*Kirk-Othmer Encyclopedia of Chemical Technology.*

# PROPYLENE OXIDE

Propylene oxide [75-56-9] (methyloxirane, 1,2-epoxypropane) is a significant organic chemical used primarily as a reaction intermediate for production of polyether polyols, propylene glycol, alkanolamines (qv), glycol ethers, and many other useful products (see Glycols). Propylene oxide was first prepared in 1861 by Oser and first polymerized by Levene and Walti in 1927 (1). Propylene oxide is manufactured by two basic processes: the traditional chlorohydrin process (see Chlorohydrins) and the hydroperoxide process, where either *tert*-butanol (see Butyl alcohols) or styrene (qv) as a co-product.

## 1. Physical Properties

Propylene oxide is a colorless, low-boiling (34.2°C) liquid. Table 1 lists general physical properties; Table 2 provides equations for temperature variation on some thermodynamic functions. Vapor–liquid equilibrium data for binary mixtures of propylene oxide and other chemicals of commercial importance are available. References for binary mixtures include 1,2-propanediol (14), water (7, 8, 15), 1,2-dichloropropane [78-87-5] (16), 2-propanol [67-63-0] (17,18), 2-methyl-2-pentene [625-27-4] (19), methyl formate [107-31-3] (20), acetaldehyde [75-07-0] (17,21), methanol [67-56-1] (22), propanal [123-38-6] (16), 1-phenylethanol [60-12-8], oxygen (24 (23), and *tert*-butanol [75-65-0] (22, 23).

## 2. Chemical Properties

Propylene oxide is highly reactive owing to the strained three-membered oxirane ring. The ring C–C and C–O bond lengths have been reported as 147 and 144 pm, respectively, whereas the C–C bond for the substituted methyl group is 152 pm (28). Although some reactions, such as those with hydrogen halides or ammonia (qv), proceed at adequate rates without a catalyst, most reactions of industrial importance employ the use of either acidic or basic catalysts. Recovery of optically active propylene oxide from a mixture of enantiomers is accomplished by the action of microorganisms (29).

### 2.1. Ring Opening

The epoxide ring of propylene oxide may open at either of the C–O bonds. In anionic (basic) catalysis, the bond preferentially opens at the least sterically hindered position, resulting in mostly (95%) secondary alcohol products (30). Cationic (acidic) catalysts provide a mixture of secondary and primary alcohol products. Weak cationic catalysts, such as zeolites, give up to 30% primary alcohol product when reacting with alcohols. Stronger cationic catalysts, such as $H_2SO_4$, give up to 55% primary alcohol product (31).

The ring-opening reactions of epoxides take place by nucleophilic substitution, ie, a $S^{N^2}$ mechanism, on one of the epoxide carbon atoms with displacement of the epoxide oxygen atom. The orientation of ring

**Table 1. Physical Property Data for Propylene Oxide**

| Property | Value | Ref. |
|---|---|---|
| molecular weight | 58.08 | |
| boiling point at 101.3 kPa[a], °C | 34.2 | 2 |
| freezing point, °C | −111.93 | 2 |
| critical pressure, MPa[a] | 4.92 | (3–5) |
| critical temperature, °C | 209.1 | (3–5) |
| critical volume, $cm^3$/mol | 186 | (4, 6) |
| critical compressibility factor, $Z_c$ | 0.228 | (3–5) |
| accentric factor | 0.269 | 5 |
| dipole moment, Cm[b] | $6.61 \times 10^{-30}$ | 6 |
| explosive limits in air, vol % | | |
| upper | 36 | 2 |
| lower | 2.3 | 2 |
| flash point, Tag closed cup, °C | −37 | (3, 7) |
| heat of fusion, kJ/mol[c] | 6.531 | 3 |
| heat of vaporization, 101.3 kPa[a], kJ/mol[c] | 27.8947 | (2, 8, 9) |
| heat of combustion, kJ/mol[c] | 1915.6 | 2 |
| specific heat, at 20°C, J/(mol·K)[c] | 122.19 | (8, 10) |
| autoignition temperature, at 101.3 kPa[a], °C | 465 | (2, 3) |
| index of refraction, at 25°C | 1.36335 | 2 |

[a] To convert kPa to psi, multiply by 0.145.

[b] To convert Cm to debye, divide by $3.336 \times 10^{-30}$.

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

**Table 2. Propylene Oxide Physical Property Data as a Function of Temperature**

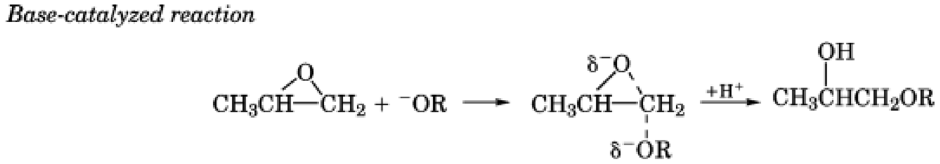
| | | Coefficients | | | | |
|---|---|---|---|---|---|---|
| Property | Equation | *A* | *B* | *C* | *D* | Ref. |
| For T in Kelvin | | | | | | |
| heat of formation, kJ/mol[a] | $A + BT + CT^2$ | −74.450 | $-7.2182 \times 10^{-2}$ | $3.4979 \times 10^{-5}$ | | 11 |
| heat capacity, J/(mol·K)[a] | | | | | | |
| vapor | $A + BT + CT^2 + DT^3$ | −7.868 | 0.32282 | $-1.9498 \times 10^{-4}$ | $4.6455 \times 10^{-8}$ | 12 |
| liquid | $A + BT + CT^2$ | 113.08 | −0.15085 | $6.728385 \times 10^{-4}$ | | 13 |
| For T in °C | | | | | | |
| liquid density, g/mL | $A + BT$ | 0.8556 | −0.00122 | | | 2 |
| viscosity, mPas(=cP) | | | | | | |
| saturated liquid | $A + BT$ | 0.413 | −0.0047 | | | 2 |
| vapor | $A + BT$ | $7.96075 \times 10^{-3}$ | $3.101 \times 10^{-5}$ | | | 3 |
| heat of vaporization, J/g[a] | $A + BT$ | 528.23 | −1.2552 | | | 3 |
| surface tension, N/m | $A + BT$ | 0.02501 | $-1.343 \times 10^{-4}$ | | | 3 |
| thermal conductivity, J/(h·cm·C)[a] | | | | | | |
| liquid | $A + BT$ | 6.5249 | −0.01582 | | | 3 |
| vapor | $A + BT$ | 0.12238 | 0.001025 | | | 3 |
| vapor pressure, kPa[b] | $\log_{10} P = A - B/(T + C)$ | 6.09689 | 1066.19 | 226.38 | | 2 |

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

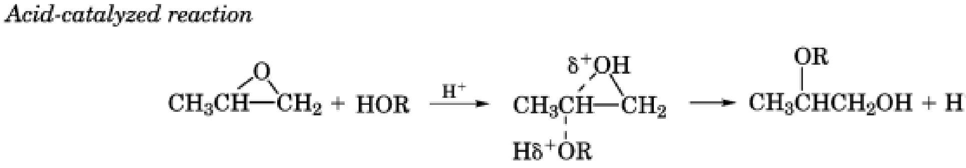
[b] To convert kPa to mm Hg, multiply by 7.5.

opening in propylene oxide is determined primarily by the steric hindrance of the substituent methyl group and secondarily by the electron-releasing effect of the methyl group. Thus acid catalysis increases substitution on the secondary carbon by increasing the positive charge on this carbon (28).

#### 2.1.1. Base-catalyzed reaction



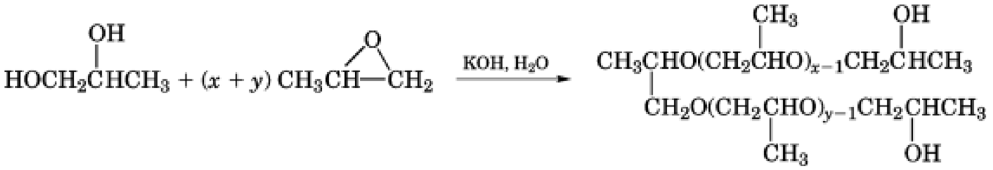
#### 2.1.2. Acid-catalyzed reaction



### 2.2. Polymerization to Polyether Polyols

The addition polymerization of propylene oxide to form polyether polyols is very important commercially. Polyols are made by addition of epoxides to initiators, ie, compounds that contain an active hydrogen, such as alcohols or amines. The polymerization occurs with either anionic (base) or cationic (acidic) catalysis. The base catalysis is preferred commercially (30, 32).

Some of the simplest polyols are produced from reaction of propylene oxide and propylene glycol and glycerol initiators. Polyether diols and polyether triols are produced, respectively (27) (see Glycols).



A variety of initiators can be used to produce polyols of varying functionality. Polymerization of propylene oxide on alcohols or mercaptans results in polymers having a single terminal hydroxyl group, whereas use of propylene glycol yields a product with two hydroxyls (diol). Triols result from initiators such as glycerol (qv), trimethylolpropane, 1,2,6-hexanetriol, and triethanolamine. Higher functionality is achieved with initiators such as sorbitol, sucrose, pentaerythritol, sorbitans, and ethylene diamine (33, 34). Mixtures of initiators (eg, glycerol and sucrose) give polymer mixtures of intermediate functionality.

Propylene oxide can be copolymerized with other epoxides, such as ethylene oxide (qv) (30, 34, 35) or tetrahydrofuran (36, 37) to produce copolymer polyols. Copolymerization with anhydrides (38) or $CO_2$ (39) results in polyesters and polycarbonates (qv), respectively.

Polyols are typically prepared by base catalysis using sodium or potassium hydroxide, aqueous ammonia, or trimethylamine (30, 32, 40). Potassium hydroxide is generally preferred for preparation of polyols for polyurethane applications, whereas sodium hydroxide may be used to prepare polyols used as surfactants (qv). Propylene oxide can also rearrange to allyl alcohol, which reacts with propylene oxide to form a polyether having one hydroxyl and one carbon–carbon double bond end group (32). Use of catalysts such as

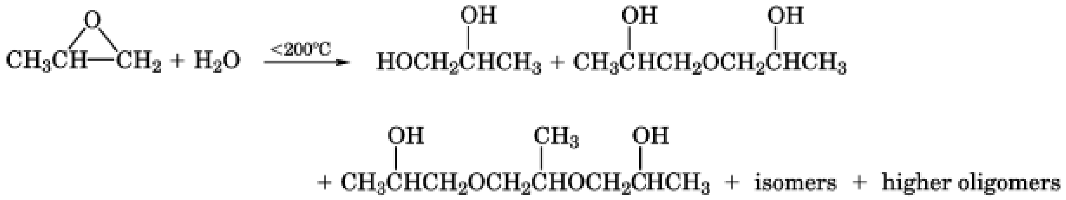
*N*-methyltetraphenylporphyrin complexes produces polymers having very narrow molecular weight distribution (41–43). Stereoselective polymerization of prochiral propylene oxide has been achieved using a chiral aluminum salt of (*R*)-(-)-3,3-dimethyl-1,2-butanediol/$ZnCl_2$ (44) or using bis-dimethylaluminum oxide (308). Polyols produced by the above methods will have molecular weights of ~200–7000 (32).

Molecular weights of poly(propylene oxide) polymers of greater than 100,000 are prepared from catalysts containing $FeCl_3$ (46, 47). The molecular weight of these polymers is greatly increased by the addition of small amounts of organic isocyanates (48). Homopolymers of propylene oxide are also prepared by catalysis using diethylzinc–water (49), diphenylzinc–water (50), and trialkylaluminum (51, 52) systems.

### 2.3. Reactions

#### *2.3.1. Water*

Propylene oxide reacts with water to produce propylene glycol [57-55-6], dipropylene glycol, tripropylene glycol, and higher-molecular-weight polyglycols. This commercial process is typically run using an excess of water (12–20 mol water/mol propylene oxide) to maximize the production of the monopropylene glycol (53).

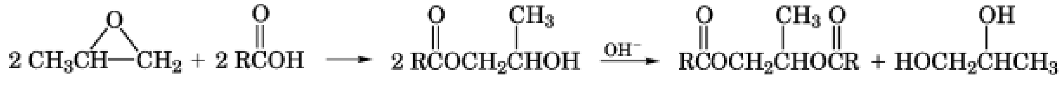


Although the commercial process normally uses heat and pressure without a catalyst, acid or base catalysts can be used to enhance reaction rates or product selectivity. Homogeneous catalyst systems, such as carbon dioxide (qv) and a quaternary phosphonium salt, reduce the excess water required (54), whereas heterogeneous hydrotalcite-type catalysts improve selectivity to monopropylene glycol (55).

