Massachusetts Chemical Fact Sheet

Sulfuric Acid and Fuming Sulfuric Acid

Sulfuric acid is a corrosive toxic chemical that causes direct effects ranging from irritation to burns on the skin, eyes, and respiratory tract. Massachusetts businesses consumed almost 45 million pounds of sulfuric acid, the world's most widely used chemical, in the production of chemicals, electricity, food products, paper products, electronics, textiles, leather goods, and electroplated parts. Fuming sulfuric acid is used to transport high concentrations of acid.

FACTS

SULFURIC ACID

Chemical Formula:	H_2SO_4
CAS Number:	7664-93-9
Vapor Pressure:	73 mm Hg at 20°C (68°F)
Water Solubility:	miscible and reactive
Flash Point:	none
Description:	dense oily liquid

FUMING SULFURIC ACID

Chemical Formula:	$H_2SO_4 \cdot SO_3$
Common Name:	Oleum
CAS Number:	8014-95-7
Description:	solution of sulfur trioxide in sulfuric acid, heavy oily liquid, fumes strongly in moist air

Hazards

Acute (Short-Term) Health Effects

- Sulfuric acid can severely irritate and burn the skin and eyes, potentially causing third degree burns and blindness.
- If inhaled, sulfuric acid can irritate the lungs and cause coughing or shortness of breath. Higher exposures can cause a build-up of fluid in the lungs (pulmonary edema); 80 milligrams per cubic meter (mg/m3) is immediately dangerous to life and health.
- Concentrated sulfuric acid vapor or mists can cause rapid loss of consciousness with serious damage to lung tissue.

Chronic (Long-Term) Health Effects

- The International Agency for Research on Cancer (IARC) classifies occupational exposure to strong, inorganic mists containing sulfuric acid as a known human carcinogen (Group 1). Limited evidence suggests that sulfuric acid causes lung cancer in refinery workers.
- Chronic inhalation of sulfuric acid mist can cause inflammation of the upper respiratory tract, shortness of breath, bronchitis, or emphysema.

Other Hazards

- Concentrated sulfuric acid can catch fire or explode when it contacts acetone, alcohols, and metals.

Exposure Routes

Worker Health

Any facility using sulfuric acid must minimize worker exposure.

- Automatically pump liquid sulfuric acid from drums to process containers. If automatic pumps are infeasible, enclose operations and use local exhaust ventilation. If exposure may exceed 1 mg/m^3 use a National Institute for Occupational Safety and Health-approved full facepiece respirator with an acid gas canister and high efficiency particulate pre-filters.
- Avoid any contact with sulfuric acid. Immediately wash any exposed area and contact a doctor.

(For section references, see endnote #1.)

The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989 • University of Massachusetts Lowell • One University Avenue • Lowell, Massachusetts 01854-2866
PH: (978) 934-3275 • FAX: (978) 934-3050 • WEB: www.turi.org

Use Nationally and in Massachusetts

U.S. manufacturers consumed 38 million metric tons (84 billion pounds) of sulfuric acid in 1993, making it the most widely used chemical (see Table 1).

- Producers of phosphate fertilizers are the largest end-user of sulfuric acid; they consume almost 75% of sulfuric acid in the U.S.

- Other large end-users include mining operations (ore processing), oil refiners (petroleum alkylation), chemical producers (caprolactum, methyl methacrylate, aluminum sulfate, hydrofluoric acid, ammonium sulfate, titanium dioxide, and surface-active ingredients), pulp and paper producers, battery manufacturers, plastics manufacturers, and iron and steel producers.

Table 1. U.S. Consumption of 100% Sulfuric Acid by End Use, 1993

End-Use	Metric Tons (000)	Pounds (000,000)	% of Total
Fertilizers	27,541	60,718	72.02%
Ore Processing	2,282	5,031	5.97%
Petroleum Alkylation	1,550	3,417	4.05%
Pulp and Paper	930	2,050	2.43%
Caprolactam	800	1,764	2.09%
Methyl Methacrylate	806	1,777	2.11%
Aluminum Sulfate	595	1,312	1.56%
Hydrofluoric Acid	436	961	1.14%
Titanium Dioxide Pigments	350	772	0.92%
Batteries	224	494	0.59%
Cellulosic Fibers and Plastics	213	470	0.56%
Iron and Steel Industry	210	463	0.55%
Ammonium Sulfate	120	265	0.31%
Surface-active Ingredients	75	165	0.20%
Miscellaneous Uses	2,111	4,654	5.52%
Total	38,243	84,311	100%

Source: SRI International, Chemical Economics Handbook, 1995 (Palo Alto, CA)

- Miscellaneous uses include water treatment, production of deionized water used in electricity generation, and chemical products (including hydrochloric acid, chrome chemicals, citric acid, boric acid, resorcinol, furfural, alcohols, and phenol).

