GLYCOLS

1. Ethylene Glycols

1.1. Introduction. Glycols are diols, compounds containing two hydroxyl groups attached to separate carbon atoms in an aliphatic chain. Although glycols may contain heteroatoms, those discussed here are composed solely of carbon, hydrogen, and oxygen. These are adducts of ethylene oxide and can be represented by the general formula, $C_{2n}H_{4n}O_{n-1}(OH)_2$.

Ethylene glycol, the adduct of water and ethylene oxide, is the simplest glycol and is the principal topic of this section. Diethylene, triethylene, and tetraethylene glycols are oligomers of ethylene glycol. Polyglycols are higher molecular weight adducts of ethylene oxide and are distinguished by intervening ether linkages in the hydrocarbon chain. These polyglycols are commercially

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important; their properties are significantly affected by molecular weight. They are water soluble, hygroscopic, and undergo reactions common to the lower weight glycols.

Ethylene glycol, EG, is a colorless, practically odorless, low viscosity, hygroscopic liquid of low volatility. It is completely miscible with water and many organic liquids. EG was first prepared by Wurtz in 1859 by hydrolysis of ethylene glycol diacetate. It did not achieve commercial interest until World War I, when it was used in Germany as a substitute for glycerol (qv) in explosives manufacture (1). The uses for ethylene glycol are numerous. Some of the applications are polyester resins for fiber, PET containers, and film applications; all-weather automotive antifreeze and coolants, defrosting and deicing aircraft; heat-transfer solutions for coolants for gas compressors, heating, ventilating, and air-conditioning systems; water-based formulations such as adhesives, latex paints, and asphalt emulsions; manufacture of capacitors; and unsaturated polyester resins. The oligomers also have excellent water solubility but are less hygroscopic and have somewhat different solvent properties. The number of repeating ether linkages controls the influence of the hydroxyl groups on the physical properties of a particular glycol.

Glycols undergo reactions common to monohydric alcohols forming esters, acetals, ethers, and similar products. For example, both simple and polyesters are produced by reaction with mono- or dibasic acids (eqs. 1 and 2):

$$\begin{gathered}\underset{\text{triethylene glycol}}{HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH} + 2\,CH_3COOH \longrightarrow \\ \underset{\text{triethylene glycol diacetate}}{CH_3COOCH_2CH_2OCH_2CH_2OCH_2CH_2OOCCH_3} + 2\,H_2O\end{gathered} \tag{1}$$

$$HOCH_2CH_2OH + HOOC{-}R{-}COOH \longrightarrow \underset{\text{polyester}}{H\!\left(OOC{-}R{-}COOCH_2CH_2\right)_{x}\!OH} + H_2O \tag{2}$$

1.2. Physical Properties. Ethylene glycol and its lower polyglycols are colorless, odorless, high boiling, hygroscopic liquids completely miscible with water and many organic liquids. Physical properties of ethylene glycols are listed in Table 1. Vapor-pressure curves of the ethylene glycols at various temperatures are illustrated in Figure 1. Ethylene glycols markedly reduce the freezing point of water (Fig. 2). Some important physical constants of ethylene glycol are given in Table 2.

1.3. Chemical Properties. The hydroxyl groups on glycols undergo the usual alcohol chemistry giving a wide variety of possible derivatives. Hydroxyls can be converted to aldehydes, alkyl halides, amides, amines, azides, carboxylic acids, ethers, mercaptans, nitrate esters, nitriles, nitrite esters, organic esters, peroxides, phosphate esters, and sulfate esters (6,7).

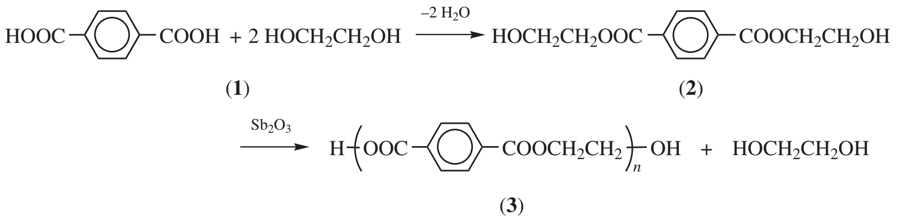
The largest commercial use of ethylene glycol is its reaction with dicarboxylic acids to form linear polyesters. Poly(ethylene terephthalate) [25038-59-9] (PET) is produced by esterification of terephthalic acid [100-21-0] (1) to form

Table 1. **Properties of Glycols**[a]

Property	Ethylene glycol	Diethylene glycol	Triethylene glycol	Tetraethylene glycol
CAS registry number	[107-21-1]	[111-46-6]	[112-27-6]	[112-60-7]
formula	$HOCH_2\text{-}CH_2OH$	$HO(CH_2\text{-}CH_2O)_2H$	$HO(CH_2\text{-}CH_2O)_3H$	$HO(CH_2\text{-}CH_2O)_4H$
mol wt	62.07	106.12	150.17	194.23
sp gr, 20/20°C	1.1155	1.1185	1.1255	1.1247
bp at 101.3 kPa,[b] °C	197.6	245.8	288	dec
mp, °C	−13.0	−6.5	−4.3	−4.1
viscosity at 20°C, mPa · s(= cP)	20.9	36	49	61.9
refractive index, n_D^{20}	1.4318	1.4475	1.4561	1.4598
heat of vaporization at 101.3 kPa,[b] kJ/mol[c]	52.24	52.26	61.04	62.63
flash point of commercial material, °C	116[d]	138[e]	172[e]	191[e]

[a] Ref. 2–5.
[b] To convert kPa to mm Hg, multiply by 7.5.
[c] To convert kJ to kcal, divide by 4.184.
[d] Determined by ASTM D56, using the Tag closed cup.
[e] Determined by ASTM D92, using the Pensky-Martens closed cup.

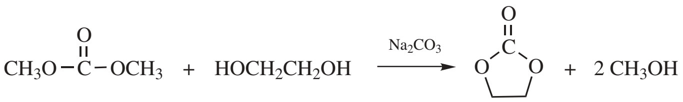
bishydroxyethyl terephthalate [959-26-2] (BHET) (2). BHET polymerizes in a transesterification reaction catalyzed by antimony oxide to form PET (3).



(3)

Ethylene glycol esterification of BHET is driven to completion by heating and removal of the water formed. PET is also formed using the same chemistry starting with dimethyl terephthalate [120-61-6] and ethylene glycol to form BHET also using an antimony oxide catalyst.

Glycols may undergo intramolecular cyclization or cyclically condense with other molecules to form a number of ring structures. Transesterification of carbonates with ethylene glycol produces ethylene carbonate [96-49-1] (eq. 4). Numerous materials catalyze carbonate transesterifications.



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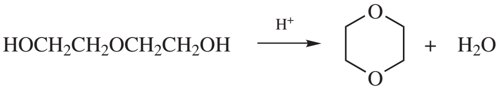
Diethylene glycol readily dehydrates using an acid catalyst to make 1,4-dioxane [123-91-1] (eq. 5).



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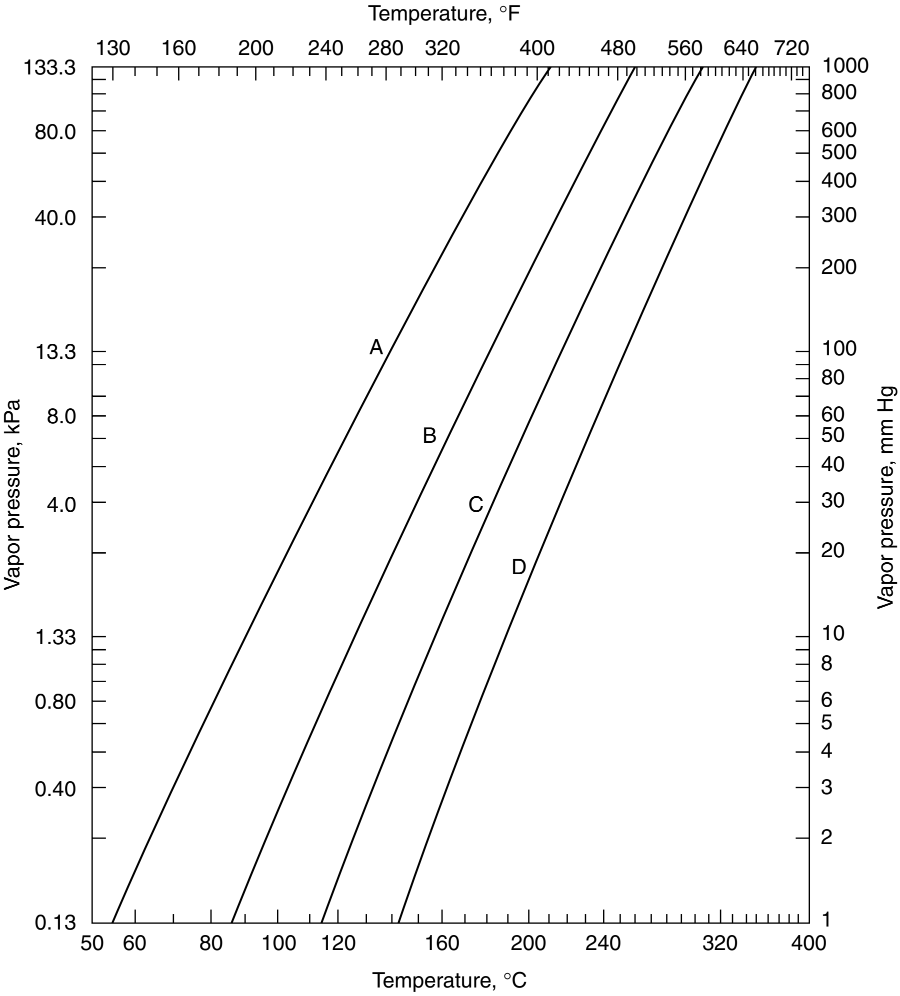
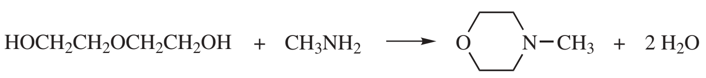


Fig. 1. Vapor pressures of glycols at various temperatures. A, ethylene glycol; B, diethylene glycol; C, triethylene glycol; and D, tetraethylene glycol.

Ethylene glycol also produces 1,4-dioxane by acid-catalyzed dehydration to diethylene glycol followed by cyclization. Cleavage of triethylene and higher glycols with strong acids also produces 1,4-dioxane by catalyzed ether hydrolysis with subsequent cyclization of the diethylene glycol fragment. Diethylene glycol condenses with primary amines to form cyclic structures (eq. 6), eg, methylamine [74-89-5] reacts with diethylene glycol to produce *N*-methylmorpholine [109-02-4].



