FEATURED REVIEW

Ethylene Glycols Technology

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Abstract−Ethylene glycol (EG) or monoethylene glycol (MEG), the adduct of ethylene oxide (EO) and water, is the simplest glycol. It is the first of a homologous series of three dihydroxy alcohols discussed in this article. Diethylene and triethylene glycols (DEG, TEG) are the other two. These glycols are composed solely of carbon, hydrogen and oxygen. Although they have similar chemical properties, their applications vary mainly with physical properties such as viscosity, hygroscopicity and boiling point. The commercial route to ethylene glycols in use today involves the non-catalyzed thermal hydrolysis of ethylene oxide in water. This process produces chiefly mono-, di- and triethylene glycols and a small amount of tetraethylene and heavier glycols. The yield of monoethylene glycol via hydrolysis is controlled by the water-to-ethylene oxide ratio in the feed to the reactor system. Removal of excess water following the glycols-forming hydrolysis is energy intensive and requires capital investment in evaporators. Such costs limit the amount of excess water which is used. In practice, reactor feed water content is such that the selectivity to monoethylene glycol achieved ranges from 89-91%. The equipment elements in a simplified process flow diagram are discussed along with recommended materials of construction. Among other items discussed are a) a brief review of economic factors; b) health, safety and environmental issues; and c) commercial applications of the three glycols, MEG, DEG and TEG. Finally, recommendations for shipping, handling and storage are discussed.

Key words: Monoethylene Glycol, Thermal Hydrolysis, Properties, Toxicology/Environmental, Applications

INTRODUCTION

1. General

Ethylene glycol (EG), the principal topic discussed in this article is also interchangeably referred to as monoethylene glycol (MEG). Ethylene glycol is the adduct of ethylene oxide (EO) and water and is the simplest glycol, the first of a homologous series of three dihydroxy alcohols, namely, mono-, di- and triethylene glycols (MEG, DEG and TEG). These glycols contain two hydroxyl groups at-tached to separate carbon atoms in an aliphatic chain. Diethylene and triethylene glycols, and tetraethylene glycols, which some authors also discuss, are oligomers of ethylene glycol. Not discussed extensively are polyglycols. Polyglycols are higher molecular weight adducts of ethylene oxide distinguished by intervening ether linkages in the hydrocarbon chain. Polyglycols are commercially important and have properties that vary with molecular weight, are water soluble, hygroscopic, and undergo reactions common to the lower molecular weight glycols.

Table 1. Properties of glycols

Property	Ethylene glycol	Diethylene glycol	Triethylene glycol
Molecular weight	62.07	106.12	150.17
Boiling point@760 mmHg, ℃	197.6	245.0	287.4
Specific gravity@20/20 ℃	1.1155	1.1184	1.1254
Density, kg/ m³@40 ℃	1099	1103	1109
Coefficient of expansion@20 ℃per ℃	0.00059	0.00063	0.00067
Flash point, cleveland open cup, ℃	115	143	165
Freezing point at 760 mmHg, ℃	−13.0	−8.0	−7.2
Refractive index, n_D@20 ℃	1.4318	1.4472	1.4559
Viscosity, @20 ℃, cp	20.9	35.7	47.8
Vapor pressure, mmHg@20 ℃	0.06	<0.01	<0.01
Heat of vaporization@760 mmHg, cal/gm	191	83	99
Thermal conductivity, cal/(sec)(cm²) (℃/cm)@60 ℃	0.000620	0.000398	0.000382
Surface tension, dynes/cm@20 ℃	50.5	47.0	47.5
Specific heat, cal/gm/℃@20 ℃	0.561	0.539	0.520
Water solubility	complete	complete	complete

Source: Shell Bull., 1993.

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The three glycols (mono-, di- and triethylene glycol) discussed are composed solely of carbon, hydrogen and oxygen and have similar chemical properties. They have applications that vary mainly with physical properties such as viscosity, hygroscopicity and boiling point.

2. Structures

The three glycols have the following structures and synonyms:

Ethylene Glycol $HOCH_2CH_2OH$
(Monoethylene Glycol, EG or MEG)

Diethylene Glycol $HOCH_2CH_2OCH_2CH_2OH$
(DEG)

Triethylene Glycol $HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$
(TEG)

PHYSICAL PROPERTIES

Table 1 lists various physical properties and constants for the ethylene glycols.

Mono-, di- and triethylene glycols are colorless, odorless, high boiling, hygroscopic liquids that are completely miscible in water and a number of organic liquids.

