22nd Department of Defense Explosives Safety Seminar

Safety and Handling of Hydrazine

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Abstract

Hydrazine products are widely used as chemical building blocks oxygen scavengers, chemical explosive intermediates, monopropellants and bipropellants. Although these forms of hydrazine have had a long history of safe and successful use, hydrazine has recently received much attention due to its toxic properties.

The latest toxicological information on hydrazine and the regulations governing its use are reviewed. Hydrazine's nature, what to do about personnel exposure, how it can be absorbed into the body and what effects exposure may create are all discussed. Discussion will focus on how employee exposure to hydrazine can be minimized by simple and effective engineering controls, supplemented by mandatory use of protective equipment and proper handling procedures. Training of employees to recognize the hazards involved and safe procedures to be used is the most important element in minimizing the hazard potential with any chemical.

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Introduction

Hydrazine's original use was as a rocket fuel in the ME-163 German fighter plane during World War II. Today, hydrazine propellants include anhydrous hydrazine (AH), monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH) and the 70% aqueous hydrazine (H-70) product. Hydrazine fuels have been historically used as bipropellants with nitrogen tetroxide and as a monopropellant. Hydrazine's use as a monopropellant, is by its decomposition over a suitable catalyst to produce gaseous products to provide attitude and in orbit control for satelites and spacecraft. Hydrazine is also produced and sold as aqueous solutions (6′ 54.4 and 35 weight percent solutions) for application as a corrosion inhibitor/oxygen scavenger; and as a chemical building block for agricultural products, chemical foaming agents and explosive intermediates along with many other uses. A number of hydrazine derivatives including the simple perchlorate, nitrate and azide salts are explosives. Hydrazine derived aminoguanidine derivatives, including 5-aminotetrazole, guanylazide, and tetracene are explosives with tetracene used as an ammunition primer component.

Hydrazine is an important industrial chemical whose historical, present and projected uses are based to a large extent upon its high degree of reactivity. This same property, however, has in the past given hydrazine the reputation of being an unstable and hazardous chemical.

Misapprehension concerning the nature of hazards involved in handling hydrazina started before the compound was isolated, and has continued for years. Curtius (1), who first prepared hydrazine in solution, expressed the conjecture that "the free base is so unstable that it can not exist in the free state." The prediction of Curtius was later proved erroneous by Labry de Bruyn (2), who isolated the anhydrous free base, and reported that "it is a very stable compound, and in contrast to hydrogen peroxide, not explosive. It can be heated above 300°C without being decomposed." Despite this observation, and in spite of other experimental evidence to the contrary, the idea of inherent instability has continued to persist. Although hydrazine products have a long history of safe and successful use, hydrazine has received much attention recently due to its toxic properties. The American Conference of Governmental Industrial Hygienists (ACGIH) and the International Agency for Research on Cancer have listed hydrazine as a suspect carcinogen. Hydrazine products are indeed hazardous commodities, but so are a great many of the chemicals , industry routinely handles. If people are aware of the properties of hydrazine so they can separate facts from misunderstandings and become knowledgeable in the best way to handle hydrazine, then it's safe use can be assured.

Hydrazine Properties

An attempt is made here to summarize some of the available information pertinent to hydrazine safe handling. For this purpose information dealing with anhydrous hydrazine and the aqueous solution products will only be covered. More detailed information is covered in a number of excellent references (3-7).

Physical. Anhydrous hydrazine (N_2H_4) is a highly polar, hygroscopic liquid that will absorb CO_2 or oxygen from the atmosphere. It melts at 2.0°C and boils at 113.5°C (760 mm Hg). Since its density as a solid (1.146/-5°c) is higher than as a liquid (1.024/2°C), there is no danger of rupturing containers under freezing conditions.

Vapor pressures for anhydrous hydrazine are represented by the following empirical equation:

$$\log_{10}P(\text{mm Hg}) = 7.80687 - 1680.745/(t + 227.74)$$

Above the atmospheric boiling point, data is less reliable due to thermal decomposition. Hydrazine and water form an azeotropic mixture which boils at 120.3°C (760 mm Hg) containing 58.5 mole % N_2H_4. Freezing point (Table I) data on the $N_2H_4.H_2O$ system show the compound $N_2H_4.H_2O$ to be a stable solid phase melting at -51.7°C. Eutectics exist at 29.5 mole % (-88°C m.p.) and at 56 mole % (-53.5°C m.p.).

