V. WORK PRACTICES

The recommended work practices for hydrazines are formulated by considering the nature of their industrial applications and their chemical, physical, and toxicologic properties, from information obtained from various sources [2,192-197], and from plant visit observations [28]. Generally, work practices adopted for hydrazine, 1,1-dimethylhydrazine, and methylhydrazine have been similar [2].

Toxicologic data discussed in Chapter III established that these hydrazines present hazards from both inhalation and skin or eye contact. From the standpoint of acute toxicity, methylhydrazine is the most toxic of the hydrazines [2,20,96,110,111]. Eye damage may depend on the basicity of the hydrazines, and if so, hydrazine would cause the most severe effect if contact occurs. When one considers vapor pressures of the various hydrazines, given in Tables XI-1 to XI-5, it can be seen that 1,1-dimethylhydrazine vapors have the greatest potential to escape into workroom air.

Although specific information on work practices for 1,2-dimethylhydrazine and phenylhydrazine was not found, the information on toxicity and chemical properties indicates that recommendations based on information available for the other three hydrazine bases should be adequate for all five compounds and their salts.

So far as is known, the salts of the hydrazines are not flammable or combustible, but all the free bases are flammable or combustible as liquids and present both fire and explosion hazards as vapors [2,195]. 1,1-Dimethylhydrazine, with a vapor pressure of about 120 mmHg at 70 F, a

flashpoint of 34 F, and flammability limits in air from 2 to 95% (v/v) at normal temperatures, presents the greatest fire hazard. Hydrazines may react explosively with some oxidizing agents, such as fuming nitric acid or nitrogen dioxide, and great care must be exercised when circumstances require handling of such combinations together, such as in rocket operations. Because of these hazards, extreme precautions must be taken in the manufacture, handling, transport, storage, and use of these compounds. Where a potential for fire or explosion exists, adequate procedures for emergency exit and reentry, decontamination of spills or leaks, firefighting, and storage are especially important. Potential sources of sparks and open flames must be prohibited where there is a fire or explosion hazard.

In all situations where hydrazines are present, engineering controls should be designed to maintain concentrations in the worker's breathing zone at or below the recommended limits, and work practices should be implemented to prevent eye and skin contact.

Storage, Handling, and Transport

The recommended procedures for safe storage, handling, and transport of hydrazines are based on an understanding of their toxicity, ease of oxidation, and flammability. Glass bottles, drums, and tank cars constructed of proper material have been used for storing or transporting hydrazines [194]. According to a bulletin prepared by Olin Chemicals [1], each drum should have a 3/4-inch and a 2-inch screw-type closure in the top head, sealed by a polyethylene gasket. The drums may be emptied with a small gear pump, sparkproof as necessary, or by nitrogen pressure. When nitrogen pressure is used to unload hydrazines, nitrogen should be supplied

at a pressure of 3 or 4 psig. When a pump is used, nitrogen should be supplied at 0.4-0.5 psig.

For storing large quantities of hydrazines, the Air Force [193] and FMC Corporation [194] have recommended using horizontal cylindrical tanks kept under slight pressure with nitrogen or other inert gases. Each tank should be electrically grounded and fitted with a fluid-inlet connection, level gauge, pressure gauge, rupture disc, relief valve, and a flame arrestor at its top. Rupture-disc discharge should be directed so that no working areas will be contaminated. A top outlet with sump and dip-leg should be used to eliminate leakage [193]. Large horizontal tanks should be mounted on reinforced-concrete saddles, and vertical tanks should be set on concrete pads. Drums should be stored on concrete pads with low curbs to control drainage [193]. Before drums are emptied, the drums and other equipment used in the operation should be electrically bonded and grounded [194].

Hydrazines should be stored at temperatures well below their respective boiling points, away from ignition sources and oxidants, and preferably outdoors. Containers of hydrazines stored outdoors should be sheltered against direct sunlight, dirt, snow, water, and ice accumulation [194,196]. Within inside storage areas, continuous ventilation should be provided [193,196]. Major storage facilities should be diked with concrete to hold at least 110% of the total storage capacity and have a concrete slab below the storage tank [193], so that the spilled hydrazines will not be soaked up by the ground. The diked area should be kept clean, and the diking system should drain to a burn basin, a collection basin, or reclamation sump [193]. The Air Force [193] has published quantity-

distance tables to be used as guidelines in determining proper tank locations within storage areas. Entrances to the storage area should be properly posted, and all containers should be properly labeled.