Vapor pressure curves for the ethylene glycols at various temperatures are illustrated in Fig. 1. Another important property, ethylene glycols can reduce the freezing point of water markedly as shown in Fig. 2.
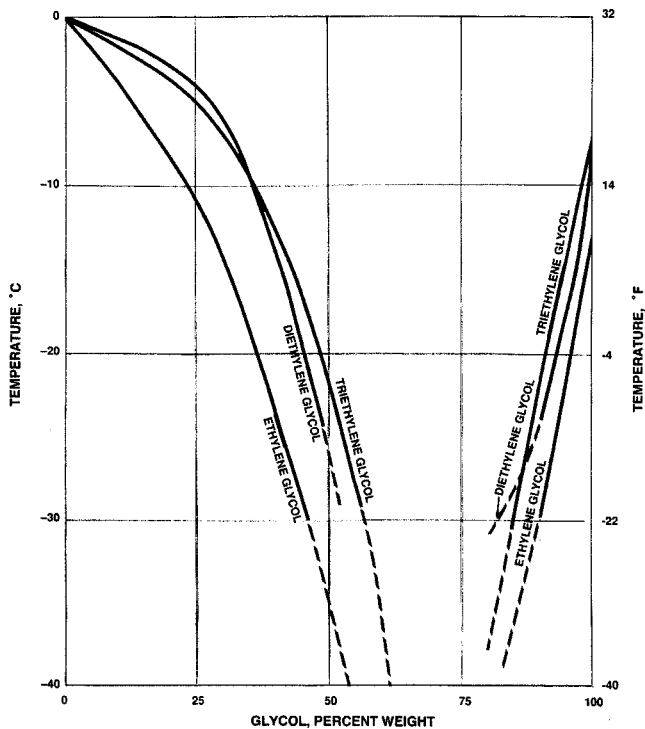
CHEMICAL PROPERTIES

The presence of two hydroxyl groups in the glycol molecule de-
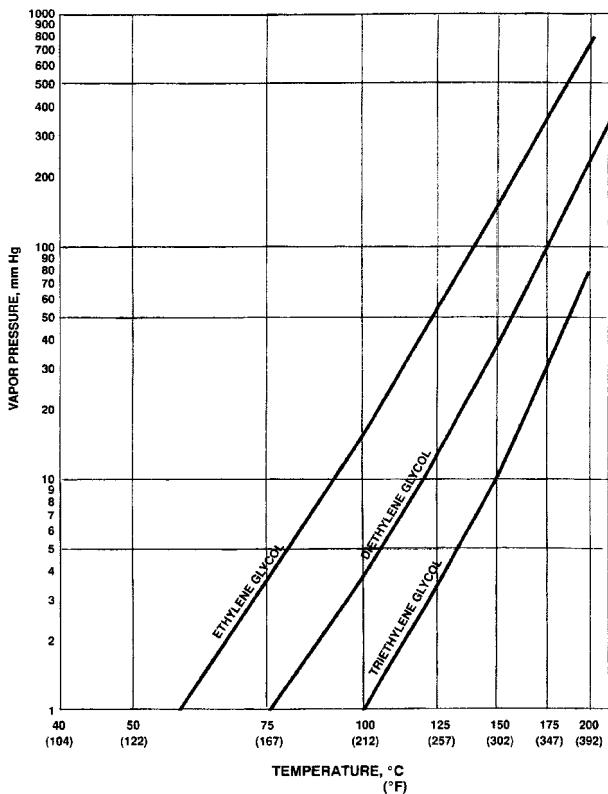
Fig. 1. Vapor pressures of glycols.
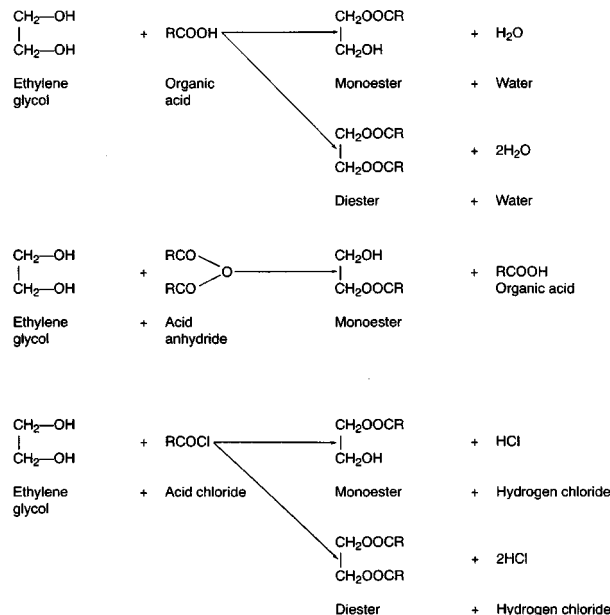Source: Shell Bull., 1993.

Fig. 2. Freezing points of monoethylene glycol, diethylene glycol and triethylene glycol aqueous solutions.
Source: Shell Bull., 1993.

termines its chemistry and permits reactions such as esterification, dehydration, oxidation, halogenation and formation of alcoholates and acetals to take place. In the following examples, ethylene glycol is used to illustrate some of its reaction characteristics.
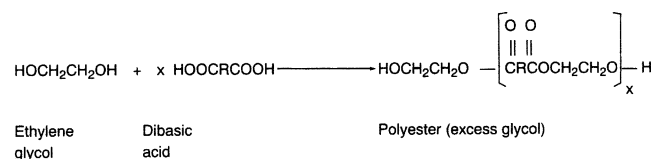
1. Esters of Organic Acids

Organic acids, anhydrides, and acid chlorides react with the glycols to yield mono- and diesters. The molar ratio of the acid to the glycol determines which product will predominate.