Chemical. From a strictly chemical standpoint, hydrazine is classified as a very strong reducing agent, and a mildly alkaline base. It reacts readily and exothermically with most oxidizing agents, and mineral acids with the speed of reaction depending upon concentration, temperature, and catalytic conditions.

Examples of oxidizing agents include not only the electronegative elements and highly oxidized compounds, but also lower oxides of some metals and even certain metal ions. Hydrazine may be liquid or vapor, concentrated or dilute, free or in combined from. Principal products are usually N_2 and H_2O, but in some cases substantial amounts of NH_3 are produced. Typical reactions include reduction of salts of oxides of copper, iron, silver, mercury and many other similar metals. Reaction MoO_3, Fe_2O_3, MnO_2, HgO, CuO, PbO_2, CrO_3, $AgNO_3$ and Cu $(NO_3)_2$ may be particularly violent with anhydrous hydrazine, although less so with the aqueous hydrazine solutions (ie) 35% hydrazine.

As with many chemicals certain precautions must be observed when handling hydrazine propellants and products. Acids such as hydrochloric, sulfuric, and nitric, and oxidizers like hypochlorites, hydrogen peroxide, permanganates, chromates etc. should be avoided in areas where hydrazine is handled or stored. Again, it is important to recognize that the intensity of the reactions of hydrazine with oxidizers or acids is dependent upon the concentration of the reactants. The lower the hydrazine concentration, the milder the reaction.

Flammability. Liquid anhydrous hydrazine is very stable and non-explosive. In the absence of decomposition catalysts, it has been heated above 500°F with very little decomposition.

Hydrazine vapors, however do present a hazard. Mixtures of hydrazine vapor in air are flammable between the limits of 4.7% and 100% hydrazine by volume. The flammability of hydrazine vapor is decreased by the use of any of several diluents. Nitrogen is generally recommended due to ready availability and cost. The lower explosive limit of a hydrazine-nitrogen-air mixture is a straight line function between 4.7% for air and 38% for nitrogen at 228° to 234°F.

In contrast to most other chemicals, hydrazine has no upper limit to the range of explosive concentrations. Combustion of cold liquid hydrazine is difficult to initiate. Ignition occurs only when the temperature has been raised above roughly 126°F, the fire and flash points for hydrazine. When burning freely in air, hydrazine behaves much like gasoline. However, at elevated temperatures it burns fiercely.

Water solutions of hydrazine at any concentration below 40% cannot be ignited. A 50% solution will burn only near its boiling point, with increasing concentration the burning temperature decreases to about 126°F for the anhydrous product (see Figure 1 and Table I). Water is the best means of combating fires, as it has the combined effect of cooling and diluting the hydrazine below its combustible limit.

Stability. Anhydrous hydrazine and aqueous hydrazine solutions under normal conditions are stable and insensitive to shock and friction. It presents no explosive hazard and storage tests over extended periods have shown negligible decompositions of the products. Decomposition of hydrazine is caused by elevated temperatures and the presence of catalytic surfaces or ion impurities.

At increased temperatures, hydrazine will slowly decompose to yield nitrogen and ammonia. Studies at temperatures up to 500°F have shown that most of the decomposition takes place in the vapor phase, and that the rate of decomposition is a direct function of temperature. No rapid decomposition has been observed, even at 500°F, in the absence of catalytic agents.

Certain metallic ions and metallic oxide surfaces exhibit a marked catalytic effect upon the decomposition of hydrazine. Laboratory studies have shown that chromic, ferric and cupric ions catalyze decomposition of hydrazine at reflux conditions under a nitrogen blanket. At ambient conditions there is no noticeable effect from dissolved ions. A surface area catalytic effect occurs when molybdenum, iron, Raney nickel, rust, copper oxide or cobalt in finely divided form come into contact with hydrazine. A film of hydrazine on iron rust will burst into flames if ventilation is inadequate to keep it cool.

Ignition has also been observed with asbestos, expanded vermiculite, sawdust, rags, paper and some metal powders when moistened with hydrazine and exposed to the atmosphere at room temperature. The phenomenon is similar to the spontaneous ignition of drying oils, starting with slow oxidation under conditions that prevent the dissipation of the heat as fast as it is liberated, and preceding faster as the temperature rises until the ignition temperature is reached. The effect of the porous solid may be either catalytic or simply that of a barrier to dissipation of heat.

