SAFETY AND HANDLING OF HYDRAZINE SOLUTIONS

Hydrazine is a versatile chemical, used in many industrial applications such as the production of chemical blowing agents, pharmaceutical and agricultural intermediates, urethane coatings and in boiler water treatment. Like any chemical, hydrazine should be handled carefully. In order to aid in properly handling and storing hydrazine, the following is presented to assure the customers safety.

Why Aqueous Hydrazine?

Hydrazine (N_2H_4) is generally sold in solution rather than anhydrous form. This reduces the hazards associated with handling, storage and processing of the anhydrous form. Hydrazine solutions are commercially available from Arch Chemicals in a range of concentrations suitable for most applications. This brochure provides the basic information to enable a potential user to evaluate the commercial aspects of handling, storing and using hydrazine solutions.

Properties of Aqueous Hydrazine

Chemical Properties

The most active chemical properties of hydrazine are its basicity, its readiness to react with oxidants, and its reactivity with organic compounds, which are evidenced by the large number of derivatives reported in trade journals and patent literature. Books on this subject have also been published.

As a base, hydrazine is weaker than ammonia. However, you can prepare more concentrated solutions of aqueous hydrazine than you can of ammonia. Since hydrazine solutions behave as fairly caustic liquids, appropriate precautions should be taken. Care should also be taken when neutralizing hydrazine solutions with strong acids.

Hydrazine solutions will attack rubber and cork and slowly leach silica from glass vessels if stored in them for periods of years.

A powerful reducing agent, hydrazine reacts with a variety of oxidants including many metal oxides, certain metal salts in their aqueous solutions, and atmospheric oxygen. Therefore, some loss of hydrazine can occur if solutions are stored under conditions that permit entry of air.

Hydrazine solutions are stable under normal storage conditions if contact with air, oxidizing or catalytic agents and impurities is avoided. Decomposition of hydrazine is caused by elevated temperatures and/or the presence of catalytic surfaces or ionic impurities. When hydrazine decomposes under these circumstances, the products formed are either nitrogen and ammonia, or nitrogen, ammonia and hydrogen, depending on the catalyst. In contact with air, the reaction products are nitrogen, ammonia and water.

Hydrazine in the vapor state is subject to auto-decomposition from catalytic effects or high energy excitation, such as an electric discharge or spark. In the case of pure or concentrated hydrazine vapor, the rate of auto-decomposition is rapid enough to cause an explosion. Thus, the upper explosive limit of hydrazine is defined as 100% N_2H_4. However, the rate of auto-decomposition is retarded when hydrazine vapors are diluted with substances which absorb a part of the energy Water vapor mixed with hydrazine has such a retarding effect. Other vapor diluents such as heptane also have a retarding effect. If a vapor diluent is used, care must be taken to ensure that reactions between hydrazine and the diluent, or the decomposition products of either, do not increase the hazard of an explosion.

Although hydrazine may exist as the monohydrate in water solutions, all of the hydrazine is readily available for chemical reaction.

Physical Properties

Pure hydrazine is a colorless, highly polar liquid with a slight ammonia-like odor. It is miscible with water in all proportions and these solutions are highly alkaline the more important properties of commonly available hydrazine solutions are listed in our Technical Data Sheet on Hydrazine.

Hazards of Hydrazine Solutions

Certain precautions must be observed in handling hydrazine solutions. These precautions require recognition of (1) the toxic and corrosive characteristics of hydrazine, (2) its ease of oxidation, and (3) the need to avoid conditions which can lead to rapid decomposition.

Toxicity

Hydrazine can he absorbed into the body in harmful or fatal amounts by ingestion, skin contact, or inhalation. Contact with the skin, eyes and respiratory tract can cause severe irritation and/or burns. Hydrazine may cause dermal sensitization.

Exposure to large single doses, or small repeated doses of hydrazine may cause death, temporary blindness, dizziness, nausea, cyanosis, and damage to internal organs. Damage may occur to the central nervous system and/or to such organs as the liver, kidneys, lungs, and those organs that form the blood. Hydrazine has been shown to cause cancer in laboratory animals. It is considered a suspect carcinogen in humans. High concentrations of hydrazine have caused embryo lethality and fetal malformation in laboratory animals.

For complete, up-to-date information, obtain and read the current Material Safety Data Sheet for the hydrazine product used. To order an MSDS, contact Arch Chemicals at the address listed on the back cover of this brochure.

Fire

It has been determined by using ASTM procedures that aqueous solutions below 40% N_2H_4 have no flash or fire point. However, as the concentration of hydrazine increases, the flash point decreases from about 113°C (235°F) at 40% concentration to about 52°C (126°F) for anhydrous hydrazine.

