Massachusetts Chemical Fact Sheet

Hydrofluoric Acid

Hydrofluoric acid is extremely corrosive. Acute exposures are especially hazardous and can result in severe burns or respiratory damage. U. S. manufacturers use hydrofluoric acid to produce fluorocarbons, aluminum and other chemical products. Metal pickling and etching applications are the primary end-uses for hydrofluoric acid in Massachusetts. Hydrofluoric acid use is on the decline in Massachusetts. However, produced as an unintended byproduct, coal-fired power plants are a potential source of public exposure to hydrofluroic acid.

FACTS

Other Name:	Hydrogen Fluoride
Chemical Formula:	HF
CAS Number:	7664-39-3
Vapor Pressure:	760 mm Hg at 20°C (68°F)
Water Solubility:	Very Soluble

Hazards

Acute (Short-Term) Health Effects

- Skin contact with hydrogen fluoride, or solutions containing more than 30% hydrogen fluoride, produces immediate pain. Reactions to more dilute solutions may be delayed for many hours. The accompanying pain is excruciating and persistent, and healing is delayed.

- Contact with eyes may result in permanent eye damage.

- Hydrofluoric acid is a poison by inhalation. If inhaled hydrofluoric acid can cause severe respiratory damage, including severe irritation of the nose, throat, and lungs and pulmonary edema (fluid build-up in the lungs). At concentrations of 30 parts per million (ppm) hydrofluoric acid is immediately dangerous to life and health.

- Hydrofluoric acid inhalation may also damage the liver and kidneys.

Chronic (Long-Term) Health Effects

- Hydrofluoric acid is not classified as a carcinogen due to lack of data. Increased rates of cancer have been observed in workers exposed to a mixture of chemicals that included fluoride, but no single chemical was identified as the cause of the cancer.

- Hydrofluoric acid is a possible teratogen (reproductive hazard). Occupational studies of women exposed to fluoride identified increased rates of menstrual irregularities. Animal studies have also found that fluoride impairs reproduction and increases the rates of fetal bone and teeth malformation.

- The chronic inhalation of hydrofluoric acid can cause irritation and congestion of the nose and throat and bronchitis. Animal studies have also found increased rates of kidney and liver damage from hydrofluoric acid inhalation.

University of Massachusetts Lowell • One University Avenue • Lowell Massachusetts 01854-2866
Ph: (978) 934-3275 • Fax: (978) 934-3050 • Web: www.turi.org

Exposure Routes

Worker Health

Facilities using hydrofluoric acid must minimize worker exposure:

- Use hydrofluoric acid in closed systems. If a closed production system is infeasible, enclose operations and use local exhaust ventilation. If hydrofluoric acid exposure may exceed 3 ppm, use a Mine Safety and Health Administration/National Institute for Occupational Safety and Health-approved supplied-air respirator with a full facepiece.

- Take precautions to avoid hydrofluoric acid contact. If hydrofluoric acid contacts skin, wash immediately and get medical attention.

Public Health

- The major sources of hydrofluoric acid are industrial facilities, aluminum smelters, coal-fired power plants, volcanoes, and dust that contain fluorspar (a naturally occurring mineral). Hydrofluoric acid is found at low levels — ranging from 1.2 to 9.1 parts per billion — in ambient air.

(For section references, see endnote #1.)

Use Nationally and in Massachusetts

Manufacturers produce hydrofluoric acid from the mineral fluorspar. Three manufacturers — Allied Signal, DuPont, and Elf Atochem North America — produce hydrofluoric acid in the U.S. They had the capacity to produce 211,000 tons of hydrofluoric acid in 1994. The major U.S. markets

Table 1. Hydrogen Fluoride: Use and Output Data for Massachusetts, 1990 and 1996 (pounds)