Health Hazards

Although anhydrous hydrazine and aqueous hydrazine solutions have a long history of safe and successful use, hydrazine received much attention recently due to its toxic properties. The American Conference of Governmental Industrial Hygienists (ACGIH) and the International Agency for Research on Cancer have listed hydrazine as a suspect carcinogen. Hydrazine solutions are indeed hazardous commodities, but so are a great many of the chemicals industry routinely handles.

Questions of occupational safety and health are never solely a matter of the toxicity of a chemical. They should be a matter of selecting and adopting the proper handling methods. Use of mandatory protective equipment is prudent and appropriate in view of the toxic and physical/chemical properties of the chemical. No chemical is completely safe unless it is properly handled and, it is well known that comparatively hazardous chemicals can be handled safely. Training of employees about th hazards involved and safe procedures to be used is the most important element in minimizing the hazard potential.

Hazardous exposure of personnel to hydrazine should only occur through accidents, since the precautions established for proper handling and storage would protect workers under normal non-accidental conditions. The two types of exposure are: 1) acute, short-term, high-dosage exposure resulting from a massive spill, truck accident or tank rupture and 2) chronic, long-term, low-dosage exposure. Hydrazine if directly contacted can cause burns to the skin, eyes and is highly irritating to th mucous membranes. The products Material Safety Data Sheet and label as required by the OSHA Hazard Communications standard should be consulted for the most up-to-date and complete information on health hazards.

Even though hydrazine can be absorbed into the body in toxic amounts by either acute or chronic exposure, employee exposure t hydrazine can be minimized by simple and effective engineering controls, supplemented by mandatory use of protective equipment and proper handling procedures. What can be done to prevent exposure to hydrazine? Most obviously don't drink it! Wearing of protective clothing is most important to prevent skin contact, Table II illustrates preferred clothing items. It should be noted that leather shoes are unsuitable since leather is not resistant to hydrazine thereby presenting an exposure concern. Hydrazine cannot be removed from leather thus contaminated shoes would have to be discarded. For different activities, less equipment is needed since exposure may be different when working in a storage area as opposed to the processing area. Finally, it is extremely important that the workplace be well ventilated to be certain ambient hydrazine concentrations in air will be at or below acceptable levels. If adequate ventilation cannot be provided, then further means must be adopted to provide protection against inhalation, such as using a closed handling system.

Exposure Limits

Currently there are several hydrazine exposure limits in use, of which the OSHA limit of 1 ppm is a required standard. Others such as the NIOSH (National Institute for Occupational Safety and Health) or ACGIH (American Conference of Governmental Industrial Hygienists), are only guidelines. The OSHA Standard was developed from ACGIH 1968 values. Table III illustrates these exposure limits. The ACGIH recommendation of 0.1 ppm is for 1985-1986 and is based on toxicology information gathered since the establishment of the OSHA standard.

The latest toxicological information on hydrazine is contained in the recently issued Air Force Aerospace Research Laboratory Report on the "Chronic Inhalation Toxicity of Hydrazine: Oncogenic Effects".[8] This study examined the exposure by the inhalation route and used hydrazine, the free base, rather than the sulfate salt of hydrazine as shown in Table IV.[8] These inhalation studies were performed in several species - rats, mice, hamsters and dogs - to assess the cancer producing potential of hydrazine. The inhalation exposures were conducted on a six hour/day, five days/week schedule (to simulate an industrial type of exposure) for a one year period followed by an observation period. Results of the studies indicated that hydrazine was a weak tumorigen capable of causing respiratory tumors, primarily benign (non-malignant), at the OSHA Permissible Exposure Limit (PEL) of 1 ppm.

Based on these results, the Air Force study concluded that the OSHA Permissible Exposure Limit expressed as an 8 hour time-weighted average exposure of 1.0 ppm hydrazine is unsatisfactory, while the American Conference of Governmental Industrial Hygienists (ACGIH) recommended Threshold Limit Value (TLV) of 0.1 ppm appears to be a <u>low-risk exposure level.</u>

Given the results of the USAF study and the ACGIH recommendation, it would appear that keeping levels of hydrazine at or below the

ACGIH recommendation of 0.1 ppm for an 8 hour day time-weighted average over a 40 hour week would provide an adequate margin of safety for the tumorigenic potential of hydrazine.

Detection of a hydrazine odor (similar to that of ammonia) indicates a vapor concentration of 3-5 ppm which is well in excess of the allowable exposure limits.[9] When ventilation or a closed handling system is not feasible or when disposing of significant spills, inhalation hazards should be controlled by protecting personnel with a self-contained breathing apparatus. Cartridge respirators are not suitable for hydrazine.