Source: Shell Bull., 1993.

2. Polyesters of Polybasic Acids

Polybasic acids or their derivatives will react with the glycols to form polyesters. Depending on whether an excess of acid or glycol is used, the polymer may be terminated with either alcohol or acid groups.

$$HOCH_2CH_2OH + x\ HOOCRCOOH \longrightarrow HOCH_2CH_2O \left[\begin{array}{c} O\ O \\ \| \ \| \\ CRCOCH_2CH_2O \end{array} \right]_x H$$

Ethylene   Dibasic   Polyester (excess glycol)
glycol   acid
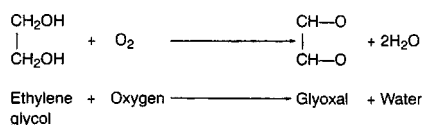
Source: Shell Bull., 1993.

3. Dehydration

Depending on the catalyst and conditions used the dehydration of ethylene glycol yields aldehydes, alkyl ethers and cyclic ethers, such as dioxane.
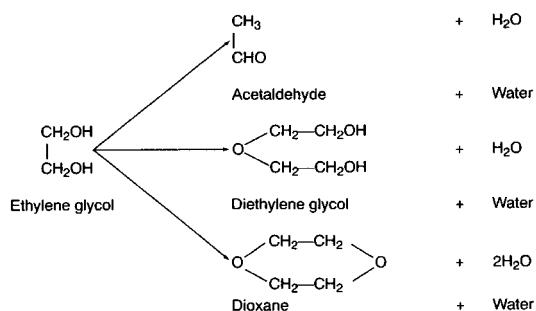
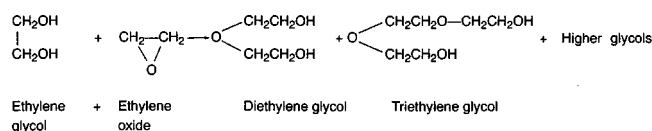Source: Shell Bull., 1993.

4. Oxidation

The oxidation of ethylene glycol by various methods yields acetaldehyde, formaldehyde, glycolic acid, oxalic acid, and glyoxal. Glyoxal is the most important oxidation product. The course of the reaction is dependent on the reaction conditions.

Sources: Shell Bull., 1993.

5. Other Reactions

The reaction of the ethylene glycols with ethylene oxide leads to the formation of ether-alcohols. The product composition is governed by the ratio of the reactants.

Sources: Kirk-Othmer, 1994; Shell Bull., 1993.

MANUFACTURING

1. Process History

Ethylene glycol was first prepared by Wurtz in 1859 by the hydrolysis of ethylene glycol diacetate but was not of commercial interest until World War I, when it was used in Germany as a substitute for glycerol in explosives production [Curme and Johnston, 1952]. Later, in the 1930's, when the commercial use of the Lefort direct oxidation route to ethylene oxide began to displace the chlorohydrin process, hydrolysis of the oxide to ethylene glycol came into favor. Ethylene glycol was originally produced commercially in the United States from ethylene chlorohydrin.

Although hydrolysis with both acid and base catalysts are proven methods for ethylene glycol production, neutral non-catalyzed hydrolysis has been shown to be equally as popular. In time, the latter gained acceptance as the favored choice used for commercial production. Today there are no known industrial producers of ethylene glycol via catalytic hydrolysis of ethylene oxide.

Neutral hydrolysis (pH 6-10) carried out in the presence of a large excess of water at high temperature and pressure, gives selectivities to monoethylene glycol in the 89-91% range. The principal by-product is diethylene glycol with minor amounts of triethylene, tetraethylene and higher molecular weight glycols accounting for the remainder [Kirk-Othmer, 1994].

Selectivity to the different glycols is in practice controlled by varying the ratio of water-to-ethylene oxide with a large excess of water favoring the selectivity to monoethylene glycol. Removing the excess water is energy intensive and requires capital investment in evaporators. Accordingly, this cost factor limits the amount of excess water which can be economically used for control of the non-catalyzed route to ethylene glycol.

2. Hydrolysis Chemistry

We cite here the three principal chemical reactions that occur in the liquid-phase, non-catalytic thermal hydrolysis of ethylene oxide (EO) in the presence of excess water.

Monoethylene glycol (MEG) is the principal product of the hydrolysis as follows:

$$C_2H_4O + H_2O \rightarrow HOCH_2CH_2OH \qquad\qquad \text{(MEG)} \quad (1)$$
$$+ 22\ kcal/gmole$$
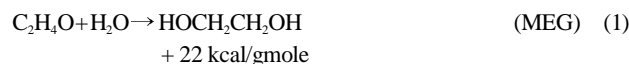
The reactions for the only significant by-products, to diethylene glycol (DEG) and triethylene glycol (TEG) follow:

$$HOCH_2CH_2OH + C_2H_4O \rightarrow HOCH_2CH_2OCH_2CH_2OH \quad \text{(DEG)} \quad (2)$$
$$+ 25\ kcal/gmole$$

$$DEG + C_2H_4O \rightarrow HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH \quad \text{(TEG)} \quad (3)$$
$$+ 24\ kcal/gmole$$

It is interesting to note that the yield of monoethylene glycol (MEG) depends only on the ethylene oxide concentration in the EO: water feed, and is not affected by temperature, pressure or contact time provided that substantially complete reaction (>99%) of the ethylene oxide occurs [Dye, 1966].