Use Data -- MA TURA	1990	1996	Change	% Change
Manufactured or Processed	10,231	156,666	146,435	1431%
Otherwise Used	665,939	484,987	-180,952	-27%
Total TURA Inputs	676,170	641,653	-34,517	-5%
Output Data -- MA TURA	**1990**	**1996**	**Change**	**% Change**
Generated as Byproduct	518,724	582,882	64,158	12%
Shipped In or As Product	10,220	0	-10,220	-100%
Total TURA Outputs	528,944	582,882	53,938	10%
Releases & Transfers Data -- US EPA, TRI	**1990**	**1996**	**Change**	**% Change**
Environmental Releases	12,263	161,075	148,812	1214%
Off-site Transfers	309,564	91,714	-217,850	-70%
Total TRI R&T	321,827	252,789	-69,038	-21%

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

for hydrofluoric acid are fluorocarbon production (46%), aluminum production (21%), chemical derivatives (13%), petroleum alkylation catalysis (4%), metal surface treatments – pickling and desmuting - (4%), uranium production (3%), and other uses, which include the etching of silicon (9%).

- Hydrofluoric acid is an intermediary in the manufacture of fluorocarbons. Prior to the 1987 Montreal Protocol, chlorofluorocarbons (CFCs) were the dominant fluorinated hydrocarbon. Today, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are the dominant fluorocarbons.

- Aluminum manufacturers use cryolite, manufactured from hydrofluoric acid, in the smelting of primary aluminum.

- The major chemical derivatives manufactured from hydrofluoric acid are fluoropolymers, inorganic fluorides, fluoborate salts, fluoboric acid, and fluoborates.

- Petroleum alkylation catalysis is a process for producing high-octane components for use in motor fuels. Hydrofluoric acid is the catalyst in this process.

- Hydrofluoric acid is used in metal surface treatments, including pickling and desmuting. Metal pickling is the process by which manufacturers remove surface oxides (scale) from stainless steel and other metals. A variety of acids can be used to accomplish this task, including nitric and sulfuric acids. Hydrofluoric acid is normally used for the pickling of stainless steel. Desmuting is necessary to remove the gray-to-black residual film deposited on the surface during cleaning and etching processes. Hydrofluoric acid is used for desmuting high-silicon aluminum alloys and aluminum die castings.

- Uranium manufacturers use hydrofluoric acid to produce uranium hexafluoride; it separates U-235 from other uranium isotopes for use in nuclear reactors

- The primary "other" use of hydrofluoric acid is etching. Etching prepares the surface for further processing in various ways, including increasing wettability, changing the appearance or texture of the finish and removing contaminants. The primary use for etching is for silicon in the manufacture of microelectronic circuits. The electronics industry uses high purity, 49% hydrofluoric acid solution, to etch silicon.

Massachusetts' facilities reported using 640,000 pounds of hydrofluoric acid in 1996 (see Table 1). In Massachusetts metal cleaning (pickling and desmuting) and etching applications accounted for 75% of reported hydrofluoric acid use (see Table 2).

- Metal cleaning (pickling and desmuting) is the primary end-use for hydrofluoric acid in Massachusetts. These applications consumed 50% of all hydrofluoric acid use in 1996.

- Etching applications consumed 26% of the state's reported hydrofluoric acid use.

- Hydrofluoric acid is also incidentally "manufactured" by coal-fired power plants. Coal contains minute levels of fluorspar which are converted to hydrofluoric acid during combustion. These facilities, which began reporting in 1991, accounted for 24% of HF use in 1996.

Table 2. Massachusetts Hydrofluoric Acid Consumption by Use Categories (1990 and 1996)

Use Category [1]	Facility Name	Use (pounds) 1990	Use (pounds) 1996	Percent Change
Etching	**Aluminum**			
	Crown Cork & Seal	56,679	58,000	2%
	Ceramics			
	Texas Instruments	10,040	0 [2]	-100%
	Quartz			
	Osram Sylvania Inc	98,706	0	-100%
	Silicon			
	Allegro Microsystems	52,011	25,445	-51%
	Analog Devices	26,000	28,963	11%
	ASE Americas Inc	0	19,967	n/a[3]
	Digital Equip Corp	15,603	22,521	44%
	Lucent Technologies Inc	20,100	0	-100%
	Microsemi Incorporated	14,000	11,517	-18%
	subtotal	293,139	166,413	-43%
Metal Cleaning: Pickling and Desmut	Independent Plating	0	36,500	n/a
	Rodney Metals	49,600	123,092	148%
	Westfield Electroplating Co	0	16,385	n/a
	Wyman Gordon Company[4]	323,200	142,600	-56%
	subtotal	372,800	318,577	-15%
Byproduct -- Fossil Fuel Combustion	Montaup Electric Co	0	64,954	n/a
	New England Power Company[5]	0	91,709	n/a
	subtotal	0	156,663	n/a
Unknown	George Mann and Co.	10,231	0	-100%
	subtotal	10,231	0	-100%
	total	676,170	641,653	-5%