#### *2.3.2. Hydroxy-Containing Organics*

Propylene oxide reacts with the hydroxyl group of alcohols and phenols to produce monoethers of propylene glycol. Suitable catalysts include sodium hydroxide, potassium hydroxide, tertiary amines, potassium carbonate, sodium acetate, boron trifluoride, and acid clays. Further addition of propylene oxide yields the di-, tri-, and poly(propylene glycol) ethers. Multiple hydroxyls (glycol, glycerol, glucose, etc) on the organic reactant lead to the polyether polyols discussed earlier (56–58).

Propylene oxide and carboxylic acids in equimolar ratios produce monoesters of propylene glycol. In the presence of basic catalysts these monoesters can undergo transesterification reactions that yield a product mixture of propylene glycols, monoesters, and diesters (56, 59).



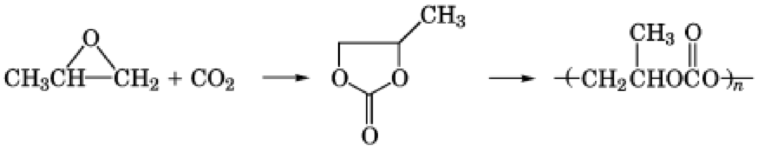
Many natural products, eg, sugars, starches, and cellulose, contain hydroxyl groups that react with propylene oxide. to yield a variety of ether and ester products (60–67).

#### *2.3.3. Ammonia and Amines*

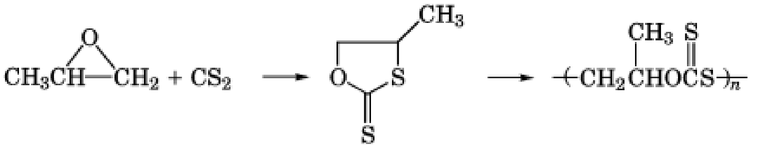
Isopropanolamine is the product of propylene oxide and ammonia in the presence of water (see Alkanolamines). Propylene oxide reacts with isopropanolamine or other primary or secondary amines to produce *N*- and *N*, *N*-disubstituted isopropanolamines. Propylene oxide further reacts with the hydroxyl group of the alkanolamines to form polyether polyol derivatives of tertiary amines (68) or of secondary amines in the presence of a strong base catalyst (69).

#### *2.3.4. Carbon Dioxide and Carbon Disulfide*

Propylene oxide and carbon dioxide react in the presence of tertiary amine, quaternary ammonium halides, anion exchange resins having a quaternary phosphonium group, or calcium or magnesium halide catalysts to produce propylene carbonate (70, 71). Use of catalysts derived from diethylzinc results in polycarbonates (72).



Similarly, carbon disulfide and propylene oxide reactions are catalyzed by magnesium oxide to yield episulfides (73), and by derivatives of diethylzinc to yield low-molecular-weight copolymers (74). Use of tertiary amines as catalysts under pressure produces propylene trithiocarbonate (75).



#### *2.3.5. Hydrogen Sulfide and Mercaptans*

Hydrogen sulfide and propylene oxide react to produce 1-mercapto-2-propanol and bis(2-hydroxypropyl) sulfide (76, 77). Reaction of the epoxide with mercaptans yields 1-alkylthio- or 1-arylthio-2-propanol when basic catalysis is used (78). Acid catalysts produce a mixture of primary and secondary hydroxy products, but in low yield (79). Suitable catalysts include sodium hydroxide, sodium salts of the mercaptan, tetraalkylammonium hydroxide, acidic zeolites, and sodium salts of an alkoxylated alcohol or mercaptan (31, 76, 77, 80, 81).

#### *2.3.6. Friedel-Crafts*

2-Phenylpropanol results from the catalytic ($AlCl_3$, $FeCl_3$, or $TiCl_4$) reaction of benzene and propylene oxide at low temperature and under anhydrous conditions (see Friedel-crafts reactions). Epoxide reaction with toluene gives a mixture of *o*-, *m*-, and *p*-isomers (82, 83).

#### *2.3.7. Grignard Reagents*

Grignard reagents, RMgX, produce a mixture of secondary alcohols, $RCH_2CHOHCH_3$, and propylene halohydrin, $CH_3CHOHCH_2X$, upon reaction with propylene oxide (23, 84, 85). Use of dialkylmagnesium eliminates the halohydrin formation and rearrangement (86) (see Grignard reactions).

#### *2.3.8. Isomerization and Hydrogenolysis*

Isomerization of propylene oxide to propionaldehyde and acetone occurs over a variety of catalysts, eg, pumice, silica gel, sodium or potassium alum, and zeolites (87, 88). Stronger acid catalysts favor acetone over propionaldehyde (88). Allyl alcohol yields of 90% are obtained from use of a supported lithium phosphate catalyst (89).

**Table 3. Global Propylene Oxide Production Capacities,** t × $10^3$/yr

| | | | Hydroperoxide | | | | |
|---|---|---|---|---|---|---|---|
| | Chlorohydrin | | Coproduct–TBA[a] | | Coproduct–styrene | | |
| Geographical location | Capacity | Number of sites | Capacity | Number of sites | Capacity | Number of sites | Total produc-tion capacity |
| United States | 940 | 2 | 783 | 2 | 554 | 1 | 2277 |
| Latin America | 250 | 1 | 0 | | 0 | | 250 |
| Europe | 1061 | 12 | 490 | 2 | 686 | 5 | 2237 |
| Pacific | 558 | 21 | 0 | | 463 | 3 | 1021 |
| Total | 2808 | 36 | 1273 | 4 | 1703 | 9 | 5784 |
| percent of total | 48.5 | | 22.0 | | 29.5 | | |

[a] TBA = *tert* − butyl alcohol.

Hydrogenolysis of propylene oxide yields primary and secondary alcohols as well as the isomerization products of acetone and propionaldehyde. The Pd and Pt catalysts favor acetone and 2-propanol formation (90–92). The Ni and Cu catalysts favor propionaldehyde and 1-propanol formation (93, 94). Reaction of hydrogen atoms on graphite covered Pt favors 1-propanol formation 95

Reduction of propylene oxide to propylene is accomplished by use of metallocenes, such as $Ti(C_5H_5)_2Cl_2$, and sodium amalgam (96).

### 2.3.9. Carbonyl Compounds

Cyclic ketals and acetals (dioxolanes) are produced from reaction of propylene oxide with ketones and aldehydes, respectively. Suitable catalysts include stannic chloride, quaternary ammonium salts, glycol sulfites, and molybdenum acetyl acetonate or naphthenate (97–99). Lactones come from $Ph_4SbI$-catalyzed reaction with ketenes (100).

### 2.3.10. Other Reactions

Propylene oxide reacts with hydrogen halides to give the corresponding isomeric halohydrins (101, 102); with sodium bisulfite to give the sodium salt of 2-hydroxypropanesulfonic acid (103, 104); with nitric acid to produce isomeric nitrate esters (105); with hydrogen cyanide to give 1-cyano-2-propanol (106); and with boric acid, boron trichloride, or diborane to give a variety of substituted boranes and borates (107–110).

2-Dioxolanimines, 2-oxathiolanimines, and 2-oxazolidinimines result from the reaction of propylene oxide with isocyanates, isothiocyanates, and carbodiimides, respectively (111, 112).

Trimethylaluminum and propylene oxide form a mixture of 2-methyl-1-propanol and 2-butanol (113, 114). Numerous other nucleophilic (115) and electrophilic (116) reactions of propylene oxide have been described in the literature.

## 3. Manufacture

Propylene oxide is produced by one of two commercial processes: the chlorohydrin process or the hydroperoxide process. The 1999 global propylene oxide capacity was estimated at about 5.78 × $10^6$ t/yr, with about half came from each of the two processes. Table 3 summarizes the global production capacities for each of the processes.

The chlorohydrin process involves reaction of propylene and chlorine in the presence of water to produce the two isomers of propylene chlorohydrin. This is followed by dehydrochlorination with caustic or lime to propylene oxide and salt. The Dow Chemical Company is the only practitioner of the chlorohydrin process in North America. However, several companies practice the chlorohydrin process at more than 30 locations in Germany, Italy, Brazil, Japan, Eastern Europe, and Asia.

The hydroperoxide process involves oxidation of propylene (qv) to propylene oxide by an organic hydroperoxide. An alcohol is produced as a coproduct. Two different hydroperoxides are used commercially that result in *tert*-butanol or 1-phenylethanol as the coproduct. The *tert*-butanol (TBA) has been used as a gasoline additive, dehydrated to isobutylene, and used as feedstock to produce methyl *tert*-butyl ether (MTBE), a gasoline additive. The 1-phenyl ethanol is dehydrated to styrene. Lyondell has plants producing the TBA coproduct in the United States, France, and the Netherlands. Huntsman has a TBA coproduct plant in the United States. Styrene coproduct plants are operated by Lyondell in the United States and Japan, Shell in the Netherlands and Singapore, Repsol in Spain, and Yukong in South Korea.

Process flow sheets and process descriptions given herein are estimates of the various commercial processes. There are also several potential commercial processes, including variations on the chlorohydrin process, variations on the hydroperoxide process, and direct oxidation of propylene.

### 3.1. Chlorohydrin Process

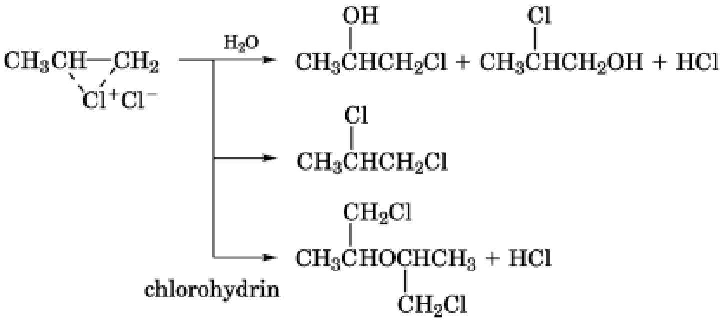
The chlorohydrin process illustrated in Figure 1 is fairly simple, requiring only two reaction steps, chlorohydrination and epoxidation, followed by product purification (117–119). Propylene gas and chlorine gas in about equimolar amounts are mixed with an excess of water to generate propylene chlorohydrin and a small amount of chlorinated organic coproducts, chiefly 1,2-dichloropropane (117). Epoxidation, also called saponification or dehydrochlorination, is accomplished by treatment of the chlorohydrin solution with caustic soda or milk of lime (aqueous calcium hydroxide). Propylene oxide and other organics are steam-stripped from the resulting sodium chloride or calcium chloride brine. The brine is treated, usually by biological oxidation, to reduce organic content prior to discharge. The propylene oxide is further purified to sales specifications by removal of lights and heavies via distillation.

#### *3.1.1. Chlorohydrination*

The mechanism for the formation of propylene chlorohydrin is generally believed to be through the chloronium ion intermediate (117, 119).

$$CH_3CH{=}CH_2 + Cl_2 \longrightarrow CH_3\underset{\diagdown\ \diagup}{CH{-}CH_2}\ \ Cl^+Cl^-$$

The chloronium ion intermediate can react with water to produce the desired propylene chlorohydrin, with chloride ion to produce 1,2-dichloropropane, or with propylene chlorohydrin to produce isomers of dichlorodipropyl ether.



$$CH_3CH{-}CH_2\,(Cl^+Cl^-) \xrightarrow{H_2O} CH_3\overset{OH}{\overset{|}{C}}HCH_2Cl + CH_3\overset{Cl}{\overset{|}{C}}HCH_2OH + HCl$$

$$\longrightarrow CH_3\overset{Cl}{\overset{|}{C}}HCH_2Cl$$

$$\xrightarrow{\text{chlorohydrin}} CH_3\overset{CH_2Cl}{\overset{|}{C}}HO\underset{\underset{CH_2Cl}{|}}{C}HCH_3 + HCl$$

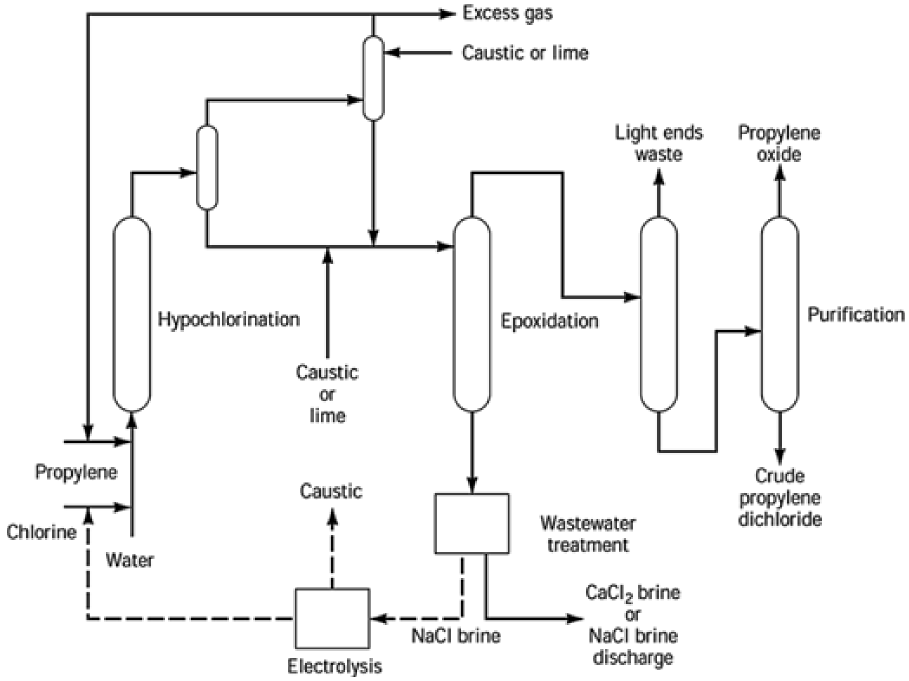


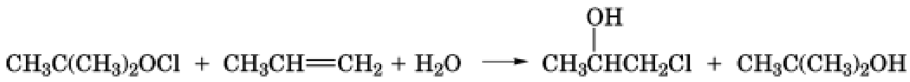
**Fig. 1.** The chlorohydrin process (117, 118, 133).