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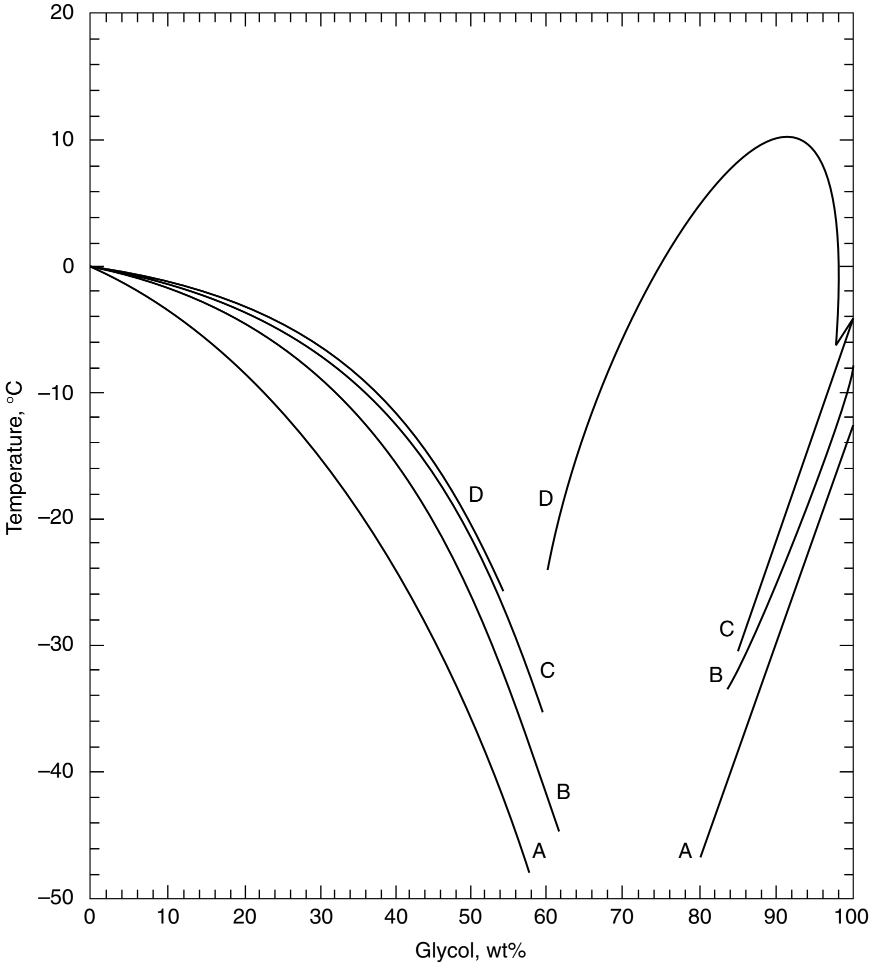
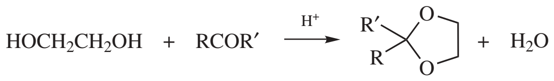


Fig. 2. Freezing points of aqueous glycol solutions. A, ethylene glycol; B, diethylene glycol; C, triethylene glycol; and D, tetraethylene glycol. Ethylene glycols form a slush with water in the apparent discontinuous ranges.

Ketones and aldehydes react with ethylene glycol under acidic conditions to form 1,3-dioxolanes (cyclic ketals and acetals) (eq. 7).



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1.4. Manufacture.

In 1937 the first commercial application of the Lefort direct ethylene oxidation to ethylene oxide [75-21-8] followed by hydrolysis of ethylene oxide became, and remains, the main commercial source of ethylene glycol production (1) (see Ethylene Oxide). Ethylene oxide hydrolysis proceeds

Table 2. **Physical Properties of Ethylene Glycol**[a]

Property	Value
flash point	
Pensky-Martens closed cup, °C	127
Cleveland open cup, °C	127
autoignition temperature, °C	400
density at 20°C, g/mL	1.1135
surface tension at 20°C, mN/m(= dyn/cm)	48.4
specific heat, J/(g · K)[b]	
as liquid, 19.8°C	2.406
as ideal gas, 25°C	1.565
electrical conductivity at 20°C, S/m	1.07×10^{-4}
solubility in water at 20°C, % by wt	100.0
solubility of water in EG at 20°C, % by wt	100.0
heat of combustion at 25°C, kJ/mol[b]	−1189.595
heat of formation at 25°C, kJ/mol[b]	−392.878
heat of fusion, kJ/mol[b]	11.63
onset of initial decomposition, °C	165
critical constants	
temperature, °C	446.55
pressure, kPa[c]	6515.73
volume, L/mol	0.186
compression factor, Z_c	0.2671
viscosity, mPa · s(= cP)	
at 0°C	51.37
at 40°C	9.20

[a] Ref. 2; see also Table 1.
[b] To convert J to cal, divide by 4.184.
[c] To convert kPa to mm Hg, multiply by 7.5.

with either acid or base catalysis or uncatalyzed in neutral medium. Acid-catalyzed hydrolysis activates the ethylene oxide by protonation for the reaction with water. Base-catalyzed hydrolysis results in considerably lower selectivity to ethylene glycol. The yield of higher glycol products is substantially increased since anions of the first reaction products effectively compete with hydroxide ion for ethylene oxide. Neutral hydrolysis (pH 6–10), conducted in the presence of a large excess of water at high temperatures and pressures, increases the selectivity of ethylene glycol to 89–91%. In all these ethylene oxide hydrolysis processes the principal by-product is diethylene glycol. The higher glycols, ie, triethylene and tetraethylene glycols, account for the remainder.

The large excess of water from the hydrolysis is removed in a series of multiple-effect evaporators (8), and the ethylene glycol is refined by vacuum distillation. Figure 3 depicts a typical process flow diagram.

Ethylene glycol was originally commercially produced in the United States from ethylene chlorohydrin [107-07-3], which was manufactured from ethylene and hypochlorous acid (eq. 8) (see CHLOROHYDRINS). Chlorohydrin can be converted directly to ethylene glycol by hydrolysis with a base, generally caustic or caustic/bicarbonate mix (eq. 9). An alternative production method is converting

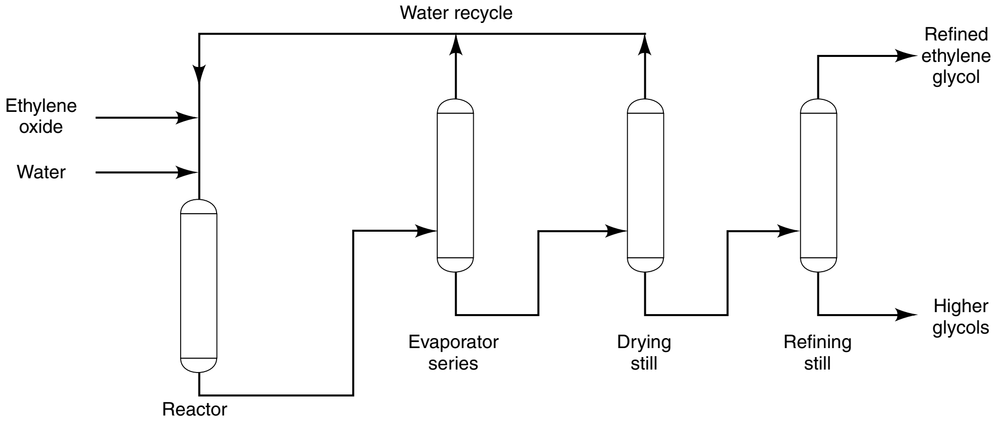


Fig. 3. Simplified glycol process flow diagram.

chlorohydrin to ethylene oxide (eq. 10) with subsequent hydrolysis (eq. 11).

$$CH_2{=}CH_2 + HOCl \longrightarrow HOCH_2CH_2Cl \tag{8}$$

$$HOCH_2CH_2Cl + NaOH \longrightarrow HOCH_2CH_2OH + NaCl \tag{9}$$

$$HOCH_2CH_2Cl + Ca(OH)_2 \longrightarrow \overset{O}{CH_2{-}CH_2} + CaCl_2 + H_2O \tag{10}$$

$$\overset{O}{CH_2{-}CH_2} + H_2O \longrightarrow HOCH_2CH_2OH \tag{11}$$

This process allows the purification of glycols without the difficulties of salt separation because the manufacturing procedure is done in two discrete steps with ethylene oxide distillation prior to hydrolysis. The hydration step is either uncatalyzed at high temperatures and pressures or utilizes an acid catalyst. A U.S. Industrial Chemicals, Inc. process uses a sulfuric acid catalyst at moderate temperatures producing an aqueous solution of glycol-containing acid (9). This process requires an additional step in the purification to remove the catalyst.

Du Pont commercially produced ethylene glycol from carbon monoxide, methanol, hydrogen, and formaldehyde (qv) until 1968 at Belle, West Virginia. The process consisted of the reaction of formaldehyde, water, and carbon monoxide with an acid catalyst to form glycolic acid. The acid is esterified with methanol to produce methyl glycolate. Subsequent reduction with hydrogen over a chromate catalyst yields ethylene glycol and methanol (eqs. 12–14). Methanol and formaldehyde were manufactured on site from syngas.

$$CO + CH_2O + H_2O \longrightarrow HOOCCH_2OH \tag{12}$$

$$HOOCCH_2OH + CH_3OH \longrightarrow CH_3OOCCH_2OH + H_2O \tag{13}$$

$$CH_3OOCCH_2OH + H_2O \longrightarrow HOCH_2CH_2OH + CH_3OH \tag{14}$$

Coal was the original feedstock for syngas at Belle; thus ethylene glycol was commercially manufactured from coal at one time. Ethylene glycol manufacture from syngas continues to be pursued by a number of researchers (10).

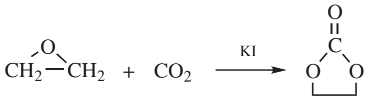
Ethylene glycol can be produced from acetoxylation of ethylene (eq. 15). Acetic acid, oxygen, and ethylene react with a catalyst to form the glycol mono and diacetate. Catalysts can be based on palladium, selenium, tellurium, or thallium. The esters are hydrolyzed to ethylene glycol and acetic acid (eq. 16). The net reaction is ethylene plus water plus oxygen to give ethylene glycol. This technology has several issues which have limited its commercial use.

$$CH_3COOH + CH_2{=}CH_2 + O_2 \xrightarrow{TeO_2,Br_2} CH_3COOCH_2CH_2OH + CH_3COOCH_2CH_2OOCCH_3 \qquad (15)$$

$$CH_3COOCH_2CH_2OH + CH_3COOCH_2CH_2OOCCH_3 + \xrightarrow{3\,H_2O} 2\,HOCH_2CH_2OH + 3\,CH_3COOH \qquad (16)$$

The catalysts and acetic acid are highly corrosive, requiring expensive construction materials. Trace amounts of ethylene glycol mono- and diacetates are difficult to separate from ethylene glycol limiting the glycol's value for polyester manufacturing. This technology (Halcon license) was practiced by Oxirane in 1978 and 1979 but was discontinued due to corrosion problems.

Ethylene glycol can be manufactured by the reaction of ethylene oxide with carbon dioxide to form ethylene carbonate (eq. 17) which can be hydrolyzed to ethylene glycol (eq. 18).



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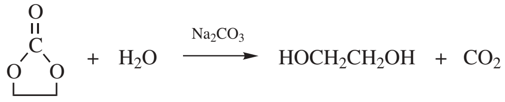
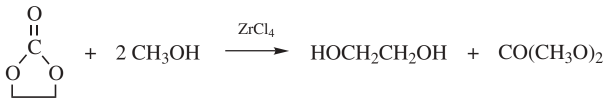


(18)

Catalysts for the reaction of ethylene oxide and carbon dioxide to produce ethylene carbonate are alkali halides, quaternary ammonium halides, and quaternary phosphonium halides; conversion of the ethylene carbonate to ethylene glycol is catalyzed by basic materials (11,12). A significant advantage of the carbonate process is almost complete conversion of ethylene oxide to ethylene glycol with only around 1% diethylene glycol and higher glycols formed. The hydrolysis of ethylene carbonate requires a ratio of <2:1 water to carbonate by weight thus allowing significant reductions in distillation evaporators and concentrators.

Ethylene glycol can be manufactured by the transesterification of ethylene carbonate. A process based on the reaction of ethylene carbonate with methanol to give dimethyl carbonate and ethylene glycol is described in a Texaco patent (13); a general description of the chemistry has also been published (14) (eq. 19). Selectivities to ethylene glycol are excellent with little diethylene glycol or higher glycols produced. A wide range of catalysts may be employed including ion-exchange resins, zirconium and titanium compounds, tin compounds, phosphines, acids, and bases. The process produces a large quantity of dimethyl carbonate which would require a commercial outlet.



