

4. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

4.1 PRODUCTION

Historically, ethylene glycol has been commercially produced on a large scale by hydration of ethylene oxide (Merck 1989). Currently, it is also produced by the oxidation of ethylene in the presence of acetic acid to form ethylene diacetate which is then hydrolyzed to the glycol, with the acetic acid recycled in the process (Rowe and Wolf 1982). Ethylene glycol was ranked 30th on a list of the top 50 chemicals produced in the United States in both 1992 and 1993 (Chemical and Engineering News 1994).

The companies that produce ethylene glycol in the United States, their production sites, and the annual capacities in millions of pounds for 1993 (the most recent year for which figures are available) are shown below (SRI 1993).

Company	Annual Production	Site Capacity
BASF Corporation	Geismar, LA	470
Dow Chemical	Plaquemine, LA	450
Eastman Chemical Company	Longview, TX	230
Hoechst Celanese Group Corp.	Clear Lake, TX	550
Occidental Petroleum Corp.	Bayport, TX	580
PD Glycol	Beaumont, TX	790
Quantum Chemical Corp.	Morris, IL	220
Shell Oil Company	Geismar, LA	525
Sun Company, Inc.	Brandenburg, KY	2
Texaco Chemical Company	Port Neches, TX	735
Union Carbide Corporation	Seadrift, TX	550
	Taft, LA	1,400
Total Production		6,502

Over the past several years, production volume of ethylene glycol has remained relatively constant at a level of approximately 6,000 million pounds per year (SRI 1989, 1991, 1993). The production volumes were 5,925, 6,250, and 6,502 million pounds in 1989, 1991, and 1993, respectively.

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A list of ethylene glycol production and processing facilities in the United States in 1993 is given in Table 4-1. Table 4-1 lists the number of facilities in each state that manufacture or process ethylene glycol, the range of maximum amounts of ethylene glycol that are stored on-site, and the intended use. The data presented in Table 4-1 are from the Toxic Release Inventory (TRI93 1995). Data from this table should be used with caution since only certain types of facilities are required to report (EPA 1995c). This is not an exhaustive list.

Propylene glycol is produced commercially from the hydration of propylene oxide (Merck 1989). Propylene glycol also is produced by the liquid-phase high pressure reaction (600 atmospheres) of synthetic gas in the presence of a rhodium cluster complex (Kirk-Othmer Encyclopedia of Chemical Technology 1978).

The companies that produce propylene glycol in the United States, their production sites, and the annual capacities in millions of pounds for 1993 (the most recent year for which figures are available) are shown below (SRI 1993).

Company	Production Site	Capacity
ARCO Chemical Company	Bayport, TX	374
Dow Chemical USA	Freeport, TX	250
	Plaquemine, LA	150
Eastman Chemical Company	South Charleston, WV	72
Olin Corporation	Brandenburg, KY	70
Texaco Chemical Company	Port Neches, TX	120
Total Production		1,036

Over the past few years, production of propylene glycol has remained relatively constant at a level of approximately 1,000 million pounds per year (SRI 1989, 1991, 1993, 1995). The production volumes were 935, 1,000, 980, and 1,036 million pounds in 1989, 1991, 1993, and 1995, respectively.

There is no information on facilities that manufacture or process propylene glycol in the United States available in the Toxic Release Inventory because information on this chemical is not required to be reported (EPA 1995c).