The 1-chloro-2-propanol isomer represents about 85% of the chlorohydrin produced. In order to minimize the coproduct formation of dichloride and ether, the reactant compositions are chosen such that the effluent liquid contains 4–5 wt % propylene chlorohydrin. Under these conditions, the yield of chlorohydrin, dichloride, and ether from the reactants is 90–93, 5–7, and 1%, respectively. Computer simulations of the reactor are useful to optimize the yields (120).

In two proposed alternative processes, the chlorine is replaced in the chlorohydrination reaction by hypochlorous acid [7790-92-3], HOCl, or *tert*-butyl hypochlorite. In the first, a concentrated (>10% by weight) aqueous solution of hypochlorous acid, substantially free of chloride, chlorate, and alkali metal ions, is contacted with propylene to produce propylene chlorohydrin (121). Advantages of the HOCl process include >95% chlorohydrin yields due to lower 1,2-dichloropropane formation. The process has the potential for water and brine recycle for reduced waste effluent (122,123). The likely mechanism of reaction is the same as that for chlorine, as chlorine is generated *in situ* through the equilibrium of chlorine and hypochlorous acid (117).

$$HOCl + HCl \rightleftarrows Cl_2 + H_2O$$

In the second proposed alternative process, *tert*-butyl hypochlorite, formed from the reaction of chlorine and *tert*-butyl alcohol, reacts with propylene and water to produce the chlorohydrin. The alcohol is a coproduct and is recycled to generate the hypochlorite (124–126). No commercialization of the hypochlorous acid and *tert*-butyl hypochlorite processes for chlorohydrin production is known.



$$CH_3C(CH_3)_2OCl + CH_3CH{=}CH_2 + H_2O \longrightarrow CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_2Cl + CH_3C(CH_3)_2OH$$

### 3.1.2. Epoxidation

Epoxidation, also referred to as saponification or dehydrochlorination, of propylene chlorohydrin (both isomers) to propylene oxide is accomplished using a base, usually aqueous sodium hydroxide or calcium hydroxide 127.

$$CH_3CH(OH)CH_2Cl + HCl + Ca(OH)_2 \longrightarrow CH_3CH(O)CH_2 + CaCl_2 + 2\,H_2O$$

About 10% excess base is used for the epoxidation and neutralization of the acid. Because propylene oxide undergoes hydrolysis to propylene glycol (128, 129) in the presence of the base, the oxide is quickly steam-stripped from the brine solution. This operation is carefully controlled to avoid stripping unreacted chlorohydrin. The exit gas, containing about 70 wt % water, 26 wt % propylene oxide, and 4 wt % miscellaneous organic compounds, is further processed to purify the propylene oxide. The brine effluent contains salt, eg, 5–6 wt % calcium chloride; base, 0.1 wt % calcium hydroxide; and 0.05–0.1 wt % propylene glycol (117–119). Although not used commercially, recovery of HCl is possible via catalytic dehydrochlorination using a $CsCl/SiO_2$ catalyst (130).

### 3.1.3. Purification

Purification of propylene oxide from the chlorohydrin process is accomplished by standard distillation (qv) in one or more packed or trayed columns. Lighter components, such as acetaldehyde (qv), are removed overhead. Heavier components, such as water and propylene dichloride, are taken off the bottom of the column (117, 118). Glycol formation can be reduced by controlling the bottoms stream at pH between 4 and 7 by adding NaCl or $Na_2SO_4$ (131). The bottoms stream is decanted into an aqueous layer and an organic layer. The aqueous layer can be recycled for additional product recovery. The organic layer contains coproducts that can be further processed for recovery and use (117, 118, 131). 1,2-Dichloropropane is used as a feedstock for chlorinated organic processes such as perchlorethylene. It is also catalytically reduced by hydrogen to propylene and anhydrous HCl (132). Epichlorohydrin is recovered for use, eg, in epoxy resins.

### 3.1.4. Effluent Wastewater Treatment

The volume of water effluent is about 40 times the volume of propylene oxide produced in the chlorohydrin process, representing a significant concern for proper disposal or reuse (119). The options for treatment of the water effluent from the epoxidation process depend on the alkali used. Use of lime in epoxidation results in a calcium chloride brine (4–6 wt %) which has little commercial value and is, therefore, discharged. Use of caustic soda in epoxidation results in a sodium chloride brine that can either be discharged or recycled to a chloralkali electrolysis unit to generate chlorine and caustic (133). The effluent is treated biologically to reduce organic content prior to discharge or recycle (134, 135). Chlorinated organic content of the effluent is reduced by activated carbon (136) or through process operating controls (137).

## 3.2. Hydroperoxide Process

The hydroperoxide process to propylene oxide involves the basic steps of oxidation of an organic to its hydroperoxide, epoxidation of propylene with the hydroperoxide, purification of the propylene oxide, and conversion of the coproduct alcohol to a useful product for sale. Incorporated into the process are various purification, concentration, and recycle methods to maximize product yields and minimize operating expenses. Commercially, two processes are used. The coproducts are *tert*-butanol, which is converted to methyl *tert*-butyl ether [1634-04-4] (MTBE), and 1-phenyl ethanol, converted to styrene [100-42-5]. The coproducts are produced in a weight ratio of 3–4:1 *tert*-butanol/propylene oxide and 2.4:1 styrene/propylene oxide, respectively. These processes use isobutane (see Hydrocarbons) and ethylbenzene (qv), respectively, to produce the hydroperoxide. Other

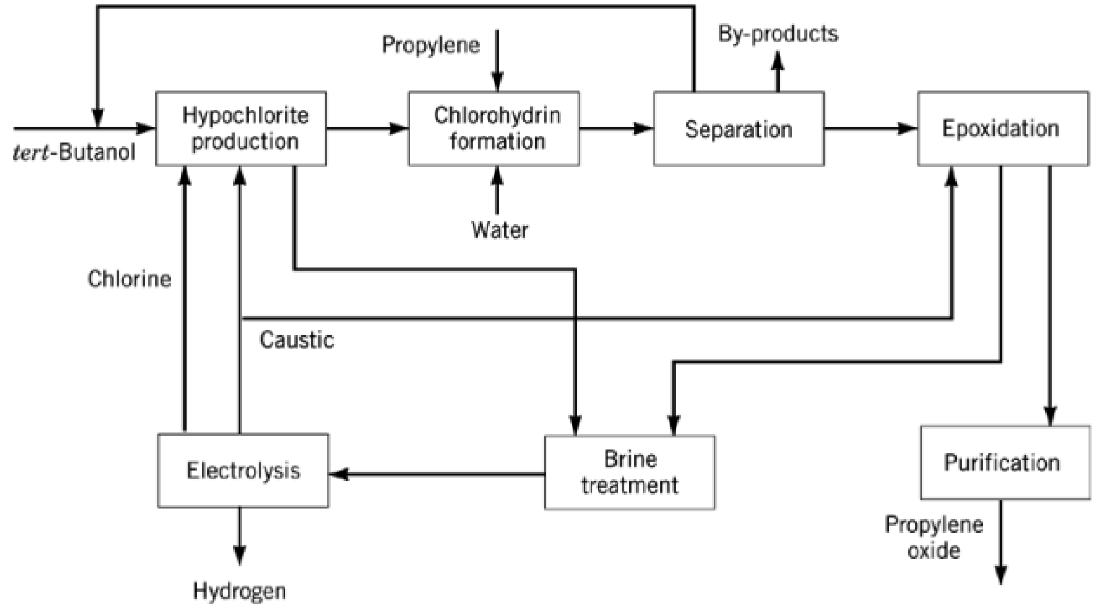


**Fig. 2.** The *tert*-butyl hydroperoxide process to propylene oxide (PO) and *tert*-butanol (TBA) (138–158).

processes have been proposed based on cyclohexane where aniline is the final coproduct, or on cumene (qv) with $\alpha$-methyl styrene as the final coproduct.

### *3.2.1. tert-Butyl Hydroperoxide Process*

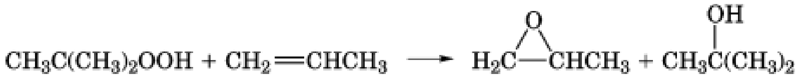
Figure 2 provides a simplified flow sheet of the propylene oxide and *tert*-butyl alcohol coproduct process. The first step of the process is the liquid-phase air oxidation of isobutane to *tert*-butyl hydroperoxide (TBHP) in the presence of 10–30 wt % *tert*-butyl alcohol (TBA). Temperature is 95–150°C and pressure is 2075–5535 kPa (300–800 psi), resulting in a conversion of 20–30% of the isobutane and a selectivity to TBHP of 60–80% and to TBA of 20–40%. Conversion can be increased at the expense of selectivity of TBHP by increasing temperature and increasing reaction time (138). Unreacted isobutane and a portion of the TBA are separated from the product and recycled back to the hydroperoxide-forming reactor.

$$\overset{\overset{CH_3}{|}}{CH_3CHCH_3} + O2 \longrightarrow CH_3C(CH_3)_2OOH$$

The *tert*-butyl hydroperoxide is then mixed with a catalyst solution to react with propylene. Some TBHP decomposes to TBA during this process step. The catalyst is typically an organometallic that is soluble in the reaction mixture. The metal can be tungsten, vanadium, or molybdenum with molybdenum complexes with naphthenates or carboxylates providing the best combination of selectivity and reactivity. Catalyst concentrations of 200–500 ppm in a solution of 55% TBHP and 45% TBA are typically used when water content is less than 0.5 wt %. The homogeneous metal catalyst must be removed from solution for disposal or recycle (139, 159). Although heterogeneous catalysts can be employed, elution of some of the metal, particularly molybdenum, from the support surface occurs (160). References 161 and 162 discuss possible mechanisms for the catalytic epoxidation of olefins by hydroperoxides.

**Table 4. Solvents for Purification of Propylene Oxide From Epoxidation Using *tert*-Butyl Hydroperoxide**

| Impurity to be removed | Extractive distillation solvent | Reference |
|---|---|---|
| water | sulfonate | 163 |
| | monohydroxy alkoxyalkanol | 164 |
| water–methanol–acetone | 1-methyl-2-pyrrolidine | 165 |
| | triethyleneglycol | 166 |
| | dipropyleneglycol | 167 |
| | 1-propanol | 168 |
| methanol | acetone–water | 169 |
| methanol–acetone | water | 170 |
| methanol–water–methyl formate | octane or propylene glycol | 158 |
| $C_4$–$C_7$ hydrocarbons | *tert*-butanol–water | 171 |
| | paraffinic hydrocarbon | 172 |
| | $C_7$–$C_{10}$ alkane hydrocarbon | 157 |



An excess of 2–10 mol propylene to hydroperoxide is used to maximize conversion of hydroperoxide and selectivity to propylene oxide. Temperature is 100–130°C, pressure is 1480–3550 kPa (215–515 psi), and residence time is sufficient (about 2 h) for $>95\%$ conversion of the hydroperoxide. An organic solvent such as benzene, chlorobenzene, or *t*-butanol may be employed. Selectivity to propylene oxide is 95–98% based on TBHP and 97–98% based on propylene. The principal by-products are propylene glycol, methyl formate, and a propylene dimer. Some of these by-products are difficult to remove from the product propylene oxide (140–142). The presence of acids, such as carboxylic acids, results in lower product selectivity (143). The reactor design is described as a horizontal tank having partitioned reaction zones, a thermosyphon reactor, or a two-stage reactor having different operating conditions in each stage (143, 159).

After epoxidation a distillation is performed to remove the propylene, propylene oxide, and a portion of the TBHP and TBA overhead. The bottoms of the distillation contains TBA, TBHP, some impurities such as formic and acetic acid, and the catalyst residue. Concentration of this catalyst residue for recycle or disposal is accomplished by evaporation of the majority of the TBA and other organics (144–146), addition of various compounds to yield a metal precipitate that is filtered from the organics (147–150), or liquid extraction with water (151). Low ($<500$ ppm) levels of soluble catalyst can be removed by adsorption on solid magnesium silicate (152). The recovered catalyst can be treated for recycle to the epoxidation reaction (135).

