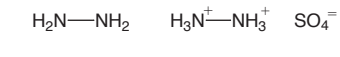
Hydrazine and Hydrazine Sulfate
CAS Nos. 302-01-2 and 10034-93-2

Reasonably anticipated to be a human carcinogen
First Listed in the *Third Annual Report on Carcinogens* (1983)



Hydrazine Hydrazine Sulfate

Carcinogenicity

Hydrazine and hydrazine sulfate are *reasonably anticipated to be human carcinogens* based on sufficient evidence of carcinogenicity in experimental animals (IARC 1974, 1982, 1987, 1999). When administered orally, hydrazine induced pulmonary adenomas and adenocarcinomas in mice. Intraperitoneal injection of hydrazine induced reticulum cell sarcomas of the mediastinum and myeloid leukemias in mice of both sexes (IARC 1974). When administered by inhalation, hydrazine induced alveolarogenic carcinomas and lymphosarcomas of the spleen in female mice (MacEwen *et al.* 1974). When administered orally, hydrazine sulfate induced pulmonary adenomas and adenocarcinomas, hepatomas, and hepatocarcinomas in mice of both sexes. When administered by stomach tube, hydrazine sulfate induced lung adenomas and adenocarcinomas in rats of both sexes and hepatic cell carcinomas and spindle cell sarcomas in male rats (IARC 1974).

There is inadequate evidence for the carcinogenicity of hydrazine and hydrazine sulfate in humans (IARC 1982, 1987, 1999). Three reports on cancer mortality among workers exposed to hydrazine have been published. One case of choroidal melanoma was observed in a man who had been exposed to hydrazine for 6 years. A study of 423 men engaged in the manufacture of hydrazine initially revealed three stomach, one prostate, and one neurogenic cancers. A follow-up study of this cohort found a slight excess of lung cancer (2 cases) in the highest exposure category. Another cohort of 427 men who worked in a hydrazine plant in the UK did not find excess cancer mortality or an excess of all cause mortality. The evidence these studies provide was considered inadequate by an IARC Working Group.

Properties

Hydrazine is a white or colorless, oily, fuming liquid with an ammonia-like odor. It is miscible with water, methyl, ethyl, propyl, and isobutyl alcohols, but is insoluble in chloroform and ether (IARC 1999). Hydrazine is a flammable liquid that may spontaneously ignite on contact with oxidizers or porous materials and may explode when exposed to heat, flame, or upon chemical reaction with alkali metals. Hydrazine is available as a propellant grade with a minimum of 97.5% purity. Solutions with varying hydrazine content are available for a variety of industrial uses (HSDB 2000a).

Hydrazine sulfate occurs as a colorless crystal or white crystalline powder. It is soluble in hot water and insoluble in alcohol. When heated to decomposition, it emits toxic fumes of sulfur oxides and nitrogen oxides. Hydrazine sulfate is available in two grades of <98% and 99% purity with heavy metal and chloride impurities (HSDB 2000b).

Use

Hydrazine is used primarily as a chemical intermediate to produce agricultural chemicals, spandex fibers, and antioxidants. Hydrazine is also used as rocket fuel, an oxygen scavenger in water boilers and heating systems, a polymerization catalyst, a blowing agent, and as a scavenger for gases. Additionally, it is used for plating metals on glass and plastics and in fuel cells, solder fluxes, and photographic developers. Hydrazine is used as a reactant in fuel cells in the military, as a reducing agent in electrodless nickel plating, as a chain extender in urethane polymerizations, as a reducing agent in plutonium extraction from reactor waste, and as a water treatment chemical. Hydrazine is also used as a chemical intermediate for blowing agents, photography chemicals, pharmaceuticals, antituberculants, textile dyes, heat stabilizers, explosives, and to make hydrazine sulfate (IARC 1974, 1999, Sax 1987, ATSDR 1997, HSDB 2000a).