2. HEALTH EFFECTS

Table 4-1. Facilities That Manufacture or Process Ethylene Glycol

State ^a	Number of facilities	Range of maximum amounts on-site in thousands of pounds ^b	Activities and uses ^c
AK	1	10-100	13
AL	16	0-10000	1, 6, 7, 8, 11, 12, 13
AR	17	1-50000	1, 2, 4, 5, 7, 8, 9, 11, 12, 13
AZ	8	0-100	1, 2, 3, 5, 8, 12, 13
CA	85	0-50000	2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 13
CO	8	1-10000	1, 5, 7, 8, 10, 12, 13
CT	9	1-100	1, 5, 7, 8, 9, 12, 13
DE	10	0-1000	1, 5, 6, 7, 8, 9, 11, 12, 13
FL	30	1-1000	2, 4, 7, 8, 9, 11, 12, 13
GA	51	0-1000	1, 2, 3, 5, 7, 8, 9, 10, 11, 12, 13
IA	18	1-10000	1, 2, 3, 5, 8, 9, 10, 11, 12, 13
ID	4	1-1000	1, 5, 8, 11, 12
IL	98	0-50000	1, 2, 4, 5, 7, 8, 9, 10, 11, 12, 13
IN	48	0-10000	1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13
KS	12	0-1000	1, 5, 8, 9, 10, 11, 12, 13
KY	36	0-10000	1, 4, 5, 7, 8, 9, 10, 11, 12, 13
LA	32	0-50000	1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 13
MA	17	0-1000	1, 2, 3, 8, 9, 11, 12, 13
MD	17	1-1000	1, 5, 7, 8, 9, 10, 11, 12, 13
ME	10	1-1000	8, 10, 11, 12, 13
MI	52	0-500000	1, 3, 7, 8, 9, 10, 11, 12, 13
MN	16	0-10000	1, 5, 7, 8, 9, 10, 12, 13
MO	32	1-50000	7, 8, 9, 10, 11, 12, 13
MS	10	1-1000	1, 5, 7, 8, 11, 12, 13
MT	4	10-1000	8, 12, 13
NC	52	0-50000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13
ND	4	1-100	9
NE	8	1-10000	8, 9, 12, 13
NH	5	1-100	1, 5, 8, 9, 10, 11, 13
NJ	59	1-10000	1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13
NM	4	1-100	8, 10, 12, 13
NV	1	10-100	8
NY	35	0-1000	1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 13
OH	93	0-100000	1, 2, 4, 5, 7, 8, 9, 10, 11, 12, 13
OK	13	1-10000	7, 8, 9, 10, 12, 13
OR	12	0-1000	7, 8, 9, 10, 12, 13
PA	56	1-50000	1, 2, 3, 5, 7, 8, 9, 10, 11, 12, 13
PR	18	1-1000	1, 2, 3, 5, 7, 8, 9, 11, 12, 13
RI	7	1-10000	1, 2, 4, 5, 7, 8, 10, 11, 12, 13
SC	54	0-50000	1, 5, 7, 8, 9, 10, 11, 12, 13
TN	36	0-50000	1, 2, 3, 5, 7, 8, 9, 10, 11, 12, 13
TX	106	0-100000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13
UT	6	1-1000	2, 5, 7, 8, 10, 12, 13
VA	25	0-10000	1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 12, 13

2. HEALTH EFFECTS

Table 4-1. Facilities That Manufacture or Process Ethylene Glycol (continued)

State ^a	Number of facilities	Range of maximum amounts on-site in thousands of pounds ^b	Activities and uses ^c
WA	14	0-100	8, 9, 10, 11, 12, 13
WI	32	0-10000	8, 9, 10, 11, 12, 13
WV	12	1-100000	1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13
WY	3	1-100	2, 3, 8, 11, 12

Source: TRI93 1995

^a Post office state abbreviations used^b Data in TRI are maximum amounts on-site at each facility^c Activities/Uses:

- | | |
|-------------------------------|----------------------------------|
| 1. Produce | 8. As a formulation component |
| 2. Import | 9. As a product component |
| 3. For on-site use/processing | 10. For repackaging |
| 4. For sale/distribution | 11. As a chemical processing aid |
| 5. As a by-product | 12. As a manufacturing aid |
| 6. As an impurity | 13. Ancillary or other uses |
| 7. As a reactant | |

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4.2. IMPORT/EXPORT

Ethylene glycol has been imported into the United States in large quantities over the last several years. Import volume since 1992 has averaged 200 million kg per year (440 million pounds per year). Import volume was 180,213,702 kg (397 million pounds) in 1992; 171,087,963 kg (377 million pounds) in 1993; and 239,109,749 kg (527 million pounds) in 1994 (NT.DB 1995).

Ethylene glycol also has been exported in large quantities over the last several years with export volume generally being twice that of the import volume for any given year. Export volume since 1990 has averaged 415 million kg per year (915 million pounds per year). Export volume for ethylene glycol was 390,056,362 kg (869 million pounds), 413,797,808 kg (912 million pounds), 396,227,465 kg (874 million pounds), 452,126,142 kg (997 million pounds), and 423,179,712 kg (933 million pounds) in 1990, 1991, 1992, 1993, and 1994 respectively (NTDB 1995).

Propylene glycol has been imported into the United States in ever increasing quantities over the last several years. Import volume increased from 198,031 kg (0.4 million pounds) in 1992, to 2,167,664 kg (4.8 million pounds) in 1993, to 5,249,265 kg (11.6 million pounds) in 1994 (NTDB 1995).