Routine air monitoring should be an integral part of any hydrazine user's employee protection program. Sensory detection of hydrazine odors at 3-5 ppm is not adequate.[9] There are a number of commercially available air monitoring instruments and detection devices listed in Table IV. This information is not necessarily all inclusive and is not meant to be a recommendation for certain commercial products but an attempt to aid hydrazine users to develop necessary personnel protection programs. In addition, there are NIOSH and Air Force approved methods for determination of hydrazine compounds in air. These procedures are based on a measured volume of air being drawn through a tube containing an acid impregnated treated packing material to chemically react with the hydrazine. The sorbent is treated to desorb the hydrazine, and the concentration of hydrazine determined colorimetrically with p-dimethylaminobenzaldehyde or gas chromatography.

Use of proper protective equipment will prevent personnel contact by any of the three routes of contact; dermal, oral or inhalation. In addition to having proper protective clothing, proper care and observance of safety and cleanliness should be observed by all workers. An important way to minimize exposure to hydrazine is by using a closed handling system, whether in a batch or continuous unloading arrangement. Nitrogen padding or blanketing should be maintained to prevent air oxidation of the hydrazine, and to raise the lower explosive limit to 38% for nitrogen-hydrazine mixtures.

Handling Accidents

From time to time, accidents not involving personnel exposure may happen such as spills or fires where hydrazine may be nearby and emergency action is clearly necessary. All spills should be immediately washed down with large volumes of water to prevent exposure and then neutralized prior to discharge. Water in large quantities is the recommended method for fighting fires involving hydrazine. A coarse spray is most effective, since it gives an immediate surface dilution effect. In addition to extinguishing the fire, a coarse water spray will cool adjacent drums and at the same time dilute the exposed solution to a less hazardous concentration, in terms of a inhalation or fire hazard. If clothing is involved, douse with water followed by immediate removal of any contaminated clothing.

Waste hydrazine from spills or process effluent presents a problem of neutralization prior to discharge. Dilute aqueous hydrazine solutions will react with the dissolved oxygen in water and will eventually consume all of the hydrazine, producing only nitrogen and water. Use of a dilute oxidizer solution will speed up the neutralization reaction. An aqueous solution (5% or less) of sodium hypochlorite or calcium hypochlorite (prepared from swimming pool dry chlorinator) or dilute hydrogen peroxide may be used as illustrated in Table V. All neutralizations must be carried out using very dilute solutions (5% or less). To insure neutralization, the discharge can be monitored for residual hydrazine using a standard boiler water test kit utilizing the p-dimethylamino benzaldehyde reagent. If an available chlorine oxidizer had been used then one could measure residual chlorine to insure neutralization. Finally hydrazine should be disposed of in a manner approved by appropriate Federal, state and local regulatory agencies.

Conclusion

Hydrazine, along with many other industrial chemicals, is classified as a hazardous material. It is reactive, the property which makes it an effective propellant, chemical intermediate and oxygen scavenger, but it is toxic. Therefore, it is necessary to protect the operator to avoid skin contact, ingestion and to provide adequate ventilation. It is also necessary to store hydrazine properly, avoid contact with heat. Like any other industrial chemical, reasonable precautions permit hydrazine to be stored, handled and dispensed safely. The successful preparation and use of hydrazine for boiler water treatment and for the government's space programs for almost 30 years is testimony to the fact that hydrazine can be handled safely on a daily basis.

TABLE I

HYDRAZINE PHYSICAL PROPERTIES

Solution Strength

Property	35%	64%	70%	AH	MMH	UDMH
Density gm/ml	1.0207	1.032	1.029	1.004	0.874	0.784
Freezing Pt. ^{o}C (^{o}F)	-65 (-85)	-51.7 (-61)	-56 (-68.8)	2.0 (35.6)	-52.4(-62.3)	-57.2(-71)
Boiling Point ^{o}C @ 760 mmhg (F^{o})	1.09.4 (228.9)	120.1 (248.2)	120 (248)	113.5 (236.3)	87.5 (189.5)	63 (146)
Flash Point ^{o}F (COC)	NONE	161	150	125	70.0	5

TABLE II

PERSONNEL PROTECTION

Clothing and Equipment	Materials
Protective Suit (or apron)	Butyl Rubber
Face Shield	Plastic
Hard Hat	Plastic
Goggles	Chemical Safety Type
Gloves	Butyl Rubber
Boots	Butyl Rubber
Respirator	Self-Contained Air

