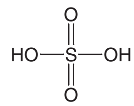
Strong Inorganic Acid Mists Containing Sulfuric Acid CAS No. 7664-93-9 (Sulfuric Acid)

Known to be a human carcinogen
First Listed in the *Ninth Report on Carcinogens* (2000)



Carcinogenicity

Strong inorganic acid mists containing sulfuric acid are *known to be human carcinogens* based on sufficient evidence of carcinogenicity from studies in humans that indicate a causal relationship between exposure to strong inorganic acid mists containing sulfuric acid and human cancer. Occupational exposures to strong inorganic acid mists containing sulfuric acid are specifically associated with laryngeal and lung cancer in humans. Steenland *et al.* (1988) reported on studies of one U.S. cohort of male workers in pickling operations in the steel industry, which showed excesses of laryngeal cancer (approximately two-fold) after adjusting for smoking and other potential confounding variables. In a ten-year follow-up, Steenland (1997) reported a two-fold laryngeal cancer rate ratio consistent with previous findings from this cohort. In a nested case-control study of workers in a U.S. petrochemical plant, Soskolne *et al.* (1984) found a dose-response for laryngeal cancer risk among workers exposed to moderate (odds ratio [OR] of 4.6; 95% CI, 0.83 to 25.35) or high levels (OR of 13.4; 95% CI, 2.08 to 85.99) of sulfuric acid. In a Canadian population-based case-control study, after controlling for tobacco and alcohol use and including only the most specific exposure scale, Soskolne *et al.* (1992) also observed a dose-response for laryngeal cancer risk in workers exposed to sulfuric acid mist. A report of a similar population-based case-control study in Canada by Siemiatycki (1991) also suggested an increase in risk for oat-cell carcinoma of the lung. Steenland and Beaumont (1989), reporting on the same U.S. cohort of male workers in pickling operations described by Steenland *et al.* (1988), found an excess of lung cancer in these workers after adjusting for smoking and other potential confounding variables.

No adequate experimental animal carcinogenicity studies of sulfuric acid or strong inorganic acid mists containing sulfuric acid have been reported in the literature.

Additional Information Relevant to Carcinogenicity

The manufacture of isopropyl alcohol by the strong acid process, which uses sulfuric acid, has been identified by IARC as known to cause an increased incidence of cancer of the paranasal sinuses in workers (IARC 1977).

The carcinogenic activity of sulfuric acid is most likely related to the genotoxicity of low pH environments. Reduced pH environments are known to enhance the depurination rate of DNA and the deamination rate of cytidine (IARC 1992).

Properties

A mist is defined as a liquid aerosol formed by condensation of a vapor or by atomization of a liquid. Strong inorganic acid mists containing sulfuric acid may be generated during a process when factors such as evaporation, solution strength, temperature, and pressure combine to effect release of a mist. Concentrations to which workers may be exposed depend on proximity to the source of the acid mist and controls of ventilation and containment (IARC 1992). Sulfuric acid mists are the most extensively studied of the acid mists. Liquid sulfuric acid may exist in air as a vapor or a mist; however, it exists most often as mist because of its low volatility and high affinity for water.

Sulfuric acid is a strong acid that is usually a clear, odorless, and colorless oily liquid; however, impure or spent sulfuric acid is a dark brown to black liquid. Acid strength is based on the position of equilibrium in an acid-base reaction and is measured by the pKa. The pKa is the negative logarithm (to the base 10) of the acid dissociation constant (Ka). The lower the pKa, the stronger the acid. Sulfuric acid has two pKa values because it releases two hydrogen atoms in aqueous solution. The first pKa cannot be measured accurately and is reported as less than 0; the second pKa is 1.92 at 18°C to 25°C. Sulfuric acid has a molecular weight of 98.1 and will oxidize, dehydrate, or sulfonate most organic compounds. It has a melting point of 10.31°C, a boiling point of 290°C, a density of 1.8 g/cm^3, and a log octanol-water partition coefficient of 1.92. Dehydration occurs because sulfuric acid has a strong affinity for water. It forms various hydrates when in contact with organic matter or water vapor. Although it is miscible with water, contact with water generates heat and may produce a violent reaction. The reaction with water releases toxic and corrosive fumes and mists. Sulfuric acid is noncombustible, but it can release flammable hydrogen gas when in contact with metals. Thermal decomposition to sulfur trioxide and water occurs at 340°C. Sulfuric acids are available in the following grades: commercial, electrolyte (high purity), textile (low organic content), and chemically pure or reagent grades (IARC 1992, ATSDR 1998, HSDB 2003).

Sulfur trioxide is added to sulfuric acid to produce fuming sulfuric acid (also known as oleum). Oleum has a molecular weight of 178.1, may contain up to 80% free sulfur trioxide, and is a colorless to slightly colored, oily liquid. Sulfur trioxide has a molecular weight of 80.1 and can exist as a gas, liquid, or solid. Liquid sulfur trioxide is colorless and fumes in air at ambient conditions. In the presence of moisture, sulfur trioxide forms solid polymers consisting of alpha and beta forms. The melting points of the alpha (62.3°C) and beta (32.5°C) forms are the temperatures where they depolymerize back to the liquid form. The liquid form has a boiling point of 44.8°C and a density of 1.92 g/cm^3 at 20°C. Both oleum and sulfur trioxide react with water and water vapor to form sulfuric acid mists. Oleum is available in several grades with free sulfur trioxide content ranging from 20% to 99.9% and corresponding sulfuric acid equivalents ranging from 104.5% to 122.5%. Sulfur trioxide is available with a minimum purity of 99.5% as a stabilized technical grade or unstabilized liquid (IARC 1992).