(19)

Oxalic acid produced from syngas can be esterified (eq. 20) and reduced with hydrogen to form ethylene glycol with recovery of the esterification alcohol (eq. 21). Hydrogenation requires a copper catalyst giving 100% conversion with selectivities to ethylene glycol of 95% (15).

$$\text{HOOCCOOH} + 2\,\text{ROH} \longrightarrow \text{ROOCCOOR} + 2\,\text{H}_2\text{O} \qquad (20)$$

$$\text{ROOCCOOR} + 4\,\text{H}_2 \xrightarrow{\text{Cu}} \text{HOCH}_2\text{CH}_2\text{OH} + 2\,\text{ROH} \qquad (21)$$

Ethylene glycol can be produced by an electrohydrodimerization of formaldehyde (16). The process has a number of variables necessary for optimum current efficiency including pH, electrolyte, temperature, methanol concentration, electrode materials, and cell design. Other methods include production of valuable oxidized materials at the electrochemical cell's anode simultaneous with formation of glycol at the cathode (17). The compound formed at the anode may be used for commercial value directly, or coupled as an oxidant in a separate process.

An early source of glycols was from hydrogenation of sugars obtained from formaldehyde condensation (18,19). Selectivities to ethylene glycol were low with a number of other glycols and polyols produced. Biomass continues to be evaluated as a feedstock for glycol production (20).

Conventional uncatalyzed hydrolysis of ethylene oxide to ethylene glycol also forms diethylene glycol, triethylene glycol, and higher weight glycols. Although the market demands for ethylene glycol and diethylene glycol are mostly independent of each other, the current manufacturing of ethylene glycol and diethylene glycol gives dependent production. Selectivity to the different glycols is currently controlled by varying the ratio of water to ethylene oxide with a large excess of water promoting ethylene glycol selectivity. Removing the excess water is energy intensive and requires capital investment in evaporators. These factors limit the amount of excess water which can be used for control of the uncatalyzed selectivity to ethylene glycol.

Although catalytic hydration of ethylene oxide to maximize ethylene glycol production has been studied by a number of companies with numerous materials patented as catalysts, there has been no reported industrial manufacture of ethylene glycol via catalytic ethylene oxide hydrolysis. Studied catalysts include sulfonic acids, carboxylic acids and salts, cation-exchange resins, acidic zeolites, halides, anion-exchange resins, metals, metal oxides, and metal salts (21–26). Carbon dioxide as a cocatalyst with many of the same materials has also received extensive study.

1.5. Economic Aspects. Current U.S. ethylene glycol producers and their capacities are given in Table 3.

Table 3. **2000 U.S. Ethylene Glycol Capacity**[a]

Producer	Location	Capacity, 10^3 t/yr
BASF	Geismer, La.	352
Dow	Plaqemine, La.	209
Dow	Seadrift, Tex.	249
Dow	Taft, La.	717
Eastman	Longview, Tex.	104
Equistar	Bayport, Tex.	263
Formosa	Point Comfort, Tex.	299
Hunsthan	Port Neches, Tex.	363
Old World Industries	Clear Lake, Tex.	318
PD Glycol	Beaumont, Tex.	363
Shell	Geismer, La.	490
Total		*3727*

The United States market is weak. Higher feedstock costs worldwide are hastening the shift of ethylene glycol production to the Middle East because of the availability of cheap gas reserves. It is expected that the U.S. will change from a major exporter of ethylene glycol to a net importer by 2010.

Strong projected growth in the polyesters fibers and poly(ethylene terephthalate) (PET) sectors are supporting the ethylene glycol market. These combined sectors should grow at the rate of 4%/yr in the U.S. (27). In 2002, 80% of the ethylene glycol consumed worldwide went into the production of PET (28). The antifreeze market in the U.S. is flat and fiber growth is slowed by the migration of textile industries to Asia.

Demand for ethylene glycol in 2000 was 2521×10^3 t (exports equaled 545×10^3 t). Demand in 2004 is expected to be ca 2730×10^3 t.

1.6. Health, Safety, and Environmental Factors. Biodegradability of a product may be evaluated by extended-term biochemical oxygen demand (BOD) tests. This procedure permits comparison of the amount of oxygen consumed by microorganisms in the oxidation of the test material to the theoretical oxygen required to completely oxidize the chemical to carbon dioxide and water. Laboratory BOD tests using unacclimated biomass show that ethylene glycol (2,29,30) is readily biodegraded in a system which attempts to simulate the dilute biological conditions of a river or lake. The mean of several BOD determinations on ethylene glycol for 5, 10, and 20 days are 51, 78, and 97% biooxidation, respectively (2). Ethylene glycol can be treated effectively in conventional wastewater treatment plants and does not persist in the environment under expected conditions. For the higher molecular weight glycols (30) the laboratory BOD tests, using acclimated biomass which should occur in a wastewater treatment plant, show the 20-day value for diethylene glycol (3), triethylene glycol (4), and tetraethylene glycol (5) to be 67, 86, and 88% biooxidation, respectively. Consequently, in an acclimated environment, the higher molecular weight glycols (tetraethylene glycol is the highest molecular weight studied) readily biodegrade and do not persist in the environment.

Acute aquatic toxicity tests on ethylene glycol (31,32), diethylene glycol (3), and triethylene glycol (4,33,35) indicate no toxicity to *Daphnia magna* and

Table 4. **Rat Acute Oral LD_{50} Values of Ethylene Glycols**

		LD_{50} rats, g/kg[a]	
Glycol	Ref. 36	Ref. 37	Ref. 38
ethylene	6.1	8.5	13.4
diethylene	16.6	20.8	
triethylene	16.8	22.1	
tetraethylene		32.8	

[a] Single oral dose.

fathead minnows at concentrations through 10,000 mg/L during the 48- and 96-h test duration. Also, bacterial inhibition tests indicate no bacterial growth inhibition at concentrations through 10,000 mg/L. Tetraethylene glycol (5) is relatively nontoxic to *Daphnia magna* and fathead minnows. The measured 48-h LC_{50} value with *Daphnia magna* was 7750 mg/L, whereas the 96-h LC_{50} value with fathead minnows was greater than 10,000 mg/L. Bacterial inhibition tests for tetraethylene glycol indicate no bacterial growth inhibition at concentrations through 5000 mg/L.

None of these glycols are highly irritating to the mucous membranes or skin (34). A splash of these neat materials in the eye may produce marked irritation, but permanent damage should not be expected. In general, each glycol is believed to have low acute dermal toxicity and vapor and inhalation toxicity when exposure is in an industrial situation at normal room temperature, since the amount absorbed through the skin is believed to be minimal and the vapor pressures are relatively low (35). Table 4 presents ranges of values for acute oral LD_{50} tests in rats (calculated dose that kills 50% of the treated animals) performed on the different glycols.

Ethylene glycol is not recommended for use as an ingredient in food or beverages, or where there is a significant contact with food or potable water. For adult humans, death has occurred after as little as 30 mL ethylene glycol has been ingested (37); yet survival has been reported following one liter and more (39). The clinical sequence of toxic response has been described as follows: Phase I: central nervous system (CNS) and metabolic abnormalities; Phase II: cardio and pulmonary abnormalities; Phase III: renal insufficiency. Urinary oxalate crystals are a common, but not invariable, feature of ethylene glycol poisoning. For adults, the reported probable oral acute lethal dose for diethylene glycol is between 1–2 g/kg which is in the same range as ethylene glycol (40). Some of the same clinical signs have been noted for diethylene glycol poisoning as in ethylene glycol poisoning. However, hepatotoxicity may be more common in diethylene glycol poisoning. There are no recorded human fatalities by any route of exposure to triethylene or tetraethylene glycols.

Human volunteers tolerated continuous (20–22 h/d) inhalation exposure to ethylene glycol aerosols up to 75 mg/m^3, but considered 140 mg/m^3 irritating and 200 mg/m^3 intolerable for more than 15 minutes (41). Repeated skin contact with undiluted ethylene glycol has a very low potential to cause the development of allergic contact dermatitis. There is no evidence for a skin sensitizing potential in a repeated insult test in guinea pigs or humans for diethylene or triethylene glycols.

There is no evidence of genetic toxicity for ethylene, diethylene, and triethylene glycols from a battery of *in vitro* tests (42–44). Tetraethylene glycol is not believed to be mutagenic. Questionable results were obtained for *in vitro* tests; however, tetraethylene glycol did not induce mutagenic effects in tests with higher levels including an *in vivo* dominant lethal test in rats. Ethylene glycol was tested under the National Toxicology Program to determine its chronic toxicity and neoplastic (tumor causing) potential. After two years of feeding mice diets with ethylene glycol as high as 50,000 ppm, there was no evidence of carcinogenic activity (42). Likewise in a chronic feeding study in rats, no treatment-related neoplastic (tumorigenic) effects were observed (45).

Effects of repeated ethylene glycol peroral overexposure in treated rats and mice can result in kidney, liver, and nervous system damage. The most sensitive indicators of ethylene glycol toxicity are disturbances in acid–base balance and nephrotoxic (kidney) effects. Effects of repeated chronic peroral overexposure of diethylene glycol in treated rats result in kidney and liver damage (46).

There were no treatment-related effects on the reproductive system or performance in a three-generation reproduction study in which rats were fed diets containing ethylene glycol as high as 1000 mg/kg. When given to pregnant laboratory animals in the diet or by cutaneous application, ethylene glycol does not induce fetal malformations. Studies conducted through the National Toxicology Program have shown teratogenic and fetotoxic effects resulting from administration to mice of high doses by gavage (47) or in drinking water (48); however, no teratogenic or fetotoxic effects were observed when rabbits were given doses high enough by gavage to cause maternal death (49). Nose-only exposure with aerosols is minimally effective in producing developmental toxicity and only at levels that would be intolerable for humans, even for one or two breaths. Occluded cutaneous application of ethylene glycol does not demonstrate a potential to cause developmental toxicity in animal tests.

In animal studies, it has been concluded that high exposure to diethylene glycol and triethylene glycol do not result in a teratogenic response. Tetraethylene glycol has not been tested for teratogenic effects, but it and ethylene glycol have been shown to have no effect on reproduction when the males alone are exposed to high doses (50).

Following administration by various routes, ethylene glycol is rapidly absorbed, distributed, and cleared. Metabolic pathways and rates of metabolism and excretion vary with species, dose, and route of administration. The principal excretory end product at low doses is carbon dioxide in expired air and at higher doses is glycolate and unchanged ethylene glycol by urinary elimination (50). The metabolic pathway for the higher glycols has not been defined.

The OSHA PEL CL = 50 ppm. The ACGIH TLV value is the same (51).

1.7. Uses.

In 2000, uses for ethylene glycol in the U.S. were as followed: PET bottle-grade resins, 34%; antifreeze, 26%; polyesters fibers, 24%; polyester film, 4%; polyester engineering resins, 3%; aircraft deicing fluids, 2%; miscellaneous, 7%. Poly(ethylene terephthalate) provides unique properties for each end use. Wrinkle resistance, strength, durability, and stain resistance are enhanced when polyester is combined with natural fibers to produce apparel, home furnishing fabrics, carpeting, and fiberfill. Polyester's strength is an asset in industrial products such as tire cord, seat-belts, flexible belts, rope, and industrial fabric. Polyester containers are preferred for packaging soft drinks, food, personal care, and other consumer products where clarity, shatter resistance, and recyclability are important. Special grades of container resin are used to produce dual-oven containers suitable for microwave or conventional ovens and thermal-formed items such as cups. The strength of thin films makes polyester ideal for manufacturing video, audio, and computer tapes as well as various packing materials.