3. Commercial Production

Fig. 3 is a simplified process flow diagram for an ethylene glycols manufacturing unit.

Finished (purified) ethylene oxide (EO) or an EO: water mixture is the principal feed to the process. This feed is mixed with recycled water, e.g., condensates from reboilers on evaporators (3) and (4). Subsequently, the pressure is boosted on this feed via a high-head pump, and it is then heated to reaction conditions. The booster pump and feed preheater are not shown in Fig. 3.
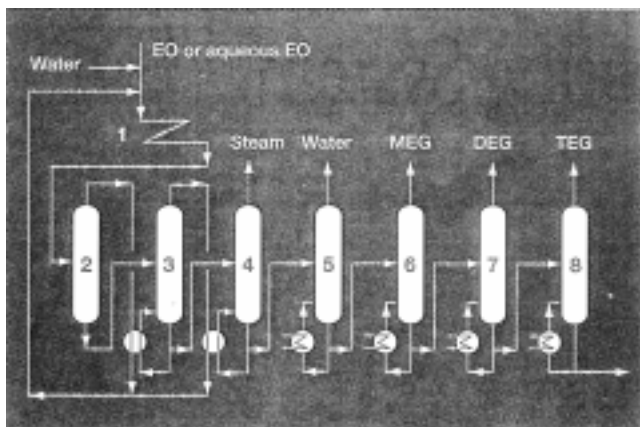
Fig. 3. Ethylene glycol process.
Source: Hydro. Proc., 1999.

The glycol reactor (1) is of tubular construction, usually arranged in a vertical serpentine-like layout for reasons of space and heat insulation.

The tube diameter is such that assures fully-developed turbulent flow is established through the reactor and back mixing is avoided.

By back mixing, the undesired reaction to higher glycols is promoted. Reactor length is set to provide three minutes residence time, which allows 99.99% of the ethylene oxide to be reacted.

The glycols-forming reactions are exothermic and the reactor product containing water and glycols due to adiabatic temperature rise exits at about 228 °C (442 °F) for an illustrative case of a 9%w EO-in water feed entering the reactor at 190 °C (374 °F). Respective inlet and outlet pressures are 35.4 kg/cm² ga (504 psig) and 35.2 kg/cm² ga (500 psig). Selectivity to monoethylene glycol of this illustration is about 90%.

Excess water (some water is consumed in the hydrolysis reaction) in the glycol reactor product is removed in evaporators (2), (3) and (4), with final reduction of water content achieved in vacuum column (5), the dehydrator.

High-pressure (circa 45.7 kg/cm² ga or 650 psig) steam drives the evaporator (2) reboiler (not shown) and the overhead vapor from this column provides the motive steam for evaporator (3) reboiler. In similar fashion, evaporator (3) overhead vapor serves evaporator (4) reboiler. The overhead vapor from evaporator (4) is 4.0-5.0 kg/cm² ga (57-71 psig) low pressure steam that is normally exported for use in an associated EO manufacturing unit or other manufacturing units on the site. Medium pressure steam, viz, 12.5-15.0 kg/cm² ga (178-213 psig), serves the reboilers of the vacuum columns (5), (6), (7) and (8).

As indicated above, vacuum column (5) completes the recovery of the glycols. This column reduces the water content of the crude glycols stream to less that 100 ppm (w). Overhead losses of MEG from this column are, typically, less than 0.01% of the feed to this final dehydration operation.

Vacuum columns (6), (7) and (8), in turn, separate the MEG, DEG, and TEG products into the required purities needed for sales.

Ethylene glycol processes in modern-day plants can turn out products of the highest quality that meet the most stringent specifications demanded by polyester fiber and PET (polyethylene terephthalate) manufacturers.

4. Some Feed Quality Requirements

The ethylene oxide, or ethylene oxide-water, feed to this process must be substantially free of aldehydes and carbon dioxide (CO_2). High levels of these components can recycle and build up to concentrations that can jeopardize finished product quality, particularly that of the MEG product.

5. Some Equipment Engineering Features

Evaporators (2) and (3) are refluxed tray columns that are included in designs to limit recycle of MEG to the glycol reactor. Recycled MEG contributes to higher DEG and TEG make in the reactor at the expense of MEG selectivity. Reflux is provided to these distillation operations by using tops condensate (water) from the dehydration column (5). Excess dehydration tops condensate is purged from the process to the plant effluents treatment system.

5-1. Materials of Construction

The aqueous EO feed to the glycol reactor is often corrosive to carbon steel at the high temperatures encountered in the reactor preheater and reactor (1). This corrosion is believed to be caused by the presence of low concentrations of CO_2. Hence, stainless steel has been specified for these two process items, a choice which has been confirmed by corrosion tests and plant observations [Dye, 1966].