Materials of Construction

Materials used in equipment that contains or directly contacts hydrazines have been selected mostly on the basis of their effects on the purity and decomposition of the hydrazines. Cloyd and Murphy [2] recommended certain materials for use with hydrazine and methylhydrazine. The US Advisory Panel on Fuels and Lubricants [192] also prepared lists of materials that are compatible with the three hydrazines used as rocket fuels. These recommendations are shown in Table V-1. Other recommendations made by the Air Force [193] and the FMC corporation [194] are also listed in the table.

Equipment Cleaning

Surfaces that will be in contact with hydrazines should be cleaned to limit the introduction of impurities and potential decomposition. In this regard, the Air Force [193] has established recommended procedures for cleaning all systems and component parts. Cloyd and Murphy [2] recommended that, before any stainless steel part is to be used with the hydrazines, it should be descaled by etching with an aqueous solution of 3-5% hydrofluoric acid and 15-20% nitric acid for approximately 1 hour. The component should be made chemically inert; for stainless steel, this may be done by immersion in 50% nitric acid for 30 minutes. Plastics can be cleaned with a 4% detergent solution for 30 minutes at 120 F [193].

TABLE V-1

MATERIAL COMPATIBILITY WITH HYDRAZINE COMPOUNDS

Compatible with Hydrazine and Methylhydrazine

Aluminum Alloy Nos. 356, B356, 1100, 2014, 2024, 4043, 5052, 6061, 6066, and Tens 50	Inconel and Inconel-X
Chromium plating	Sinclair L743
Dow Corning Number 11	Kel-F and polyethylene
Graphite	Stainless Steel 304,321,347, and 1707 PH
	Teflon

Not Compatible with Hydrazine and Methylhydrazine

Carbon steel	Johns-Manville Packing No. 76
Copper	Nickel
Iron-Base Superalloy A-236*	Stainless steel AM-350* and AM-355*

Not Compatible with Methylhydrazine

Lead	Monel
Hastelloys	Zinc
Iron	

Compatible with 1,1-Dimethylhydrazine

Aluminum and its alloys	Mylar A
Hydropol OT Plastic	Nickel
Kel-F and polyethylene	Silicone rubber AMS 3305
Mild steel	Teflon
Monel	Graphite
Stainless steel types-303,304 321,347	

Not Compatible with 1,1-Dimethylhydrazine

Copper and its alloys	Isocyanate polyester
Phenolic resin	Phenolic-asbestos plastic
Polyvinyl alcohol polymer	Vinylchloride-vinylidene copolymer
Cellulose acetate butyrate	Organic polysulfide
Vinyl chloride-acetate copolymer	

*Contains over 0.5% molybdenum; should not be used with hydrazine or methylhydrazine at temperatures above 160 F

Adapted from references 2,192-194

Special precautions are necessary for entering tanks or vessels that may contain the hydrazines to clean or perform flame- or spark-generating operations such as welding and cutting. Before any employee enters a vessel, all pipelines leading into or out of the vessel must be blanked to prevent the entry of hydrazines. The vessel interior should then be washed with water and purged with air or with nitrogen followed by air. After purging the vessel interior, trained personnel should test the vessel atmosphere with suitable instruments to ensure that no hazards from fire, explosion, oxygen deficiency, or vapor inhalation exist. No one should enter a tank or vessel without first being equipped with an appropriate respirator (if necessary) and a secured lifeline and harness. Mechanical ventilation should be provided continuously when workers are inside the tank. At least one other worker should watch at all times from outside the vessel. This worker should be equipped with similar respiratory protection and secured lifelines and harnesses. An effective communication system should be established between workers in the tank and those outside. Two additional employees should be available to assist in the event of an emergency. Cutting or welding may be performed only when an authorized representative of the employer signs a permit indicating that all necessary safety precautions have been taken..

Spills and Leaks

Spills and leaks may present hazards from inhalation, skin or eye contact, ingestion, and fire and explosion. Cloyd and Murphy [2] recommended the following basic design considerations to decrease the likelihood of these hazards:

(1) Reduce mechanical joints to a minimum.

(2) Consider maximum pressure in system design.

(3) Eliminate low-lying liquid traps wherever possible.

(4) Provide an inert gas purge system.

(5) Install high stack or scrubber for vent.

