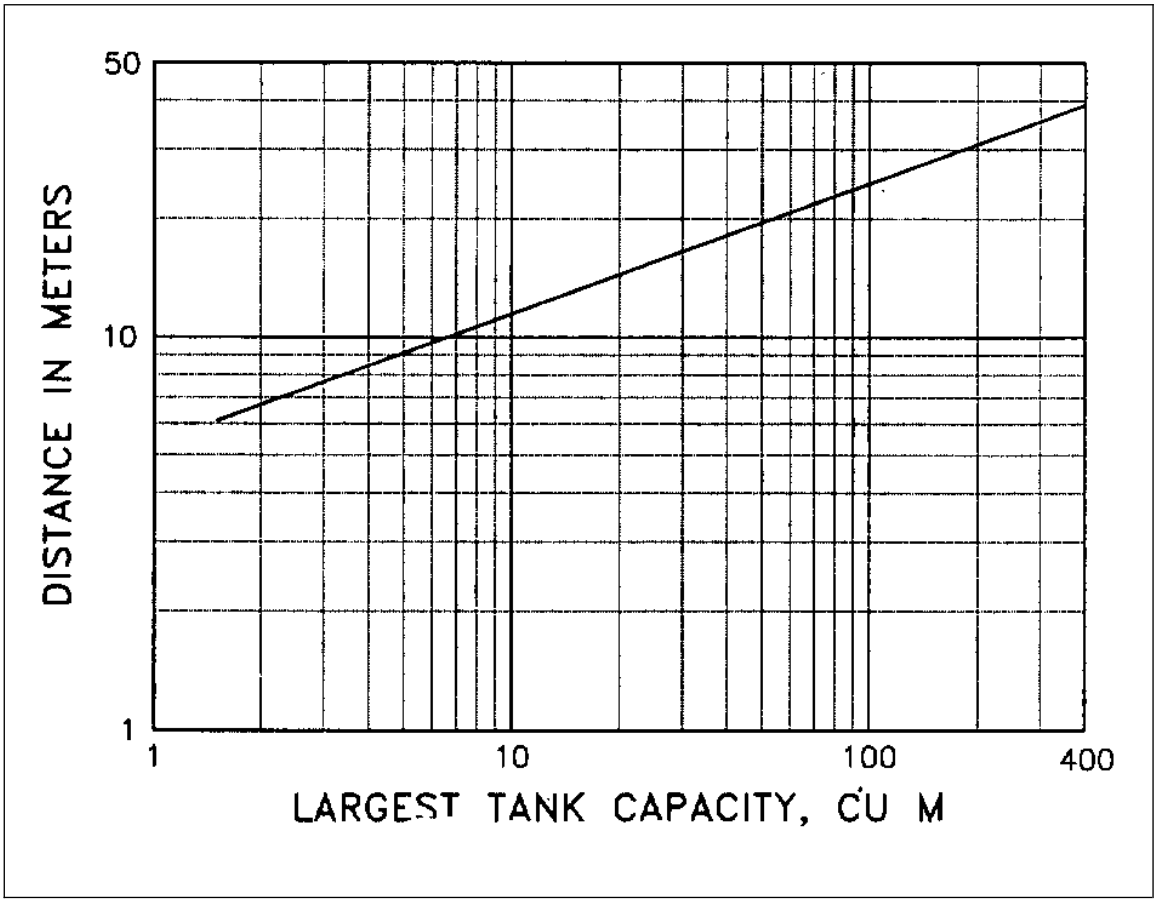

Fig. 1b. Spacing of outdoor storage tanks for AH, MMH and UDMH (Metric units).

2.1.4 Drums should be constructed and stored as follows:

a) Drums for AH, MMH, and UDMH should be constructed in accordance with Department of Transportation (DOT) regulations, manufacturer's requirements or comparable international regulation. These would be 304 stainless steel except for UDMH where mild steel is permitted.

b) Drums for hydrazine monohydrate and its solutions should be constructed in accordance with DOT, manufacturer's or international regulations. These could be Type 304L, 316, or 347 stainless steel, Teflon-lined steel, or polyethylene.

c) All drum storage should be limited to one high on end, protected from excessive temperatures less than 124°F (51°C) and kept out of direct sunlight.

d) All drums are shipped with a nitrogen pad that should be maintained if the drum is partially emptied.

2.1.5 Spacing, location and construction for drum storage pads or buildings for hydrazine and its derivatives should be in accordance with requirements for ordinary ignitable liquids (excluding nonignitable solutions).