Ethylene glycol is used as a nonvolatile antifreeze for liquid-cooled motor vehicles (see ANTIFREEZES AND DEICING FLUIDS). With smaller cars and reduced change frequency, antifreeze demand is stable. Miscellaneous markets typically utilize the freeze point depressing, polarity, and reactivity of ethylene glycol. Specially formulated fluids are used for defrosting and deicing aircraft; anti-icing or deicing airport runways and taxi-ways; and heat-transfer solutions for a wide temperature range (−51 to 135°C). Ethylene glycol is used in adhesive, latex paint, and asphalt-emulsion water-based formulations to provide freeze protection. High purity ethylene glycol is a solvent and suspending medium for ammonium perborate, the conductor used in most electrolytic capacitors. Polyester resins based on maleic and phthalic anhydrides, ethylene glycol and higher glycols, and vinyl-type monomers are important in the low pressure laminating of glass fibers for furniture, suitcases, boat hulls, aircraft parts, and automobile bodies.

1.8. Derivatives. In addition to oligomers ethylene glycol derivative classes include monoethers, diethers, esters, acetals, and ketals as well as numerous other organic and organometallic molecules. These derivatives can be of ethylene glycol, diethylene glycol, or higher glycols and are commonly made with either the parent glycol or with sequential addition of ethylene oxide to a glycol alcohol, or carboxylic acid forming the required number of ethylene glycol subunits.

Ethylene glycol monoethers are commercially manufactured by reaction of an alcohol with ethylene oxide. The resulting glycol ether contains an ether and an alcohol functional group in the same molecule, thus providing unique solvency characteristics for diverse applications. Glycol monoethers having longer hydrocarbon-like alkoxide groups display solubility more characteristic of hydrocarbons. Thus glycol ethers produced from higher molecular weight alcohols have limited water solubility. The ether groups introduce additional sites for hydrogen bonding with improved hydrophilic solubility performance. These glycol ethers are miscible with a wide range of polar and nonpolar organic solvents and miscible with water in most cases (52). These properties allow applications as mild-ordered solvents for many resins, oils, waxes, fats, and dyestuffs, and as coupling agents for many water/organic systems.

Applications for glycol monoethers are found in a broad array of end uses (Table 5). Glycol monoethers are widely used in cleaning formulations to facilitate the removal of grease and greasy soils, to aid in solubilizing other components in the cleaner formulation, and to improve the storage stability of the formulations (53). Glycol monoethers are used as jet fuel additives to inhibit icing in fuel systems (54). They are used as solvents and cosolvents for conventional solvent-based lacquer, enamel, and wood stain industrial coating systems as well as cosolvents for waterborne industrial coating systems (55). Other

Table 5. **Applications for Glycol Monoalkyl Ethers, $RO(CH_2CH_2O)_nH$**[a]

				Industrial application[c]					
Glycol monoether[b]	CAS Registry number	n	R	Agriculture	Chemical	Food	Cleaning[d]	Textile	Transportation
methyl Cellosolve[e]	[109-86-4]	1	CH_3	X					X
methyl Carbitol	[111-77-3]	2	CH_3	X		X		X	X
methoxytriglycol	[112-35-6]	3	CH_3		X			X	X
cellosolve[f, g]	[110-80-5]	1	C_2H_5						
carbitol	[111-90-0]	2	C_2H_5	X		X	X	X	X
ethoxytriglycol	[112-50-5]	3	C_2H_5		X			X	X
propyl Cellosolve	[2807-30-9]	1	C_3H_7						
propyl Carbitol	[6881-94-3]	2	C_3H_7				X		X
butyl Cellosolve	[111-76-2]	1	C_4H_9	X		X	X	X	X
butyl Carbitol[e, f]	[112-34-5]	2	C_4H_9	X	X	X	X		X
butoxytriglycol	[143-22-6]	3	C_4H_9		X			X	X
hexyl Cellosolve	[112-25-4]	1	C_6H_{13}				X		
hexyl Carbitol[g]	[112-59-4]	2	C_6H_{13}				X		

[a] Ref. 52.

[b] Monoethylene glycol derivatives are termed "cellosolves"; diethylene glycol derivatives, "carbitols"; and triethylene glycol derivatives, triglycols. CELLOSOLVE and CARBITOL are registered trademarks of Union Carbide Corp.

[c] All but methyl Cellosolve are used for coatings.

[d] Household and institutional.

[e] Also used in electronics.

[f] Used in pharmaceuticals.

[g] Also used in printing.

applications include dye solvents in the textile, leather, and printing industries; solvents for insecticides and herbicides for agricultural applications; couplers and mutual solvents for soluble oils, hard-surface cleaners, and other soap–hydrocarbon systems; semiconductor manufacture; printed circuit board laminating formulations; freeze–thaw agents in latex emulsions; diluents for hydraulic brake fluids; chemical reaction solvents; and chemical intermediates (52).

Ethylene glycol diethers are made by derivatizing both glycol hydroxyl groups. Glycol diethers contain only the ether functional group; thus they are aprotic polar molecules which are relatively inert chemically with excellent solvent properties (56). Glycol dimethyl ethers are miscible in water, ethanol, acetone, benzene, diethyl ether, and octane. Glycol diethers with larger alkoxide end groups show more hydrophobic character and less water solubility. Strong solvating and stability properties allow numerous applications for glycol diethers including adhesives and coatings, ink formulations, cleaning compounds, batteries, electronics, polymer solvents, polymer plasticizers, gold refining, and gas purification.

Cyclic polyethers, or crown ethers, are cyclic structures containing ethylene glycol units as $\mathrm{-\!\!(CH_2CH_2O)\!\!-}_n$ with $n>2$ and generally between 4 and 8. The oxygen atoms are arranged in a cavity which is efficient in complexing cations. The number of glycol units determines the size of the cavity and effects the ability to complex specific cations. The closer the fit in size between the cavity and cation, the more stable the complex. Crown ethers greatly improve the solubility of salts in organic solvents and have a wide range of applications in organic reactions, especially as phase-transfer reagents (57) (see Catalysis, Phase-Transfer).

Glycols can be used in the manufacture of poly(ethylene glycol) (PEG). Ethylene glycol, ethylene oxide, and a base catalyst react to form a family of linear polymers containing repeating $\mathrm{-\!\!(CH_2CH_2O)\!\!-}$ ether groups with hydroxyl functions on the ends. Length of the chains is controlled by addition of ethylene oxide. PEGs find applications in agriculture products, ceramics, chemical intermediates, coatings and adhesives, cosmetics and toiletries, electronics, foods and feeds, household products, lubricants, metal processing, mining, paper, petroleum, pharmaceuticals, photography, plastics and resins, printing, rubber chemicals, textiles and leather, and wood products (58). Ethylene glycols can also react with other alkylene oxides as well as other alkylene glycols reacted with ethylene oxide to form mixed oxide polyglycols which can be used in many applications similar to those already mentioned (see Polyethers, Aromatic).

Ethylene glycol (as well as the higher glycols) can be esterified with traditional reagents such as acids, acid chlorides, acid anhydrides, and via transesterification with other esters. Preference between mono- and diesters can be controlled by the molar ratio of reactants. Low molecular weight glycol esters are good solvents for cellulose esters and printing inks, and are employed in industrial extraction processes and the protective coating industry. Fatty acid esters, together with other surfactants, are good-emulsifying, stabilizing, dispersing, wetting, foaming, and suspending agents.

Ethylene glycol monoethers contain a hydroxyl function which is readily derivatized to glycol ether–esters utilizing the same chemistry as glycol esters. Ether–ester applications are in cellulose acetate, acrylic, urethane, and polyester coatings, generally in conjunction with other oxygenated solvents (56).

Other uses include retarder solvents for organic coatings and coalescing aids for latex paints.

Ethylene glycol in the presence of an acid catalyst readily reacts with aldehydes and ketones to form cyclic acetals and ketals (59). 1,3-Dioxolane [646-06-0] is the product of condensing formaldehyde and ethylene glycol. Applications for 1,3-dioxolane are as a solvent replacement for methylene chloride, 1,2-dichloroethane, 1,1,1-trichloroethane, and methyl ethyl ketone; as a solvent for polymers; as an inhibitor in 1,1,1-trichloroethane; as a polymer or matrix interaction product for metal working and electroplating; in lithium batteries; and in the electronics industry (60). 1,3-Dioxolane can also be used in the formation of polyacetals, both for homopolymerization and as a comonomer with formaldehyde. Cyclic acetals and ketals are used as protecting groups for reaction-sensitive aldehydes and ketones in natural product synthesis and pharmaceuticals (61).

Glyoxal [107-22-2] is a highly reactive dialdehyde produced commercially by the vapor-phase oxidation of ethylene glycol. Glyoxal has utility in paper manufacture as a wet-strength agent, to confer water resistance to starch-clay paper coatings, and with other pigment coating binders. Other applications include improving resistance to shrinkage and creasing of cotton, rayon, and other cellulosics; leather tanning; intermediate for biologically active molecules; reaction with hydrocolloids for modification of adhesives containing starch, carbohydrates, and other reactive materials; and in hardening gelatin (qv), either alone or condensed with diols or amino alcohols in photography.

Diethylene Glycol. Physical properties of diethylene glycol are listed in Table 1. Diethylene glycol is similar in many respects to ethylene glycol, but contains an ether group. It was originally synthesized at about the same time by both Lourenco and Wurtz (1) in 1859, and was first marketed by Union Carbide in 1928. It is a coproduct (9–10%) of ethylene glycol produced by ethylene oxide hydrolysis. It can be made directly by the reaction of ethylene glycol with ethylene oxide, but this route is rarely used because more than an adequate supply is available from the hydrolysis reaction. The 2000 U.S. capacity was estimated to be 379,210 t/yr (62).

Manufacture of unsaturated polyester resins and polyols for polyurethanes consumes ca 44% of the diethylene glycol. Approximately 8.6% is blended into antifreeze. Triethylene glycol from the ethylene oxide hydrolysis does not meet market requirements, which leads to 10% of the diethylene glycol being converted with ethylene oxide to meet this market need. About 6.5% of diethylene glycol is converted to morpholine. Another significant use is natural gas dehydration, which uses 3.9%. The remaining portion is used in such applications as plasticizers for paper, fiber finishes, compatiblizers for dye and printing ink components, latex paint antifreeze, and lubricants in a number of applications (62).

Triethylene Glycol. Physical properties of triethylene glycol are listed in Table 1. Triethylene glycol is a colorless, water-soluble liquid with chemical properties essentially identical to those of diethylene glycol. It is a coproduct of ethylene glycol produced via ethylene oxide hydrolysis. Significant commercial quantities are also produced directly by the reaction of ethylene oxide with the lower glycols. U.S. capacity in 2000 was 118,390 t/yr (63).

Triethylene glycol is an efficient hygroscopicity agent with low volatility, and about 53% is used as a liquid drying agent for natural gas (see DRYING).

Its use in small packaged plants located at the gas wellhead eliminates the need for line heaters in field gathering systems (see GAS, NATURAL). As a solvent (12%) triethylene glycol is used in resin impregnants and other additives, steam-set printing inks, aromatic and paraffinic hydrocarbon separations, cleaning compounds, and cleaning poly(ethylene terephthalate) production equipment. The freezing point depression property of triethylene glycol is the basis for its use in heat-transfer fluids (63).