Reflecting its versatility and wide use, 166 Massachusetts businesses used 45 million pounds of sulfuric acid in 1996 (see Table 2) in at least 15 different applications (see Table 3). In 1996, it was the second most frequently reported chemical, ranked fifth in total use, and ranked third in byproduct generation.

- Chemical manufacturers are one of the dominant users of sulfuric acid in Massachusetts. Chemical products manufactured using sulfuric acid include photographic gelatin, polyamide resins, polyvinyl butyral resin, sulfonated oils, electroplating baths, and photoactive chemicals.

- Two chemical distributors reported repackaging and distributing 6.6 million pounds of sulfuric acid in 1996, or 15% of the total reported that year. This industry sector was not required to report in 1990.

- Many industries use sulfuric acid in water and wastewater treatment processes, consuming at least 25% of the total used in Massachusetts. It is used to control pH and in the deionization of water. Industries that report the largest use for these purposes include: textiles, food and beverage processing, electronics, metals, and pulp and paper. The quantity used for waste treatment has, in many cases, been estimated from available data. Facilities are not required to separate out and report the amount used for waste treatment.

- Electricity generators are the third largest end-user; they consume 17% of all sulfuric acid in Massachusetts. Electric utilities use it to regenerate ion exchange resins, and they produce it incidentally in flue gas scrubbers.

- Massachusetts food and beverage processors used 2.9 million pounds of sulfuric acid in 1996. Kraft Foods dominates this use with 2.87 million pounds of sulfuric acid in the manufacture of edible gelatin.

- Electronics manufacturers used 2.1 million pounds of sulfuric acid in 1996 to produce printed circuit boards, semiconductors, and silicon wafers. Electronics producers use sulfuric acid in copper-sulfate baths and micro-etch solutions.

- Electroplaters and anodizers used 2.9 million pounds of sulfuric acid in 1996. Electroplaters use sulfuric acid to remove oxides from metals prior to plating (pickling) and in copper-sulfate and tin-sulfate plating baths. Anodizers use sulfuric acid to produce an oxide layer on aluminum surfaces and to remove smut from cast aluminum.

- Paper manufacturers used 2.1 million pounds of sulfuric acid in 1996 to control pH in processes including: deinking recycled paper, manufacturing cotton pulp, and treating water.

Massachusetts reported use of sulfuric acid rose incrementally, by 3%, between 1990 and 1996 (see Tables 2 and 3).

- Two industries that reported significant amounts of sulfuric acid use in 1996 were not required to report in 1990. In 1996, electric utilities reported 7.6 million pounds and chemical distributors reported 6.6 million pounds. If these industries are omitted from the analysis, there was a 28% decrease in sulfuric acid use from 1990 to 1996.

- Sulfuric acid use in food processing increased by almost 50%, due to a 30% rise in use by Kraft Foods and new uses reported by AgriMark, Cumberland Farms, and H.P. Hood. The latter three companies use sulfuric acid to clean process equipment.

- Sulfuric acid use in chemical products dropped by 57%. This change is primarily due to an aggregate decrease of 10 million pounds from 1990 to 1996 by three large facilities, only one of which still reported in 1996. The majority of chemical companies (15 out of 21) reporting decreased their use from 1990 to 1996.

- Electronics, textiles and leather, and metal pickling significantly reduced use of sulfuric acid from 1990 to 1996. Paper manufacturing increased use by almost 50%, due to approximately half the companies reporting increases and half reporting decreases.

Outputs of sulfuric acid were considerably lower than inputs because sulfuric acid is often consumed or transformed in the process. "Outputs" are measured by the Massachusetts Toxics Use Reduction Act (MA TURA) as product and byproduct. MA TURA output data include all non-product material created by a process line prior to releases, on-site treatment, or transfer ("byproduct") and the amount of toxic chemical incorporated into a product ("shipped in or as product"). Outputs of sulfuric acid rose slightly, by 6%, between 1990 and 1996.

