4. PRODUCTION, IMPORT, USE, AND DISPOSAL

4.1 PRODUCTION

For most uses, hydrazine is produced as hydrazine hydrate in a formulation with water. The hydrate may be produced commercially by three methods: the Raschig process, the ketazine process, and the peroxide process. The Raschig process, the original commercial production process for hydrazine, involves oxidation of ammonia to chloramine with sodium hypochlorite, then further reaction of the chloramine with excess ammonia and sodium hydroxide to produce an aqueous solution of hydrazine with sodium chloride as a by-product. Fractional distillation of the product yields hydrazine hydrate solutions. Currently, most hydrazine is produced by the ketazine process, which is a variation of the Raschig process. Ammonia is oxidized by chlorine or chloramine in the presence of an aliphatic ketone, usually acetone. The resulting ketazine is then hydrolyzed to hydrazine. In the peroxide process, hydrogen peroxide is used to oxidize ammonia in the presence of a ketone. Anhydrous hydrazine is the formulation used in rocket fuels and is produced by dehydration of the hydrate by azeotropic distillation with aniline as an auxiliary fluid (Budavari et al. 1989; IARC 1974; Schmidt 1988; WHO 1987).

1,1-Dimethylhydrazine is currently prepared commercially by a modified Raschig process: reacting dimethylamine with the chloramine produced from ammonia and sodium hypochlorite. Formerly, it was prepared by the reduction of dimethylnitrosamine or by the reductive catalytic alkylation of carboxylic acid hydrazides with formaldehyde and hydrogen, followed by basic hydrolysis (Budavari e al. 1989; EPA 1984a, 1992b; IARC 1974; Schmidt 1988). 1,2-Dimethylhydrazine may be prepared from dibenzoylhydrazine or by electrosynthesis from nitromethane (Budavari et al. 1989).

The two current chemical producers of hydrazine in the United States are the Olin Corporation in Lake Charles, Louisiana, and Miles Inc. in Baytown, Texas. The chemical was also produced by Fairmount Chemical Company, Inc., Newark, New Jersey, as recently as 1987. 1,1-Dimethylhydrazine is produced by Olin and Uniroyal Chemical Company, Inc., Geismar, Louisiana. Estimates of past production (based on anhydrous hydrazine, although most production was of the hydrate) indicate that U.S. production volume was about 7,000 metric tons (15 million pounds) per year in the mid-1960s and increased to 17,000 metric tons (37 million pounds) per year in the mid-1970s. Production

capacity in the United States was estimated at 17,240 metric tons (38 million pounds) in 1979 and about 14,000 metric tons (30 million pounds) in 1984, the most recent year for which information was located. 1,1-Dimethylhydrazine production volume was estimated to be at least 45 metric tons (99,000 pounds) in 1977 and more than 4.5 metric tons (9,900 pounds) in 1982 (HSDB 1995; Schmidt 1988; SRI 1987, 1988, 1992; WHO 1987). Information on current production volume is not publicly available for either hydrazine or 1,1-dimethylhydrazine (EPA 1991d).

Tables 4-l and 4-2 list information on U.S. companies that reported the manufacture and use of hydrazine and 1,1-dimethylhydrazine, respectively, in 1993 (TRI93 1995). The data listed in the Toxics Release Inventory (TRI) should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

4.2 IMPORT/EXPORT

There is some indication that hydrazine was imported into the United States from Japan during the 1970s (IARC 1974), but no data were located on past or current U.S. import or export quantities of hydrazine or 1,1-dimethylhydrazine.

4.3 USE

Hydrazine (anhydrous or as the hydrate) has numerous commercial uses. The principal current use for hydrazine is as an intermediate in the production of agricultural chemicals such as maleic hydrazide. It is also used as an intermediate in the manufacture of chemical blowing agents which are used in the production of plastics such as vinyl flooring and automotive foam cushioning, as a corrosion inhibitor and water treatment agent, as a rocket propellant, and, to a lesser extent, as a reducing agent, in nuclear fuel reprocessing, as a polymerization catalyst, as a scavenger for gases, and several other uses. It has also been used as a medication for sickle cell disease and cancer.