Approximately 12% triethylene glycol is used in some form as a vinyl plasticizer. Triethylene glycol esters are important plasticizers (qv) for poly(vinyl butyral) resins, nitrocellulose lacquers, vinyl and poly(vinyl chloride) resins, poly(vinyl acetate) (see VINYL ACETAL POLYMERS), and synthetic rubber compounds and cellulose esters. The fatty acid derivatives of triethylene glycol are used as emulsifiers, demulsifiers, and lubricants. The remaining uses are polyurethanes (8%), humectants (4%), unsaturated polyester resins (4%), miscellaneous (7%). Miscellaneous includes coating resins and textile lubricants.

Tetraethylene Glycol. Physical properties of tetraethylene glycol are listed in Table 1. Tetraethylene glycol has properties similar to diethylene and triethylene glycols and may be used preferentially in applications requiring a higher boiling point, higher molecular weight, or lower hygroscopicity (5).

Tetraethylene glycol is miscible with water and many organic solvents. It is a humectant that, although less hygroscopic than the lower members of the glycol series, may find limited application in the dehydration of natural gases. Other possibilities are in moisturizing and plasticizing cork, adhesives, and other substances.

Tetraethylene glycol may be used directly as a plasticizer or modified by esterification with fatty acids to produce plasticizers (qv). Tetraethylene glycol is used directly to plasticize separation membranes, such as silicone rubber, poly(vinyl acetate), and cellulose triacetate. Ceramic materials utilize tetraethylene glycol as plasticizing agents in resistant refractory plastics and molded ceramics. It is also employed to improve the physical properties of cyanoacrylate and polyacrylonitrile adhesives, and is chemically modified to form polyisocyanate, polymethacrylate, and to contain silicone compounds used for adhesives.

Tetraethylene glycol has found application in the separation of aromatic hydrocarbons from nonaromatic hydrocarbons (BTX extraction) (64) (see BTX PROCESSING). In general, the critical solution temperature of a binary system, consisting of a given alkyl-substituted aromatic hydrocarbon and tetraethylene glycol, is lower than the critical solution temperature of the same hydrocarbon with triethylene glycol and is considerably lower than the critical solution temperature of the same hydrocarbon with diethylene glycol. Hence, at a given temperature, tetraethylene glycol tends to extract the higher alkylbenzenes at a greater capacity than a lower polyglycol.

2. Propylene Glycols

2.1. Introduction.

The propylene glycol family of chemical compounds consists of monopropylene glycol (PG), dipropylene glycol (DPG), and tripropylene glycol (TPG). The proper IUPAC chemical name for PG is 1,2-propanediol and it is listed on the U.S. EPA Toxic Substances Control Act (TSCA) inventory of chemical substances by its CAS Registry Number, [57-55-6]. The IUPAC name and TSCA listing for DPG is oxybispropanol [25265-71-8] and for TPG [(1-methyl-1,2-ethanediyl)bis(oxy)]bispropanol [24800-44-0]. These chemicals are manufactured as coproducts and are used commercially in a large variety of applications. They are available as highly purified products which meet well-defined manufacturing and sales specifications. All commercial production is via the hydrolysis of propylene oxide. A fourth propylene glycol product, trimethylene glycol or 1,3-dihydroxypropane [504-63-2], has been available in commercial quantities in the past, but is not an important product (65). It was obtained as a by-product in the production of glycerol by either saponification or fermentation of animal fats (see GLYCEROL).

The propylene glycols are clear, viscous, colorless liquids that have very little odor, a slightly bittersweet taste, and low vapor pressures. The most important member of the family is monopropylene glycol, also known as 1,2-propylene glycol, 1,2-dihydroxypropane, 1,2-propanediol, methylene glycol, and methyl glycol. The more common commercial names are Propylene Glycol Industrial (PGI) and Propylene Glycol USP (PG USP), which designates the grade for general industrial as opposed to the food and drug grade. All of the glycols are totally miscible with water.

Propylene glycol, when produced according to the U.S. Food and Drug Administration good manufacturing practice guidelines at a registered facility, meets the requirements of the U.S. Food, Drug, and Cosmetic Act as amended under Food Additive Regulation CFR Title 21, Parts 170–199. It is listed in the regulation as a direct additive for specified foods and is classified as generally recognized as safe (GRAS). In addition, it meets the requirements of the *Food Chemicals Codex* and the specifications of the *U.S. Pharmacopeia XXII.* Because of its low human toxicity and desirable formulation properties it has been an important ingredient for years in food, cosmetic, and pharmaceutical products.

2.2. Physical and Chemical Properties. Table 6 lists various physical and chemical properties and constants for the propylene glycols. A comprehensive source for additional physical and chemical properties is Reference 66.

2.3. Chemical Properties. Monopropylene glycol (1,2-propanediol) is a difunctional alcohol with both a primary and a secondary hydroxyl. Chemically, the presence of the secondary hydroxyl group differentiates propylene glycol from ethylene glycol, which has two primary hydroxyl groups. Coproducts dipropylene glycol and tripropylene glycol have several possible structural and stereochemical isomers. Examination of the mechanisms for addition of an alcohol to an oxirane ring under various reaction conditions explains the distribution of the various isomers in the product mix (67). In the high pressure, high temperature process for hydrolysis of propylene oxide to propylene glycol and the subsequent formation of dipropylene and tripropylene glycol, the neutral to slightly acidic conditions dictate a nonspecific opening of the oxirane ring. The nonspecific nature of the acid-catalyzed reaction is seen in the approximately 50:50 product distribution for the primary to secondary alcohol isomers in the dipropylene glycol produced in the process. In the base-catalyzed propoxylation of an alcohol, for example in poly(propylene glycol) manufacture, attack is at the less

Table 6. **Properties of Glycols**

Physical properties	Propylene glycol	Dipropylene glycol	Tripropylene glycol
formula	$C_3H_8O_2$	$C_6H_{14}O_3$	$C_9H_{20}O_4$
molecular weight	76.1	134.2	192.3
boiling point at 101.3 kPa[a], °C	187.4	232.2[b]	265.1[b]
vapor pressure, kPa[a], 25°C	0.017	0.0021	0.0003
density, g/mL			
25°C	1.032	1.022	1.019
60°C	1.006	0.998	0.991
freezing point, °C	supercools	supercools	supercools
pour point, °C	<-57	-39	-41
viscosity, mPa · s(=cP)			
25°C	48.6	75.0	57.2
60°C	8.42	10.9	9.7
surface tension, mN/m(=dyn/cm), 25°C	36	35	34
refractive index at 25°C	1.431	1.441	1.442
specific heat at 25°C, J/(g · K)[c]	2.51	2.18	1.97
flash point, °C, PMCC[d]	104	124	143
coefficient of expansion $\times 10^4$, 0–60°C	7.3	7.0	8.1
thermal conductivity at 25°C, W/(m · K)	0.2061	0.1672	0.1582
heat of formation, kJ/mol[c]	-422	-628	-833
heat of vaporization at 25°C, kJ/mol[c]	67.0	45.4	35.4

[a] To convert kPa to mm Hg, multiply by 7.5.

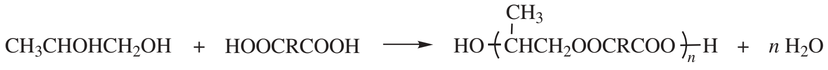
[b] Varies with isomer distribution.

[c] To convert J to cal, divide by 4.184.

[d] PMCC=Penskey-Martens closed cup.

substituted position of the oxirane ring, leading to the preferential formation of the secondary alcohol.

The primary and secondary alcohol functionalities have different reactivities, as exemplified by the slower reaction rate for secondary hydroxyls in the formation of esters from acids and alcohols (68). 1,2-Propylene glycol undergoes most of the typical alcohol reactions, such as reaction with a free acid, acyl halide, or acid anhydride to form an ester; reaction with alkali metal hydroxide to form metal salts; and reaction with aldehydes or ketones to form acetals and ketals (69,70). The most important commercial application of propylene glycol is in the manufacture of polyesters by reaction with a dibasic or polybasic acid.



$$\mathrm{CH_3CHOHCH_2OH} + \mathrm{HOOCRCOOH} \longrightarrow \mathrm{HO}\!\left(\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2OOCRCOO}\right)_{n}\!\mathrm{H} + n\,\mathrm{H_2O}$$

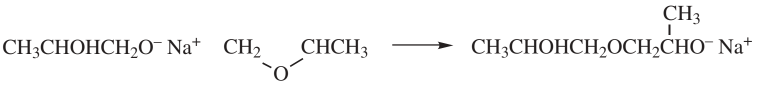
In the manufacture of unsaturated polyester resins the polyester is synthesized and then diluted with a vinyl reactive monomer such as styrene (see POLYYESTERS, UNSATURATED). A portion of the dibasic acid of the polyester is maleic or some other vinyl reactive diacid that can be polymerized with the styrene to yield a highly cross-linked, high performance polymer system. Other esters made with propylene glycol, dipropylene glycol, and tripropylene glycol are used as emulsifiers in foods, as plasticizers in polymer systems, and as part of acrylate resin systems.

Polyethers are also products of commercial importance. Ethers can be formed by thermal dehydration, as shown for the formation of dipropylene glycol from propylene glycol. Cyclic ethers can form by elimination of water from di- or tripropylene glycol.

$$2\,CH_3CHOHCH_2OH \longrightarrow CH_3CHOHCH_2OCH_2CHOHCH_3 + H_2O$$

The principal product obtained when heating propylene glycol in the presence of aluminum silicate at 200 to 400°C is the cyclic ether 2,5-dimethyl-1,4-dioxane (71). The synthesis practiced in industry to make the important class of polyethers called polyols or polyglycols is the acid- or base-catalyzed addition of an epoxide such as propylene oxide to an active hydrogen compound such as a glycol. Any of the propylene glycols may be used for this purpose. Polyglycols can be tailored to meet rigorous application specifications for use in polyesters, polyurethanes, or other systems where active hydrogen compounds are needed.

$$CH_3CHOHCH_2OH + NaOH \longrightarrow CH_3CHOHCH_2O^- Na^+$$

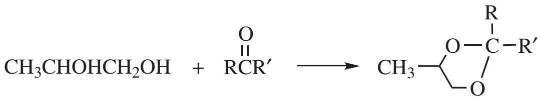


$$CH_3CHOHCH_2O^- Na^+ \quad CH_2\overset{O}{-}CHCH_3 \longrightarrow CH_3CHOHCH_2OCH_2\overset{CH_3}{\overset{|}{C}}HO^- Na^+$$

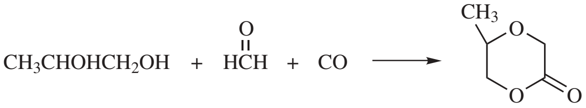
Oxidation of a glycol can lead to a variety of products. Periodic acid quantitatively cleaves 1,2-glycols to aldehydes and is used as an analysis method for glycols (70,72). The oxidation of propylene glycol over Pd/C modified with Pb, Bi, or Te forms a mixture of lactic acid, hydroxyacetone, and pyruvic acid (73). Air oxidation of propylene glycol using an electrolytic crystalline silver catalyst yields pyruvic aldehyde.

Certain bacterial strains convert propylene glycol to pyruvic acid in the presence of thiamine (74); other strains do the conversion without thiamine (75). Propylene oxide is the principal product of the reaction of propylene glycol over a cesium impregnated silica gel at 360°C in the presence of methyl ethyl ketone and xylene (76).