Use

Strong inorganic acid mists containing sulfuric acid are not used *per se* in industry or in commercial products but are generated from both natural and industrial sources. In particular, sulfuric acid mists may be produced during the manufacture or use of sulfuric acid, sulfur trioxide, or oleum. Sulfur trioxide is primarily used to make sulfuric acid, but it also is used as a sulfonating or oxidizing agent. Oleum is used as a sulfonating or dehydrating agent, in petroleum refining, and as a laboratory reagent. Sulfuric acid is one of the most widely used industrial chemicals; however, most of it is used as a reagent rather than an ingredient. Therefore, most of the sulfuric acid used ends up as a spent acid or a sulfate waste. Exacting purity grades are required for use in storage batteries and for the rayon, dye, and pharmaceutical industries. Sulfuric acids used in the steel, chemical, and fertilizer industries have less exacting standards (IARC 1992, ATSDR 1998, HSDB 2003).

Sulfuric acid is used in the following industries: fertilizer, petroleum refining, mining and metallurgy, ore processing, inorganic and organic chemicals, synthetic rubber and plastics, pulp and paper, soap and detergents, water treatment, cellulose fibers and films, and inorganic pigments and paints. Between 60% and 70% of the sulfuric acid used in the United States is used by the fertilizer industry to convert phosphate rock to phosphoric acid. All other uses account for less than 1% to less than 10% of the total consumption. Sulfuric acid use is declining in some industries. There is a trend in the steel industry to use hydrochloric acid instead of sulfuric acid in pickling, and hydrofluoric acid has replaced sulfuric acid for some uses in the petroleum industry. The primary consumer product that contains sulfuric acid is the lead-acid battery; however, this accounts for a small fraction of the overall use. It is also used as a general purpose food additive (IARC 1992, ATSDR 1998).

Production

Strong inorganic acid mists containing sulfuric acid may be produced as a result of the use of mixtures of strong inorganic acids, including sulfuric acid, in industrial processes such as acid treatment of metals, phosphate fertilizer manufacture, lead battery manufacture, and various other industries (IARC 1992). The degree of vapor or mist evolution varies with the process and method. In pickling, for instance, mist may escape from acid tanks when hydrogen bubbles and steam rises from the surface of the solution.

Sulfuric acid is the largest volume chemical produced in the United States (CEN 1996). Production volume increased from approximately 28.3 million metric tons/yr (62.4 billion pounds/yr) in 1972 to 40.1 million metric tons/yr (88.4 billion pounds/yr) in 1980 (IARC 1992, ATSDR 1998). Between 1981 and 2002, annual production remained fairly steady with a low of 32.6 million metric tons (71.9 billion pounds) in 1986 (IARC 1992) and a high of 44 million metric tons (97 billion pounds) in 1998 (CEN 2003). Between 1992 and 2002, annual production declined by only one percent (CEN 2003). Many different grades and strengths are produced. The primary method of production is called the contact process which consists of the following steps: (1) oxidation of sulfur to sulfur dioxide, (2) cooling the gases, (3) oxidation of sulfur dioxide to sulfur trioxide, (4) cooling the sulfur trioxide gas, and (5) adding sulfur trioxide to water to produce sulfuric acid. Oleum is produced at sulfuric acid plants by adding sulfur trioxide to sulfuric acid. In addition to primary production, large quantities of spent sulfuric acid are reprocessed (IARC 1992, ATSDR 1998). ChemSources (2003) identified 41 suppliers of sulfuric acid and 15 suppliers of oleum in the United States in 2003.

The United States is a net importer of sulfuric acid and oleum. Imports for 2002 were approximately 1 million metric tons (2.2 billion pounds), and exports were 147,000 metric tons (324 million pounds) (ITA 2003). U.S. imports were 275,000 metric tons (600 million pounds) in 1975, 426,000 metric tons (940 million pounds) in 1984, and 2.3 million metric tons (5 billion pounds) in 1993 compared to exports of 129,000 metric tons (284 million pounds) in 1975, 119,000 metric tons (262 million pounds) in 1984, and 136,000 metric tons (300 million pounds) in 1993 (HSDB 2003).

Exposure

Exposure to strong inorganic acid mists containing sulfuric acid may occur by inhalation, ingestion, and dermal contact. Exposure depends on many factors including particle size, proximity to the source, and control measures such as ventilation and containment. Data on particle size distribution of acid mists are limited, and sampling methods have generally not differentiated between liquid and gaseous forms of acids. One study of sulfuric acid mists in several U.S. battery manufacturing plants indicated a mass median aerodynamic diameter of 5 to 6 µm; therefore, the available data indicate that sulfuric acid mists contain aerosol particles that can be deposited in both the upper and lower airways (IARC 1992).