In the event of spills or leaks, a self-contained breathing apparatus and protective clothing should be worn during the cleanup operation [193]. All areas of operation involving hydrazines should have proper drainage systems so that leaks and spills can be flushed away immediately. For small quantities, spilled hydrazines can be flushed with water and collected in holding tanks [198]. Hydrazine will decompose to water, nitrogen, and ammonia by oxidation or by bacterial action. Hydrazines should not be discharged into the sewers or waterways, unless first decomposed. Dilute solutions of hydrazines, at concentrations less than 2%, can be collected in open containers and oxidized by adding 10% hydrogen peroxide, calcium hypochlorite, or household bleach [198]. Comparatively large quantities may be disposed of by burning under proper supervision. If leaks develop during transit, the spilled material should be washed away with water before the remaining materials are salvaged [193].

Fire and Explosions

The hydrazine bases are flammable or combustible. In aqueous solutions, hydrazine at a concentration higher than 50%, methylhydrazine higher than 50%, and 1,1-dimethylhydrazine higher than 25% are ignitable at normal temperatures [199]. Vapors of hydrazines are explosive in a wide range of mixtures with air, 4.7-100% for hydrazine, 2.5-92% for

methylhydrazine, and 2-95% for 1,1-dimethylhydrazine [9]. The lower limits for all but hydrazine can easily be reached in a confined space because of relatively high vapor pressures. To avoid the formation of such a mixture, and also to retard oxidation, an inert gas such as nitrogen should be used to blanket the hydrazine compounds in containers. Hydrazines can ignite spontaneously in air when in contact with porous materials such as earth, asbestos, wood, or cloth [9,193]. If these materials become soaked with hydrazines, they must be thoroughly wetted with water [1] before disposal. Rags should never be used to wipe up spills because of the danger of spontaneous ignition [29].

Buildings that house equipment for handling or processing hydrazines must be well ventilated to prevent the accumulation of vapors or aerosols. Automatic water sprinkler systems should be installed in these buildings to provide deluge water for fires and with an appropriate triggering device to dilute the concentrations of spilled hydrazines [1]. In an enclosed space, all personnel must be evacuated when the atmospheric concentration reaches 20% of the lower explosive limit [193] because of the imminent danger of fire and explosion. Oxidants such as hydrogen peroxide, nitric acid, and halogens should be kept away from storage areas for hydrazines because of the potential for spontaneous ignition.

When an explosion occurs in a closed vessel with nitrogen present, the pressure will increase 12-14 times. If air is present, even higher pressure will be generated [200]. All equipment used with hydrazines should have a working pressure sufficiently greater than the venting pressure to accommodate any pressure resulting from an explosion [196]. Processing or manufacturing equipment should be located away from open

flame, high temperatures, and congested areas.

Fire involving hydrazines may be supported either by air or by oxidants. Air-supported fires may be extinguished by diluting hydrazines with a quantity of water one to three times the original volume [193,194]. Applying water in a coarse spray is the most efficient method [193]. Water both cools and dilutes, and the diluted solution of hydrazines is nonflammable. For fires supported by oxidants, water may be used if it does not aggravate the situation with the specific oxidant involved. Dry chemicals and carbon dioxide may be used to extinguish both air- and oxidant-supported fires, but flooding with water will also be necessary to prevent reignition [9]. Chemical foam extinguishers are not recommended, because hydrazine compounds may deactivate the foam-forming surfactant and destabilize the foam [193,194]. Protective clothing and a self-contained breathing apparatus must be worn by any person involved in firefighting [9]. Advanced or large fires must be fought from a safe distance or from a protected location because of the explosion hazard.

Regulated Areas

Regulated areas must be established and maintained where hydrazines are manufactured, processed, stored, or otherwise used. To limit the number of employees exposed to hydrazines, only those persons needed for the job should be allowed access to these areas. A daily roster of the employees who enter the regulated areas must also be maintained along with environmental monitoring records for later reference. Signs warning of the hazards of entry into regulated areas must be prominently displayed.