Stainless steel is specified for all reboiler tubes in the glycol recovery system, namely, reboilers for evaporators (2), (3), and (4), as well as the reboiler tubes for dehydrator (5).

Stainless steel is also prescribed for reboilers serving the MEG column (6), the DEG column (7) and TEG column (8). Except for reboilers for evaporators (3) and (4), shells of all the reboilers are carbon steel. For the two evaporators cited, the shells are normally specified of carbon steel construction with a corrosion allowance, typically, 3-5 mm. Extra corrosion allowance is also specified for the carbon steel column shell and overhead line from evaporator (2) and the condensate line from the evaporator (3) reboiler. This corrosion allowance is provided due the possible presence of CO_2. Most glycol producers select stainless steel internals (distributors, trays, packing, etc.) for all distillation columns serving glycol operations, a common "housekeeping" practice.

To avoid iron contamination of the finished MEG, DEG and TEG products, carbon steel construction is avoided for all equipment in contact with the overhead product streams of the glycol purification columns (6), (7) and (8). Hence, stainless steel construction is specified for reflux accumulators, the product lines and pumps. Although the distillation column shells in this finishing section are normally of carbon steel construction, the top third of each vacuum column, viz. (6), (7) and (8), along with the top head have stainless steel cladding.

Normally two rundown tanks (holding vessels awaiting analysis confirming a product meets sales specifications) are provided for each product, each sized for 24-hours' production. Products held in these tanks are normally maintained under 0.1 kg/cm² ga (1.5 psig) dry N_2 pressure to assure dryness. Glycol product rundown tanks have been fabricated of stainless steel (to assure no iron contamination), but this choice is quite rare in the industry. Use of aluminum in this service is commonplace. In the U.S., tank construction of carbon steel lined with Amercoat® 385 (an epoxy product marketed by Ameron International, Alpharetta, Georgia) has met wide acceptance. Vinyl epoxy resins are no longer favored for this service due to environmental restrictions.
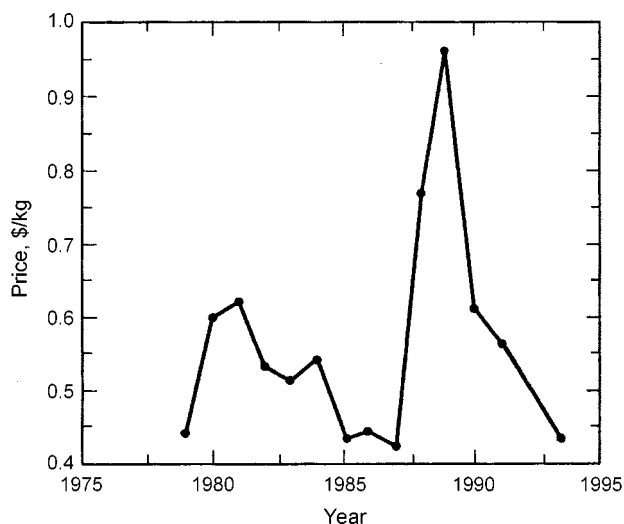
Fig. 4. Ethylene glycol prices in the U.S.
Source: Kirk-Othmer, 1994.

ECONOMIC ASPECTS

During the 1980's through early 1990's, ethylene glycol prices have varied widely, a divergence believed to have been due largely to capacity variations and supply imbalances.

Recent U.S price history covering a 15-year period is illustrated in Fig. 4 [Kirk-Othmer, 1994]. A mid-1999 published price was 39.7-44 c/kg (18-20 c/lb) delivered [Chem. Week, 1999]. A year later in August 2000, a market report gave a price essentially unchanged at 44 c/kg (20 c/lb) for both fiber grade and antifreeze grade ethylene glycol [Chem. Mar. Rep., 2000].

A listing of world producers of ethylene glycol and estimates of their capacities are given in Table 2. This table gives a North American ethylene glycol capacity estimate of 5.31×10^6 metric tons (m.t.)/yr. (11.70×10^9 lb/yr) and a worldwide ethylene glycol capacity estimate of 12.45×10^6 m.t./yr (27.44×10^9 lb/yr).

HEALTH, SAFETY AND ENVIRONMENTAL FACTORS

1. Toxicology

None of these glycols as liquids are highly irritating to human skin. Laboratory studies have shown that ethylene glycol penetrates animal skin slowly and that absorption through human skin takes place even more slowly. This slow-rate of absorption prevents high concentrations of ethylene glycol and its toxic breakdown products from accumulating in the bloodstream.

A splash of glycol liquids in the eyes many cause temporary discomfort or irritation, but permanent damage is not likely.

In contrast, monoethylene and diethylene glycols are regarded as toxic for applications where there is a possibility of ingestion. In general, no treatment is necessary in the case of triethylene glycol ingestion unless large quantities are swallowed. In any event, medical advice should be sought.

Feeding rats for two years on diets containing 0.5 and 1.0 gm/kg (animal weight) of monoethylene glycol caused a toxic action centered chiefly in the kidneys and shortened the life span of the test animals.