- Sulfuric acid "shipped in or as product" appeared to increase by 43% primarily because of the addition in 1991 of chemical distributors to those that must report chemical use in Massachusetts. Astro Chemicals and

Table 2. Massachusetts Sulfuric Acid: Use and Output Data for 1990 and 1996 (pounds)

Use Data -- MA TURA	1990	1996	Change	% Change
Manufactured or Processed	17,136,291	16,268,472	-867,819	-5%
Otherwise Used	26,485,884	28,579,312	2,093,428	8%
Total TURA Inputs	43,622,175	44,847,784	1,225,609	3%
Output Data -- MA TURA	**1990**	**1996**	**Change**	**% Change**
Generated as Byproduct	13,212,639	12,136,313	-1,076,326	-8%
Shipped In or As Product	5,074,571	7,234,290	2,159,719	43%
Total TURA Outputs	18,287,210	19,370,603	1,083,393	6%
Releases and Transfers -- US EPA, TRI	**1990**	**1996**	**Change**	**% Change**
Environmental Releases	180,271	1,515,905	1,335,634	741%
Off-site Transfers	1,968,581	368,605	-1,599,976	-81%
Total TRI R&T	2,148,852	1,884,510	-264,342	-12%

Sources: MA TURA -- Massachusetts Toxics Use Reduction Act data, 1998; and US EPA, TRI -- US Environmental Protection Agency, Toxics Release Inventory data, 1998.

Boremco Specialty Chemicals reported distributing 6.6 million pounds of sulfuric acid-based products in 1996 (as compared to 0 pounds in 1990). Offsetting this was a decrease from 3.4 million pounds shipped by Proctor and Gamble in 1990 to 0 pounds in 1996.

- Sulfuric acid "generated as byproduct" dropped by 8%. The trend in byproduct generation was influenced by facilities which stopped reporting sulfuric acid after 1990 (a reduction of 2.3 million pounds), and facilities which began reporting after 1990 (an increase of 4 million pounds, mostly from electric utilities). Those "consistent" facilities that reported in both years reduced their byproduct by 2.8 million pounds, or 25%.

Environmental releases and transfers of sulfuric acid in Massachusetts dropped by 12% between 1990 and 1996. The U.S. EPA, TRI output data include information on the waste materials generated by a facility after on-site treatment including: releases to air, land, and water ("environmental releases") and transfers off-site for treatment or disposal ("off-site transfers").

Table 3. Massachusetts Sulfuric Acid Consumption by Use Categories (1990 and 1996)

Use Category [1]	Number of Businesses [2]	Use (pounds) 1990	Use (pounds) 1996	% Change
Batteries, Lead-Acid	1	47,637	42,567	-11%
Chemical Products	19	19,121,986	8,172,215	-57%
Chemical Distributors [3]	2	0	6,575,038	N/A
Electronics -- Printed Circuit Boards, Semiconductors, Silicon Wafers	34	2,714,160	2,086,732	-23%
Electroplating and Anodizing	57	3,006,217	2,932,595	-2%
Pickling Metal	11	802,369	178,559	-78%
Electricity or Steam Generation [3]	22	1,115,178	7,608,732	582%
Food and Beverage Processing	9	2,457,069	2,903,157	18%
Medical Products	2	45,707	73,723	61%
Photographic Film	1	179,223	172,959	-3%
Paper Manufacturing	12	1,420,676	2,114,665	49%
Silver and Gold Refining	3	538,000	527,398	-2%
Textiles and Leather	10	787,083	344,316	-56%
Water & Wastewater Treatment [4]	84 [5]	11,326,230	10,970,739	-3%
Unknown Uses (no production unit data)	2	60,640	144,389	138%
Totals	**210**	**43,622,175**	**44,847,784**	**3%**

[1] Use Categories were assigned based on the Institute's examination of TURA data and in some cases may not represent the actual use; [2] Number of businesses that reported in 1990 and/or 1996; [3] Chemical Distributors and most Electricity Generators were not required to report until 1991; [4] Wastewater treatment quantities were estimated from available data. In 1990, companies did not report the quantity of a chemical used for waste treatment. In subsequent years, facilities reported a range for the amount used in waste treatment or, optionally, the exact quantity; [5] 25 businesses reported sulfuric acid in waste treatment only, an additional 59 reported some portion used in waste treatment; Source: Massachusetts Toxics Use Reduction Act data, 1998.