Personal Protective Clothing and Equipment

Because hydrazine compounds are dermal irritants and can penetrate the skin to cause systemic toxicity, dermal exposure must be prevented. All hydrazine-processing equipment or systems should be designed to be as enclosed as possible. The immediate surrounding areas should be provided with ventilation to prevent the buildup of vapors or aerosols. Personal protective equipment for safeguarding the health of workers should not be used as a substitute for adequate engineering controls; however, where adequate engineering controls are impractical, personal protective equipment must be used. Workers in regulated areas must wear work clothing consisting of coveralls or any other combination of clothing that offers the same protection, hat or head covering, and shoes or shoe covering. If there is any possibility of spilling or splashing hydrazines, a plastic full-face shield (8-inch minimum) and goggles, rubber or plastic wrist and arm protectors, gloves, boots, and a rubber-type apron must be worn [193]. Gloves should be made of an impervious material such as natural rubber, reclaimed rubber, or vinyl-coated cotton, and footwear should be "fireman-type" rubber boots [193,194]. Whenever the splashing of hydrazines is likely, such as during loading, unloading, or transfer, impervious clothing must be worn. This clothing may be made of rubber, rubberized, or fiberglass material impregnated with a corrosion-resistant plastic or vinyl-coated cotton [193].

When it is necessary to work in an atmosphere in which the vapor or aerosol concentration exceeds the recommended environmental limits, approved respirators, as specified in Chapter I, must be used. In confined spaces or where concentrations of hydrazines may be high, a self-contained

breathing apparatus should be used [193]. The employer must establish a respiratory protection program in accordance with 29 CFR 1910.134 to ensure that clean and well-maintained respirators are available to employees required to wear them in the course of their work. In addition, workers who are required to wear respirators must be trained in their proper use and be able to know how to test them for leakage and proper fit and operation.

Safety showers and eyewash fountains must be installed in or close to storage and handling areas. Emergency exits must be provided and be accessible at all times. The water supply provided should be adequate for dilution, flushing, washing, decontamination, and firefighting. All emergency eyewash, shower, protective, and firefighting equipment should be checked periodically to ensure its serviceability.

Sanitation

Good sanitation and personal hygiene must be practiced to minimize the risk of exposure to hydrazines, especially by ingestion. Oral intake has been shown to be one of the routes by which hydrazines cause health effects [42,145]. Thus, food and beverage consumption, vending machines, and open smoking or chewing materials must not be allowed in any area where the hydrazines are manufactured, processed, stored, or otherwise used. A separate changing room, adjacent to such areas, with showers, washing facilities, and lockers that permit separation of street and work clothing should be provided for and used by employees working in regulated areas. Separate toilet facilities and designated smoking areas, if needed, must be provided adjacent to or near the changing room. When leaving the work

area, employees must wash their hands and face. After a spill or when exiting from regulated areas for the last time in a workshift, workers should place work clothing in a suitably marked and covered container for disposal or laundering prior to further use. Before the last exit from the regulated area and before changing into street clothes, the employee must shower. Work clothes should not be taken home, and the employer must provide for the laundering of the work clothes. Persons laundering the clothing must be apprised of the hazards from hydrazines.

Emergency and Decontamination

In case of accidental exposure, the exposed worker should be removed from the hazardous environment immediately and all contaminated clothing should be removed. The worker should then shower with water for 15 minutes; if the worker is unconscious, then emergency personnel should wash the worker's skin with water. If hydrazines have contacted the eyes, they must be flushed copiously with water [193]. Signs and symptoms of poisoning by the hydrazines include irritation of eyes, nose, and throat, dizziness, nausea, vomiting, and convulsions [196]. Medical assistance should be obtained if these signs and symptoms are present. Gross contamination must be taken off of protective clothing before removal from the wearer. Contaminated work clothes and protective equipment should be rinsed with water and stored in a container prior to being cleaned and decontaminated for reuse or final disposal. Equipment contaminated by hydrazines should be flushed thoroughly with a large volume of water or with diluted acid and dried before it is returned to service [194].

Laboratory Activities

When the hydrazines are used for research or quality-control purposes, several precautions should be taken. For this purpose, guidelines established by the National Cancer Institute as published in Safety Standards for Research Involving Chemical Carcinogens [201] should be followed.

Experiments that are conducted in an open hood should be in a hood with an average face velocity of 150 feet/minute or higher [191]. Glove boxes kept under a negative pressure of 0.5 inches water gauge or more or laminar flow biologic cabinets with the face velocity required in an open hood can also be used [201]. Discharge of exhaust air from laboratory-type hoods should comply with the appropriate Federal and local regulations. All work surfaces should be covered with material impervious to absorption or penetration by hydrazines. All pipetting should be performed with mechanical devices to prevent accidental ingestion of hydrazines. Contaminated wastes and animal carcasses should be collected in impermeable containers. These containers must be kept closed until being removed for disposal.