Sulfuric acid and mists and vapors containing sulfuric acid are present in the environment because of releases of sulfur compounds from both natural and anthropogenic sources. Volcanic eruptions, biogenic gas emissions, and oceans are the primary natural sources of sulfur emissions. Volcanoes release 0.75 to 42 million metric tons (1.7 billion pounds to 93 billion pounds) of sulfur/yr and airborne sea spray and marine organisms release between 12 to 15 million metric tons/yr (26 billion to 33 billion pounds/yr). Coal combustion by electric plants is the major anthropogenic source of sulfur dioxide release. Sulfur dioxide emissions in the United States declined by more than 60% between the early 1970s (28 million metric tons [62 billion pounds]) and 1994 (18 million metric tons [40 billion pounds]). Between 1994 and 1995, emissions decreased by another 13% (ATSDR 1998).

Ambient air may contain particulate-associated mixtures of sulfuric acid and ammonium sulfates (sulfuric acid partially or completely neutralized by atmospheric ammonia). The relative amounts of sulfuric acid and total sulfates depend on meteorological and chemical parameters. The presence of sulfuric acid and sulfates in the atmosphere is believed to be due to oxidation of sulfur dioxide in cloud water and other atmospheric media. Ambient air concentrations of sulfuric acid are at least an order of magnitude lower than concentrations in occupational settings (IARC 1992).

EPA's Toxics Release Inventory (TRI) for 2001 (TRI01 2003) includes a total of 1,163 facilities reporting environmental releases of sulfuric acid. These facilities reported releasing more than 147 million pounds (67,000 metric tons) of sulfuric acid to the environment. More than 99% of the releases were to the air. The TRI data show that sulfuric acid emissions have fluctuated from year to year but have remained in the range of 26 million pounds (12,000 metric tons) to 42 million pounds (19,000 metric tons) between 1994 and 2001.

Sulfuric acid is used with other strong inorganic acids in many manufacturing processes, during which strong inorganic acid mists containing sulfuric acid may be generated. The industries in which occupational exposure to strong acid mists may occur include chemical manufacture (sulfuric acid, nitric acid, synthetic ethanol, and vinyl chloride); building and construction; lead-acid batteries; phosphate fertilizers; pickling and other acid treatments of metals; petroleum and coal products; oil and gas extraction; printing and publishing; paper and allied products; and the tannery industry. Most of the available occupational exposure data comes from the pickling and plating industries. Average concentrations of strong inorganic acid mists containing sulfuric acid reported in workplace air in the 1970s and 1980s were less than 0.01 to 7.3 mg/m^3 (pickling and acid cleaning), less than 0.07 to 0.57 mg/m^3 (phosphate fertilizer manufacture), 0.01 to 1.03 mg/m^3 (lead battery manufacture), and less than 0.005 to 0.5 mg/m^3 for other industries (IARC 1992).

The National Institute of Occupational Health and Safety (NIOSH) reported results of the National Occupational Exposure Survey (NOES), conducted from 1981-1983, which reported on more than 54,500 plants with potential workplace exposure to strong inorganic acids. NIOSH estimated that 775,587 workers, including 173,653 women, were exposed to sulfuric acid; 1,238,572 workers, including 388,130 women, were exposed to hydrochloric acid; 297,627 workers, including 76,316 women, were exposed to nitric acid; and 1,256,907 workers, including 450,478 women, were exposed to phosphoric acid in the workplace. NIOSH also conducted the National Occupational Hazard Survey (NOHS) from 1972-1974 and estimated that 499,446 workers were exposed to sulfuric acid, 824,985 to hydrochloric acid, 132,401 to nitric acid, and 454,920 to phosphoric acid (RTECS 2003).

Regulations

CPSC

Sulfuric acid and any preparation containing sulfuric acid in a concentration of 10% or more must have a label containing the word "poison"

DOT

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

EPA

<u>Comprehensive Environmental Response, Compensation, and Liability Act</u>
Reportable Quantity (RQ) = 1,000 lb (sulfuric acid)
<u>Emergency Planning and Community Right-To-Know Act</u>
Toxics Release Inventory: Aerosol forms of sulfuric acid are listed and thus subject to reporting requirements
Threshold Planning Quantity (TPQ) = 1,000 lb (sulfuric acid)
Reportable Quantity (RQ) = 1,000 lb (sulfuric acid)

OSHA

Permissible Exposure Limit (PEL) = 1 mg/m^3 (sulfuric acid)

Guidelines

ACGIH

Threshold Limit Value - Time-Weighted Average Limit (TLV-TWA) = 1 mg/m^3 (sulfuric acid contained in strong inorganic acid mists)
Threshold Limit Value - Short Term Exposure Limit (TLV-STEL) = 3 mg/m^3 (sulfuric acid contained in strong inorganic acid mists)

NIOSH

Recommended Exposure Limit (REL) = 1 mg/m^3 (sulfuric acid)
Immediately Dangerous to Life and Health (IDLH) = 15 mg/m^3 (sulfuric acid)

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