Methyl formate and propylene oxide have close boiling points, making separation by distillation difficult. Methyl formate is removed from propylene oxide by hydrolysis with an aqueous base and glycerol, followed by phase separation and distillation (154, 155). Methyl formate may be hydrolyzed to methanol and formic acid by contacting the propylene oxide stream with a basic ion-exchange resin. Methanol and formic acid are removed by extractive distillation (156).

Final purification of propylene oxide is accomplished by a series of conventional and extractive distillations. Impurities in the crude product include water, methyl formate, acetone, methanol, formaldehyde, acetaldehyde, propionaldehyde, and some heavier hydrocarbons. Conventional distillation in one or two columns separates some of the lower boiling components overhead, while taking some of the higher boilers out the bottom of the column. The reduced level of impurities are then extractively distilled in one or more columns to provide a purified propylene oxide product. The solvent used for extractive distillation is distilled in a conventional column to remove the impurities and then recycled (157, 158). A variety of extractive solvents have been demonstrated to be effective in purifying propylene oxide, as shown in Table 4.

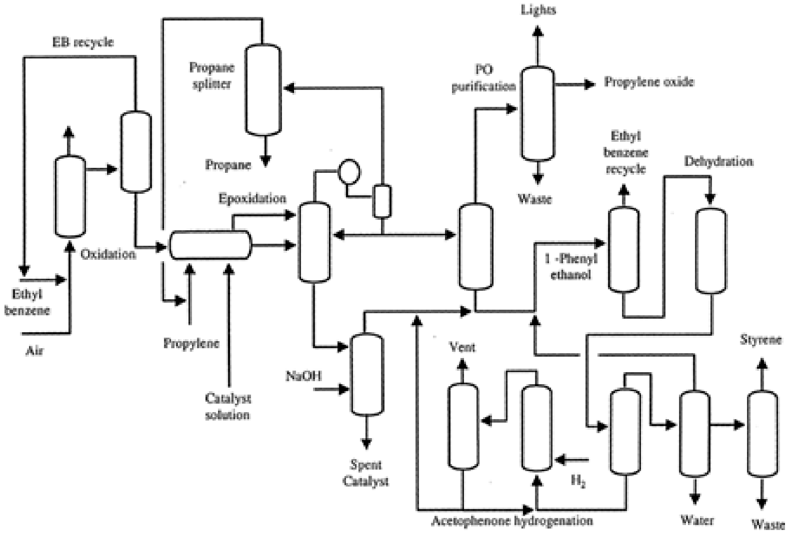
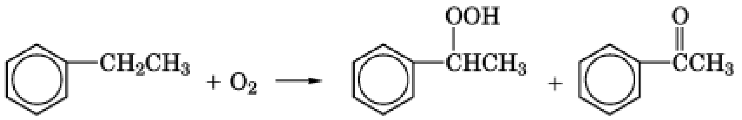


**Fig. 3.** The ethylbenzene (EB) hydroperoxide process to propylene oxide (PO) and styrene (173–196).

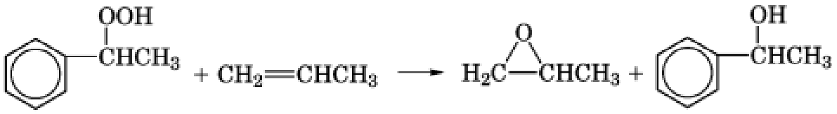
The *tert*-butanol coproduct is purified for further use as a gasoline additive. Upon reaction with methanol, methyl *tert*-butyl ether (MTBE) is produced. Alternatively the TBA is dehydrated to isobutylene, which is further hydrogenated to isobutane for recycle in the propylene oxide process.

### *3.2.2. Ethylbenzene Hydroperoxide Process*

Figure 3 shows the process flow sheet for production of propylene oxide and styrene via the use of ethylbenzene hydroperoxide (EBHP). Liquid-phase oxidation of ethylbenzene with air or oxygen occurs at 206–275 kPa (30–40 psia) and 140–150°C, and 2–2.5 h are required for a 10–15% conversion to the hydroperoxide. Recycle of an inert gas, such as nitrogen, is used to control reactor temperature. Impurities in the ethylbenzene, such as water, are controlled to minimize decomposition of the hydroperoxide product and are sometimes added to enhance product formation. Selectivity to by-products include 8–10% acetophenone, 5–7% 1-phenylethanol, and $<1\%$ organic acids. EBHP is concentrated to 30–35% by distillation. The overhead ethylbenzene is recycled back to the oxidation reactor (173–175). Because the by-product organic acids decompose EBHP and decrease epoxidation catalyst activity, an alkali hydroxide or carbonate wash is used to neutralize the acids (176–178).



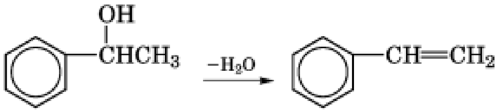
EBHP is mixed with a catalyst solution and fed to a horizontal compartmentalized reactor where propylene is introduced into each compartment. The reactor operates at 95–130°C and 2500–4000 kPa (360–580 psi) for 1–2 h, and 5–7 mol propylene/1 mol EBHP are used for a 95–99% conversion of EBHP and a 92–96% selectivity to propylene oxide. The homogeneous catalyst is made from molybdenum, tungsten, or titanium and an organic acid, such as acetate, naphthenate, stearate, etc (173, 179). Heterogeneous catalysts consist of titanium oxides on a silica support (174–176).



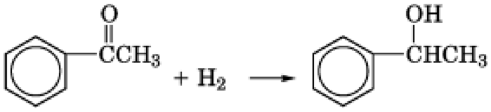
After epoxidation, propylene oxide, excess propylene, and propane are distilled overhead. Propane is purged from the process; propylene is recycled to the epoxidation reactor. The bottoms liquid is treated with a base, such as sodium hydroxide, to neutralize the acids. Acids in this stream cause dehydration of the 1-phenylethanol to styrene. The styrene readily polymerizes under these conditions (184–186). Neutralization, along with water washing, allows phase separation such that the salts and molybdenum catalyst remain in the aqueous phase (186). Dissolved organics in the aqueous phase are further recovered by treatment with sulfuric acid and phase separation. The organic phase is then distilled to recover 1-phenylethanol overhead. The heavy bottoms are burned for fuel (187–189).

Crude propylene oxide separated from the epoxidation reactor effluent is further purified by a series of conventional and extractive distillations to reduce the content of aldehydes, ethylbenzene, water, and acetone (190–192).

The co-product 1-phenylethanol from the epoxidation reactor, along with acetophenone from the hydroperoxide reactor, is dehydrated to styrene in a vapor-phase reaction over a catalyst of silica gel (193) or titanium dioxide (173, 194) at 250–280°C and atmospheric pressure. This product is then distilled to recover purified styrene and to separate water and high-boiling organics for disposal. Unreacted 1-phenyl ethanol is recycled to the dehydrator.



Acetophenone is separated for hydrogenation to 1-phenylethanol, which is sent to the dehydrator to produce styrene. Hydrogenation is done over a fixed-bed copper-containing catalyst at 115–120°C and pressure of 8100 kPa (80 atm), a 3:1 hydrogen-to-acetophenone ratio, and using a solvent such as ethyl benzene, to give 95% conversion of the acetophenone and 95% selectivity to 1-phenyl ethanol (195, 196).



## 4. Developmental Processes

Since each of the commercial processes has issues of effluent treatment, by-product treatment, co-product sales, and cost, development of alternative processes that address one or more of these issues is on-going.

### 4.1. Hydrogen Peroxide Processes

A titanium silicalite catalyst (TS-1) is used to produce propylene oxide from propylene and hydrogen peroxide. Alcohol or alcohol–water mixtures are used as solvent. Methanol is the preferred alcohol. Yields on peroxide are quantitative and propylene selectivity is high (95%). TS-1 is a molecular sieve having an average pore diameter of 0.55 nm and a $TiO_2$ content of 2.6 wt % (197, 198). The catalyst deactivates due to polymer formation and is regenerated by calcining or treatment with hydrogen peroxide solutions (199). Propylene oxide selectivity is improved by treating the catalyst with neutral (200) or basic (201) salts, tin (202), or metal cations (203) at the expense of catalyst activity. Peroxide decomposition to water and oxygen is reduced by use of chelating agents (204), but is increased by Pd in the catalyst (205).

Fully integrated processes have been proposed that include hydrogen peroxide production, propylene reaction to propylene oxide, product purification, and solvent recycle. Peroxide formation can be from catalytic hydrogen and oxygen reaction in alcohol solvent (206) or the anthraquinone process (207, 208). Purification of propylene oxide by extractive distillation using water or propylene glycol effectively removes impurities such as acetaldehyde (209).

### 4.2. Direct Oxidation of Propylene to Propylene Oxide

Comparison of ethylene (qv) and propylene gas-phase oxidation on supported silver and silver–gold catalysts shows propylene oxide formation to be 17 times slower than ethylene oxide (qv) formation and the $CO_2$ formation in the propylene system to be six times faster, accounting for the lower selectivity to propylene oxide than for ethylene oxide (210). In propylene oxidation a polymer forms on the catalyst surface that is oxidized to $CO_2$ (211).

To improve the selectivity of propylene to propylene oxide, the silver-based catalysts have been prepared in a variety of methods, using a variety of supports and modifiers (212–218). Addition of water, nitrous oxide, ethyl chloride, or 1,2-dichloroethane to the gas feed has also provided higher selectivities (216–221). In spite of significant research efforts, an economically acceptable combinaiton of propylene conversion, propylene oxide selectivity, and catalyst productivity has not been achieved.

Recent developments have demonstrated propylene oxide selectivity $>90\%$ using a gold on titania or titanosilicate catalyst (222–226). Such gas-phase processes consume hydrogen and oxygen, yielding water as a coproduct. Propylene conversion is typically less than 2%. Generally, hydrogen selectivity is low and the catalyst activity deteriorates in hours. Use of Pd or Pt in place of gold results in higher propylene conversion, but lower selectivity (227, 228).

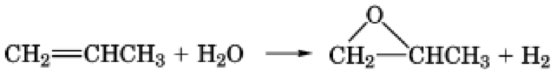
Gas-phase oxidation of propylene using oxygen in the presence of a molten nitrate salt such as sodium nitrate, potassium nitrate, or lithium nitrate and a co-catalyst such as sodium hydroxide results in propylene oxide selectivities greater than 50%. The principal by-products are acetaldehyde, carbon monoxide, carbon dioxide, and acrolein (229, 230). This same catalyst system oxidizes propane to propylene oxide and a host of other by-products (231). Higher selectivities ($>70\%$) are achieved by supporting nitrate or nitrite salts on silicates (232, 233).

Propylene oxide is also produced in liquid-phase homogeneous oxidation reactions with various molybdenum-containing catalysts (234, 235), cuprous oxide (236), rhenium compounds (237), or an organomonovalent gold(I) complex (238). Propylene oxide selectivity is typically $<60\%$. Selectivity $>90\%$ has been achieved with a $EuCl_3$ catalyst (239, 240). Whereas gas-phase oxidation of propylene on silver catalysts results primarily in propylene oxide, water, and carbon dioxide as products, the liquid-phase oxidation of propylene results in an array of oxidation products, such as propylene oxide, acrolein, propylene glycol, acetone, acetaldehyde, and others.

Noncatalytic oxidation of propylene to propylene oxide is also possible. Use of a small amount of aldehyde in the gas-phase oxidation of propylene at 200–350°C and up to 6900 kPa (1000 psi) results in about 44% selectivity to propylene oxide. About 10% conversion of propylene results (242, 243). Photochemical oxidation of propylene with oxygen to propylene oxide has been demonstrated in the presence of $\alpha$-diketone sensitizers and an aprotic solvent (244).

### 4.3. Electrochemical Process

Applying an electrical current to a brine solution containing propylene results in oxidation of propylene to propylene oxide. The chemistry is essentially the same as for the halohydrin process. All the chemistry takes place in one reactor. Most of the reported work uses sodium or potassium bromide as the electrolyte. Bromine, generated from bromide ions at the anode, reacts with propylene and water to form propylene bromohydrin. Hydroxide generated at the cathode then reacts with the bromohydrin to yield propylene oxide (245–248). The net reaction involves transfer of two electrons:



$$CH_2{=}CHCH_3 + H_2O \longrightarrow \overset{O}{\overbrace{CH_2{-}CHCH_3}} + H_2$$

More recently, electrocatalytic systhesis of propylene oxide has been demonstrated. Oxygen generated from water at the anode made of Pt black (249, 250) or nickel (251) epoxidizes propylene to propylene oxide. Oxygen consumed at the cathode, made of carbon or carbon/titanium silicalite, also produces propylene oxide from propylene (251). Gas-phase epoxidation at a Pt black anode has been demonstrated (252).