Propylene glycol also has been exported over the last several years with export volume greatly exceeding the import volume in any given year. Export volume for propylene glycol has declined slightly since 1990, but has averaged 77,000,000 kg per year (170 million pounds per year). Export volumes for propylene glycol were 94,606,830 kg (209 million pounds), 64,850,502 kg (143 million pounds), 62,940,802 kg (139 million pounds), 81,531,357 kg (180 million pounds), and 78,997,747 kg (174 million pounds) in 1990, 1991, 1992, 1993, and 1994, respectively (NTDB 1995).

4.3 USE

Ethylene glycol has been used extensively in many different industrial applications because of its chemical and physical properties. Ethylene glycol dissolves in water and is miscible in alcohol and acetone, has the capacity to hold large amounts of heat before boiling, and lowers the freezing point of water (Lewis 1993). In addition, ethylene glycol is hygroscopic (has the ability to absorb twice its weight in water), is suitable for use as an industrial humectant (drying agent), and possesses excellent

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solvent properties (Lewis 1993; Merck 1989; Rowe and Wolf 1982). Approximately 39% of all ethylene glycol produced is used to make antifreeze, 29% is used to make polyester fibers, 26% is exported, and 23% is used to make polyethylene terephthalate (PET) bottles, films, resin products, and in other miscellaneous industrial applications (HSDB 1995a).

The major use of ethylene glycol is in the transportation industry, where it has been used as an ingredient in hydraulic brake fluids, as the major component in automotive antifreeze/coolant, and as a component of de-icing fluids for aircraft, runways, and taxiways (Klecka et al. 1993; Lewis 1993; Merck 1989; Rowe and Wolf 1982). Ethylene glycol also has been used as an intermediate in the synthesis of esters, ethers, and resinous products, particularly polyester fibers (Terylene, Dacron) and resins, and as a solvent (Merck 1989; Rowe and Wolf 1982). As a solvent, ethylene glycol has been used in the paint and plastic industries in the formulation of printers' inks, stamp pad inks, and inks for ball point pens, and as a softening agent in cellophane (Merck 1989; Rowe and Wolf 1982).

Ethylene glycol is also used as a stabilizer for soy bean foam used in fire extinguishers, in photographic developing solutions, and in the manufacture of explosives, plasticizers, elastomers, and synthetic waxes (Lewis 1993; Merck 1989). Small amounts of ethylene glycol are used in pharmaceutical preparations (components of skin lotions, powders, and as a substitute for glycerin) (Browning 1965) and as a preservative in pitfall traps for sampling beetles and other surface-active soil arthropods (Holopainen 1992).

Like ethylene glycol, propylene glycol has been used extensively in many different industrial applications because of its chemical and physical properties. Propylene glycol dissolves in water and is miscible with alcohol, acetone, chloroform, and other organic solvents; has the capacity to hold large amounts of heat before boiling; and lowers the freezing point of water (EPA 1987a; Lewis 1993). In addition, propylene glycol is hygroscopic, is suitable for use as an industrial humectant, and possesses excellent solvent properties (Lewis 1993; Merck 1989; Rowe and Wolf 1982).

Approximately 41% of all propylene glycol produced is used for unsaturated polyester resin production, 29% is exported, 11% is used in foods, pharmaceutical products, and cosmetics, 7% is used in semi-moist pet food, 4% is used as a humectant for tobacco, 4% is used in functional fluids, and 4% is for miscellaneous uses (HSDB 1995b).

The major use of propylene glycol is as an intermediate in the manufacture of cross-linked polyesters and hydroxylated polyester resins. In the airline industry, ethylene glycol has been used as a base

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component of de-icing fluids for aircraft, runways, and taxiways (Klecka et al. 1993; Kirk-Othmer Encyclopedia of Chemical Technology 1978). Propylene glycol is a solvent and humectant for various pharmaceuticals, hair colorant formulations, and food and tobacco products (Kirk-Othmer Encyclopedia of Chemical Technology 1978; Merck 1989). In addition, the use of small amounts of propylene glycol is permitted in foods as an anticaking agent, antioxidant, dough strengthener, emulsifier, processing aid, stabilizer and thickener, surface active agent or texturizer (EPA 1979). In veterinary medicine, propylene glycol is used in oral medications for ruminants and as a solvent for various drugs (Merck 1983). As a nontoxic antifreeze, propylene glycol is used in breweries and dairy establishments and as an inhibitor of fermentation and mold growth (Merck 1989). The chemical has been used as an emollient in pharmaceutical and cosmetic creams because it readily absorbs water. Propylene glycol has even been used in vapor form as an air sterilizer in hospitals and public buildings, and in veterinary applications to protect animals against the spread of airborne bacteria and influenza virus (Kirk-Othmer Encyclopedia of Chemical Technology 1978; Rowe and Wolf 1982). Used as a mist, propylene glycol is deployed as a special effect fog/smoke during theatrical performances, rock concerts, private parties, and in fire training programs to simulate fire fighting conditions (Ross01 1993).