[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] "0" indicates that the facility either is not using the chemical or has dropped below the reportable threshold; [3] n/a = not applicable; [4] Wyman Gordon reported hydrogen fluoride at two facilities in 1990 (Worcester and Grafton) and one facility in 1996 (Grafton); [5] New England Power reported hydrogen fluoride emissions at two facilities in 1996 (Salem and Somerset); Source: Massachusetts Toxics Use Reduction Act data, 1998.

Hydrofluoric acid use in Massachusetts declined slightly, by 5%, between 1990 and 1996. Excluding power plants, who were first required to report in 1991, hydrofluoric acid use declined by 28% between 1990 and 1996. Etching use declined by 43% and metal cleaning use declined by 15%. HF manufactured by power plants decreased by 17% from 189,000 in 1991 to 157,000 in 1996.

Table 1 includes two sources of "output" data: MA TURA and U.S. Environmental Protection Agency (EPA), Toxics Release Inventory (TRI) data. The MA TURA database includes all non-product material created by a process line prior to release, on-site treatment, or transfer ("byproduct") and the amount of toxic chemical incorporated into a product ("shipped in or as product"). The U.S. EPA, TRI database includes 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").

- MA TURA "byproduct" outputs grew by 12% due to the additional reporting of power plants (145,000 pounds in 1996) and increased byproduct generation by Allegro Microsystems, Crown Cork and Seal, and Rodney Metals. Byproducts probably increased for Allegro (25,000 pounds) and Crown Cork and Seal (58,000 pounds) because they incorrectly reported byproduct for 1990, the first year of reporting. Byproduct increased for Rodney Metals due to increased use of hydrofluoric acid.

TRI releases and transfers are much less than TURA outputs because the majority of hydrofluoric acid is treated on-site (neutralized) before being discharged.

- Off-site transfers declined dramatically due to reductions by Rodney Metals (49,000 pounds), Wyman Gordon (70,000 pounds), and Osram Sylvania (99,000 pounds). The Osram Sylvania plant closed in 1995. The Wyman Gordon facility in Worcester stopped reporting hydrofluoric acid use in 1993 (it accounted for 32,000 pounds of hydrofluoric acid off-site transfers in 1990).

- The increase in environmental releases is due to air emissions from power plants, which were required to report in 1991.

(For section references, see endnote #2.)

Alternatives

Due to the hazards associated with the use of hydrofluoric acid, manufacturers are investigating alternatives. Some alternatives for MA TURA-reported uses are discussed in this section.

In metal finishing operations the fluoride ion is often used to accomplish functions such as pickling stainless steel, desmuting high silicon aluminum alloys and die castings, and etching aluminum and some specialty metals.

- The fluoride ion can be introduced either by using hydrofluoric acid or by adding the ion in the form of a salt (e.g., ammonium and sodium fluoride salts)

- For etching, pickling and cleaning other metals, alternative acids (e.g., nitric, hydrochloric, phosphoric) should theoretically accomplish these functions.

Historically metal finishers neutralized their spent acids and landfilled the resulting solid byproduct. Due to increasing material and disposal costs, metal finishers increasingly minimize their acid waste by acid purification and reuse. Although one of the more challenging applications for the technology, diffusion dialysis can be used to recycle spent hydrofluoric acid in mixed acid baths, reducing virgin hydrofluoric acid consumption by as much as 85%. Two Massachusetts manufactures currently offer diffusion dialysis units: Pure Cycle Environmental Technologies Inc. of Palmer and Zero Discharge Technologies, Inc. of Chicopee.