Further, monoethylene glycol produced calcium oxalate bladder stones and caused severe renal tubular atrophy and fatty degeneration in the liver. With diethylene glycol, two-year feeding studies revealed that 1.0 percent concentrations retarded growth slightly and produced a lower incidence of calcium oxalate bladder stones than for monoethylene glycol and only slight kidney damage. In the case of triethylene glycol, even lower effects were observed [Patty's, 1981].

In rat acute oral tests, LD_{50} values (the calculated dose that kills 50% of the test animals) reported for single oral doses of monoethylene, diethylene and triethylene glycols were 8.5, 20.8, and 22.1 gm/kg, respectively [Kirk-Othmer, 1994].

Due to their low vapor pressures, inhalation of the vapors of these glycols appears to present no significant health hazard in ordinary applications. Yet human experience and animal test data served at one time as a sufficiently convincing basis for the U.S. Office of Safety and Health Administration (OSHA) to set in 1989 an interim permissible atmospheric exposure limit (PEL) for monoethylene and diethylene glycols of 50 ppm(m) and a value of 10 mg/m^3 of ethylene glycol as particulate matter such as mist.

Shortly thereafter, OSHA rescinded the interim PEL standard cited here. Nevertheless, many U.S. glycol producers that adopted the 1989 OSHA PEL standard have retained the 50 ppm(m) ceiling in the *Exposure Control/Personal Protection* sections of their Material Safety Data Sheets (MSDS). U.S. Federal regulations require the distribution of product MSDS documents to glycol customer-users.

Prolonged inhalation of saturated vapors of triethylene glycol have produced no ill effects in animals, but such concentrations would likely be irritating to the upper respiratory tracts and possibly the eyes of humans [Dow MSDS, 2000; Shell MSDS, 1999].

Ethylene glycol has not been shown to cause cancer. The Agency for Toxic Substances and Disease Registry has reviewed the available genotoxicity data reported by various studies and concludes, "ethylene glycol is negative for genotoxic effects". In considering a potential cancer-causing classification for ethylene glycol the U.S. Environmental Protection Agency (EPA) has concluded that ethylene glycol is either "not classifiable" (Group D) or had "evidence of no carcinogenicity" (Group E). EPA further stated that "Substances in groups 'D' and 'E' are not given a hazard ranking for carcinogenicity because the Agency does not consider them to be potential carcinogens" [Am. Chem. Coun., 2000].

2. Safety

Due to the relatively high flash points, viz., 115 °C (240 °F), 143 °C (290 °F) and 165 °C (330 °F), for mono-, di- and triethylene glycols, respectively, these glycols are not readily ignited but can burn when exposed to heat and flames.

In the case of an accidental release, protective measures include 1) eliminate potential sources of ignition (no smoking, flares, sparks or flames in the immediate area); 2) prevent all bodily contact with all spilled material; and 3) wear appropriate personal protective equipment when responding to spills. Personal protective equipment selections vary based on potential exposure conditions such as handling practices, concentration and ventilation.

Chemical goggles should be worn for eye protection. Protective clothing which is chemically resistant to the material should be worn.

Table 2. World ethylene glycol capacity

(in thousands of metric tons/year)			
NORTH AMERICA		**(EUROPE Cont'd.)**	
Union Carbide		Dow	
Taft, LA	740	Terneuzen	140
Seadrift, TX	300	Shell Chemicals	
Shell Chemical		Moerdijk	110
Geismar, LA	500	Spain	
Equistar		Industrias Quimicas	
Beaumont, TX	413	Tarragona	75
Bayport, Tx	307	Turkey	
Huntsman		Alpet	82
Port Neches, Tx	390	**U.K.**	
Formosa Plastics		Union Carbide	
Point Comfort, TX	330	Wilton	85
Dow Chemical		CIS	333
Plaquemine, LA	325	Poland	80
Celanese		Slovakia	70
Clear Lake, TX	315	Romania	30
BASF		Sweden	20
Geismar, LA	270	**ASIA/MIDEAST**	
Eastman Chemical		China	582
Longview, TX	120	India	
Canada		Reliance	295
Alberta & Orient Glycol		Others	155
Prentiss, AB	300	Indonesia	
Union Carbide		GT Petrochem	100
Prentiss	300	Japan	
Dow		Mitsubishi Chemical	286
Fort Saskatchewan, AB	270	Mitsui Chemical	245
Mexico		Nippon Shokubai	235
Idesa		Nisso-Maruzen	100
Morelos, Veracruz	200	Nisso Petrochemical	75
Pemex		Kuwait	
Morelos	150	Union Carbide (Equate)	
Polioles		Shuaiba	350
Lerma, Mexico	76	Saudi Arabia	
EUROPE		Sharq	
Belgium		Al Jubail	850
BASF		Yanpet	
Antwerp	225	Yanbu	350
Inspec		Singapore	125
Antwerp	200	South Korea	
Bulgaria		Honam Petrochemical	410
Neftochim		Hyundai Petrochemicals	410
Burgas	90	Samsung	80
Germany		Taiwan	
Erdšlchemie		Oriental Union	180
Koln	110	China Man-Made Fiber	130
Clariant		**SOUTH AMERICA**	
Gendorf	100	Brazil	
Dow		Oxiteno Nordeste	206
Schkopau	65	Oxiteno	25
Italy		Venezuela	
Enichem		Pralca	86
Gela	50		

Source: Parpinelli Tecnon (London) via www.chemweek.com, 1998.

