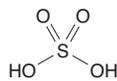


## Strong Inorganic Acid Mists Containing Sulfuric Acid

### CAS No. 7664-93-9 (Sulfuric acid)

Known to be human carcinogens

First listed in the *Ninth Report on Carcinogens* (2000)



Sulfuric acid

### Carcinogenicity

Strong inorganic acid mists containing sulfuric acid are *known to be human carcinogens* based on sufficient evidence of carcinogenicity from studies in humans.

#### Cancer Studies in Humans

Occupational exposure to strong inorganic acid mists containing sulfuric acid is specifically associated with laryngeal and lung cancer. Studies of one U.S. cohort of male workers in pickling operations in the steel industry found excesses of laryngeal cancer (approximately twofold) after adjustment for smoking and other potentially confounding variables (Steenland *et al.* 1988). A ten-year follow-up of this cohort also found a twofold excess of laryngeal cancer, consistent with the earlier findings (Steenland 1997). The same cohort showed an excess of lung cancer after adjustment for smoking and other potentially confounding variables (Steenland and Beaumont 1989). A nested case-control study of workers in a U.S. petrochemical plant found a dose-related increase in the risk of laryngeal cancer among workers exposed to sulfuric acid at moderate levels (odds ratio [OR] = 4.6; 95% confidence interval [CI] = 0.83 to 25.35) or high levels (OR = 13.4; 95% CI = 2.08 to 85.99) (Soskolne *et al.* 1984). A Canadian population-based case-control study also found a dose-related risk of laryngeal cancer for workers exposed to sulfuric acid mist, after controlling for tobacco and alcohol use and using only the most specific exposure scale (Soskolne *et al.* 1992). A similar Canadian population-based case-control study suggested an increased risk of lung cancer (oat-cell carcinoma) (Siemiatycki 1991).

#### Additional Information Relevant to Carcinogenicity

The manufacture of isopropyl alcohol by the strong-acid process, which uses sulfuric acid, has been classified by the International Agency for Research on Cancer as carcinogenic to humans, based on 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, which are known to increase the rates of depurination of DNA and deamination of cytidine (IARC 1992a).

#### Cancer Studies in Experimental Animals

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

### Properties

Sulfuric acid is a strong acid that is a clear, colorless oily liquid at room temperature. Impure or spent sulfuric acid is a dark-brown to black liquid. Sulfuric acid is soluble in water and ethanol and is very corrosive (IARC 1992b). Physical and chemical properties of sulfuric acid are listed in the following table.

Property	Information
Molecular weight	98.1 <sup>a</sup>
Density	1.8 g/cm <sup>3a</sup>
Melting point	10.31°C <sup>a</sup>
Boiling point	290°C <sup>a</sup>
Log $K_{ow}$	1.92 <sup>b</sup>
Vapor pressure	5.93 × 10 <sup>-5</sup> mm Hg at 25°C <sup>a</sup>
Vapor density relative to air	3.4 <sup>a</sup>
Dissociation constant (pK <sub>a</sub> )	1.98 at 25°C <sup>a</sup>

Sources: <sup>a</sup>HSDB 2009, <sup>b</sup>ATSDR 1998.

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 result in release of a mist (IARC 1992a). 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.

Acid strength is based on the position of equilibrium in an acid-base reaction and is measured by the negative logarithm (to the base 10) of the acid dissociation constant (pK<sub>a</sub>). The lower the pK<sub>a</sub>, the stronger the acid. Sulfuric acid has two pK<sub>a</sub> values because it releases two hydrogen atoms in aqueous solution, but the first pK<sub>a</sub> cannot be measured accurately and is reported as less than 0. 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 1992b, ATSDR 1998, HSDB 2009).

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 at which 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<sup>3</sup> 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 1992b).

### 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 is also 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 1992b, ATSDR 1998, HSDB 2009).

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 individual 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. Sulfuric acid is also used as a general-purpose food additive (IARC 1992b, 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, and lead battery manufacture (IARC 1992b). 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 rise from the surface of the solution. Many different grades and strengths of sulfuric acid are produced. The primary method of production is the contact process, which consists of the following steps: (1) oxidation of sulfur to sulfur dioxide, (2) cooling of the gases, (3) oxidation of sulfur dioxide to sulfur trioxide, (4) cooling of the sulfur trioxide gas, and (5) addition of sulfur trioxide to water to produce sulfuric acid. Oleum (a mixture used to transport sulfuric acid) 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 1992b, ATSDR 1998). In 2009, sulfuric acid was available from 76 U.S. suppliers, and oleum from 6 U.S. suppliers (ChemSources 2009).

Sulfuric acid is the largest-volume chemical produced in the United States (CEN 1996). From 1972 to 2003, annual production was between 50 billion and 100 billion pounds (IARC 1992b, ATSDR 1998, CEN 2003), and in 2017, U.S. production plus imports fell in this same range (as shown in the table below). The United States is a net importer of sulfuric acid and oleum. Imports varied from year to year from the 1970s through the 1990s, but generally exceeded 250 million pounds annually (HSDB 2009, USITC 2009). In 2017, U.S. imports exceeded 6 billion pounds, over 11 times the volume of exports.