From the late 1950s through the 1960s the primary use of hydrazine was as a rocket propellant. In 1964, 73% of the hydrazine consumed in the United States was used for this purpose. By 1982, other commercial uses dominated the market; 40% of the hydrazine consumed was used in agricultural

Table 4-1. Facilities That Manufacture or Process Hydrazine

Facility	Location[a]	Range of maximum amounts on site in pounds	Activities and uses
OCCIDENTAL CHEMICAL CORP.	MUSCLE SHOALS, AL	10,000-99,999	As a chemical processing aid
HALL CHEMICAL CO.	ARAB, AL	10,000-99,999	As a chemical processing aid
OLIN CORP.	MCINTOSH, AL	10,000-99,999	In repackaging only
GREAT LAKES CHEMICAL CORP.	EL DORADO, AR	10,000-99,999	As a chemical processing aid
GREAT LAKES CHEMICAL CORP.	EL DORADO, AR	10,000-99,999	As a formulation component
NA	AZ	100-999	Ancillary uses
DEEPWATER IODIDES INC.	CARSON, CA	10,000-99,999	As a reactant
AEROJET SACRAMENTO OPS.	SACRAMENTO, CA	100,000-999,999	Ancillary uses
HERCULES INC.	BRUNSWICK, GA	10,000-99,999	As a reactant
AMOCO	WOOD RIVER, IL	10,000-99,999	As a reactant
3M	IL	10,000-99,999	As a reactant
SUNDSTRAND AEROSPACE	ROCKFORD, IL	1,000-9,999	Ancillary uses
ALLIED-SIGNAL INC.	PITTSBURG, KS	10,000-99,999	As a reactant
VANDERBILT CHEMICAL CORP.	MURRAY, KY	10,000-99,999	As a reactant
UNIROYAL CHEMICAL CO. INC.	GEISMAR, LA	100,000-999,999	As a reactant
OLIN CORP.	WESTLAKE, LA	100,000-999,999	Produce; For sale/distribution; Ancillary uses
SHELL OIL PRODS.	NORCO, LA	1,000-9,999	As a chemical processing aid
NA	MA	100-999	As a reactant
ZENECA RESINS	WILMINGTON, MA	1,000-9,999	As a reactant
BF GOODRICH	LEOMINSTER, MA	1,000-9,999	As a reactant
BAYER CORP.	KANSAS CITY, MO	100,000-999,999	As a reactant
FAIRMOUNT CHEMICAL CO. INC.	NEWARK, NJ	10,000-99,999	As a reactant
JOHNSON MATTHEY INC.	WEST DEPTFORD, NJ	1,000-9,999	As a chemical processing aid
DEGUSSA CORP.	SOUTH PLAINFIELD, NJ	10,000-99,999	As a reactant; As a chemical processing aid
E. I. DU PONT DE NEMOURS & CO.	NJ	10,000-99,999	As a chemical processing aid
PROCTER & GAMBLE	NORWICH, NY	10,000-99,999	As a reactant
OLIN CORP.	ROCHESTER, NY	10,000-99,999	As a reactant; As a formulation component
HALL CHEMICAL CO.	WICKLIFFE, OH	1,000-9,999	As a chemical processing aid
LUBRIZOL CORP.	PAINESVILLE, OH	10,000-99,999	As a reactant
BF GOODRICH	AVON LAKE, OH	10,000-99,999	As a reactant

Table 4-1. Facilities That Manufacture or Process Hydrazine (continued)