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Table 3. Biodegradation of glycols

Glycol	ThOD[1]	BOD[2]-20 Day
Monoethylene glycol	1.29 p/p[3]	1.15 p/p
Diethylene glycol	1.51	0.88
Triethylene glycol	1.60	0.27

Source: Dow MSDS, 2000.
[1]ThOD: Theoretical oxygen demand.
[2]BOD: Biological oxygen demand.
[3]p/p: Parts per part, units of oxygen needed per unit of biodegradation.

The particular selection of protective clothing depends on potential exposure conditions and may include gloves, boots, suits and other items. Respiratory protection should be worn by workers if engineering controls do not maintain airborne glycol concentrations at levels which are adequate for the protection of worker health. Respiratory equipment selection should be in accordance with regulatory requirements. In the U.S., requirements set out in OSHA Respiratory Protection Standard, 29 CFR 1910.134 applies [Shell MSDS, 1999].

3. Environmental Considerations

3-1. Biodegradation

The three glycols discussed in this article are expected to be readily biodegradable and thus will not remain in the environment. The data in Table 3 indicate that biodegradation is expected to be moderate to high under both aerobic and anaerobic conditions.

3-2. Aquatic Toxicity

Aquatic toxicity, basis LC_{50} s (concentrations at which 50% of the test species die), on monoethylene, diethylene and triethylene glycols indicate no toxicity to *Daphnia magna* and fathead minnows through 10,000 mg/L during 48-hour and 96-hour tests. Also, bacterial inhibition tests indicate no bacterial growth inhibition at concentrations through 10,000 mg/L [Kirk-Othmer, 1994].

Acute toxicity values (LC_{50} s) are classed "practically non-toxic" by the U.S. Environmental Protection Agency, basis that organization's acute toxicity evaluation criteria, $LC_{50} > 100$ mg/L effect concentrations [EPA, 1985a, b].

APPLICATIONS

1. General

Table 4 compares the percentages of the ethylene glycols consumed in the U.S. for 1983 with 1998. Data on pounds produced for 1983 are not readily available, but for 1998, 5.77 billion pounds with a value of $1.27 billion (at 22 c/lb) were produced in the U.S. that year [Am. Chem. Coun., 2000].

Table 4. U.S. ethylene glycol usage

Item/Year	1983	1998
Polyester fiber	27.0%	34.5%
PET bottles, film and packaging	18.5%	31.0%
Antifreeze	42.0%	27.0%
Misc. other and inventory change	12.5%	7.5%
	100.0	100.0

Sources: Kirk-Othmer, 1994; Am. Chem. Coun., 2000.

In 1983, the largest fraction of domestically-produced ethylene glycol, 42%, was consumed in antifreeze production. By 1998, with smaller cars and reduced change frequency, antifreeze usage appears to have stabilized at about 27%. On the other hand, the polyester markets have grown to 34.5%.

The largest consumption, polyester fibers, was 34.5% in 1998 vs. 27% in 1983. PET (polyethylene terephthalate) bottles, film and packaging products were 31.0% in 1998 vs. 18.5% in 1983. Miscellaneous industrial uses for 1998 vs. 1983, were 7.5% and 12.5%, respectively.

The attractiveness of ethylene glycol usage for polyester fiber is that the polyester product imparts wrinkle resistance, strength, durability and stain resistance when combined with natural fibers to produce apparel, home furnishing fabrics, and carpeting. Polyester strength is an asset in industrial products such as tire cord, seat belts and rope.

Polyester containers are widely preferred for packaging soft drinks, food, personal care and other consumer products where water resistance and recyclability are important.

Special manufactures derived from ethylene glycol are container resin products and thermally-formed cups. The strength of polyester film makes the material ideal for the production of audio, computer and videotapes as well as a number of film-wrapped products [Kirk-Othmer, 1994].

2. Product Profiles

Mono-, di- and triethylene glycols are colorless, essentially odorless stable liquids with high boiling points. The three have many similar chemical properties. Differences in their applications are due chiefly to variations in physical properties such as viscosity, hygroscopicity and boiling points.

Monoethylene Glycol (*MEG*) is by far the largest volume of the glycol products sold by the industry and is normally sold in three grades: fiber grade, industrial grade, and antifreeze grade. Each of these grades can be distinguished by their glycol and water contents. Fiber grade MEG is typically 99.9% (w) minimum MEG. Industrial grade is 99.0% (w) minimum MEG, and antifreeze grade is 95.0% (w) minimum MEG.

We directed attention in an earlier paragraph to the important role ethylene glycol plays as an intermediate in the manufacture of polyester products. Fiber grade MEG is the principal raw material sought by processors to assure production of the highest quality polyester products for sale in the marketplace. Some illustrative manufacturing specifications for fiber grade MEG are given in Table 5.