4.4 DISPOSAL

Ethylene glycol is listed as a toxic substance under Section 313 of the Emergency Planning and Community Right-to Know Act (EPCRA) under Title III of the Superfund Amendments and Reauthorization Act (EPA 1995).

Two promising methods for the complete (>99%) destruction of ethylene glycol in waste water are ultraviolet (UV) light-catalyzed oxidation and supercritical oxidation. In the UV light-catalyzed oxidation method, ethylene glycol-containing waste water in the presence of 10% hydrogen peroxide is oxidized by UV irradiation (200-250 nm) with light from a mercury lamp (Wang et al. 1993). The W/hydrogen peroxide undergoes photochemical decomposition to produce OH radicals that are strong oxidants capable of oxidizing most organic compounds stepwise to complete mineralization (e.g., carbon dioxide and water). In the supercritical water oxidation method, the waste water is subjected to oxidation at >550 °C and 4,000 psi pressure with a residence time of <30 seconds (Rice et al. 1993).

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A new technology, *in situ* vitrification (a thermal treatment technology) (Drajun 1991) has shown potential for the remediation of soil contaminated with ethylene glycol. During the *in situ* vitrification process, contaminated soil is transformed into silicate glass using large amounts of electrical energy and a crystalline product similar to obsidian is formed. Another novel approach involving an encapsulated biooxidation method proposes that sodium percarbonate encapsulated in polyvinylidene chloride be inserted in subsurface soil by a method called hydraulic fracturing. Oxygen slowly released from the encapsulated sodium percarbonate increases the number of glycol-degrading organisms. This method is expected to remediate soils contaminated with glycols via enhanced aerobic biodegradation in subsurface soils (Vesper et al. 1994).

Distillation of used automobile and heavy duty engine coolant under reduced pressure has been assessed to be an acceptable technology for recycling ethylene glycol in terms of economic potential, waste reduction potential, and product quality that meets both American Society for Testing and Materials (ASTM) and SAE standards (Randall and Gavaskar 1993).

Propylene glycol is currently listed as a Generally Recognized as Safe (GRAS) additive in foods (FDA 1982) and is not listed as a toxic substance under Section 313 of the Emergency Planning and Community Right-to Know Act under Title III of the Superfund Amendments and Reauthorization Act (EPA 1995c).

Two methods for treatment of waste water containing propylene glycol include a methane fermentation process and a newly developed biotreatment process that uses mixed cultures of bacteria to degrade the compound. The methane fermentation process has proven to be a reliable as well as cost and energy efficient method for the treatment of domestic sludges and certain industrial waste water containing propylene glycol and other organic compounds (Chou et al. 1979). Propylene glycol in effluents from propylene oxide production plants contains both high biological oxygen demand/chemical oxygen demand (BOD/COD) loads and high chloride concentrations. The high salinity poses problems to waste water treatment such as activated sludge and activated carbon absorption processes. A novel and economically viable propylene glycol biotreatment process recently has been developed that uses a mixed culture of engineered bacterial species from the genera *Pseudomonas* and *Aerobacter*. The *Pseudomonas* use propylene glycol to produce volatile acids, while *Aerobacter* were effective in degrading the volatile acids to carbon dioxide and water (Raja et al. 1991).

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A new encapsulated biooxidation method has shown potential for the remediation of soil contaminated with propylene glycol (Vesper et al. 1994). The encapsulated biooxidation method proposes that sodium percarbonate encapsulated in polyvinylidene chloride be inserted in subsurface soil by a method called hydraulic fracturing. Oxygen slowly released from the encapsulated sodium percarbonate increases the number of glycol-degrading organisms. In a laboratory experiment conducted over a 30-day period at 12 °C that simulated subsurface soil temperatures, the concentration of propylene glycol was reduced 10-fold and the number of propylene glycol degrading organisms increases 10-fold compared to live controls without the encapsulated sodium percarbonate. This method is expected to remediate soils contaminated with glycols via enhanced aerobic biodegradation in subsurface soils. The hydraulic fracturing technique that would be used to deliver the encapsulated sodium percarbonate to the subsurface soils involves creating horizontal pancake-shaped fractures that are 5 meters in diameter and 1-2 cm in thickness. These fractures are stacked vertically in the subsoil, and granular material is injected into each fracture (Vesper et al. 1994). The advantage of this method is that oxygen can be delivered deep into contaminated subsurface soil and then made available slowly to stimulate bacterial growth.