Hydrazine sulfate is used in refining rare metals, as an antioxidant in soldering flux for light metals, in analytical tests for blood, a reducing agent in the analysis of minerals and slag, and in the preparation of hydrazine hydrate. Hydrazine sulfate is also used as a biocide for fungi and molds; although, it is not registered for use as a biocide in the United States. Investigators have studied hydrazine sulfate as an adjunct to antineoplastic drug treatment, but extensive use is not foreseeable (IARC 1974, Sax, 1987, HSDB 2000b).

Production

Only one current producer and 19 suppliers of hydrazine and one current producer and 28 suppliers of hydrazine sulfate were identified in the United States (HSDB 2000a,b, Chem Sources 2001). Annual production estimates for hydrazine ranged from 15 million lb to 38 million lb from the mid 1960s to 1984 (ATSDR 1997). U.S. production capacity estimates for hydrazine hydrate was 55 million lb in 1988 and production capacity estimates for hydrazine solutions were approximately 36.3 million lb in 1992 (IARC 1999). More recent production data were not found. In 2000, U.S. exports and imports of hydrazine and hydroxylamine and their inorganic salts were reported to be approximately 27.6 million lb and 10.7 million lb, respectively (ITA 2001). The 1979 TSCA Inventory identified four companies producing 11 million lb of hydrazine in 1977 and 13 companies importing 660,500 lb. The 1979 TSCA Inventory also identified seven companies producing 562,000 lb of hydrazine sulfate and three companies importing an unspecified amount (TSCA 1979).

Exposure

Hydrazine and hydrazine sulfate may be released to the environment through production, use, and waste disposal. Hydrazine is rapidly degraded in most environmental media by oxidation. High concentrations of hydrazine are toxic to microorganisms, but at low concentrations, biodegration may occur. Use of hydrazine in boiler water treatment may result in its brief occurrence in discharged waste, but it would be rapidly oxidized (ATSDR 1997, HSDB 2000a).

The primary routes of potential human exposure to hydrazine are ingestion, inhalation, and dermal contact. The exposure potential for the general population is low, but it may occur through inhalation of cigarette smoke or ingestion of trace amounts in processed foods. Hydrazine has been detected in cigarette smoke at a concentration of 32 µg/cigarette (OSH 1982). Occupational exposure is more likely to occur by inhalation or dermal contact (HSDB 2000a). The National Occupational Exposure Survey estimated that 59,147 workers, including 2,840 females, were potential exposed to hydrazine in the United States between 1981 and 1982 (IARC 1999). NIOSH estimated that about 11,000 workers were possibly exposed to hydrazine in the workplace between 1972 and 1974 (NIOSH 1976). In 1978, NIOSH estimated that 9,000 workers in the United States may have been potentially exposed to hydrazine and that over 90,000 may have been exposed to various hydrazine salts (NIOSH 1978).

The Toxic Chemical Release Inventory (TRI99 2001) listed 36 industrial facilities that reported releases of hydrazine in 1999. The facilities reported releases of hydrazine to the environment which were estimated to total 143,727 lb (10,278 lb total on-site air release, 642

lb surface water discharges, 88,378 lb underground injections, 372 lb total land release, and 44,057 off-site releases). Only one industrial facility reported environmental releases of hydrazine sulfate in 1999 (TRI99 2001). This facility reported that 190,000 lb were disposed by underground injection.