2.2 Occupancy

2.2.1 Transfer

2.2.1.1 Hydrazine and its derivatives should be transferred in dedicated systems constructed of compatible materials. This includes gaskets, valves, fittings, etc. This generally includes Type 304 or 347 stainless steel except for hydrazine monohydrate solutions where polyethylene or Teflon may be used.

2.2.1.2 All metallic piping and apparatus should be grounded and bonded to prevent accumulations of static electricity that could ignite the vapor present.

2.2.2 Processing

These recommendations do not cover manufacture of hydrazine or its derivatives. Such facilities require careful study, design and assistance from specialists familiar with the unique hazards of the products.

2.2.2.1 Process all hydrazine materials in structures suitable for ignitable-liquid occupancies.

2.2.2.2 Locate process equipment containing anhydrous hydrazine or monomethyl hydrazine vapors and exceeding 50 ft^3 (1.4 m^3) in volume at least 100 ft (30 m) from important buildings. For all other hydrazine derivatives, follow the distances recommended for ordinary ignitable liquids.

2.2.2.3 Use the recommended safeguards in Data Sheet 7-77, *Testing Internal Combustion Engines and Accessories,* as a guide where monopropellant testing in cells is encountered. Cell construction for an internal pressure of 150 psf (7.2 kPa) with 1 ft^2 of venting for every 15 ft^3 of room volume (1 m^2/4.5 m^3) is satisfactory for quantities up to 30 gal (115 L).

2.3 Fire Protection

2.3.1 Provide automatic water spray protection for storage or processing tanks containing AH, MMH, or UDMH having capacities in excess of 500 gal (1.9 m^3). System design should be based on 0.3 gpm/ft^2 (12 mm/min) for the entire tank surface area, plus at least 500 gpm (1.9 m^3/min) for monitor nozzle or hose use.

2.3.2 Provide protection for storage tanks containing other hydrazine derivatives as for ignitable liquids.

2.3.3 Hydrant protection is adequate for outdoor drum storage arranged according to this standard. However, provision of a noncombustible canopy with automatic deluge sprinkler protection may be advisable over anhydrous hydrazine drum storage if firefighting manpower is limited.

2.3.4 Provide automatic sprinkler or water spray protection for areas processing hydrazine or its ignitable derivatives in accordance with Data Sheet 7-14, *Fire & Explosion Protection for Ignitable Liquid, Flammable Gas, & Liquefied Flammable Gas Processing Equipment & Supporting Structures.*

2.3.5 First aid firefighting equipment should be provided as for other ignitable liquids. Carbon dioxide or dry chemical extinguishers are satisfactory. Small hose with spray nozzles are particularly effective in diluting spilled liquid below its ignitable concentrations.

2.4 Equipment and Processes

2.4.1 Maintain a nitrogen atmosphere in all storage tanks. The major manufacturer recommends storage pressures of approximately 14 in. (35 cm) of water and transfer pressures of 5 psig (0.3 bar g). Storage tanks will usually be designed to contain 35 psig (2.4 bar g) pressure. All storage tanks should be equipped with relief valves set to discharge at less than the design pressure and of sufficient capacity to relieve potential pressures developed by an exposure fire. The heat capacity and latent heat of vaporization of hydrazine and its derivatives are such that the required capacities for emergency relief of aboveground ignitable liquid storage tanks may be used.

2.5 Contingency Planning

2.5.1 Information about disposal of wastes, spill handling procedures and protective equipment for personnel should be obtained from the manufacturer's literature.

2.6 Ignition Source Control

2.6.1 Provide electrical equipment in accordance with the *National Electric Code,* Article 500, Group C, static grounding, safety ventilation, and other safeguards in areas where hydrazine or its ignitable derivatives are stored or handled, the same as for equivalent quantities of other ignitable liquids.

3.0 SUPPORT FOR RECOMMENDATIONS

3.1 Illustrative Losses

There has been only one fire or explosion in the last 15 years recorded at FM insured locations.

3.1.1 Hydrazine Distillation Column Experiences Mild Explosion

In 1977, a process involving distillation of 9% hydrazine in an acetone-water solution to produce hydrazine monohydrate experienced an overpressure condition. The cause of the incident was apparently exposure of the solution to bare steam coils at about 500°F (260°C). This resulted in formation of pure hydrazine vapor. The resulting decomposition dislodged all the trays in the column but did no damage to the shell. Apparently an operator accidently drained solution from the column, exposing the steam coils in the reboiler.

4.0 REFERENCES

4.1 FM

Data Sheet 7-14, *Fire & Explosion Protection for Ignitable Liquid, Flammable Gas, & Liquefied Flammable Gas Processing Equipment & Supporting Structures.*

Data Sheet 7-77, *Testing Internal Combustion Engines and Accessories.*

4.2 Others

National Electric Code, Article 500.