Although the above process has not been commercialized, Daicel operated a 12,000 t/yr propylene oxide plant based on a peracetic acid [79-21-0] process during the 1970s. The Daicel process involved metal ion-catalyzed air oxidation of acetaldehyde in ethyl acetate solvent, resulting in a 30% peracetic acid solution in ethyl acetate. Epoxidation of propylene followed by purification gives propylene oxide and acetic acid as products (256). As of this writing (ca 1999), this process is not in operation.

Enzymes, such as monooxygenase, produced from certain microorganisms, oxidize propylene to propylene oxide. The capital and operating costs result in production costs of \$1.00/lb or greater (257).

## 5. Economic Aspects

Production of propylene oxide in the United States in 1999 was estimated at 2.28 × metric tons, and as having a 10-yr average annual growth rate of 3.9% (258). Projections were for continued growth at about 4%/yr. Producers include Dow Chemical's chlorohydrin plants in Freeport, Texas, and Plaquemine, Louisiana; Lyondell's hydroperoxide plants in Bayport and Channelview, Texas; and Hunstman's hydroperoxide plant in Port Neches, Texas. Globally, about half of the $5.78 \times 10^6$ t/yr capacity is in the chlorohydrin process (see Table 3). About 60% of the capacity increase in the past 5 yr has been through debottlenecking existing plants. All new grass-roots plants in this time period have used the hydroperoxide technology with styrene as the coproduct. More than 95% of the propylene oxide produced is converted to derivatives. Polyether polyols (ca 60%) and propylene glycol (ca 25%) are the principal products.

Cost of manufacture is based on capital required to build the production facilities and the operating costs (raw materials, utilities, maintenance, etc). Owing to the high pressure and large volume of recycle streams in the coproduct hydroperoxide processes, the capital required for these processes is considerably higher than for the chlorohydrin process. However, the raw material cost for chlorohydrin is higher than for the hydroperoxide routes. Because the coproducts of styrene and *tert*-butanol are produced in higher volume than propylene oxide, ie, 2.4 styrene/propylene oxide and 3-4 *tert*-butanol/propylene oxide, the profitability of the coproduct is also tied to the market conditions for sale.

## 6. Storage and Materials of Construction

The National Fire Protection Association (NFPA) has given propylene oxide a flammability rating of 4 and a reactivity rating of 2, indicative of the low flash point of $-37^{\circ}\mathrm{C}$, flammability range of 2.3–36% by volume in air, and reactivity with water. OSHA classifies propylene oxide as a Class 1A flammable liquid (259). Storage should be in steel or stainless steel vessels in an inert atmosphere such as nitrogen. Pumps (qv) and other electrical devices involved in the transfer of propylene oxide should have explosion-proof motors and housings meeting the electrical requirements of the National Electric Code (NEC-NFPA 70) of Class 1, Division 1, Group B. In addition, all pumps should use mechanical seals to minimize the potential for leaks. For pressures of 103 kPa (15 psig) or less, vessels should be designed according to API-620 code. Higher pressure design should be according to the Code for Unfired Pressure Vessels, Section VIII of the ASME Boiler and Pressure Vessel Code. Propylene oxide feed should be entered below the liquid surface, avoiding free-falling liquid through the vapor space, which could cause a spark. All vessels are required to be properly grounded. Storage in drums should be done in accordance with NFPA Codes for storage facilities for flammable and combustible liquids, eg, NFPA 30 and NFPA 80 (2, 3).

The reportable quantity (RQ) of propylene oxide under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) is 100 lbs (45.4 kg). The relative risk of refrigerated storage compared to pressurized storage has been assessed (260). The potential for leaks from propylene oxide storage and transfer facilities should be minimized by use of mechanical seals on pumps, all-welded tanks and pipes, a minimum of flanged connections and vessel nozzles, sprial-wound stainless steel with Teflon resin fill gaskets, Kalrez 1050 or Teflon O-rings, graphite valve packing, and Teflon paste or tape for pipe threads. Instrumentation on tanks should include high-level alarms or shutdowns, temperature indicators, pressure gauges, automatic pad/depad system using nitrogen with less than 200 ppm oxygen, and combustible gas detectors. All storage and handling facilities should have provision for spill containment such as diking and remote containment. Vapor containment from tank vents can be accomplished through use of scrubbers, flares, or closed pad/depad systems. Flame arrestors may be required to prevent flame propagation into the vessel (2, 3).

## 7. Transportation

Propylene oxide is classified as a flammable liquid and hazardous substance in the U.S. Department of Transportation (DOT) Hazardous Materials Table. The DOT shipping requirement is Propylene Oxide, 3, UN1280, PG 1. The red flammable liquid label and red flammable placard are required on all shipments (2, 3, 261).

Shipment by rail is done in DOT 105A 100W tank cars equipped with a 517-kPa (75-psig) safety relief valve and having a capacity of 25,000 gallons (95,000 L). Such tank cars are welded carbon steel having 10 cm of fiber glass insulation and a steel jacket. Loading and unloading are done through the top using a dip pipe that extends to the bottom of the car into a shallow sump. Shipment by truck is done in DOT MC-331 steel tanks of about 5,500-gal (20,800-L) capacity, having a pressure rating of 15–35 psig (205–340 kPa). ISO tanks are specified by DOT 51 and IM 101 and have a capacity of about 6,000 gal (22,700 L). All shipments of propylene oxide employ a nitrogen pad of 15–35 psig (205–340 kPa). Procedures for loading and unloading are found in References (2, 3), and 8.

Marine transportation is done by ship or barge in permanent containers on board or by ISO containers. Propylene oxide can be shipped by air freight, but specific regulations for domestic and international transport must be followed. No shipment of propylene oxide can be made on passenger ships or airlines (3, 261).

UN Standard 1A1 steel nonremovable head drums or DOT 17C steel drums are used to transport propylene oxide. These drums must be tested to 36 psia (250 kPa) and a stacking height of 10 ft (3 m) (3, 8, 261).

**Table 5. Specifications for Propylene Oxide**[a]

| Description | Value[b] |
|---|---|
| acidity, as acetic acid, wt % | 0.005 |
| aldehyde, as propionaldehyde, wt % | 0.040 |
| color, Pt–Co scale | 10.0 |
| nonvolatile residue, g/100 mL | 0.002 |
| residual odor | none |
| specific gravity, 20/20°C | 0.829[c]<br>0.831 |
| water, wt % | 0.050 |

[a] Ref. 8.
[b] Values given are maximum unless otherwise indicated.
[c] Value given is minimum.

## 8. Specifications and Analysis

Propylene oxide is a high-purity product and thus only the impurities are analyzed and reported. Table 5 lists typical sales specifications (8). The sales specification may vary depending on the application.

Detection of propylene oxide has practical applications in the manufacturing process, in quality control of reaction products, and in environmental monitoring. Propylene oxide content in manufacturing streams is determined by chemical methods such as hydrochlorination (262), gas chromatography, infrared spectrophotometry (263), Raman spectrometry (264), and chemical ionization mass spectrometry (265). These methods can also be applied to analyze unreacted propylene oxide in applications. Reaction with 4-(*p*-nitrobenzyl) pyridine followed by absorbance measurement at 570 nm is another method (266). In addition, the chemical method involving the use of periodate has been found useful in determining nanomole quantities of propylene oxide (267). Determination of propylene oxide in ambient air can be accomplished by adsorption, followed by thermal desorption in a gas chromatograph and quantification by flame ionization detection (268) or a quadrupole ion trap mass spectrometer (269). Analysis of impurities and physical properties of propylene oxide is accomplished by a variety of methods described in Reference 8.

Removal of low levels of close-boiling impurities or poly(propylene oxide) is accomplished by treatment of the oxide with activated carbon, diatomaceous earth, zeolites, or membranes (270–275).

## 9. Health and Safety Factors

Propylene oxide has a variety of toxic effects on humans. Thus exposure to propylene oxide during manufacture, storage and handling, and use should be minimized. Potential for high exposure to propylene oxide can occur during such routine activities as sampling, analysis, maintenance, and in disconnecting hoses used for product transfer. Exposure is first minimized through proper design of sampling devices and the handling equipment and use of job procedures for both routine work and maintenance activity. A last resort is the use of personal protective equipment such as respirators, breathing air, gloves, and chemical suits (276, 277). Reference 2 provides some recommended methods for safe sampling of propylene oxide.

Propylene oxide released to the atmosphere is relatively stable, having a half-life of 3–10 d. Propylene oxide reacts with hydroxide, producing formaldehyde and acetaldehyde. Reference 278 discusses possible reaction mechanisms for atmospheric reactions. In aqueous systems, propylene oxide is hydrolyzed by water to propylene glycol, or reacts with halides to form halohydrins. Some microorganisms degrade propylene oxide to propylene glycol and other products. Persistence in the environment and bioaccumulation are not likely owing to the high reactivity of propylene oxide (279). Spills and releases to the atmosphere of greater than 100 lb (45.4 kg) are regulated and reportable to various governmental agencies (280).

Design of processes handling propylene oxide should avoid explosive mixtures (2.3–36% by volume). Reference 281 provides literature references on documented explosions and uncontrolled reactions involving propylene oxide. Reaction vessels and storage tanks must be designed to handle operating pressures and be provided with adequate relief devices to prevent overpressure. Overpressure can result from thermal expansion caused by heating or heat of reaction, runaway reactions, or vaporization (282). Firefighting equipment should include use of Class B dry chemical or foam extinguishers for small fires and deluge systems or 6% foam systems with a capacity of at least a 0.25 gal/min/ft$^2$ (10.2 L/min/m$^2$) of storage area (3).

### 9.1. Physiological Effects

Propylene oxide has been studied extensively for its effects on humans and animals. Accordingly, it is regulated under several U.S. Federal statutes and agencies. OSHA has established a time-weighted-average 8-h permissable exposure limit of 20 ppm (50 mg/m$^3$). Because the odor threshold is about 200 ppm, the sweet penetrating odor of propylene oxide is not an adequate warning to prevent overexposure. Exposure to vapors above the permissable exposure limit can be irritating to the eyes and respiratory tract. Low concentrations can cause nausea; high concentrations can cause pulmonary edema (2, 3). Although there are no epidemiologic data for long-term exposure to humans, studies on animals suggest that propylene oxide is a possible human carcinogen and is classified as such by NIOSH, IARC, and NTP (3). References 279 and (283–285) provide a summary of the published findings on propylene oxide carcinogenicity, mutagenicity, and teratogenicity in animals. Propylene oxide has been shown to cause central nervous system effects such as ataxia, incoordination, and depression in rats (286–288).

Skin contact can result in irritation, blistering, or burns if confined to the skin by clothing or shoes, but is not injurious if it evaporates readily. Liquid propylene oxide exposure to the eyes causes injury in rabbits. Ingestion of aqueous solutions of 5 and 10% propylene oxide showed $LD_{50}$ values of 1.14 g/kg for rats and 0.69 g/kg for guinea pigs (287).

## 10. Uses

Propylene oxide is a useful chemical intermediate. Additionally, it has found use for etherification of wood (qv) to provide dimensional stability (289, 290), for purification of mixtures of organosilicon compounds (291), for disinfection of crude oil and petroleum products (292), for sterilization of medical equipment and disinfection of foods (293, 294), and for stabilization of halogenated organics (295–297).

Propylene oxide has found use in preparation of polyether polyols from recycled poly(ethylene terephthalate) (298), halide removal from amine salts via halohydrin formation (299), preparation of flame retardants (303), alkoxylation of amines (301, 302), modification of catalysts (303), and preparation of cellulose ethers (304, 305).

### 10.1. Derivatives

#### *10.1.1. Polyether Polyols*

Polyether polyols produced by polymerization of propylene oxide on polyhydric alcohols account for the largest use of propylene oxide. The starting polyhydric alcohols have from two to eight hydroxyl groups and can be mixtures of two or more alcohols. Molecular weights of the products range from about 400 to about 8000. Some of the polyether polyols may be made with copolymerization of ethylene oxide. The ethylene oxide can either be in blocks or randomly distributed in the polymer. The products are useful for making flexible and rigid urethane foams, adhesives (qv), coatings (qv), sealants (qv), and reaction moldable products (306).

#### *10.1.2. Propylene Glycol*

Propylene glycol, the second largest use of propylene oxide, is produced by hydrolysis of the oxide with water. Propylene glycol has very low toxicity and is, therefore, used directly in foods, pharmaceuticals (qv), and cosmetics, and indirectly in packaging materials (qv). Propylene glycol also finds use as an intermediate for numerous chemicals, in hydraulic fluids (qv), in heat transfer fluids (antifreeze), and in many other applications (307).

Dipropylene glycol is produced in the manufacture of propylene glycol and finds utility as an indirect food additive, in brake-fluid formulations, cutting oils, soaps, and solvents. Tripropylene glycol also finds use as a solvent, as textile soaps, and as lubricants (307).