Since hydrazine is miscible with water, the use of water in fighting a fire involving hydrazine not only cools the flame but also dilutes the hydrazine to a point where it will no longer support combustion.

Hydrazine in liquid form, even anhydrous hydrazine, is very stable and insensitive to shock. However, hydrazine vapors can present a hazard and precautions must be taken to avoid their auto- or catalytic decomposition, such as might be induced by flame or spark.

Hydrazine is a strong reducing agent, as well as a base. Therefore, it should not be stored near organic materials, oxidizing agents or acids. These include sawdust, rags, hydrogen peroxide, sodium hypochlorite solution (bleach), halogens such as chlorine, fluorine, and bromine; and fuming nitric acid. Contact with metal oxides such as iron, copper, lead, manganese and molybdenum should be avoided. Contact with any of these oxidizing agents can result in immediate ignition followed by an explosion due to rapid gas formation. 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 lack of reactivity 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 109°C to 112°C (228°F to 234°F). Exposure of all hydrazine solutions to direct sunlight or to high temperatures should be avoided.

Personnel Protection

Persons handling aqueous solutions should wear protective equipment: apron or protective suit, chemical safety goggles and/or face shield, and butyl rubber gloves and boots . Butyl rubber is the material of choice when handling hydrazine. Other compatible materials for protective clothing include: Neoprene[1], nitrile rubber and polyvinyl chloride.

Protective clothing and equipment should be worn whenever the potential exists for contact with hydrazine. This includes:

1. Opening drum plugs or tank truck manway covers.
2. Connecting and disconnecting lines.
3. Placing pumps into drums.
4. Operating manual pumps.
5. Starting and stopping electrical pumps where the switches are near the pumps.
6. Breaking hydrazine piping, even if previously decontaminated.
7. Flushing out empty drums.

[1] Trademark of E.I. du Pont de Nemours, Inc.

Workers should change into clean working clothes each day. If hydrazine is spilled or splashed on articles of clothing, they should be removed immediately and laundered before reuse. Leather shoes should not be worn when handling hydrazine since hydrazine cannot be removed from leather. If hydrazine should be spilled on leather shoes, remove them immediately and discard.

Dilute aqueous solutions of hydrazine are capable of releasing hydrazine vapors to the surrounding atmosphere. Because of the toxicity of hydrazine vapors, care should be taken to assure adequate local exhaust ventilation whenever hydrazine is handled in open containers.

Ventilation in areas where hydrazine is handled should be adequate to limit the vapor concentration of hydrazine to values below the current Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) for hydrazine, which is 1.0 part per million as an eight-hour time-weighted average (TWA) with a skin designation. The American Conference of Governmental hygienists (ACGIH) has established an 8 hour threshold Limit value (TLV) for hydrazine of 0.01 ppm, with a skin designation.

Detection of a hydrazine odor (similar to that of ammonia) indicates a vapor concentration of 3-5 ppm that is in excess of the allowable exposure limits. If hydrazine odors are detected, control measures should be taken immediately.

When ventilation is not feasible, or when disposing of significant spills, inhalation hazards should be controlled by protecting personnel with a NIOSH/MSHA approved positive-pressure supplied-air respirator. Follow the OSHA regulations for respirator use (See Title 29, Section 190.134, Code of Federal Regulations).

First Aid

Ingestion: Drink large amounts of water immediately induce vomiting by sticking finger down throat. Call a physician immediately

Eye Contact: Wash with gently flowing water for at least 15 minutes. Call a physician immediately

Skin Contact: Immediately flush with water for at least 15 minutes. Follow by thorough soap and water washing. Call a physician immediately

Inhalation: Remove victim to fresh air. Call a physician immediately

For complete, up-to-date information, obtain and read the current Material Safety Data Sheet for the hydrazine product being used. To order an MSDS, call 1-800-511-MSDS.

Spill and Leak Procedures

Wear a NIOSH approved full-face positive-pressure supplied-air respirator or self-contained breathing apparatus. Follow OSHA regulations for respirator use (See Title 29, Section 1910. 134 Code of Federal Regulations). Wear chemical safety goggles, butyl rubber gloves, boots and slicker suit.

Remove all sources of ignition. Isolate area of spill by diking. Stop source of leak. Transfer contents to a non-leaking container or storage vessel.

Neutralize spilled hydrazine by diluting with water to a 5% or less solution. Add an equal volume of 5% calcium hypochlorite aqueous solution. Test for neutralization. After neutralization, transfer material to appropriate DOT container for proper disposal. Wash all contaminated clothing before reuse. Discard any contaminated leather articles.