APPENDIX A GLOSSARY OF TERMS

Ignitable Liquid: Any liquid or liquid mixture that is capable of fueling a fire, including flammable liquids, combustible liquids, inflammable liquids, or any other reference to a liquid that will burn. An ignitable liquid must have a fire point.

APPENDIX B DOCUMENT REVISION HISTORY

January 2012. Terminology related to ignitable liquids has been revised to provide increased clarity and consistency with regard to FM Global's loss prevention recommendations for ignitable liquid hazards.

January 2000. This revision of the document has been reorganized to provide a consistent format.

June 1992 — This data sheet has been updated to reflect current format as well as to provide some updated hazard description and to clarify different requirements for the highly reactive compounds and the less hazardous solutions. There are no new recommendations.

January 1967 — Updated.

June 1957 — Original document.

APPENDIX C GENERAL HAZARD INFORMATION

Hydrazine and its derivatives are active reducing agents that react with a wide variety of chemicals, both organic and inorganic. Anhydrous hydrazine (AH), monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH) are used primarily as rocket fuels. The number of manufacturers is small and the materials will nearly always be found in commercial facilities connected with military or space agencies.

Hydrazine monohydrate (64% by weight hydrazine) and its solutions would be used as building blocks in the manufacture of drugs, insecticides, blowing agents and plastics. A major use is as a water treatment chemical for boilers.

The physical properties of hydrazine and its derivatives are shown in Table 1.

The safeguards recommended in this data sheet consider anhydrous hydrazine and monomethyl hydrazine as substances whose *vapors* are subject to explosive decomposition, but the liquid phase itself is not considered explosive.

Hydrazine and its derivatives are ignitable liquids with comparatively low auto-ignition temperatures and high chemical reactivity. Aqueous solutions of hydrazine do not burn when containing less than 40% by weight hydrazine.

Decomposition or ignition of all compounds can be initiated by common ignition sources, and by the catalytic action of oxygen, metallic oxides (particularly iron, copper, molybdenum and chromium), and other materials.

The pressure developed by the decomposition under constant volume conditions is approximately 15 times the initial absolute pressure. All storage containers should have a nitrogen pad above the liquid.

Flash points, explosive ranges and auto-ignition temperatures of hydrazine and its derivatives exhibit characteristics of ignitable liquids. A notable exception is anhydrous hydrazine with an upper explosion limit of 100% at elevated temperatures. This is because the vapor can undergo decomposition even in the absence of oxygen. When stored in open containers, hydrazine solutions can become more concentrated due to evaporation. Due to the presence of an azeotrope, the maximum concentration in the liquid would be about 70% by weight.

Avoid contact of hydrazine, its solutions and derivatives with organic materials having large surface areas or porous surfaces. Absorption by rags, cotton waste, sawdust or similar organic materials will eventually result in spontaneous combustion.

Except for potential spontaneous combustion hazards (see above), no special precautions are needed for hydrazine solutions that do not burn.

Table 1. Physical Properties of Hydrazine and its Derivatives

	Flash Point[1]	*LEL*	*UEL*	*Boiling Point*	*Freezing Point*	*Liquid Density*	*Vapor Density*	*Auto-ignition Temp.*	*Water Solu-bility*	*NFPA 704*[2] *Hazard Identification*		
										Health	*Flam.*	*React.*
Hydrazine N_2H_4	126°F (52°C)	4.7%	100%	236°F (114°C)	36°F (2°C)	1.004	1.1	518°F (270°C)	∞	3	3	2
Hydrazine Monohydrate $N_2H_4 \bullet H_2O$	167°F (75°C)	NA	NA	248°F (120°C)	–60°F (–51°C)	1.03	1.1	536°F (280°C)	∞	3	2	2
35% Hydrazine Solution	None	None	None	228°F (109°C)	–85°F (–65°C)	1.03	NA	None	∞	3	0	0
Monomethyl Hydrazine $CH_3N_2H_3$	70°F (21°C)	2.5%	98%	190°F (88°C)	–62°F (–52°C)	0.87	1.6	382°F (194°C)	∞	3	3	2
Unsymmetrical Dimethyl Hydrazine $(CH_3)_2N_2H_2$	5°F (–15°C)	2%	95%	146°F (63°C)	–71°F (–57°C)	0.78	2.1	482°F (250°C)	∞	3	3	1

NA-Not available
[1]Cleveland Open Cup
[2]NFPA 704 does not list hydrazine monohydrate or 35% hydrazine solutions. These figures were estimated from MSDS information.

APPENDIX D NFPA STANDARD

There are no comparable NFPA standards.

FM Engr. Comm. Nov. 1966