#### *10.1.3. Poly(propylene glycol)*

Polymers of propylene oxide based on reaction with water or propylene glycol are liquids of 400 to about 4000 molecular weight. Viscosity increases and water solubility decreases with increasing molecular weight. Poly(propylene glycol)s find use in cosmetics, as synthetic lubricants, as metalworking fluids, antifoam agents, heat transfer fluids, nonionic surfactants, and chemical intermediates (308, 309).

#### *10.1.4. Glycol Ethers*

Glycol ethers are produced by reaction of propylene oxide with various alcohols such as methanol, ethanol, butanol, and phenol. The products are the mono-, di-, and tripropylene glycol ethers. These products are used in protective coatings, inks, textile dyeing, cleaners, antiicing additives for jet fuel, and as chemical intermediates (310).

#### *10.1.5. Isopropanolamines*

Reaction of propylene oxide with ammonia yields mono-, di-, and triisopropanolamines. These products find use as soluble oils and solvents, emulsifiers, waterless hand cleaners, cosmetics, cleaners, and detergents. In industrial applications isopropanolamines are used in adhesives, agricultural products, corrosion inhibitors, coatings, epoxy resins, metalworking, and others (69).

## BIBLIOGRAPHY

"Propylene Oxide" under "Ethylene Oxide," in *ECT* 1st ed., Vol. 5, pp. 922–923, by R. S. Aries, Consulting Chemical Engineer, and H. Schneider, R. S. Aries & Associates; "Propylene Oxide" in *ECT* 2nd ed., Vol. 16, pp. 595–609, by L. H. Horsley, The Dow Chemical Co.; in *ECT* 3rd ed., Vol. 19, pp. 246–274, by R. O. Kirk and T. J. Dempsey, The Dow Chemical Co.; "Propylene Oxide" in *ECT* 4th ed., Vol. 20, pp. 271–302, by D. L. Trent, The Dow Chemical Company; "Propylene Oxide" in *ECT* (online), posting date: December 4, 2000, by D. L. Trent, The Dow Chemical Company.

### Cited Publications

1. J. H. Saunders and K. C. Frisch, *Polyurethanes Chemistry and Technology*, Part I: *Chemistry*, Robert E. Krieger Publishing Co., Malabar, Fla., 1962, 32–35.
2. *Safe Handling and Storage of DOW Propylene Oxide, Product Bulletin*, Form 109-609-788 SMG, The Dow Chemical Co., Midland, Mich., 1988.
3. *Propylene Oxide, Product Safety Bulletin*, ARCO Chemical Co., Newton Square, Pa., Mar. 24, 1992.
4. C. L. Yaws and M. P. Rackley, *Chem. Eng.* **83**(8), 129–137 (1976).
5. C. L. Yaws, D. Chen, H. C. Yang, L. Tan, and D. Nico, *Hydrocarbon Process.* **68**(7), 61–64 (1989).

6. M. T. Rogers, *J. Am. Chem. Soc.* **69**, 2544–2548 (1947).
7. G. O. Curme, Jr. and F. Johnston, *Glycols*, ACS Monograph No. 114, Reinhold Publishing Corp., New York, 1952, Chapt. 11.
8. *Propylene Oxide, Product Bulletin*, Texaco Chemical Co., Austin, Tex., 1986.
9. G. C. Sinke and D. L. Hildenbrand, *J. Chem. Eng. Data* **1**(1), 74 (1962).
10. E. S. Domalski and E. D. Hearing, *J. Phys. Chem. Ref. Data* **19**(4), 881 (1990).
11. C. L. Yaws and P. Y. Chiang, *Chem. Eng.* **95**(13), 81–88 (1988).
12. C. L. Yaws, H. M. Ni, and P. Y. Chiang, *Chem. Eng.* **95**(7), 91–98 (1988).
13. C. L. Yaws and X. Pan, *Chem. Eng.* **99**(4), 130–135 (1992).
14. L. C. Wilson, W. V. Wilding, and G. M. Wilson, in T. T. Shih and D. K. Jones, eds., *AIChE Symposium Series*, Number 271, Vol. **85**, 25–41, New York, 1989.
15. J. Gmehling and U. Onken, *Vapor–Liquid Equilibrium Data Collection, Aqueous Organic Systems*, DECHEMA, Frankfurt, Germany, 1977.
16. S. A. Newman, ed., *Chemical Engineering Thermodynamics*, Ann Arbor Science, The Butterworth Group, Ann Arbor, Mich., 1983, Chapt. 8.
17. V. M. Muhlenbruch and G. Figurski, *Z. Phys. Chemie* **270**(2), 305–314 (1989).
18. G. Figurski and S. Malanowski, *Int. DATA Ser., Sel. Data Mixtures, Ser. A.*, **24**(3), 237 (1996).
19. L. C. Wilson, W. V. Wilding, and G. M. Wilson, in T. T. Shih and D. K. Jones, ed., *AIChE Symposium Series, Number 271, Vol. 85*, pp. 51–72.
20. C. Yokoyama, G. Chen, H.-M. Lin, L.-S. Lee, and K.-C. Chao, in T. T. Shih and D. K. Jones, ed., *AIChE Symposium Series, Number 271, Vol. 85*, pp. 79–83.
21. G. Figurski and S. Malanowski, *Int. DATA Ser., Sel. Data Mixtures, Ser. A.*, **24**(3), 227 (1996).
22. J. Gmehling, U. Onken, and W. Arlt, *Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Supplement 1)*, DECHEMA, Frankfurt, Germany, 1982.
23. J. Gmehling, U. Onken, and U. Weidlich, *Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols (Supplement 2)*, DECHEMA, Frankfurt, Germany, 1982.
24. N. F. Giles and L. C. Wilson, G. M. Wilson, and W. V. Wilding *J. Chem. Eng. Data* **42**(6), 1067–1074 (1997).
25. J. Gmehling, U. Onken, and J. R. Rarey, *Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols, (Supplement 4)*, Frankfurt, 1990.
26. J. Gmehling, U. Onken, and W. Arlt, *Vapor–Liquid Equilibrium Data Collection, Organic Hydroxy Compounds: Alcohols and Phenols*, DECHEMA, Frankfurt, Germany, 1978.
27. B. Srinivasa, M. G. Parande and R. V. Naik, *J. Chem. Eng. Data*, **40**(4), 927-30 (1995).
28. R. E. Parker and N. S. Isaacs, *Chem. Rev.* **59**, 737–799 (1959).
29. Eur. Pat. 611,826 (Aug. 24, 1994), A. Matsuyama and Y. Kobayashi (to Daicel Chemical Industries Co., Ltd.).
30. G. Woods, *The ICI Polyurethanes Book, Second Edition*, ICI Polyurethanes and John Wiley & Sons, Inc., New York, 1990, p. 36.
31. H. Takeuchi, K. Kitajima, Y. Yamamoto, and K. Mizuno, *J. Chem. Soc. Perkin Trans. 2*, 199–203 (1993).
32. J. H. Saunders and K. C. Frisch, *Polyurethanes Chemistry and Technology, Part I, Chemistry*, Robert E. Krieger Publishing Co., Malabar, FL, 1962, p. 32–35.
33. U.S. Pat. 3,370,056 (Feb. 20, 1968), M. Yotsuzuka, K. Kodama, and K. Ogino (to Takeda Chemical Industries, Ltd.).
34. U.S. Pat. 3,433,751 (Mar. 18, 1969), M. Yotsuzuka, A. Keshi, N. Hashimoto, K. Kodama, and S. Nakahara (to Taketa Chemical Industries, Ltd.).
35. U.S. Pat. 3,865,806 (Feb. 11, 1975), L. R. Knodel (to The Dow Chemical Co.).
36. L. A. Dickinson, *J. Polym. Sci.* **58**, 857–868 (1962).
37. L. P. Blanchard, J. Singh, and M. D. Baijal, *Can. J. Chem.* **44**, 2679–2689 (1966).
38. S. Inoue, K. Kitamura, and T. Tsuruta, *Die Makromol. Chem.* **126**, 250–265 (1969).
39. K. Soga, K. Hyakkoku, and S. Ikeda, *J. Polym. Sci. Poly. Chem. Ed.* **17**, 2173–2180 (1979).
40. U.S. Pat. 4,166,172 (Aug. 28, 1979), H. P. Klein (to Texas Development Corp.).
41. S. Inoue, T. Aida, Y. Watanabe, and K. Kawaguchi, *Makromol. Chem., Macromol. Symp.* **42/43**, 365–371 (1991).
42. M. Kuroki, T. Aida, and S. Inoue, *Makromol. Chem.* **189**(6), 1305–1313 (1988).
43. Y. Watanabe, T. Aida, and S. Inoue, *Macromolecules* **23**(10), 2612–2617 (1990).
44. H. Haubenstock, V. Panchalingam, and G. Odian, *Makromol. Chem.* **188**(12), 2789–2799 (1987).

45. Z. Öktem, and K. Alyürük, *Polymer* **39**(3), 583–590 (1998).
46. S. Aksoy, H. Altinok, H. Tumturk, and K. Alyuruk, *Polymer* **31**(6), 1142–1148 (1990).
47. G. Gee, W. C. E. Higginson, and J. B. Jackson, *Polymer* **3**, 231–242 (1962).
48. U.S. Pat. 3,338,873 (Aug. 29, 1967), A. E. Gurgiolo (to The Dow Chemical Co.).
49. M. Nakaniwa, K. Ozaki, and J. Furukawa, *Die Makromol. Chem.* **138**, 197–208 (1970).
50. F. M. Rabagliati and F. Lopez-Carrasquero, *Polymer Bull.* **14**(3–4), 331–337 (1985).
51. U.S. Pat. 3,468,817 (Sept. 23, 1969), H. L. Hsieh (to Phillips Petroleum Co.).
52. Z. Shen, J. Wu, and G. Wang, *J. Polym. Sci.: Part A: Polym. Chem.* **28**(7), 1965–1971 (1990).
53. *A Guide To Glycols*, Form No. 117-00991-89, Dow Chemical U.S.A., Midland, Mich., 1981.
54. U.S. Pat. 4,160,116 (July 3, 1979), M. Mieno, H. Mori, J. Naknaishi, and J. Kasai (to Showa Denko KK).
55. U.S. Pat. 5,260,495 (Nov. 9, 1993), M. W. Forkner (to Union Carbide Chemicals & Plastics Technology Corp.).
56. J. D. Malkemus, *J. Am. Oil Chem. Soc.* **33**, 571–574 (1956).
57. J. Chlebicki, *Roczniki Chemii* **48**, 1241 (1974).
58. A. Rosowsky, in A. Weissberger, ed., *Heterocyclic Compounds with Three- and Four-Membered Rings*, Part One, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1964, pp. 289, 308.
59. F. Scholnick, H. A. Monroe, Jr., E. J. Saffese, and A. N. Wrigley, *J. Am. Oil Chem. Soc.* **44**, 40–42 (1967).
60. U.S. Pat. 3,890,300 (June 17, 1975), M. Huchette and G. Fleche (to Roquette Freres).
61. G. Lammers, E. J. Stamhuis, and A. A. C. M. Beenackers, *Ind. Eng. Chem. Res.* **32**(5), 835–842 (1993).
62. T. Viswanathan, A. Toland, R. Liu, and N. R. Jagannathan, *J. Polym. Sci.: Part C: Polym. Lett.* **28**(3), 95–100 (1990).
63. J. S. Ayers, M. J. Petersen, B. E. Sheerin, and G. S. Bethell, *J. Chromatography* **294**, 195–205 (1984).
64. A. N. Wrigley, F. D. Smith, and A. J. Stirton, *J. Am. Oil Chem. Soc.* **36**, 34–36 (1959).
65. M. A. Rousselle, M. L. Nelson, H. H. Ramey, Jr., and G. L. Barker, *Ind. Eng. Chem. Prod. Res. Dev.* **19**, 654–659 (1980).
66. U.S. Pat. 4,609,729 (Sept. 2, 1986), J. L. Garner (to The Dow Chemical Co.).
67. U.S. Pat. 4,661,589 (Apr. 28, 1987), G. L. Adams and C. D. Messelt (to The Dow Chemical Co.).
68. K. Slipko and J. Chlebicki, *Pol. J. Chem.* **53**, 2331–2337 (1979).
69. *The Alkanolamines Handbook*, Form No. 111-1159-88R-SAI, The Dow Chemical Co., Midland, Mich., 1988.
70. W. J. Peppel, *Ind. Eng. Chem.* **50**(5), 767–770 (1958).
71. Jpn. Pat. 09235252 (Sep. 9, 1987), S. Ichikawa, H. Iwane, and (to Mitsubishi Chemical Industries Ltd.).
72. W. Kuran and T. Listos, *Makromol. Chem.* **193**(4), 945–956 (1992).
73. U.S. Pat. 3,542,808 (Nov. 24, 1970), R. C. Vander Linden, J. M. Salva, and P. A. C. Smith (to Esso Research and Engineering Co.).
74. N. Adachi, Y. Kida, and K. Shikata, *J. Polym. Sci. Poly. Chem. Ed.* **15**, 937–944 (1977).
75. J. A. Durden, Jr., H. A. Stansbury, Jr., and W. H. Catlette, *J. Am. Oil Chem. Soc.* **82**, 3082–3084 (1960).
76. U.S. Pat. 5,283,368 (Feb. 1, 1994), J. E. Shaw (to Phillips Petroleum Co.).
77. Ref. 58, p. 328.
78. Ref. 58, p. 331.
79. Ref. 58, p. 337.
80. U.S. Pat. 5,218,147 (June 8, 1993), J. E. Shaw (to Phillips Petroleum Co.).
81. M. Prochazka and P. Durdovic, *Coll. Czech. Chem. Comm.* **42**, 2401–2407 (1977).
82. Ref. 58, p. 433.
83. M. Inoue, K. Chano, O. Itoh, T. Sugita, and K. Ichikawa, *Bull. Chem. Soc. Japan* **53**(2), 458–463 (1980).
84. Ref. 58, pp. 399–400.
85. N. G. Gaylord and E. I. Becker, *Chem. Rev.* **49**, 413–533 (1951).
86. S. Winstein and R. B. Henderson, in R. C. Elderfield, ed., *Heterocyclic Compounds*, Vol. **1**, John Wiley & Sons, Inc., New York, 1950, p. 57.
87. M. J. Astle, *The Chemistry of Petrochemicals*, Reinhold Publishing Corp., New York, 1956, 184–185.
88. T. Imanaka, Y. Okamoto, and S. Teranishi, *Bull. Chem. Soc. Japan*, **45**, 3251–3254 (1972).
89. U.S. Pat. 5,262,371 (Nov. 16, 1993), M. K. Faraj (to ARCO Chemical Technology, L.P.).
90. D. Ostgard, F. Notheisz, A. G. Zsigmond, G. V. Smith, and M. Bartok, *J. Catal.* **129**(2), 519–523 (1991).
91. I. Palinko, F. Notheisz, and M. Bartok, *J. Mol. Catal.* **63**(1), 43–54 (1990).
92. M. Bartok, F. Notheisz, A. G. Zsigmond, and G. V. Smith, *J. Catal.* **100**(1), 39–44 (1986).
93. M. Bartok, F. Notheisz, and A. G. Zsigmond, *J. Catal.* **63**(2), 364–371 (1980).