Facility	Location[a]	Range of maximum amounts on site in pounds	Activities and uses
DOWELL SCHLUMBERGER INC.	TULSA, OK	10,000-99,999	As a reactant
BILCHEM LTD.	PONCE, PR	10,000-99,999	As a reactant
GREAT LAKES CHEMICAL CORP.	NEWPORT, TN	10,000-99,999	As a chemical processing aid
NA	TN	10,000-99,999	As a reactant
DREXEL CHEMICAL CO.	MEMPHIS, TN	10,000-99,999	As a reactant
MILES INC.	BAYTOWN, TX	1,000,000-9,999,999	Produce; For sale/distribution
PHELPS DODGE CORP.	TX	1,000-9,999	As a reactant
LUBRIZOL CORP.	PASADENA, TX	10,000-99,999	As a reactant
HOECHST-CELANESE CHEMICAL GROU	TX	1,000-9,999	Ancillary uses
SHELL OIL CO.	DEER PARK, TX	10,000-99,999	Ancillary uses
ASHLAND CHEMICAL CO.	HOUSTON, TX	100,000-999,999	Import; For sale/distribution; As a formulation component; As a product component; In repackaging only
MOBIL OIL BEAUMONT REFINERY	BEAUMONT, TX	10,000-99,999	As a manufacturing aid
MERCK & CO. INC.	ELKTON, VA	10,000-99,999	As a reactant
SPECIALTYCHEM PRODS. CORP.	MARINETTE, WI	10,000-99,999	As a reactant
BAYER CORP.	NEW MARTINSVILLE, WV	100,000-999,999	As a reactant

Source: TRI93 1995

[a] Post office state abbreviations used

NA = not available

Table 4-2. Facilities That Manufacture or Process 1,1-Dimethylhydrazine

Facility	Location [a]	Range of maximum amounts on site in pounds	Activities and uses
OLIN CORP.	AL	10,000-99,999	In repackaging only
AEROJET SACRAMENTO OPS.	SACRAMENTO, CA	100,000-999,999	Ancillary uses
UNIROYAL CHEMICAL CO. INC.	GEISMAR, LA	100,000-999,999	Import; For on-site use/processing; As a reactant
OLIN CORP.	WESTLAKE, LA	100,000-999,999	Produce; For sale/distribution

Source: TRI93 1995

[a] Post office state abbreviations used

chemicals, about 33% for blowing agents, 15% as a corrosion inhibitor in boiler water and only 5% as an aerospace propellant (Budavari et al. 1989; Fajen and McCammon 1988; HSDB 1995; Schmidt 1988; WHO 1987).

1,1-Dimethylhydrazine is used mainly as a component of jet and rocket fuels. Other uses include an adsorbent for acid gases, a stabilizer for plant growth regulators, an intermediate for organic chemical synthesis, and in photography. 1,2-Dimethylhydrazine is used only as a research chemical and has no known commercial uses (ACGIH 1991a; Budavari et al. 1989; HSDB 1995).

4.4 DISPOSAL

Hydrazine, 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, and wastes containing these chemicals are classified as hazardous wastes by EPA. Generators of waste containing these contaminants must conform to EPA regulations for treatment, storage, and disposal (see Chapter 7). Liquid injection or fluidized bed incineration methods are acceptable disposal methods for these wastes. Oxidation of spills of hydrazine fuels with sodium or calcium hypochlorite or hydrogen peroxide prior to disposal has been recommended. However, incomplete reaction of 1,1-dimethylhydrazine with hypochlorite leads to formation of several by-products, including carcinogenic *N*-nitrosoalkylamines. Ozonation of wastewater containing hydrazine fuels has been shown to reduce concentrations of the fuels, their associated impurities, and oxidation products to environmentally acceptable levels. Biodegradation is also an acceptable treatment for wastewaters containing hydrazine wastes (Brubaker 1988; EPA 1991a; HSDB 1995; Jody et al. 1988; WHO 1987).

According to the TRI, about 106,000 pounds of hydrazine and 3,000 pounds of l,l-dimethylhydrazine were transferred to landfills and/or treatment/disposal facilities in 1993 (see Section 5.2) (TRI93 1995). Of this quantity, about 1,400 pounds of hydrazine were discharged to publicly owned treatment works.