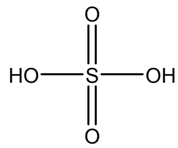
STRONG INORGANIC ACID MISTS CONTAINING SULFURIC ACID
CAS No. 7664-93-9 (Sulfuric Acid)

First Listed in the *Ninth Report on Carcinogens*



CARCINOGENICITY

Occupational exposure to strong inorganic acid mists containing sulfuric acid is *known to be a human carcinogen*, 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 (IARC 1992).

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 after adjusting for smoking and other potential confounding variables [standardized incidence rate ratio (SIR) for laryngeal cancer was 2.30 (95% confidence interval [CI], 1.05 to 4.36)]. In a ten-year follow-up, Steenland (1997) reported a laryngeal cancer rate ratio of 2.2 (95% CI, 1.2 to 3.7), 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, with ORs of 2.52 (95% CI, 0.80 to 7.91) at the lowest exposure level and 6.87 (95% CI, 1.00 to 47.06) at the highest exposure level. A report of a similar population based case-control study in Canada by Siemiatycki (1991) suggested an increase in risk for oat-cell carcinoma of the lung (rate ratio [RR] of 2.0; 90% CI, 1.3 to 2.9). 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 [standardized mortality ratio (SMR) for lung cancer was 1.36 (95% CI, 0.97 to 1.84)].

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 CARCINOGENESIS OR POSSIBLE MECHANISMS OF CARCINOGENESIS

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 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. 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 <0; the second pKa is 1.92 at 18 to 25°C (IARC 1992).

Sulfuric acid is a clear, odorless, and colorless oily liquid; however, impure or spent sulfuric acid is a dark brown to black liquid. It is a strong acid and will oxidize, dehydrate, or sulfonate most organic compounds. 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 2001).

Sulfur trioxide is added to sulfuric acid to produce fuming sulfuric acid (also known as oleum). Oleum may contain up to 80% free sulfur trioxide and is a colorless to slightly colored oily liquid. Sulfur trioxide can exist as a gas, liquid, or solid. Liquid sulfur trioxide is colorless and fumes in air at ambient conditions. The liquid and solid forms of sulfur trioxide can react with trace amounts of moisture to form solid polymers. 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 dioxide 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 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 1992, ATSDR 1998, HSDB 2001).

Sulfuric acid is used in the following industries: fertilizer, petroleum refining, mining and metallurgy, ore processing, inorganic chemicals and pigments, 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 U.S. is used by the fertilizer industry to convert phosphate rock to phosphoric acid. All other uses account for <1% to <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 rise from the surface of the solution.

Sulfuric acid production has varied over twenty years from approximately 30 million metric tons/yr to more than 40 million metric tons/yr and is the largest volume chemical produced in the U.S. 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). Chem Sources (2001) identified 47 suppliers of sulfuric acid and 15 suppliers of oleum in the U.S.

The U.S. is a net importer of sulfuric acid and oleum. During the early 1990s, the U.S. imported an average of approximately 2,000,000 metric tons/yr and exported an average of approximately 148,000 metric tons/yr (sulfuric acid and oleum combined) (ATSDR 1998). Imports and exports for 2000 were approximately 1,420,000 and 192,000 metric tons, respectively (ITA 2001).

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. Acid aerosols as a group have been designated as one of the criteria pollutants by the U.S. EPA because of their increasing presence from various human activities and their potential to cause or aggravate health effects, particularly within the respiratory tract. 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 of sulfur/yr and airborne sea spray and marine organisms release between 12 to 15 million metric tons/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) and 1994 (18 million metric tons). 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 Toxic Chemical Release Inventory for 1999 (TRI99 2001) includes a total of 1,259 facilities reporting environmental releases of sulfuric acid. These facilities reported releasing more than 181 million lb (~82,000 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 declined dramatically since the late 1980s and early 1990s.

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 air in the 1970s and 1980s were <0.01 to 7.3 mg/m^3 (pickling and acid cleaning), <0.07 to 0.57 mg/m^3 (phosphate fertilizer manufacture), 0.01 to 1.03 mg/m^3 (lead battery manufacture), and <0.005 to 0.5 mg/m^3 for other industries (IARC 1992).

The National Institute of Occupational Health and Safety (NIOSH 1990) listed results of the National Occupational Exposure Survey (1981-1983), which reported on more than 54,500 plants with potential workplace exposure to strong inorganic acids. This list estimated that approximately 776,000 workers were exposed to sulfuric acid, 1,239,000 workers were exposed to hydrochloric acid, 298,000 workers were exposed to nitric acid, and 1,257,000 workers were exposed to phosphoric acid in the workplace.

REGULATIONS

EPA regulates sulfuric acid atmospheric emissions under the Clean Air Act (CAA), the Comprehensive Emergency Response, Compensation, and Liability Act (CERCLA) and the Emergency Planning and Community Right-to-Know Act (EPCRA).

The American Conference of Governmental Hygienists (ACGIH) recommends a workroom air threshold limit value (TLV) for sulfuric acid in strong inorganic mists (considered to be a suspected human carcinogen) of 1 mg/m^3 as an 8-hour time-weighted average (TWA) for a 40-hour work week. In addition, ACGIH recommends a short-term exposure limit (STEL) of 3 mg/m^3. Worker exposure by all routes should be controlled as low as possible below the TLV. NIOSH also recommends a 10-hour TWA exposure of 1 mg/m^3. The OSHA permissible exposure limit (PEL) for sulfuric acid in workroom air, the construction industry, and shipyards is also 1 mg/m^3 as an 8-hour TWA. OSHA also regulates strong inorganic acid mists containing sulfuric acid under the Hazard Communication Standard and as a chemical hazard in laboratories. Regulations are summarized in Volume II, Table 164.

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