In the event of a large spill, call the Arch Chemicals Emergency Action Network at (800) 6546-911.

Storage and Handling

Materials of Construction

The selection of proper materials of construction for use with hydrazine is necessary not only to prevent the hydrazine solution from attacking the materials, but also to avoid decomposition of the hydrazine or contamination of the hydrazine solution with impurities.

It has also been found that some materials which have proven satisfactory for use with hydrazine at one concentration may become unsuitable at another concentration. Compatibility of materials with several concentrations of hydrazine is found in the hydrazine technical data sheet.

Due to the complexity of the factors involved, it is only possible to offer general comments about the selec-

tion of materials of construction. It is recommended that each application is reviewed and tests conducted to ensure proper selection of materials of construction.

Materials generally considered satisfactory for all ranges of concentrations are type 304L and 347 stainless steels with less than 0.5 wt.% molybdenum as well as high density polyethylene.

Safety Practices

Care must be exercised to prevent explosive conditions either in storage or processing. As previously stated, hydrazine in the vapor state might represent a hazard under certain conditions. To minimize hazardous conditions and maintain integrity of strength, a padding of nitrogen gas should be maintained in process equipment and storage vessels. Hydrazine solutions should be transferred by a pump made of an appropriate material or by pressurizing with nitrogen at a safely regulated pressure.

Storage

Hydrazine can be stored without adverse effects, either to the container or to the product, when proper materials of construction are used. All systems should be cleaned thoroughly before introduction of the hydrazine, and a nitrogen atmosphere should be maintained over the system at all times.

For general storage, the approved container for transporting hydrazine can be used. For extended bulk storage, stainless steel tanks, piping and valves should be employed.

Hydrazine should be stored in easily accessible areas, with good natural drainage and prevailing wind. A large water supply should be nearby

Do not store near combustible materials. Storage areas should be isolated from oxidizing materials and operating areas. Storage tanks should be properly diked to contain any major spills.

Design Criteria

To maintain safe operating conditions, several design criteria are recommended.

Level gauges. Bubbler-type (using nitrogen gas) liquid level gauges should be used to eliminate the possibility of hydrazine spillage. Sight glass gauges can be used, but they should be equipped with excess flow valves. A magnetic-type level gauge can also be used.

Pressure requirements. Storage and transfer systems should be designed to safely withstand pressure up to 35 psig. Systems must be hydrostatically tested before being put into operation.

Vacuum and pressure relief system. Storage tanks should be provided with a seal pot in connection with a gas wash bottle and trap to provide the tank with a means of "breathing". The depth of water (about 14 inches is generally recommended) maintained in the seal pot will effectively establish the padding pressure. The line to the seal pot can be closed when higher nitrogen pressure is needed for transferring hydrazine from tank to process. Protect the seal pot from freezing.

Joints. Welded fittings are preferred and should be used whenever possible. Threaded fittings are not generally satisfactory for hydrazine service. They tend to leak unless back-welded. When screwed joints are mandatory Teflon ribbon dope can be used.

Valves. The selection of valves for use with hydrazine involves certain design requirements, but generally these requirements are not as stringent or critical as for many other solutions. As a rule, any valve design acceptable for handling other more common liquids can be employed successfully with hydrazine if compatible materials of construction are used. Leakage cannot be tolerated in valves handling hydrazine.

Any quality relief valve with good relief-reseat characteristics and bubble-tight shutoff upon reseat can be used. Valves should be constructed of special stainless steel with suitable seating materials.

Gaskets. Gaskets of fully-sintered annealed Teflon[2], polyethylene (within its temperature limits), and type 304L stainless steel spiral-wound (Flexitallic[3], Spirotallic[4] or equivalent) are preferred.

Water Supply. An adequate nearby water supply should be available to wash down any accidental spillage. In areas where there is a possibility of spillage, such as unloading and handling points, it is good practice to install a sprinkler system operated by both local and remote con-

trols. Hoses supplying a heavy stream of water should be provided for flushing down spills or extinguishing fires.

Explosion-proofing. To guard against the possibility of igniting an explosive mixture of hydrazine vapor and air, such as might be formed when spillage is not immediately recognized and flushed, several precautions should be taken. Buildings which house equipment for handling or processing hydrazine should be well ventilated to prevent accumulation of hydrazine vapors. All electrical equipment in areas where hydrazine vapors may be present must be explosion-proof (All metallic apparatus
must be grounded and bonded to prevent the possibility of sparking.)