94. F. Notheisz, A. Molnar, A. G. Zsigmond, and M. Bartok, *J. Catal.* **98**(1), 131–137 (1986).
95. A. Dinger, C. Lutterloh, J. Biener and J. Küppers, *Surf. Sci.*, **421**(1–2), 44–52 (1999).
96. M. Berry, S. G. Davies, and M. L. H. Green, *J. Chem. Soc. Chem. Comm.*, 99 (1978).
97. J. L. E. Erickson and F. E. Collins, Jr., *J. Org. Chem.* **30**, 1050–1052 (1965).
98. U.S. Pat. 3,725,438 (Apr. 3, 1973), B. J. Barone and W. F. Brill (to PetroTex Chemical Corp.).
99. J. F. W. McOmie, *Protective Groups in Organic Chemistry*, Plenum Press, New York, 1973, p. 326.
100. M. Fujiwara, M. Imada, A. Baba, and H. Matauda, *J. Org. Chem.* **53**(25), 5974–5977 (1988).
101. Ref. 58, 350–351.
102. N. I. Shuikin and I. F. Bel'skii, *J. Gen. Chem. USSR* **29**, 2936–2938 (1959).
103. G. S. Yoneda, M. T. Griffin, and D. W. Carlyle, *J. Org. Chem.* **40**(3), 375–377 (1975).
104. Ref. 58, p. 346.
105. Ref. 58, p. 365.
106. Ref. 58, p. 384.
107. H. Steinberg and R. J. Brotherton, *Organoboron Chemistry*, John Wiley & Sons, Inc., New York, 1966, pp. 82, 520, and 549.
108. Ref. 107, p. 487.
109. J. D. Edwards, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 348 (1957).
110. F. G. A. Stone and H. J. Emeleus, *J. Chem. Soc.*, 2755–2759 (1950).
111. I. Shibata, A. Baba, H. Iwasaki, and H. Matsuda, *J. Org. Chem.* **51**, 2177–2184 (1986).
112. N. Watanabe, S. Uemura, and M. Okano, *Bull. Chem. Soc. Japan* **52**(12), 3611–3614 (1979).
113. W. Kuran, S. Pasynkiewicz, and J. Serzyko, *J. Organomet. Chem.* **73**, 187–192 (1974).
114. A. J. Lundeen and A. C. Oehlschlager, *J. Organomet. Chem.* **25**, 337–344 (1970).
115. Ref. 58, 340–342, 421, 428, 430, and 432.
116. Ref. 58, pp. 440, 442–443, 451, and 456.
117. A. C. Fyvie, *Chem. Ind. London* (10), 384–388 (1964).
118. R. B. Stobaugh, V. A. Calarco, R. A. Morris, and L. W. Stroud, *Hydrocarbon Process.* **52**(1), 99–108 (1973).
119. A. J. Gait, in E. G. Hancock, ed., *Propylene and Its Industrial Derivatives*, Halsted Press, a division of John Wiley & Sons, Inc., New York, 1973, 273–297.
120. H. J. Warnecke, M. Schäfer, J. Prüss, and M. Weidenbach, *Chem. Eng. Sci.*, **54**(13–14), 2513–2519 (1999).
121. U.S. Pat. 5,146,011 (Sept. 8, 1992), M. Shen and J. A. Wojtowicz (to Olin Corp.).
122. U.S. Pat. 5,486,627 (Jan. 23, 1996), G. J. Quarderer Jr C. N. Swisher D. L. Trent (to The Dow Chemical Co.).
123. U.S. Pat. 5,532,389 (July 2, 1996), D. L. Trent and co-workers (to The Dow Chemical Co.).
124. U.S. Pat. 4,008,133 (Feb. 15, 1977), A.P. Gelbein and J. T. Kwon (to The Lummus Co.).
125. *Hydrocarbon Process* **58**(11), 239 (1979).
126. U.S. Pat. 4,496,777 (Jan. 29, 1985), G. D. Suciu J. T. Kwon A. M. Shaban (to The Lummus Co.).
127. E. Milchert, W. Goc, E. Meissner, and J. Myszkowski, *J. Chem. Technol. Biotechnol.*, **61**(3), 251–254 (1994).
128. S. Carra, E. Santacesaria, M. Morbidelli, and L. Cavalli, *Chem. Eng. Sci.* **34**(9), 1123–1132 (1979).
129. S. Carra, E. Santacesaria, M. Morbidelli, and G. Buzzi, *Chem. Eng. Sci.* **34**(9), 1133–1140 (1979).
130. I. Mochida, T. Miyazaki, and H. Fujitsu, *Applied Catalysis* **32**, 37–44 (1987).
131. U.S. Pat. 4,243,492 (Jan. 6, 1981), T. Yamamura Y. Osawa I. Ouchi N. Oda M. Yamazaki and Y. Nishiyama (to Showa Denko K. K.).
132. World Pat. Appl. WO 97/03035 (Jan. 30, 1997), M.T. Holbrook, et al. (to The Dow Chemical Co.).
133. K. H. Simmrock, *Hydrocarbon Process.* **57**(11), 105–113 (1978).
134. M. A. Zeitoun and W. F. McIlhenny, *Treatment of Wastewater from the Production of Polyhydric Organics*, EPA Project, 12020-EEQ, 1971, 1–24.
135. L. M. V. Raja, G. Elamvaluthy, R. Palaniappan, and R. M. Krishnan, *Appl. Biochem. Biotechnol.* **28–29**, 827–841 (1991).
136. G.B. Pat. 2320020 (Jun. 10,1998), F. Schwerdtner (to Dow Deutschland Inc.).
137. Ger. Pat. 19614683 (Oct. 16, 1997), D. Schnurpfeil and R. Wagner (to Buna Sow Leuna Olefinverbund Gmbh).
138. U.S. Pat. 4,128,587 (Dec. 5, 1978), J. C. Jubin (to Atlantic Richfield Co.).
139. J. Sobczak and J. J. Ziolkowski, *J. Molecular Catal.* **13**, 11–42 (1981).
140. U.S. Pat. 5,107,067 (Apr. 21, 1992), E. T. Marquis, K. P. Keating, J. R. Sanderson, and W. A. Smith (to Texaco, Inc.).

141. U.S. Pat. 4,703,027 (Oct. 27, 1987), E. T. Marquis, J. R. Sanderson, and K. P. Keating (to Texaco Chemical Co.).
142. Eur. Pat. 0188912 (July 30, 1986), E. T. Marquis and co-workers (to Texaco Development Corp.).
143. U.S. Pat. 5,274,138 (Dec. 28, 1993), K. P. Keating, E. T. Marquis, and M. A. Mueller (to Texaco Chemical Co.).
144. U.S. Pat. 4,977,285 (Dec. 11, 1990), E. T. Marquis, K. P. Keating, R. A. Meyer, and J. R. Sanderson (to Texaco Chemical Co.).
145. U.S. Pat. 4,992,566 (Feb. 12, 1991), E. T. Marquis, K. P. Keating, J. R. Sanderson, and R. A. Meyer (to Texaco Chemical Co.).
146. U.S. Pat. 4,455,283 (June 19, 1984), N. H. Sweed (to Atlantic Richfield Co.).
147. U.S. Pat. 4,485,074 (Nov. 27, 1984), R. B. Poenisch (to Atlantic Richfield Co.).
148. U.S. Pat. 5,101,052 (Mar. 31, 1992), R. A. Meyer and E. T. Marquis (to Texaco Chemical Co.).
149. U.S. Pat. 5,128,492 (July 7, 1992), W. A. Smith, R. A. Meyer, and E. T. Marquis (to Texaco Chemical Co.).
150. U.S. Pat. 4,939,281 (July 3, 1990), E. T. Marquis, J. R. Sanderson, and K. P. Keating (to Texaco Chemical Co.).
151. U.S. Pat. 4,315,896 (Feb. 16, 1982), P. D. Taylor and M. T. Mocella (to Atlantic Richfield Co.).
152. U.S. Pat. 5,093,509 (Mar. 3, 1992), R. A. Meyer and E. T. Marquis (to Texaco Chemical Co.).
153. U.S. Pat. 4,598,057 (July 1, 1986), B. H. Isaacs (to Atlantic Richfield Co.).
154. U.S. Pat. 4,691,034 (Sept. 1, 1987), J. R. Sanderson, W. A. Smith, E. T. Marquis, and K. P. Keating (to Texaco, Inc.).
155. U.S. Pat. 4,691,035 (Sept. 1, 1987), J. R. Sanderson, E. T. Marquis, W. A. Smith, and K. P. Keating (to Texaco, Inc.).
156. U.S. Pat. 5,106,458 (Apr. 21, 1992), R. A. Meyer, E. T. Nguyen, and A. Smith (to Texaco Chemical Co.).
157. U.S. Pat. 5,262,017 (Nov. 16, 1993), R. A. Meyer, W. A. Smith, M. A. Mueller, and G. B. Demoll (to Texaco Chemical Co.).
158. U.S. Pat. 5,133,839 (July 28, 1992), T. T. Shih (to ARCO Chemical Technology, L.P.).
159. U.S. Pat. 5,286,884 (Feb. 15, 1994), R. S. Cowley and D. D. Kinzler (to Texaco Chemical Co.).
160. M. B. Ward, K. Mizuno, and J. H. Lunsford, *J. Molecular Catal.* **27**, 1–10 (1984).
161. H. Mimoun, *J. Molecular Catalysis* **7**, 1–29 (1980).
162. R. A. Sheldon, *J. Molecular Catalysis* **7**, 107–126 (1980).
163. U.S. Pat. 5,116,467 (May 26, 1992), E. T. Marquis, G. P. Speranza, Y. E. Sheu, W. K. Culbreth III, and D. G. Pattratz (to Texaco Chemical Co.).
164. U.S. Pat. 5,116,465 (May 26, 1992), E. L. Yeakey and E. T. Marquis (to Texaco Chemical Co.).
165. U.S. Pat. 5,116,466 (May 26, 1992), E. T. Marquis, G. P. Speranza, Y. E. Sheu, W. K. Culbreth III, and D. G. Pattratz (to Texaco Chemical Co.).
166. U.S. Pat. 5,139,622 (Aug. 18, 1992), E. T. Marquis, G. P. Speranza, Y. E. Sheu, W. K. Culbreth III, and D. G. Pattratz (to Texaco Chemical Co.).
167. U.S. Pat. 5,160,587 (Nov. 3, 1992), E. T. Marquis, G. P. Speranza, Y. E. Sheu, W. K. Culbreth III, and D. G. Pattratz (to Texaco Chemical Co.).
168. U.S. Pat. 5,620,658 (Apr. 15, 1997), W. A. Smith, M. A. Mueller, (to Texaco Chemical Inc.).
169. U.S. Pat. 4,971,661 (Nov. 20, 1990), R. A. Meyer, K. P. Keating, W. A. Smith, and R. M. Steinberg (to Texaco Chemical Co.).
170. U.S. Pat. 4,140,588 (Feb. 20, 1979), J. P. Schmidt (to Halcon Research and Development Corp.).
171. U.S. Pat. 5,006,206 (Apr. 9, 1991), T. T. Shih and W. J. Sim (to ARCO Chemical Technology, Inc.).
172. U.S. Pat. 5,127,997 (July 7, 1992), W. A. Smith, R. A. Meyer, and E. T. Nguyen (to Texaco Chemical Co.).
173. U.S. Pat. 3,351,635 (Nov. 7, 1967), J. Kollar (to Halcon International, Inc.).
174. U.S. Pat. 3,459,810 (Aug. 5, 1969), C. Y. Choo and R. L. Golden (to Halcon International, Inc.).
175. U.S. Pat. 4,066,706 (Jan. 3, 1978), J. P. Schmidt (to Halcon International, Inc.).
176. Jpn. Pat. 11152279 (Jun. 8, 1999), M. Yoshii and M. Ishino (to Sumitomo Chemical Co., Ltd.).
177. U.S. Pat. 5,883,268 (Mar. 16, 1999), S. Lin, J. B. Danner, and J. C. Jubin Jr. (to ARCO Chemical Technology, L.P.).
178. Jpn. Pat. 09157265 (Jun. 17, 1997), M. Tamura, K. Uchida, and J. Tsuji (to Sumitomo Chemical Co., Ltd.).
179. U.S. Pat. 3,849,451 (Nov. 19, 1974), T. W. Stein, H. Gilman, and R. L. Bobeck (to Halcon International, Inc.).
180. U.S. Pat. 3,642,833 (Feb. 15, 1972), H. Wulff and P. Haynes (to Shell Oil Co.).
181. U.S. Pat. 3,702,855 (Nov. 14, 1972), C. S. Bell and H. P. Wulff (to Shell Oil Co.).
182. U.S. Pat. 3,829,392 (Aug. 13, 1974), H. P. Wulff (to Shell Oil Co.).
183. Jpn. Pat. 11140068 (May 25, 1999), J. Tsuji, M. Ishino, and K. Uchida (to Sumitomo Chemical Co., Ltd.).
184. U.S. Pat. 3,860,662 (Jan. 14, 1975), J. Kollar (to Halcon International, Inc.).