- Releases to the environment increased sharply due to the addition of electric generation facilities to the TURA reporting universe in 1991. Those "consistent" facilities that reported in 1990 and 1996, reduced their environmental releases by 18%.

- "Off-site transfers" fell sharply due to two large users reporting 1.3 million pounds of transfers to POTW's in 1990 only. This is likely due to a change in how they reported neutralized acids in the waste stream, rather than real waste reductions.

(For section references, see endnote #2.)

Alternatives

In Massachusetts, sulfuric acid is considered integral to many processes making the search for alternatives challenging. In some applications however, alternatives for reducing byproduct or eliminating use are both cost and technically effective.

Sulfuric acid is often used to control pH and to regenerate ion exchange resins. Alternatives processes or creating new vendor relationships have reduced or eliminated the use of sulfuric acid in many companies.

- Carbon dioxide is an alternative to sulfuric acid when used for pH control. As demonstrated in the Toxics Use Reduction Institute's Demonstration Sites Program, Massachusetts' Cranston Print Works eliminated 1.9 million pounds of sulfuric acid by substituting a liquid carbon dioxide process to neutralize wastewater. A case study by the Office of Technical Assistance documents a 99% reduction of sulfuric acid at Standard Uniform Services in Agawam by installing a similar system.

- Reverse osmosis can be used instead of ion exchange so that acid is not needed to regenerate the ion exchange resins. Traditionally ion exchange has been more popular than reverse osmosis due to a lower capital cost and 100% use of the treated water (compared to 70%-90% with reverse osmosis). However, the capital costs of reverse osmosis systems are becoming more competitive and they do not require the use and associated cost of any regeneration chemical. In 1994 The Robbins Company of Attleboro reduced its acid use by nearly 100% by replacing an ion exchange system with a reverse osmosis system for water treatment.

- Refuse Energy System Company in Saugus won a Governor's Award for Outstanding Achievement in Toxics Use Reduction partly for reducing its sulfuric acid use by 67%. The company first determined the true water quality needs for its boiler operations. The company then negotiated a service performance contract with its supplier to pay a flat fee for a certain level of water conditioning. The chemical supplier then has motivation to minimize chemical use.

Sulfuric acid is commonly used for cleaning. Previously regulations may have been a barrier to companies to reduce use or switch to alternatives.

- When used to clean food processing tanks, its use may be specifically required by regulations of the U.S. Food and Drug Administration (FDA). However, a search of the Toxics Use Reduction Institute's database of cleaning chemistries found 10 non-sulfuric acid-containing chemistries that have FDA approval. These products may be substitutes, depending on the application.

- The semiconductor industry uses ultra-pure, concentrated sulfuric acid to clean silicon wafers. Recycling or reusing the spent acid is inhibited by perceived RCRA (Resource Conservation and Recovery Act) barriers identified through the U.S. EPA's Common Sense Initiative. The EPA is currently preparing an information sheet to encourage recycling of this acid.

In electronics and surface finishing operations, sulfuric acid is used in many processes including etching, pickling and anodizing.

- In electronics manufacture, two sulfuric-acid containing micro-etch solutions are used: sulfuric acid/hydrogen peroxide, and persulfate (typically peroxydisulfate). The sulfuric/peroxide systems use considerably more sulfuric acid than the persulfate systems, but the bath life of the sulfuric/peroxide systems can be increased by continuously removing the copper using an electrolytic plate-out cell and reusing the etch solution.

- In the electroplating pickling process, sulfuric acid can be replaced by hydrochloric acid or phosphoric acid, each with their own associated hazards. Diffusion dialysis can extend the bath life of an acid pickling solution with substantial savings in sulfuric acid purchases and waste volumes. For copper and tin plating, the pickling baths do not degrade readily and the major losses can be reduced by reducing dragout.

- Dragout is a continual source of loss and must be minimized. This can be accomplished by removing the workpiece at a slower rate, increasing drip time, installing drain boards or drip bars between baths, maintaining racking designs for maximum draining, and installing air knives or spray or fog rinses above process tanks.