Regulations

DOT

Hydrazine is considered a hazardous material and special requirements have been set for marking, labeling, and transporting this material

EPA

Clean Air Act

- NESHAP: Hydrazine listed as a Hazardous Air Pollutant (HAP)
- Prevention of Accidental Release: Threshold Quantity (TQ) = 15,000 lb (hydrazine only)
- Urban Air Toxics Strategy: Hydrazine identified as one of 33 HAPs that present the greatest threat to public health in urban areas

Comprehensive Environmental Response, Compensation, and Liability Act

- Reportable Quantity (RQ) = 1 lb (hydrazine only)

Emergency Planning and Community Right-To-Know Act

- Toxics Release Inventory: Listed substances subject to reporting requirements
- Reportable Quantity (RQ) = 1 lb (hydrazine)
- Threshold Planning Quantity (TPQ) = 1,000 lb (hydrazine)

Resource Conservation and Recovery Act

- Hydrazine listed as a Hazardous Constituent of Waste
- Listed Hazardous Waste: Waste codes in which listing is based wholly or partly on hydrazine - U133

FDA

Hydrazine is not permitted in steam in food treatment processes

OSHA

Permissible Exposure Limit (PEL) = 1 ppm (1.3 mg/m^3)

Guidelines

ACGIH

Threshold Limit Value - Time-Weighted Average Limit (TLV-TWA) = 0.01 ppm (hydrazine)

NIOSH

Immediately Dangerous to Life and Health (IDLH) = 50 ppm

Ceiling Recommended Exposure Limit = 0.03 ppm (0.04 mg/m^3) (2-hour exposure)

Listed as a potential occupational carcinogen

REFERENCES

ATSDR. 1997. Toxicological Profile for Hydrazine. (Final Report). NTIS Accession No. PB98-101025. Atlanta, GA: Agency for Toxic Substances and Disease Registry. 203 pp.

ChemSources. 2001. Chemical Sources International, Inc. http://www.chemsources.com.

HSDB. 2000. Hazardous Substances Data Base. National Library of Medicine. http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.

IARC. 1974. Some Aromatic Amines, Hydrazine and Related Substances, *N*-Nitroso Compounds and Miscellaneous Alkylating Agents. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, vol. 4. Lyon, France: International Agency for Research on Cancer. 286 pp.

IARC. 1982. Chemicals, Industrial Processes and Industries Associated with Cancer in Humans. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, Supplement 4. Lyon, France: International Agency for Research on Cancer. 292 pp.

IARC. 1987. Overall Evaluations of Carcinogenicity. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, Supplement 7. Lyon, France: International Agency for Research on Cancer. 440 pp.

IARC. 1999. Re-evaluation of Some Organic Chemicals, Hydrazine, and Hydrogen Peroxide. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, vol. 71. Lyon, France: International Agency for Research on Cancer. 1589 pp.

ITA. 2001. Subheading 282510: Hydrazine and Hydroxylamine and Their Inorganic Salts. International Trade Administration. U.S. Department of Commerce. http://www.ita.doc.gov/td/industry/otea/Trade-Detail/.

MacEwen, J. D., E. E. McConnell and K. C. Back. 1974. The Effect of a Six-Month Chronic Level Inhalation Exposure to Hydrazine on Animals. AD-A-011865. Springfield, VA: National Technical Information Service, U.S. Department of Commerce.

NIOSH. 1976. National Occupational Hazard Survey (1972-74). Cincinnati, OH: Department of Health, Education and Welfare.

NIOSH. 1978. Criteria for a Recommended Standard - Occupational Exposure to Hydrazines. DHEW (NIOSH) Publication No. 78-172. Cincinnati, OH: Department of Health, Education and Welfare.

OSH. 1982. The Health Consequences of Smoking, Cancer, a Report of the Surgeon General. DHHS (PHS) Publication No. 82-50179. Rockville, MD: Department of Health and Human Services. 322 pp.

Sax, N. I. and R. J. Lewis. 1987. Hawley's Condensed Chemical Dictionary, 11th ed. New York: Van Nostrand Reinhold Co. p. 276, 490, 633, 635 and 732.

TRI99. 2001. Toxic Chemical Release Inventory 1999. Data contained in the Toxic Chemical Release Inventory (TRI). National Library of Medicine. http://www.epa.gov/triexplorer/.

TSCA. 1979. Toxic Substances Control Act, Chemical Substances Inventory.