Emergency equipment. Safety showers and eyewash fountains should be provided to permit immediate treatment of personnel in case of accidental contact with hydrazine. A NIOSH approved positive-pressure supplied-air respirator should be available if it is necessary to enter an area containing hydrazine vapors.

Area drainage system. Waste hydrazine from spills or process effluent should not be allowed to enter a common sewer or stream. Hydrazine is an avid oxygen scavenger which will reduce the dissolved oxygen content of water on a pound-for-pound basis. All drains which contain hydrazine should lead to a sump or holding pond where the hydrazine may be destroyed.

Destruction. Destruction should be carried out in very dilute solutions (5% or less). A water solution of sodium hypochlorite [NaOCl], calcium hypochlorite [$Ca(OCl)_2$] or hydrogen peroxide [H_2O_2] can be used for destruction (see Waste Disposal below for recommended procedure). Aeration may be used, but it is seldom practical.

Waste Disposal/Destruction

Hydrazine should be disposed of in a manner approved by federal, state and local regulatory agencies. They should be consulted to ascertain the proper disposal procedures.

If the destruction of hydrazine from spills or process effluent is necessary the following is recommended: Sodium hypochlorite diluted to less than 5% available chlorine (approximately 5 wt% in water) is recommended for spill treatment. The reaction between sodium hypochlorite and hydrazine yields nitrogen, water and sodium chloride. To avoid excessive heat generated in the reaction, hydrazine should be diluted to less than 5% prior to treatment.

Drains from areas of hydrazine handling should lead to a sump or holding pond where hydrazine can be destroyed in a very dilute solution.

Two moles Of NaOCl are required per mole of N_2H_4:

$$N_2H_4 + 2NaOCl \longrightarrow N_2 + 2H_2O + 2NaCl$$

On a 100% weight basis, 4.7 lbs. of NaOCl are required per pound of hydrazine. A calculation must be made based on the relative strengths of NaOCl and N H~ used to determine the exact charges. Excess NaOCl should be added to insure complete destruction. The optimum pH range for this reaction is 5-8.

Commercial calcium hypochlorite (e.g. HTH® dry chlorinator) containing 65% available chlorine can also be used. The chlorine content is roughly 5 times that of industrial strength bleach. Care must be taken to insure that a dilute solution of 5:1 water and calcium hypochlorite be used. Never add dry powdered calcium hypochlorite to hydrazine because a serious, flame-generating heat evolution may result

A dilute solution of hydrogen peroxide may also be used to decompose dilute hydrazine wastes. Two moles of hydrogen peroxide are required per mole of hydrazine. A slight excess over this amount of peroxide is recommended to ensure complete destruction of the hydrazine. The addition of a trace amount of copper sulfate will catalyze the reaction, causing it to proceed more rapidly.

Cleaning

Before filling any system with hydrazine, make certain that it is clean and free from scale or other contaminating materials. Cleaning can be achieved by sandblasting, pickling with dilute inhibited acid, or by alkali clean-

[2] Trademark of E. I. du Pont de Nemours, Inc.

[3] Trademark of Flexitallic Gasket Company

[4] Trademark of Johns Manville Corporation

ing, followed by a water wash. If the system is such that the hydrazine will be subjected to elevated temperatures, pickling should be followed by a water wash and the system should be filled with a 10% solution of hydrazine. The system should then be heated above the expected operating temperature to ensure reduction of any oxidizing material present. All cleaning procedures should end with a rinse with 10% hydrazine solution.

Weldments must be carefully polished and cleaned to remove the heavy oxidation.

Shipping Information

Global DOT Regulations

Aqueous hydrazine solutions are manufactured at the Arch Chemicals facility in Lake Charles, Louisiana.

Aqueous hydrazine solutions are regulated by the Global Transport Regulations and are therefore considered to be dangerous goods.

U.S. DOT Regulations

The U.S. DOT Hazardous Material Regulations in 49 CFR 172.101, Appendix A lists "hydrazine" as a hazardous substance with a reportable quantity (RQ) of 1-lb. If a hazardous material is also a hazardous substance under U.S. DOT regulations, "RQ" must be indicated as part of the proper shipping name and description if a package contains the RQ or greater. The designation of hazardous substance is a U.S. transport requirement only; the objective of the requirement is for environmental protection.

Hydrazine aqueous solutions from 15.5% to 37%, in transport, must indicate a primary hazard classification of toxic (hazard division 6.1). There is no subsidiary hazard class designation.

Hydrazine aqueous solutions from 38% to 70%, in transport, must indicate a primary hazard classification of corrosive (hazard class 8) and subsidiary hazard classification of toxic (hazard division 6.1).