- Sulfuric acid losses from anodizing operations are partially a function of dragout, but also of aluminum build-up in the bath. Both diffusion dialysis and acid sorption can extend the lives of these baths and are generally cost effective, even for smaller operations.

- Anodizers also use sulfuric acid combined with hydrofluoric acid and nitric acid to remove smut from cast aluminum. The triacid combination is necessary due to silicon addition prior to casting, which must be removed by the presence of the fluoride ion. Non-cast aluminum can be desmutted using either a 1:1 concentrated nitric acid to water solution or with a low concentration nitric acid solution (~4% HNO_3 with an iron salt). If an anodizer is processing both cast and non-cast aluminum, and if the facility has available space, two desmutting processes can be used to lessen the load on the sulfuric acid-containing bath.

- In addition, the less acid that must be treated by the waste treatment process in these operations, the less neutralization chemical will be required.

(For section references, see endnote #3.)

Regulatory Context

The U.S. Occupational Safety and Health Administration (OSHA) and U.S. Environmental Protection Agency (EPA) regulate sulfuric acid.

The OSHA permissible exposure limit (PEL) for sulfuric acid, averaged over an 8-hour workshift, is 1.0 milligram per cubic meter (mg/m3).

The U.S. EPA regulates sulfuric acid under the authority of three environmental statutes. Under the:

- Comprehensive Environmental Responsibility, Compensation and Liability Act (popularly known as "Superfund"), sulfuric acid is regulated as an "extremely hazardous substance."
- Emergency Planning and Community Right-to-Know Act, TRI program, all large quantity users of sulfuric acid aerosols only must submit data on environmental releases, off-site transfers, and production-related waste.
- Federal Insecticide, Fungicide, and Rodenticide Act, sulfuric acid is a "registered pesticide."

(For section references, see endnote #4.)

Endnotes

1 Environmental Defense Fund (EDF), 1999, "Chemical Profile: Sulfuric Acid" (New York: EDF; see webpage: http:/www.scorecard.org/chemical-profiles/); Environmental Health Center (EHC), a division of the National Safety Council, 1997, "Environment Writer: Sulfuric Acid (H2SO4) Chemical Backgrounder" (Washington, D.C.: EHC; see webpage: http://www.nsc.org/ehc/ew/chems/sulfacid.htm); Richard J. Lewis, Sr. (ed.), 1993, Hazardous Chemicals Desk Reference (New York: Van Nostrand Reinhold); and New Jersey Department of Health and Senior Services, 1995, "Hazardous Substance Fact Sheet: Sulfuric Acid" (Trenton, New Jersey; see webpage: http://www.state.nj.us/health/eoh/rtkweb/rtkhsfs.htm).

2 Stanford Research Institute (SRI) International, 1995, Chemical Economics Handbook, "Sulfuric Acid" (Palo Alto, California: SRI). The Massachusetts chemical use data are from the Massachusetts Department of Environmental Protection (MA DEP), 1998, "Massachusetts Toxics Use Reduction Act Chemical Reporting Data" (Boston: MA DEP).

3 US Environmental Protection Agency, 1992, "Guides to Pollution Prevention The Metal Finishing Industry" (Washington, D.C.); Toxics Use Reduction Institute, Printed Wiring Board Industry Module, TUR Planner's Certification Course, Rev 2.1, (Lowell Massachusetts, TURI), Toxics Use Reduction Institute 1996, Technical Report No. 31 "Toxics Use Reduction Through Process Improvement, Substitution & Integral Recycling" (Lowell Massachusetts, TURI); EPA website http://www.epa.gov/ooaujeag/csi/computer/accomp12.htm; Office of Technical Assistance, Toxics Use Reduction Case Study, "Elimination of TURA Chemical Reporting at The Robbins Company," (Boston, Massachusetts, see webpage: http://www.state.ma.us/ota/cases/robbins.htm); Office of Technical Assistance, Toxics Use Reduction Case Study, "Sulfuric Acid Reduction at Standard Uniform Services," (Boston, Massachusetts, see webpage: http://www.state.ma.us/ota/cases/standard.htm).

4 The data in this section are from the following sources: EDF, 1999; Lewis, 1993; and New Jersey Department of Health and Senior Services, 1995 (see endnote #1 for full citations).