For a number of users, fiber grade MEG must also meet specific ultra violet (UV) light transmittance requirements. For example, a 98% minimum UV transmittance at 350 nanometers is set forth in some sales contracts [Dye, 1966].

Table 5. Manufacturing composition limits for fiber grade MEG

Component	Composition
MEG, % (w) min.	99.9
DEG , % (w) max.	0.05
Water, % (w) max.	0.03
Iron (as Fe), ppm (w), max.	0.08
Aldehyde (as acetaldehyde), ppm (w) max.	10

Source: Dye, 1966.

Diethylene Glycol (*DEG*) is an important chemical intermediate in the manufacture of some unsaturated polyester resins, polyurethanes and plasticizers. In natural gas processing, DEG serves as a dehydration agent. It also finds use as a humectant in the tobacco industry and in the treatment of corks, paper and cellophane.

The textile industry uses DEG as a conditioning agent and lubricant for various natural and synthetic fibers. DEG also finds use as a solvent in the dyeing industry and in printing ink [Shell Bull., 1993].

Triethylene Glycol (*TEG*) is used mainly for its hygroscopic properties. TEG is used as a desiccant for natural gas. It has been used as a humectant for tobacco.

TEG is used as a vinyl plasticizer and as an intermediate in the manufacture of polyols, and as a solvent in a number of miscellaneous applications.

Specialized Applications of these glycols are numerous. High purity, low conductivity MEG is used as a solvent and suspending medium in electrolytic capacitors. MEG fits this application because of its low volatility, excellent electrical properties, and because it does not corrode aluminum.

In foundries, DEG is added to the molding sand mixes for magnesium and aluminum castings to inhibit reaction of the molten metal with the sand and reaction with moisture in the sand and air.

The solvent properties of DEG and TEG are employed in the selective extraction of high purity aromatic compounds such as benzene, toluene and xylene from refinery process streams.

Since these glycols are surface active agents, a number of processors use them as emulsifiers in cosmetics and shampoos. Some gylcols are also used as stabilizers in creams and lotions [Shell Bull., 1993].

SHIPPING, HANDLING AND STORAGE

1. Shipping

Monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) are transported in commerce via bulk delivery in 20 m^3 (5,300 gallons) tank trucks, 75 m^3 (19,840 gallons) railroad tank cars and 1,200 m^3-1,600 m^3 (7,560-10,000 bbl) river barges. Some shipments are also made via ocean-going tankers, which vary in size.

2. Storage

MEG, DEG, and TEG are considered stable and noncorrosive materials with high flash points. Under ordinary storage conditions, these glycols can be stored in mild steel tanks. If traces of iron contamination and color changes are objectionable, use of stainless steel, aluminum, or resin-lined tanks are recommended.

Glycols are hygroscopic and readily absorb atmospheric mois-

Table 6. Data for shipping

Property	Monoethylene glycol	Diethylene glycol	Triethylene glycol
Kg/m^3 @40 °C	1099	1103	1109
Coeff. of expansion @20 °C, per °C	0.00059	0.00063	0.00067
Flash point, cleveland open cup °C	115	143	165

Source: Table 1 this article.

ture. If low water content is to be maintained in storage, tank contents should be kept under dry N$_2$ pressure (circa 1.5 psig or 0.1 kg/cm^{2}ga). For remote offsite storage situations, desiccant units on glycol storage tank vent lines are commonplace and preferred over the installation of lengthy nitrogen piping from battery limits.

Glycols become very viscous at low temperatures. Hence, for long term storage in cold climates, heated or insulated tanks may be required to guard against problems connected with pumping highly viscous material. If internal heating is required, use of tempered water or low-pressure steam circulated through stainless steel coils is recommended. However, product degradation can result from careless storage tank heating practices.

These glycols are not readily ignited, but glycols can burn when exposed to heat and flames.

In enclosed work areas, sufficient ventilation should be provided to keep vapor concentrations below established permissible exposure limit (PEL) values.

SOME RELEVANT COMMENTS

Stand-alone glycol plants as described herein are very rare in the industry. In the typical situation, a glycols process operates in conjunction with an upstream EO production unit. Such a combination allows the integration of a number of utilities.

A recent journal article by this writer describes an EO production operation [Dye, 1999].

NOMENCLATURE

@	: at; commonly used with a pressure or temperature value
bbl	: barrel or barrels, a measure of volume
c	: cents, fraction of one dollar
°C	: degrees Celsius (centigrade)
cal	: calorie or calories
cm	: centimeter or centimeters, a measure of length or thickness; sometimes used with pressure, viz. [kg/cm^{2}ga]
cp	: centipoise or centipoises
°F	: degrees Fahrenheit
gm	: gram or grams
kg	: kilogram or kilograms
m^3	: cubic meters, volume
mm	: millimeter or millimeters, commonly used to express height of a column of Hg as pressure
n$_D$	: refractive index
p/p	: parts per part
ppm	: parts per million, usually used to express compositions, volume or weight bases
%	: percent, basis a whole divided into one hundred parts
% (w)	: percent composition, weight basis
% (v)	: percent composition, volume basis
>	: greater than (6>5)
<	: less than (3<4)

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