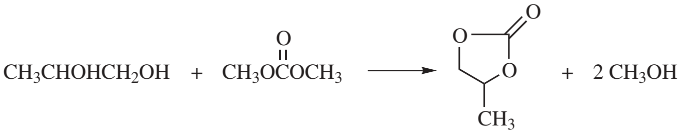
Aldehydes and ketones react with glycols to form acetals and ketals which are easily hydrolyzed, making this a convenient method for protecting aldehyde or ketone functionality in organic synthesis. Propylene glycol in the presence of an acid catalyst reacts with aldehydes and ketones with concurrent removal of water to give 4-methyl-1,3-dioxolanes (77). The reaction of chloroacetaldehyde with propylene glycol in the presence of an acid catalyst gives 2-(chloromethyl)-4-methyl-1,3-dioxolane ($R = CH_2Cl$; $R' = H$) (78).



Lactones are prepared from formaldehyde and carbon monoxide by cyclocondensation with propylene glycol in the presence of a strong acid and a Cu(I) or Ag carbonyl catalyst (79).



Cyclic carbonates are made by treating 1,2-diols with dialkyl carbonates using an alkyl ammonium and tertiary amine catalyst. The combination of propylene glycol and dimethyl carbonate has been reported to result in a 98% yield of propylene carbonate (80).



2.4. Stereochemical and Structural Isomers. Propylene glycol, dipropylene glycol, and tripropylene glycol all have several isomeric forms. Propylene glycol has one asymmetric carbon and thus there are two enantiomers: (*R*)-1,2-propanediol and (*S*)-1,2-propanediol. 1,3-Propanediol is a structural isomer. Dipropylene glycol exists in three structural forms and since each structural isomer has two asymmetric carbons there are four possible stereochemical isomers per structure or a total of twelve isomers. These twelve consist of four enantiomer pairs and two meso- compounds. Tripropylene glycol has four structural isomers and each structural isomer has three asymmetric carbons so each structural isomer has eight possible stereochemical isomers or a total of 32 isomers of tripropylene glycol. Table 7 gives a listing of the IUPAC names, unique structures, and CAS Registry Numbers for the various isomers of propylene glycol, dipropylene glycol, and tripropylene glycol that have been reported in the literature.

2.5. Manufacturing. Wurtz (84) first prepared propylene glycol in 1859 by hydrolysis of propylene glycol diacetate, and it was commercialized in 1931 by Carbide and Carbon Chemicals Corp. (85). This first commercial production used the chlorohydrin process to make propylene oxide, which was subsequently hydrolyzed to the glycol. In the mid-1930s Du Pont Co. operated a high pressure coconut oil hydrogenation plant which yielded propylene glycol as a by-product. Propylene glycol was gaining acceptance as a substitute for glycerol in pharmaceuticals, and shortages during World War II led to new production facilities by Dow Chemical Co. in 1942 and Wyandotte Chemical Corp. in 1948.

All commercial production of propylene glycol is by high pressure, high temperature, noncatalytic hydrolysis of propylene oxide (qv). A large excess of water is used in the conversion of propylene oxide to a mixture of mono-, di-, and tripropylene glycols. Typical product distribution is 90% PG and 10% coproducts. Hydration reactor conditions are 120–190°C at pressures up to 2170 kPA. After the hydration reaction is completed, excess water is removed in multieffects evaporators and drying towers, and the glycols are purified by high vacuum distillation.

Table 7. **Propylene Glycol Isomers**

IUPAC name	Formula	CAS Registry number	Boiling point,[a] °C
Propylene glycol			
1,2-propanediol	$CH_3CH(OH)CH_2OH$	[57-55-6]	189, 115.9[b,c]
(±)-1,2-propanediol		[4254-16-4]	
(R)-1,2-propanediol		[4254-14-2]	
(S)-1,2-propanediol		[4254-15-3]	
Dipropylene glycol			
oxybispropanol		[25265-71-8]	152.5[b,d]
1,1′-oxybis-2-propanol	$[CH_3CH(OH)CH_2]_2O$	[110-98-5]	222.2[c], 229–32[d]
(R*,R*)-(±)-1,1′-oxybis-2-propanol		[55716-55-7]	
(R*,R*)-1,1′-oxybis-2-propanol		[55716-54-6]	
[S-(R*,R*)]-1,1′-oxybis-2-propanol		[61217-63-8]	
2,2′-oxybis-1-propanol	$[HOCH_2CH(CH_3)]_2O$	[108-61-2]	225.7[c]
(R*,R*)-(±)-2,2′-oxybis-1-propanol		[20753-87-1]	
(R*,S*)-2,2′-oxybis-1-propanol		[20753-88-2]	
[S-(R*,R*)]-2,2′-oxybis-1-propanol		[125948-51-8]	
2-(2-hydroxypropoxy)-1-propanol	$HOCH_2CH(CH_3)OCH_2CH(CH_3)OH$	[106-62-7]	224.0[c]
(R*,R*)-(±)-2-(2-hydroxypropoxy)-1-propanol		[62376-49-2]	
(R*,S*)-2-(2-hydroxypropoxy)-1-propanol		[62376-50-5]	
[S-(R*,R*)]-2-(2-hydroxypropoxy)-1-propanol		[110813-96-2]	
Tripropylene glycol			
[(1-methyl-1,2-ethanediyl)bis(oxy)]bispropanol		[24800-44-0]	181.6[b,d]
1,1′-[(1-methyl-1,2-ethanediyl)bis(oxy)]bis-2-propanol	$HOCH(CH_3)CH_2OCH(CH_3)CH_2OCH_2CH(CH_3)OH$	[1638-16-0]	
2,2′-[(1-methyl-1,2-ethanediyl)bis(oxy)]bis-1-propanol	$HOCH_2CH(CH_3)OCH(CH_3)CH_2OCH(CH_3)CH_2OH$		
2-[1-(2-hydroxypropoxy)-2-propoxy]-1-propanol	$HOCH_2CH(CH_3)OCH(CH_3)CH_2OCH_2CH(CH_3)OH$		
2-[2-(2-hydroxypropoxy)-propoxy]-1-propanol	$HOCH_2CH(CH_3)OCH_2CH(CH_3)OCH_2CH(CH_3)OH$	[45096-22-8]	268[e]

[a] At 101.3 kPa=1 atm, unless otherwise noted.

[b] At 6.7 kPa (50 mm Hg).

[c] Ref. 81.

[d] Ref. 82.

[e] Ref. 83.

Table 8. **U.S. Producers of Propylene Glycols, in 2000**[a]

Producer	Location	Annual capacity, 10^3 t
Lyondell	Bayport, Tex.	249
Dow[a]	Freeport, Tex.	125
Dow[a]	Plaquemine, La.	118
Huntshan	Port Neches, Tex.	54
Arch Chemicals	Brandenburg, Ky.	34
Total		*580*

[a] Ref. 87.

Propylene oxide [75-56-9] is manufactured by either the chlorohydrin process or the peroxidation (coproduct) process. In the chlorohydrin process, chlorine, propylene, and water are combined to make propylene chlorohydrin, which then reacts with inorganic base to yield the oxide. The peroxidation process converts either isobutane or ethylbenzene directly to an alkyl hydroperoxide which then reacts with propylene to make propylene oxide, and *t*-butyl alcohol or methylbenzyl alcohol, respectively.

2.6. Economic Aspects. World capacity for propylene glycols in mid-2000 was ca 1.6 × 106 t. Production was concentrated in the United States (43%) and Western Europe (36%). Japan (5%) and the Republic of Korea (3%) comprised the next group. The remaining capacity was located in Mexico, India, Eastern Europe, Singapore, China, and Australia (86).

United States producers of propylene glycol and their capacities are given in Table 8 (87).

Propylene glycol's total growth rate should drop from 5%/yr to 2–2.5%. Propylene glycol's growth in cosmetics and liquid detergents continue strong, growing at the rate of 3–3.5%. The aircraft deicing market has matured. Unsaturated polyesters resins, polyethylene glycol's largest application is eroding because of competition from dicyclopentadiene-based resin.

U.S. demand in 2000 was 395×10^3 t (exports were 14.5×10^3 t). Expected demand in 2004 should be 428×10^3 t (87).

2.7. Health and Safety Factors. All of the propylene glycols display a low acute oral toxicity in laboratory rats as shown in Table 9 (57). Information for sucrose is shown for comparison.

Investigations have revealed that rats can tolerate up to 4.9% propylene glycol in the diet for two years without significant effects on growth rate (88). However, minor liver damage was observed. In a more recent study (89), dogs

Table 9. **Acute Oral Toxicity of Propylene Glycols**[a]

Compound	Oral rat LD_{50}, g/kg
propylene glycol	20.0
dipropylene glycol	14.9
tripropylene glycol	3.0
sucrose	29.7

[a] Ref. 51.

were fed a diet containing 8% propylene glycol for two years and were unaffected, as judged by mortality, body weight changes, diet utilization, histopathology, organ weights, and blood, urine, and biochemical parameters. Because of its low chronic oral toxicity, propylene glycol is considered safe for use in foods and pharmaceuticals.

Rats showed no adverse effects from 5.0% dipropylene glycol in their drinking water for 77 days, but at a dose of 10.0% in the drinking water, kidney and liver injury and some deaths occurred (90). A sufficient number of studies have not been carried out on tripropylene glycol to permit conclusions to be drawn regarding its chronic oral toxicity.

Propylene glycols produce a negligible degree of irritation upon eye or skin contact. From tests on New Zealand white rabbits (91) in 1982 it was concluded that propylene glycol is a slight eye irritant. Other tests conducted both *in vitro* and *in vivo* have shown propylene glycol to be a nonirritant to the eye. Both dipropylene glycol and tripropylene glycol have been tested for skin and eye irritation in rabbits and have been found to be nonirritating. The expert panel of the *Cosmetic Ingredient Review,* after conducting a comprehensive safety assessment, has concluded that propylene glycol may be used in cosmetic products in concentrations up to 50% (92).

Inhalation of the vapors of any of the propylene glycols appears to present no significant hazard in ordinary applications. OSHA PEL and the ACGIH TLV is 100 ppm, STEL 150 ppm (51). Limited data indicate that breathing mists of di- and tripropylene glycol may be harmful. Prolonged inhalations of saturated vapors of propylene glycol have produced no ill effects in animals, but such concentrations would likely be irritating to the upper respiratory tract and possibly the eyes of humans. Only limited work has been done on the vapor toxicity of the other glycols; however, because of their very low vapor pressures and low systemic toxicities, it is unlikely that injury would occur as a result of limited vapor inhalation.

2.8. Environmental Considerations. The propylene glycols vary in biodegradability, as shown in Table 10. The tests involved were conducted with standard municipal inoculum, and other studies (86) have shown that biodegradability can be greatly enhanced when using an acclimated bacteria. For example, tripropylene glycol has shown 66% of theoretical oxygen demand at 20 days with an industrial seed. Thus it is expected that all of the propylene glycols will exhibit moderate to high biodegradability in a natural environment.

Table 10. **Biodegradation of Propylene Glycols with Standard Municipal Inoculum**

Glycol	Theoretical O_2 demand	5-Day O_2 demand	10-Day O_2 demand	20-Day O_2 demand
PG	1.68	1.16	1.18	1.45
DPG	1.91	[a]	0.14	0.71
TPG	1.38	[a]	[a]	[a]

[a] Data not available.

All of the propylene glycols are considered to be practically nontoxic to fish on an acute basis ($LC_{50} < 100$ mg/L) and practically nontoxic to aquatic invertebrates, also on an acute basis. Acute marine toxicology testing (93) on propylene glycol showed that the 96-h LC_{50} for fathead minnows was 54,900 mg/L and the 48-h LC_{50} for *Daphnia magna* was 34,400 mg/L. A 24-h NOEL of 50,000 mg/L was also observed for fingerling trout. Similar results were observed for guppies and rainbow trout (94).