TABLE III

CURRENT EXPOSURE LIMITS

		Hydrazine	MMH	UDMH
OSHA	Current Standard	1 ppm	.2 ppm	.5 ppm
NIOSH	Recommendation	0.03 ppm	.04 ppm	.06 ppm
ACGIH	Recommendation	0.1 ppm	.2 ppm	.5 ppm

TABLE IV

HYDRAZINE MONITORING EQUIPMENT & PRACTICES

Monitoring Practice	Method	Equipment
Area	Absorbtion	Bendix/Gastec
Area/Personnel	Dry Agent	MDA Scientific Glenview, IL
Area	Adsorbtion	MSA Pittsburgh, PA
Area/Personnel	Adsorbtion	National Draeger Pittsburgh, PA
Area	Electrochemical Voltammetric Sensor	Interscan Chatsworth, CA
Area/Personnel	Absortion Colorimetric Gas Chromatography	NIOSH S237 NIOSH P & CAM 248
Personnel	Colorimetric Badge	American Gas & Chem Northvale, NJ

TABLE V

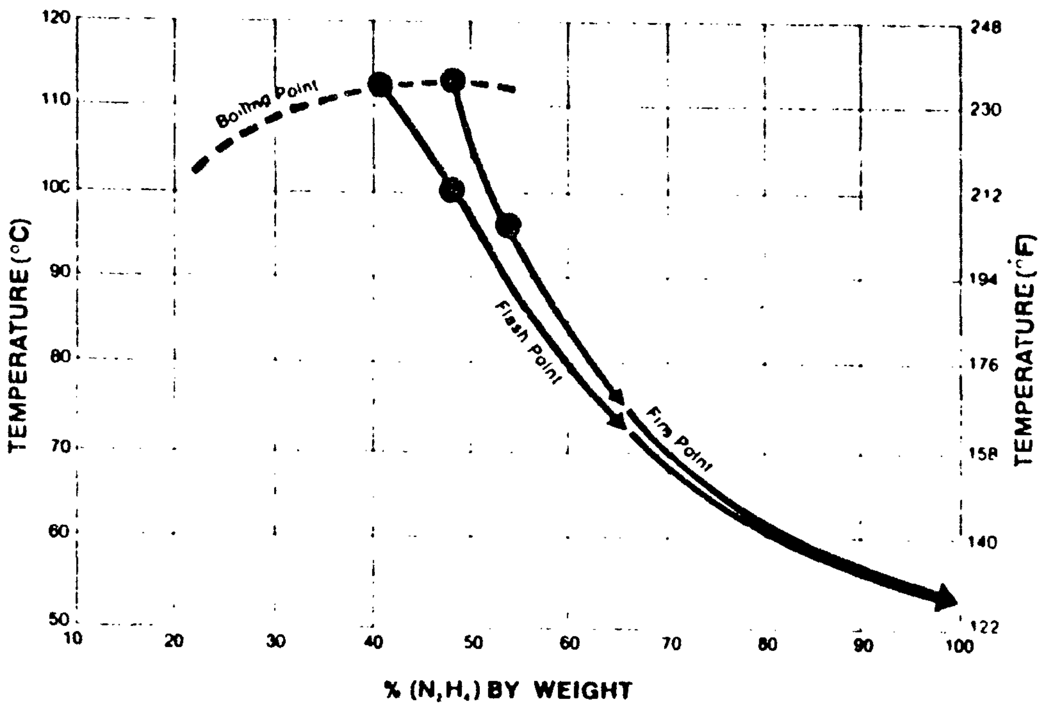
RECOMMENDED NEUTRALIZING AGENTS FOR SPILLS

The Wash Solutions should be diluted to
1- 5% N_2H_4, Prior to Neutralization

Reagent	Reaction Products	Heat Evolved KCAL/Mole N_2H_4
Water	$N_2H_4 \times H_2O$	3.9
Cl_2	N_2, HCl	160
Calcium hypochlorite	N_2, $CaCl_2$	177
H_2O_2	NH_3, N_3H	91-121

Neutralization should be complete before waste is discharged to sewer. Follow Local and Federal Regulations concerning liquid discharges from your plant site.

FIGURE I



Open Cup Flash & Fire Points For
Aqueous Hydrazine Solutions Using
ASTM Open Cup Method (D92-46)
With A Glass Cup

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