Category	Year	Quantity (lb)
Production + imports <sup>a</sup>	2015	70 billion to 80 billion
U.S. imports <sup>b</sup>	2017	6.4 billion
U.S. exports <sup>b</sup>	2017	560.9 million

Sources: <sup>a</sup>EPA 2016. <sup>b</sup>USITC 2018 (reported as "sulfuric acid and oleum").

## Exposure

Human exposure to strong inorganic acid mists containing sulfuric acid may occur by inhalation, ingestion, or 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 found that particles had a mass median aerodynamic diameter of 5 to 6  $\mu\text{m}$ , which indicates that sulfuric acid mists contain aerosol particles that can be deposited in both the upper and lower airways (IARC 1992a).

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 million to 42 million metric tons (1.7 billion to 93 billion pounds) of sulfur per year, and airborne sea spray and marine organisms release between 12 million and 15 million metric tons per year (26 billion to 33 billion pounds). 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% from the early 1970s (28 million metric tons [62 billion pounds]) to 1994 (18 million metric tons [40 billion pounds]) and decreased by another 13% from 1994 to 1995 (ATSDR 1998).

According to the U.S. Environmental Protection Agency's Toxics Release Inventory, environmental releases of sulfuric acid fluctuated from year to year, but remained in the range of 26 million to 197 million pounds from 1994 and 2007. In 2007, 840 facilities released over 138.5 million pounds of sulfuric acid, of which over 99% was released to air (TRI 2009). 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 1992a).

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, manufacture of lead-acid batteries, manufacture of phosphate fertilizers, pickling and other acid treatments of metals, manufacture of petroleum and coal products, oil and gas extraction, printing and publishing, manufacture of paper and allied products, and tanneries. Most of the available occupational exposure data comes from the pickling and plating industries. In the 1970s and 1980s, average concentrations of strong inorganic acid mists containing sulfuric acid in workplace air were less than 0.01 to 7.3  $\text{mg}/\text{m}^3$  for pickling and acid cleaning, less than 0.07 to 0.57  $\text{mg}/\text{m}^3$  for phosphate fertilizer manufacture, 0.01 to 1.03  $\text{mg}/\text{m}^3$  for lead battery manufacture, and less than 0.005 to 0.5  $\text{mg}/\text{m}^3$  for other industries (IARC 1992a).

The National Occupational Hazard Survey (conducted from 1972 to 1974) 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 (NIOSH 1976). The National Occupational Exposure Survey (conducted from 1981 to 1983), which reported on more than 54,500 plants with potential workplace exposure to strong inorganic acids, estimated that 775,587 workers, including 173,653 women, potentially were exposed to sulfuric acid; 1,238,572 workers, including 388,130 women, to hydrochloric acid; 297,627 workers, including 76,316 women, to nitric acid; and 1,256,907 workers, including 450,478 women, to phosphoric acid (NIOSH 1990).

## Regulations

### Coast Guard (Dept. of Homeland Security)

Minimum requirements have been established for safe transport of sulfuric acid on ships and barges.

### Consumer Product Safety Commission (CPSC)

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

### Department of Transportation (DOT)

Sulfuric acid and numerous sulfuric acid mixtures are considered hazardous materials, and special requirements have been set for marking, labeling, and transporting these materials.

### Environmental Protection Agency (EPA)

#### Clean Air Act

*New Source Performance Standards:* Standards of performance have been established for sulfuric acid production units, including a limit on acid mist (expressed as H<sub>2</sub>SO<sub>4</sub>) emissions of 0.15 lb/ton of acid produced.

#### Clean Water Act

Sulfuric acid is designated a hazardous substance.

#### Comprehensive Environmental Response, Compensation, and Liability Act

Reportable quantity (RQ) = 1,000 lb for sulfuric acid.

#### Emergency Planning and Community Right-To-Know Act

*Toxics Release Inventory:* Aerosol forms of sulfuric acid are listed and thus subject to reporting requirements.

Threshold planning quantity (TPQ) = 1,000 lb for sulfuric acid.

Reportable quantity (RQ) = 1,000 lb for sulfuric acid.

#### Resource Conservation and Recovery Act

*Listed Hazardous Waste:* Waste codes for which the listing is based wholly or partly on the presence of sulfuric acid = U103, P115.

### Occupational Safety and Health Administration (OSHA, Dept. of Labor)

While this section accurately identifies OSHA's legally enforceable PELs for this substance in 2018, specific PELs may not reflect the more current studies and may not adequately protect workers. Permissible exposure limit (PEL) = 1 mg/m<sup>3</sup> for sulfuric acid.

## Guidelines

### American Conference of Governmental Industrial Hygienists (ACGIH)

Threshold limit value – time-weighted average (TLV-TWA) = 0.2 mg/m<sup>3</sup> for sulfuric acid contained in strong inorganic acid mists.

### National Institute for Occupational Safety and Health (NIOSH, CDC, HHS)

Recommended exposure limit (REL) = 1 mg/m<sup>3</sup> for sulfuric acid.

Immediately dangerous to life and health (IDLH) limit = 15 mg/m<sup>3</sup> for sulfuric acid.

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