Hydrazine solutions are shipped via following transport modes: highway, rail, air and ocean vessel. Product is shipped in bulk (>119 gallon receptacle) and non bulk packagings.

The following types of containers are available.

For 64%, 54.4% and 51.2% solutions:

- 345-gallon returnable stainless steel small bulk tank
- 180-gallon returnable stainless steel small bulk tank
- 55-gallon non-returnable EZ ™ Drum plastic container
- 55-gallon non-returnable plastic drum

For 35% or less solutions:

- 345-gallon returnable stainless steel small bulk tank
- 180-gallon returnable stainless steel small bulk tank
- 55-gallon non-returnable E-Z Drum plastic container
- 55-gallon non-returnable plastic drum
- 30-gallon non-returnable plastic drum
- 6-gallon pails

All concentrations are also available in tank truck quantities. Prior to shipment, hydrazine aqueous solutions are properly packaged, labeled, marked, described, placarded, etc. in accordance with applicable transport regulations.

Unloading Hydrazine

Precautions When Unloading Drums or Tanks

- Always wear protective clothing and equipment, as previously described, when unloading drums and tanks.
- Before unloading, the eductor pipe, hoses, pump, etc. must be clean. It is recommended that the equipment be dedicated for hydrazine.
- The material of construction of the unloading equipment should be limited to polyethylene, Teflon, 304L SS (< than 0.5 wt% Mo) or 316 SS, when at all possible. Propylene fittings or valves are also suitable.
- Use explosion-proof electric devices or air-operated devices. Arch Technical Service can be contacted to help answer any hydrazine concerns.

Drum Handling Procedure

Arch recommends using an E-Z Drum system to unload hydrazine drums. The primary components of the E-Z Drum system are a special dip-tube-equipped, non-returnable drum and a unique dispensing head attachment. Remove the dip-tube's protective cap, align the dispens-

ing head and tighten. Connect the tubing outlet of the dispensing head and tighten. Connect the tubing outlet of the dispensing head to the suction of the self-priming pump and you are ready to transfer hydrazine.

When the drum is empty, disconnect the dispensing head and reconnect to a full drum. A check valve in the product line helps prevent hydrazine Leaks and drips while switching drums.

The system is simple and effetive. As always, appropriate personnel protection equipment must be worn when handling hydrazine. Consult Arch Chemicals' MSDS and product literature for complete handling information. For more information, including a video describing the E-Z drum system, call 1-800-654-6018.

Hydrazine can also be unloaded similarly to other chemicals that you handle. The precautions that should be adhered to when unloading hydrazine are:

- Dedicate the equipment used to empty hydrazine drums.
- Once hydrazine drums have been exposed to air, they should be re-padded with nitrogen.

Unloading Small Bulk Tanks

The following steps should be taken to safely unload Arch 345- and 180-gallon stainless steel tanks:

- Dedicate the pump, hoses, etc. only to hydrazine.
- Apply a slight nitrogen purge (< 1 psi) when emptying the tank to prevent air leakage into the container.
- Do not move tank while unloading.
- If a sight glass gauge is used, it should be constructed to insure against breakage that would cause a spill of hydrazine. A magnetic-type level gauge is recommended.
- Do not use pressure to unload tank.
- Do not rinse the tank when empty. Just close all valves and replace all caps and valve handles and then return tank to Arch.
- A positive displacement pump should be used which will totally evacuate hydrazine from the hose prior to disconnecting (insure that a nitrogen purge is applied).
- The tank should be grounded.

In Case of Emergency

For help with emergencies involving Arch products, we have developed an emergency network that can be reached 24 hours a day by dialing 1-800-6546-911.

After you've provided some basic information (your name, location, telephone, reasons for requesting assistance, products involved) you'll be asked to stand by your phone and await a call from a technical expert or Response Team Leader who is experienced with hydrazine and knows its properties and characteristics. He will be able to advise you on immediate action to be taken and on how to deal with almost any emergency.

In addition, the Chemical Manufacturers Association has established CHEMTREC to give advice on emergencies involving transportation and transportation equipment.

The CHEMTREC number is 800-424-9300. (In Washington, D.C., call 483-7616).

Please refer to the Material Safety Data Sheet (MSDS) for complete information on Storage and Handling, Toxicological Properties, Personal Protection, First Aid, Spill and Leak Procedures, and Waste Disposal. To order an MSDS, call the Arch Chemicals sales office listed below or MSDS Control at (800) 511-MSDS. Before using or handling this product, the MSDS should be thoroughly reviewed.

Sales Office: 960 I-10 Service Rd., Westlake, LA 70669 (337) 430-4023