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

5.1 PRODUCTION

1,4-Dioxane is manufactured in a closed system by acid catalyzed conversion of diethylene glycol via dehydration and ring closure. The use of mono-, tri-, and polyethylene glycol and their ethers as raw materials has also been reported. Concentrated sulfuric acid (ca. 5%) is used as the acid catalyst, although phosphoric acid, *p*-toluenesulfonic acid, strongly acidic ion-exchange resins, and zeolites are alternatives. Operating conditions vary; temperatures range from 130 to 200 °C and pressures range from a partial vacuum to slight pressure (i.e., 188–825 mm Hg). The ideal temperature is reported to be 160 °C. The reaction process is continuous and carried out in a heat vessel. The raw 1,4-dioxane product forms an azeotrope with water which is then vaporized from the reaction vessel by distillation. 1,4-Dioxane vapors are passed through an acid trap and two distillation columns to remove water and purify the product. Yields of ca. 90% are achievable. 2-Methyl-1,3-dioxolane, 2-ethyl-1,3-dioxolane, and acetaldehyde are the main by-products. To a lesser extent, crotonaldehyde, and polyglycol are also formed during the production. The crude 1,4-dioxane is further cleaned by heating with acids, distillation (to remove glycol and acetaldehyde), salting out with NaCl, $CaCl_2$, or NaOH, and fine subsequent distillation (EC 2002; Surprenant 2002).

While the latter production process is the most important industrially, two other processes are especially useful for the production of substituted dioxanes. 1,4-Dioxane can be prepared by ring closure of 2-chloro-2'-hydroxydiethyl ether (formed from ethylene glycol reacting with 1,2-dibromoethane) through heating with 20% sodium hydroxide, and by catalysed cyclo-dimerisation of ethylene oxide either over $NaHSO_4$, SiF_4, or BF_3, or at an elevated temperature with an acidic cation-exchange resin (EC 2002; Surprenant 2002).

Commercial production of 1,4-dioxane in the United States was first reported in 1951, but semi-commercial quantities were available in 1929 (NCI 1985). Currently, 1,4-dioxane is produced in the United States by two manufacturers: Dow Chemical (production site, Freeport, Texas) and Ferro Corporation (production site, Baton Rouge, Louisiana) (SRI 2003). Outside of the United States, 1,4-dioxane is produced by BASF AG in Lugwigshafen, Germany, Osaka Yuki and Toho Chem, Japan, and also in other countries around the world (ChemChannels 2004; EC 2002).

Recent information was not available on the production volumes of 1,4-dioxane in the United States. The total production of 1,4-dioxane for 1982 was estimated at 15 million pounds (6,800 metric tons), up from 12 million pounds (5,400 metric tons) reported in 1977 (HSDB 2005). The worldwide production capacity in 1985 was estimated to be 11,000–14,000 metric tons/year. In 1995, the production capacity of known producers and the worldwide production volume was estimated at 8,000 and 10,000 metric tons/year, respectively. In Europe, the production volume in 1997 was estimated to be 2,000–2,500 metric tons (EC 2002). However, current production levels of 1,4-dioxane are expected to be significantly less due to changing use patterns.

Table 5-1 lists the facilities in each state that manufacture or process 1,4-dioxane, the intended use, and the range of maximum amounts of 1,4-dioxane that are stored on-site. There are 368 facilities that produce or process 1,4-dioxane in the United States. The data from the Toxics Release Inventory (TRI) listed in Table 5-1 should be used with caution, however, since only certain types of facilities were required to report (EPA 1995). This is not an exhaustive list (TRI04 2007).

5.2 IMPORT/EXPORT

No information was located on the current import/export levels of 1,4-dioxane for the United States. In 1977, at least $9.1x10^4$ kg of 1,4-dioxane were imported into the United States (HSDB 2005). However, current import levels of 1,4-dioxane are expected to be significantly less due to changing use patterns.

5.3 USE

Because of its broad range of solvent properties, 1,4-dioxane has found a variety of applications. 1,4-Dioxane is used as a solvent for chemical processing (e.g., adhesives, cleaning and detergent preparations, cosmetics, deodorant fumigants, emulsions and polishing compositions, fat, lacquers, pulping of wood, varnishes, waxes). 1,4-Dioxane has also been used as a laboratory reagent (e.g., mobile phase in chromatography); in plastic, rubber, insecticide, and herbicides; as a chemical intermediate; as part of a polymerization catalyst; and as an extraction medium of animal and vegetable oils. Other minor uses are in the manufacture of membrane filters, for measuring optical activity, and for cryoscopic determination. 1,4-Dioxane has been reported to be used in the production processes of the following product categories: pharmaceuticals/pesticides, magnetic tape, and adhesives. In the past, 1,4-dioxane was used primarily as a stabilizer in chlorinated solvents, particularly 1,1,1-trichloroethane. Approximately 90% of former production of 1,4-dioxane was used in this application. 1,4-Dioxane was typically used at a concentration of about 3.5% in chlorinated solvents. However, at the end of 1995, the