In other etching processes manufacturers continue to search for alternatives to HF and new processes to minimize HF byproducts.

- In 1999, as part of the Institute's Demonstration Sites Program, ASE Americas Inc. in Billerica demonstrated a hydrofluoric acid vapor acid etch process for silicon wafers using an ultra-small volume chamber. This new process reduced their use of hydrofluoric acid by nearly 99% compared to the liquid batch etching process. However, the use of hydrofluoric acid vapor rather than liquid introduced new safety concerns to the process that had to be addressed by implementing strict procedures.

- Texas Instruments implemented a new metal spraying technique for coating ceramic parts that decreased the need for hydrofluoric acid etching of the ceramic parts prior to metal application.

In another etching process ASE Americas, Inc. is researching electrochemical etching in an alkaline solution to replace the acid solution. To aid this research, ASE partnered with UMass Lowell Electrical Engineering Department and received funding through the Institute's University Research in Sustainable Technologies Program.

New non-chemical etch processes (e.g., plasma etch) are being developed for processes where acids and other hazardous materials are currently being used to perform functions such increasing wettability and removing epoxy contamination.

(For section references, see endnote #3.)

Regulatory Context

A well-known hazard to human and environmental health, the U.S. Occupational Safety and Health Administration (OSHA), U.S. EPA, and Consumer Product Safety Commission regulate hydrofluoric acid.

- The OSHA permissible exposure limit (PEL) for an eight-hour workshift for hydrofluoric acid is 3 ppm averaged over an 8-hour workshift.

The U.S. EPA regulates hydrofluoric acid under the authority of five environmental statutes. Under the:

- Clean Air Act, hydrofluoric acid is both a "hazardous air pollutant" and a "regulated toxic, explosive, or flammable substance."
- Comprehensive Environmental Responsibility, Compensation and Liability Act (popularly known as "Superfund"), hydrofluoric acid is an "extremely hazardous substance."
- Emergency Planning and Community Right-to-Know Act, TRI program, all large quantity users of hydrofluoric acid must submit data on environmental releases and off-site transfers.
- Resource Conservation and Recovery Act, hydrofluoric acid is a "hazardous constituent."

(For section references, see endnote #4.)

Endnotes

1 Environmental Defense Fund (EDF), 1999, "Chemical Profile: Hydrofluoric Acid" (New York: EDF; see webpage: http://www.scorecard.org/chemical-profiles/); Environmental Health Center (EHC is a division of the National Safety Council), 1997, "Environment Writer: Hydrogen Fluoride (Hydrofluoric Acid) (HF) Chemical Backgrounder" (Washington, D.C.: EHC; see webpage: http://www.nsc.org/ehc/ew/chems/hydrfluo.htm); Richard J. Lewis, Sr. (ed.), 1993, *Hazardous Chemicals Desk Reference* (New York: Van Nostrand Reinhold); New Jersey Department of Health and Senior Services, 1998, "Hazardous Substance Fact Sheet: Hydrogen Fluoride" (Trenton, New Jersey; see webpage: http://www.state.nj.us/health/eoh/rtkweb/rtkhsfs.htm); and U.S. EPA, Office of Air Quality Planning and Standards, 1998, "Hydrogen Fluoride (and Related Compounds)" (Washington, D.C.: U.S. EPA; see webpage: http://www.epa.gov/ttn/uatw/hlthef/hydrogen.html); Gosselin RE, Smith RP, Hodge HC, 1984, "Clinical Toxicology of Commercial Products," 5th edition, (Baltimore, MD: Williams & Wilkins).

2 The national chemical use data are from Stanford Research Institute (SRI) International, 1995, *Chemical Economics Handbook,* "Fluorine Compounds" (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 SRI, 1995 (see endnote #2 for full citation); Unknown, "Process Fine Tuning Reduces HF Use," *Chemical Engineering Progress*, October 1996, pp. 20-22.

4 EDF, 1999; and New Jersey Department of Health and Senior Services, 1998 (see endnote #1 for full citations).