2.9. Uses. Consumption of propylene glycol in the United States in 2000 was as follows: Unsaturated polyester resins, 27%; functional fluids (antifreeze, deicing, heat transfer), 20%; food, drug, and cosmetics, 20%; liquid detergents, 17%; paints and coatings, 5%; humectants, 2%; miscellaneous uses including plasticizers, 9% (87).

Propylene glycol is unique among the glycols because it is safe for humans to take internally. Propylene glycol intended for human use is designated as USP grade and is commonly found in foods, pharmaceuticals, cosmetics, etc. The U.S. Food and Drug Administration has approved the use in food. The food sector and the maximum content, wt% of propylene glycol allowed is as follows: Alcoholic beverages, 5%; confections and frostings, 24%; frozen dairy products, 2.5%; seasons and flavorings, 97%; nuts and nut products, 5%; all others, 2%.

An industrial grade of propylene glycol is usually specified for other uses. In common with most other glycols, propylene glycol is odorless and colorless, and has a wide range of solvency for organic materials, besides being completely water soluble. Propylene glycol is also a known antimicrobial and is an effective food preservative (95). Use in an antiviral formulation has been reported (96).

Propylene glycol is an important solvent for aromatics in the flavor concentrate industry, enabling manufacturers to produce low cost flavor concentrates of high quality. It is also an excellent wetting agent for natural gums, greatly simplifying the compounding of citrus and other emulsified flavors. PG also finds use as a solvent in elixirs and pharmaceutical preparations containing some water-soluble ingredients, and as a solvent and coupling agent in the formulation of sunscreen lotion, shampoos, shaving creams, and other similar products. Certain esters of propylene glycol such as propylene glycol monostearate [1323-39-3] are also popular as an emulsifier in cosmetic and pharmaceutical creams (97).

Propylene glycol can be administered therapeutically to effectively reverse thrombocytopenia and increase platelet cell counts, particularly in patients suffering from medical conditions such as HIV/AIDS or undergoing chemotherapy (98).

Aqueous solutions of propylene glycol display excellent antifreeze properties and are therefore valuable as low temperature heat-transfer fluids. For applications involving indirect food contact, heat-transfer fluids formulated with the USP grade product are preferred, since there could be inadvertent contact with a food product. These fluids are commonly used in the brewing and dairy industries as well as in refrigerated display cases in retail grocery stores.

Propylene glycol is also an effective humectant, preservative, and stabilizer and is found in such diverse applications as semimoist pet food, bakery goods, food flavorings, salad dressings, and shave creams. Humectancy, or the capability of retaining moisture in a product, is a result of the vapor–liquid equilibria of the glycol–water system and can be estimated from tables provided by suppliers (99).

The industrial grade of propylene glycol is an important intermediate in the production of alkyd resins for paints and varnishes. It is the preferred glycol for manufacturing high performance, unsaturated polyester resins for many uses, eg, reinforced plastic laminates for marine construction, gel coats, sheet molding compounds (SMC), and synthetic marble castings. It is also used as a solvent and plasticizer in printing inks, as a preservative in floral arrangements, and as a stabilizer in hydraulic fluids. Heat-transfer fluids used in commercial and industrial building heating and cooling systems, chemical plants, stationary engines, and solar heat recovery can be formulated with the industrial grade of propylene glycol. More recently, propylene glycol-based coolants for automobiles and heavy-duty diesel engine trucks have been introduced which compete with traditional ethylene glycol-based products (100,101). ASTM standard D5216 specifies aqueous propylene glycol-based engine coolants for automobile and light-duty truck service. All heat-transfer applications require corrosion inhibitor additives and are designed for specific operating temperature ranges and types of materials of construction. Operation at low temperature without freezing and at high temperature without excessive pressure are the principal features of these systems.

Due in large part to its lower toxicity and the concomitant lesser concern about its environmental impact, propylene glycol use in the air transportation industry as an airplane and runway deicing agent has grown substantially in recent years (see ANTIFREEZES AND DEICING FLUIDS). Other glycols, such as ethylene glycol, have historically been used in this industry.

Dipropylene Glycol. Dipropylene glycol is similar to the other glycols in general properties, and its fields of use are comparable. However, its greater solvency for certain materials and higher viscosity make it of interest in certain applications for which the other glycols are not as well suited. The greater solvency of dipropylene glycol for castor oil indicates its usefulness as a component of hydraulic brake fluid formulations; its affinity for certain other oils has likewise led to its use in cutting oils, textile lubricants, and industrial soaps. It is also used as a reactive intermediate in manufacturing polyester resins, plasticizers, and urethanes. Fragrance or low odor grades of dipropylene glycol are established standard base formulating solvents in the fragrance industry and for some personal care products such as deodorants.

U.S. consumption of dipropylene glycol in 2000 was as follows: Plasticizers, 22%; unsaturated polyesters resins, 18%; cosmetics and fragrances, 20%, polyurethane polyols, 12%; alkyd resins, 8%, miscellaneous, including solvents and functional fluids, 20% (102).

Tripropylene Glycol. Tripropylene glycol is an excellent solvent in many applications where other glycols fail to give satisfactory results. Its ability to solubilize printing ink resins is especially marked, so much so that it finds its way into creams designed to remove ink stains from the hands. A combination of water solubility and good solvent power for many organic compounds plus low volatility and a high boiling point also have led to its use by formulators of textile soaps and lubricants, cutting oil concentrates, and many similar products. Tripropylene glycol is also used as a reactant to produce acrylate resins which are useful in radiation-cured coatings, adhesives, and inks. Polyethers used in the manufacture of urethane rigid foam insulation are made by alkoxylation of tripropylene glycol.

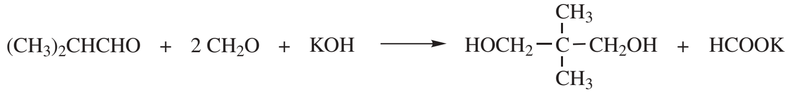
3. Other Glycols

3.1. Properties. Glycols such as neopentyl glycol, 2,2,4-trimethyl-1,3-pentanediol, 1,4-cyclohexanedimethanol, and hydroxypivalyl hydroxypivalate are used in the synthesis of polyesters, unsaturated (qv) and urethane foams (see Foamed Plastics). Their physical properties are shown in Table 11 (1–6) (103–107).

3.2. Neopentyl Glycol. Neopentyl glycol, or 2,2-dimethyl-1,3-propanediol [126-30-7] (1) (104) is a white crystalline solid at room temperature, soluble in water, alcohols, ethers, ketones, and toluene but relatively insoluble in alkanes (104). Two primary hydroxyl groups are provided by the 1,3-diol structure, making this glycol highly reactive as a chemical intermediate. The *gem*-dimethyl configuration is responsible for the exceptional hydrolytic, thermal, and uv stability of neopentyl glycol derivatives.

Chemical Properties. Neopentyl glycol can undergo typical glycol reactions such as esterification (qv), etherification, condensation, and oxidation. When basic kinetic studies of the esterification rate were carried out for neopentyl glycol, the absolute esterification rate of neopentyl glycol with n-butyric acid was approximately 20 times that of ethylene glycol with n-butyric acid (107).

Manufacture. Commercial preparation of neopentyl glycol can be via an alkali-catalyzed condensation of isobutyraldehyde with 2 moles of formaldehyde (crossed Cannizzaro reaction) (103,108). Yields are ~70%.



$$(CH_3)_2CHCHO + 2\,CH_2O + KOH \longrightarrow HOCH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2OH + HCOOK$$

(1)

Toxicity. Acute toxicity data for neopentyl glycol are reported in Table 12.

Uses. Neopentyl glycol is used extensively as a chemical intermediate in the manufacture of polyester resins (see Alkyd Resins), polyurethane polyols (see Urethane Polymers), synthetic lubricants, polymeric plastizers (qv), and other polymers. It imparts a combination of desirable properties to properly formulated esterification products, including low color, good weathering and chemical resistance, and improved thermal and hydrolytic stability.

The weatherability and hydrolytic stability of unsaturated polyesters based on neopentyl glycol have made it a popular intermediate for use in formulations exposed to severe conditions, eg, in gel coats for cultured marble and marine applications (see Coatings, Marine) (110).

Reactive saturated polyester resins (oil-free alkyds) based on neopentyl glycol are produced for use in formulating premium-quality surface coatings (111–113). These coatings exhibit excellent water, detergent, and stain resistance, and excellent weatherability, acid rain resistance, and gloss retention. (114). They may be formulated as conventional solvent-borne coatings, as high solids coatings, or as dry powders for electrostatic coatings applications.

Table 11. **Physical Properties of Several Glycols**

Properties	Neopentyl glycol (1)	2,2,4-Trimethyl-1,3-pentanediol (2)	1,4-Cyclohexane-dimethanol[a] (3)	Hydroxypivalyl hydroxypivalate (4)
CAS registry number	[126-30-7]	[144-19-4]	[105-08-5]	[1115-20-4]
molecular formula	$C_5H_{12}O_2$	$C_8H_{18}O_2$	$C_8H_{16}O_2$	$C_{10}H_{20}O_4$
mol wt	104.2	146.2	144.2	204.3
melting range, °C	124–130	46–55	45–50[b]	46–50
sublimation temp, °C	128			
boiling point, °C, at kPa[c]				
at 0.13			118	
at 0.45	93–94			
at 1.33			160	
at 101.3	212	236	286	290
boiling range, °C		215–235		
assay (commercial grade), wt% min	97	96	99	98
density, g/cm^3				
at 20°C	1.06		1.02	1.02
at 15°C		0.937		
pour point, supercooled, °C			10	
crystallization point, °C			35	
viscosity at 50°C, mPa · s=cP)			675	70
heat of combustion, kJ/mol[d]	−3100	−5050	−4849[e]	
flammability				
fire point, COC,[f] °C	135	118	174	
flash point, COC,[f] °C	129	113	167	161
autoignition temp,[g] °C	388	346	316	404
heat of fusion,[h] kJ/mol[d]	21.77	8.63		
heat of vaporization, kJ/mol[d]				
at 32 kPa,[e] 170°C	67.1			
at 101.3 kPa[e]				95.6
at 101.3 kPa,[e] 204°C	56.5			
hygroscopity,[i] wt % H_2O				
at 50% rh		0.1–0.2		
at 51% rh	0.3			
at 78% rh	11.3			

[a] Mixture of isomers, cis/trans ratio (wt%) = ~32/68.

[b] Mp of cis isomer [3236-47-3] = 41°C; mp of trans isomer [3236-48-4] = 70°C.

[c] To convert kPa to mm Hg, multiply by 7.5.

[d] To convert kJ to kcal, divide by 4.184.

[e] Paar bomb.

[f] Cleveland open cup.

[g] ASTM D286.

[h] Estimated.

[i] At equilibrium; neopentyl glycol at 25–38°C, and 2,2,4-trimethyl-1,3-pentanediol at 25°C.

A comparison of coatings formulations based on various glycols to determine the effects of the various glycol structures on the performance properties of the coatings has been made. Properties compared included degree of cure, flexibility, hardness, hydrolytic stability, processibility, chemical and stain resistance, and viscosity (115,116).

Table 12. **Toxicity Data for Various Glycols**[a]

Parameter	Structure number (**1**)	(**2**)	(**3**)	(**4**)
oral LD_{50} (rat), mg/kg	6,400–12,800	3,730	3,200–6,400	>3,200
oral LD_{50} (mouse), mg/kg	3,200–6,400	1,600–3,200	1,600–3,200	1,600–3,200
inhalation LC_{50} (rat),[b] mg/L/6 h[b]	168	73.3[c]		>1.18[d]
dermal LD_{50} (guinea pig), g/kg	14[e]	slight	>1	>1
eye irritation (rabbit)	slight[f]	moderate–strong	slight	moderate

[a] Ref. 109.