Table 5-1. Facilities that Produce, Process, or Use 1,4-Dioxane

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AL	5	1,000	999,999	1, 5, 6, 7, 10, 11
AR	6	1,000	999,999	1, 5, 7, 10, 12
AZ	1	1,000	9,999	12
CA	34	0	99,999	2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13
CO	1	1,000	9,999	10
CT	4	100	99,999	1, 2, 3, 5, 6, 8, 10
GA	3	0	9,999	1, 5, 7
IA	4	0	99,999	8, 12
IL	14	100	9,999,999	1, 2, 4, 5, 7, 9, 10, 11, 12
IN	12	0	99,999	2, 7, 10, 11, 12
KS	2	0	999	1, 2, 3, 7, 11
KY	2	100	999	7, 12
LA	22	0	49,999,999	1, 4, 5, 7, 9, 12, 13
MA	5	1,000	99,999	7, 10, 11, 12
MD	1	1,000	9,999	7
ME	2	100	9,999	11, 12
MI	8	0	99,999	7, 9, 11, 12
MN	9	0	99,999	1, 2, 3, 4, 5, 7, 10, 11, 12, 13
MO	15	0	999,999	1, 3, 5, 6, 7, 8, 9, 10, 12, 13
MS	12	0	999,999	1, 2, 5, 6, 7, 9, 11, 12
NC	20	0	99,999	1, 2, 5, 6, 7, 9, 12, 13, 14
NE	2	10,000	99,999	12
NH	2	100	99,999	11
NJ	6	0	99,999	1, 2, 4, 5, 7, 9, 10, 12, 14
NY	17	100	99,999	1, 5, 7, 9, 10, 11, 12, 13
OH	21	0	999,999	1, 5, 7, 9, 10, 11, 12
OK	2	100	9,999	7, 8
OR	2	1,000	99,999	10
PA	9	100	99,999	7, 9, 10, 11, 12
PR	4	0	999,999	10, 12
SC	23	0	9,999,999	1, 5, 6, 7, 9, 11, 12, 13, 14
TN	15	0	99,999	1, 5, 10, 12, 13
TX	38	0	9,999,999	1, 3, 4, 5, 6, 7, 8, 9, 11, 12, 13, 14
UT	10	0	999,999	7, 10, 11, 12
VA	7	0	99,999	1, 2, 5, 10, 12
WA	1	1,000	9,999	11
WI	8	100	999,999	1, 5, 7, 9, 10, 11, 12, 13

Table 5-1. Facilities that Produce, Process, or Use 1,4-Dioxane

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
WV	18	0	999,999	1, 3, 5, 6, 7, 8, 12, 13, 14
WY	1	0	99	12

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses
14. Process Impurity

Source: TRI04 2007 (Data are from 2004)

use of 1,1,1-trichloroethane was limited under the Montreal Protocol due to the ozone depletion potential of 1,1,1-trichloroethane. Thus, current use of 1,4-dioxane as a stabilizer of 1,1,1-trichloroethane will not be significant (EC 2002; Hartung 1989; HSDB 2005; NICNAS 1998).

1,4-Dioxane has been found as an impurity in cosmetics, household and industrial detergents, and pharmaceuticals due to its occurrence as a by-product in ethoxylated emulsifiers (Hartung 1989). Currently, most manufacturers utilize vacuum stripping to remove 1,4-dioxane before formulation of ethoxylated surfactants in consumer cosmetics and household products (EC 2002).

5.4 DISPOSAL

The primary method of disposal of 1,4-dioxane is by incineration. Small amounts of 1,4-dioxane can be diluted with large amounts of water and subsequently discharged to waste water treatment plants (United Nations 1985). However, since 1,4-dioxane does not undergo significant biodegradation in waste water treatment plants, much of the 1,4-dioxane disposed by this method will end up in the environment.
In contrast to biological or physical methods, chemical treatment has been found to be highly effective for the removal of 1,4-dioxane from water. 1,4-Dioxane is rapidly degraded by hydrogen peroxide in combination with a ferrous salt. Chlorination has also been found to be highly effective for the removal of 1,4-dioxane from water. For example, chlorine and hypochlorous acid are capable of oxidizing 1,4-dioxane (Dow Chemical Co. 1989). However, the extent to which 1,4-dioxane is removed from waste streams by these methods is unknown.