[b] Unless otherwise noted.

[c] Also mouse.

[d] 1.18 mg/L/6 h.

[e] No skin sensitization (guinea pig).

[f] Skin irritation (rabbit) is moderate.

The polyurethane industry provides other uses for neopentyl glycol as an intermediate in the manufacture of hydroxy-terminated polyester polyols. Beginning with basically the same ingredients, products with a wide range of properties, varying from soft to rigid foams to elastomers, synthetic, survey (qv) and adhesives (qv) may be produced from polyols based on neopentyl glycol. This glycol also is employed to improve thermal, hydrolytic, and uv stability (117–120).

Synthetic lubricants are made with neopentyl glycol in the base-stock polyester (121). Excellent thermal stability and viscosity control are imparted to special high performance aviation lubricants by the inclusion of polyester thickening agents made from neopentyl glycol (122,123) (see LUBRICATION AND LUBRICANTS). Neopentyl glycol is also used to manufacture polymeric plasticizers that exhibit the improved thermal, hydrolytic, and uv stability necessary for use in some exterior applications (124).

Neopentyl glycol can be used for thermal energy storage by virtue of its solid-phase transition, which occurs at 39–41°C, a temperate range useful for solar heating and cooling (125–129).

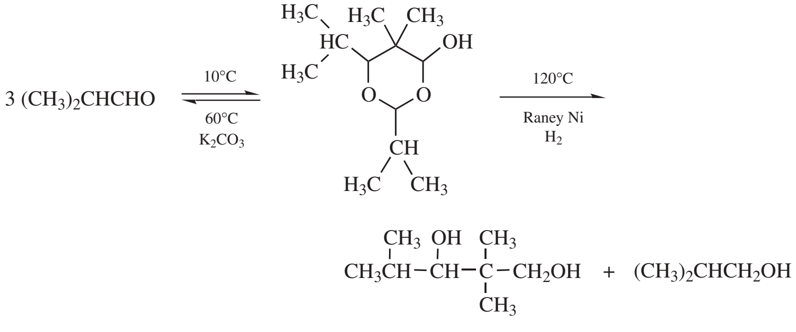
3.3. 2,2,4-Trimethyl-1,3-Pentanediol.

2,2,4-Trimethyl-1,3-pentanediol (**2**) is a white, crystalline solid. It is used in surface coating and unsaturated polyester resins. It also appears promising as an intermediate for synthetic lubricants and polyurethane elastomers and foams.

Trimethylpentanediol is soluble in most alcohols, other glycols, aromatic hydrocarbons, and ketones, but it has only negligible solubility in water and aliphatic hydrocarbons.

Chemical Properties. Trimethylpentanediol, with a primary and a secondary hydroxyl group, enters into reactions characteristic of other glycols. It reacts readily with various carboxylic acids and diacids to form esters, diesters, and polyesters (130). Some organometallic catalysts have proven satisfactory for these reactions, the most versatile being dibutyltin oxide. Several weak bases such as triethanolamine, potassium acetate, lithium acetate, and borax are effective as stabilizers for the glycol during synthesis (131).

Manufacture and Processing. 2,2,4-Trimethyl-1,3-pentanediol can be produced by hydrogenation of the aldehyde trimer resulting from the aldol condensation of isobutyraldehyde [78-84-2].



(**2**)

Toxicity. Acute toxicity data for this glycol are reported in Table 12.

Uses. The versatility of trimethylpentanediol as an intermediate is reflected by the diversity of its commercial applications.

Unsaturated polyesters derived from trimethylpentanediol are characterized by a low exotherm, low shrink curing, and a product that has good electrical properties and excellent hydrolytic stability and chemical resistance (109,116, 130,131). These unsaturated resins exhibit low viscosity, low density, and good glass–fiber or filler wetting (131). They are resistant to hydrolytic action, probably because of the protection of the ester linkage by the pendent methyl groups, and by virtue of the lesser number of ester groups in a given weight of material than would be afforded with lower molecular weight glycols (132). Chemically resistant applications where trimethylpentanediol-based unsaturated resins are used include reinforced polyester storage tanks and pipelines for hot, concentrated acids, some solvents, mild bases, hypochlorite solution, and ammonia (see Polyesters, Unsaturated).

Saturated polyester resins based on trimethylpentanediol are used in various coating applications, most notably in water-borne (133) and high solids coatings (134,135). Resins manufactured with this diol are characterized by low viscosities, which permits formulation of enamels with 85% nonvolatiles when sprayed. Such formulations are cross-linked with isocyanates or melamines to give premium coatings useful for industrial applications, appliance coil coatings, and the like (134–136). Other saturated polyester resins based on trimethylpentanediol are useful in high gloss hypoallergenic nail polishes (137) (see Polyesters, Thermoplastic).

The monoisobutyrate ester of trimethylpentanediol is especially useful as a coalescing aid in flat and semigloss (138) latex pain formulations (see Paint, Architectural). This product is commercially available from Eastman as Texanol ester alcohol.

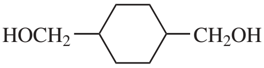
The diisobutyrate ester of trimethylpentanediol is an economical, low color primary plasticizer for use in surface coatings, vinyl flooring, moldings, and other vinyl products (139).

Various other diesters, mixed esters, and polyesters of trimethylpentanediol are useful as monomeric or polymeric plasticizers for coatings and plastic film and sheeting (139). They are compatible with, and useful in, cellulosics, vinyls, polystyrenes, and some other plastics.

Trimethylpentanediol is used in hard-surface cleaners as a coupling agent (140) and in temporary or semipermanent hair dyes (141). Other applications involving trimethylpentanediol, or a derivative, are in urethane elastomers (142), in foams (143), as a reactive diluent in urethane coatings (see URETHANE POLYMERS) (144), as a sound-insulating, glass–laminate adhesive (see ADHESIVES) (145), as a bactericide–fungicide (146), and as a cross-linking agent in poly(vinyl chloride) adhesive (147).

3.4. 1,4-Cyclohexanedimethanol.

1,4-Cyclohexanedimethanol, 1,4-dimethylolcyclohexane, or 1,4-bis(hydroxymethyl) cyclohexane (**3**), is a white, waxy solid. The commercial product consists of a mixture of cis and trans isomers (6). This diol is used in the manufacture of polyester fibers (qv) (148), high performance coatings, and unsaturated polyester molding and laminating resins (105).



(**3**)

1,4-Cyclohexanedimethanol is miscible with water and low molecular weight alcohols and appreciably soluble in acetone. It has only negligible solubility in hydrocarbons and diethyl ether (106).

Chemical Properties. The chemistry of 1,4-cyclohexanedimethanol is characteristic of general glycol reactions; however, its two primary hydroxyl groups give very rapid reaction rates, especially in polyester synthesis.

Manufacture. The manufacture of 1,4-cyclohexanedimethanol can be accomplished by the catalytic reduction under pressure of dimethyl terephthalate in a methanol solution (137,149). This glycol also may be prepared by the depolymerization and catalytic reduction of linear polyesters that have alkylene terephthalates as primary constituents. Poly(ethylene terephthalate) may be hydrogenated in the presence of methanol under pressure and heat to give good yields of the glycol (see POLYESTERS, UNSATURATED) (150,151).

Toxicity. Acute toxicity data are reported in Table 12.

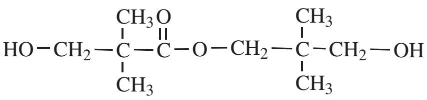
Uses. The most important application for 1,4-cyclohexanedimethanol is in the manufacture of linear polyesters for use as fibers (152,153) (see FIBERS, POLYESTER). Compared with fibers made from poly(ethylene terephthalate), fibers made from poly(1,4-cyclohexanedimethanol terephthalate) have lower densities and higher melting points. Linear polyesters produced from dicarboxylic acids, eg, terephthalic acid, generally have greater hydrolytic stability and better electrical properties than similar polyesters made from other glycols. The high dielectric strength, good dielectric constant, and low dielectric loss make them useful for many electrical applications, eg, in capacitors, wire coatings, and magnetic tape coatings (154,155).

Unsaturated resins based on 1,4-cyclohexanedimethanol are useful in gel coats and in laminating and molding resins where advantage is taken of the properties of very low water absorption and resistance to boiling water. Thermal stability is imparted to molding resins, both thermoplastic (156,157) and thermoset (158–161), enabling retention of physical and electrical properties at elevated temperatures (162). Additionally, resistance to chemical and environmental exposure is characteristic of products made from these resins (163).

High performance polyester enamels are manufactured from saturated resins containing 1,4-cyclohexanedimethanol. Such enamels may be formulated as electrostatically applied powder coatings (164–167), water-borne (168,169), cationic electrodeposition coatings (170), or solvent-based coatings (see Coating Processes, Survey). These coatings are characterized by an extremely hard, durable, stain- and detergent-resistant finish (171–173). Other polyester resins based on 1,4-cyclohexanedimethanol are also used as plasticizers (174), in hot-melt adhesives (175,176), in elastomers (177,178), and urethane elastomeric coatings (179) (see Coatings).

Another area in which 1,4-cyclohexanedimethanol is commercially important is in the manufacture of polyurethane foams (see Foamed Plastics). The two primary hydroxyl groups provide fast reaction rates with diisocyanates, which makes this diol attractive for use as a curative in foams. It provides latitude in improving physical properties of the foam, in particular the load-bearing properties. Generally, the ability to carry a load increases with the amount of 1,4-cyclohexanedimethanol used in producing the high resilience foam (180). Other polyurethane derivatives of 1,4-cyclohexanedimethanol include elastomers useful for synthetic rubber products with a wide range of hardness and elasticity (181).

3.5. Hydroxypivalyl Hydroxypivalate. Hydroxypivalyl hydroxypivalate or 3-hydroxy-2,2-dimethylpropyl 3-hydroxy-2,2-dimethylpropionate (**4**) is a white crystalline solid at room temperature. It is used to manufacture polyester resins for use in surface coatings where good resistance to weathering and acid rain are of particular importance (106).



$$HO{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}OH$$

(**4**)

Hydroxypivalyl hydroxypivalate is soluble in most alcohols, ester solvents, ketones, and aromatic hydrocarbons. It is partially soluble in water (106).

Chemical Properties. Both hydroxy groups on hydroxypivalyl hydroxypivalate are primary, which results in rapid reactions with acids during esterification. The absence of hydrogens on the carbon atom beta to the hydroxyls is a feature this glycol shares with neopentyl glycol, resulting in excellent weatherability. The relatively high molecular weight of this glycol requires lower levels of aromatic acid to produce polyester resins, thus contributing to the improved weatherability of polyesters made from this glycol.

Manufacture. Hydroxypivalyl hydroxypivalate may be produced by the esterification of hydroxypivalic acid with neopentyl glycol or by the intermolecular oxidation–reduction (Tishchenko reaction) of hydroxypivaldehyde using an aluminum alkoxide catalyst (182,183).

Toxicity. Acute toxicity data for hydroxypivalylyl hydroxypivalate appear in Table 12.

Uses. Saturated polyesters made from hydroxypivalyl hydroxypivalate are most often used for formulating coatings which have very low initial color and which retain the low color exposure to weathering. The most typical example is in clear topcoat useful in automotive finishes (184). This glycol is often used as a partial replacement for neopentyl glycol in polyester resins to provide better resin solubility, reduced crystallinity, lower glass-transition temperatures, and lower melt viscosity. These characteristics make this glycol particularly useful for resins used in coil coatings, powder coatings, waterborne coatings, and unsaturated polyester gel coats (106,185).

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