185. U.S. Pat. 3,947,500 (Mar. 30, 1976), J. Kollar (to Halcon International, Inc.).
186. U.S. Pat. 5,171,868 (Dec. 15, 1992), R. S. Albal, R. N. Cochran, and T. B. Hsu (to ARCO Chemical Technology, L.P.).
187. U.S. Pat. 5,276,235 (Jan. 4, 1994), W. S. Dubner (to ARCO Chemical Technology, L.P.).
188. U.S. Pat. 5,210,354 (May 11, 1993), W. S. Dubner and R. N. Cochran (to ARCO Chemical Technology, L.P.).
189. 189. Eur. Pat. 767,171 (Apr. 9, 1997), T. I. Evans, B. Cooker, and R. S. Albal (to ARCO Chemical Technology, L.P.).
190. U.S. Pat. 3,881,996 (May 6, 1975), J. P. Schmidt (to Oxirane Corp.).
191. U.S. Pat. 3,632,482 (Jan. 4, 1972), S. E. Heary and S. F. Newmann (to Shell Oil Co.).
192. Jpn. Pat. 09169751 (Jun. 30, 1997), M. Yoshii, N. Oku, and M. Ishino (to Sumitomo Chemical Co., Ltd.).
193. U.S. Pat. 4,049,736 (Sept. 20, 1977), J. J. Lamson, R. H. Hall, E. Stroiwas, and L. D. Yats (to The Dow Chemical Co.).
194. U.S. Pat. 3,442,963 (May 6, 1969), E. I. Korchak (to Halcon International, Inc.).
195. U.S. Pat. 3,927,120 (Dec. 16, 1975), H. R. Grane and T. S. Zak (to Atlantic Richfield Co.).
196. U.S. Pat. 3,927,121 (Dec. 16, 1975), H. R. Grane and T. S. Zak (to Atlantic Richfield Co.).
197. M. G. Clerici, G. Bellussi, and U. Romano, *J. Catal.* **129**, 159–167 (1991).
198. R. L. Burwell, Jr., *Chemtracts Inorg. Chem.* **3**, 344–346 (1991); see Ref. 188.
199. G. F. Thiele and E. Roland, *J. Mol. Catal. A: Chem.*, **117**(1–3), 351–356 (1997).
200. U.S. Pat. 5,646,314 (Jul. 8, 1997), G. L. Crocco, and J. G. Zajacek (to ARCO Chemical Technology, L.P.).
201. Eur. Pat. 757,043 (Feb 5, 1997), G. Thiele (to Degussa Aktiengesellschaft).
202. U.S. Pat. 5,780,654 (Jul. 14, 1998), L. Nemeth, G. J. Lewis, and R. R. Rosin (to UOP LLC).
203. Eur. Pat. 930,308 (Jul. 21, 1999), V. Arca, P. Furlan, and R. Buzzoni (to Enichem S.p.A.).
204. U.S. Pat. 5,591,875 (Jan. 7, 1997), T. Chang, D. W. Leyshon, and G. L. Crocco.
205. W. Laufer, R. Meiers, and W. Hölderich, *J. Mol. Catal. A: Chem.*, **141**(1–3), 215–21 (1999).
206. Eur. Pat. 812,836 (Dec. 17, 1997), F. Goto, S. Shibata, T. Sasaki, and K. Tanaka (to Sumitomo Chemical Co. Ltd.).
207. Eur. Pat. 819,683 (Jan. 21, 1998), M. G. Clerici, A. De Angelis, and P. Ingallina (to Enichem S.p.A.).
208. U.S. Pat. 5,463,090 (Oct. 31, 1995), C. L. Rodriguez, and J. G. Zajacek (to ARCO Chemical Technology, L.P.).
209. U.S. Pat. 5,849,938 (Dec. 15, 1998), M. A. Rueter, and J. C. Jubin, Jr. (to ARCO Chemical Technology, L.P.).
210. P. V. Greenen, H. J. Boss, and G. T. Pott, *J. Catal.* **77**, 499–510 (1982).
211. M. Stoukides and C. G. Vayenas, *J. Catal.* **82**, 45–55 (1983).
212. World Pat. Appl. WO 97/34693 (Sep. 25, 1997), A. Kahn, A. Gaffney, and R. Pitchai (to ARCO Chemical Technology, L.P.).
213. U.S. Pat. 5,703,254 (Dec. 30, 1997), A. M. Gaffney, A. P. Kahn, and R. Pitchai (to ARCO Chemical Technology, L.P.).
214. U.S. Pat. 5,780,657 (Jul. 14, 1998), B. Cooker, A. M. Gaffney, J. D. Jewson, and W. H. Onimus (to ARCO Chemical Technology, L.P.).
215. U.S. Pat. 4,859,786 (Aug. 22, 1989), G. E. Vrieland (to The Dow Chemical Co.).
216. U.S. Pat. 4,994,587 (Feb. 19, 1991), T. M. Notermann and E. M. Thorsteinson (to Union Carbide Chemicals and Plastics Co., Inc.).
217. U.S. Pat. 5,698,719 (Dec. 16, 1997), A. M. Gaffney, A. Jones, R. Pitchai, and A. P. Kahn (to ARCO Chemical Technology, L.P.).
218. U.S. Pat. 5,770,746 (Jun. 23, 1998), B. Cooker, A. M. Gaffney, J. D. Jewson, A. P. Kahn, and R. Pitchai (to ARCO Chemical Technology, L.P.).
219. Ger. Pat. 19529679 (Feb. 13, 1997), W. Mueller-Markgraf (to Linde Ag).
220. J. T. Ranney, S. R. Bare, and J. L. Gland, *Catal. Lett.*, **48**(1,2), 25–29 (1997).
221. J. T. Ranney, J. L. Gland and S. R. Bare, *Surf. Sci.*, **401**(1), 1–11 (1998).
222. B. S. Uphade, S. Tsubota, T. Hayashi, and M. Haruta, *Chem. Lett.* (**12**), 1277–1278 (1998).
223. Y. A. Kalvachev, T. Hayashi, S. Tsubota, and M. Haruta, *Stud. Surf. Sci. Catal.*, **110**, 965–972 (1997).
224. T. A. Nijhuis, B. J. Huizinga, M. Makkee, and J. A. Moulijn, *Ind. Eng. Chem. Res.*, **38**(3), 884–891 (1999).
225. U.S. Pat. 5,965,754 (Oct. 12, 1999), H. W. Clark, and co-workers (to The Dow Chemical Co.).
226. World Pat. Appl. WO 98/00414 (Jan. 8, 1998), R. G. Bowman, and co-workers (to Dow Chemical Co.).
227. R. Meiers, U. Dingerdissen, and W. F. Hölderich, *J. Catal.*, **176**(2), 376–386 (1998).
228. 228. Jpn. Pat. 08269030 (Oct. 15, 1996), A. Sato, M. Oguri, S. Tokumaru, and T. Myake (to Tosoh Corp.).
229. U.S. Pat. 4,883,889 (Nov. 28, 1989), B. T. Pennington (to Olin Corp.).
230. U.S. Pat. 4,943,643 (July 24, 1990), B. T. Pennington and M. C. Fullington (to Olin Corp.).
231. U.S. Pat. 4,885,374 (Dec. 5, 1989). B. T. Pennington (to Olin Corp.).

232. Jpn. Pat. 10316669 (Dec. 2, 1998), K. Sugita (to Sumitomo Chemical Co., Ltd.).
233. Jpn. Pat. 10314594 (Dec. 2, 1998), K. Sugita, and Y. Oda (to Sumitomo Chemical Co., Ltd.).
234. C. Daniel and G. W. Keulks, *J. Catal.* **24**, 529–535 (1972).
235. U.S. Pat. 4,046,783 (Sept. 6, 1977), S. B. Cavitt (to Texaco Development Corp.).
236. C. Daniel, J. R. Monnier, and G. W. Keulks, *J. Catal.* **31**, 360–368 (1973).
237. U.S. Pat. 3,316,279 (Apr. 25, 1967), D. M. Fenton (to Union Oil Co.).
238. U.S. Pat. 4,391,756 (July 5, 1983), P. L. Kuch, D. R. Herrington, and J. M. Eggett (to The Standard Oil Co.).
239. I. Yamanaka, K. Nakagaki, and K. Otsuka, *Appl. Catal., A*, **171**(2), 309–314 (1998).
240. I. Yamanaka, K. Nakagaki, and K. Otsuka, *J. Chem. Soc., Chem. Commun.*, (**11**), 1185–1186 (1995).
241. U.S. Pat. 5,892,066 (Apr. 6, 1999), R. A. Grey (to ARCO Chemical Technology, L.P.).
242. U.S. Pat. 5,241,088 (Aug. 31, 1993), J. L. Meyer, B. T. Pennington, and M. C. Fullington (to Olin Corp.).
243. U.S. Pat. 5,117,011 (May 26, 1992), B. T. Pennington and M. C. Fullington (to Olin Corp.).
244. U.S. Pat. 4,481,092 (Nov. 6, 1984), K. T. Mansfield (to Ciba-Geigy Corp.).
245. T. Bejerano, S. Germain, F. Goodridge, and A. R. Wright, *Trans. Inst. Chem. Eng.* **58**(1), 28–32 (1980).
246. A. Manji and C. W. Oloman, *J. Appl. Electrochem.* **17**, 532–544 (1987).
247. F. Goodridge, S. Harrison, and R. E. Plimley, *J. Electroanal. Chem.* **214**, 283–293 (1986).
248. K. Scott, C. Odouza, and W. Hui, *Chem. Eng. Sci.* **47**(9–11), 2957–2962 (1992).
249. K. Otsuka, T. Ushiyama, I. Yamanaka, and K. Ebitani, *J. Catal.* **157**(2), 450–60 (1995).
250. K. Otsuka, *Stud. Surf. Sci. Catal.* **110**, 93–102 (1997).
251. Eur. Pat. 712,851 (May 22, 1996), B. Cooker, and R. N. Cochran (to ARCO Chemical Technology, L.P.).
252. I. Yamanaka, K. Sato, and K. Otsuka, *Electrochem. Solid-State Lett.* **2**(3), 131–2 (1999).
253. B. K. Soni, R. L. Kelley, and V. J. Srivastava, *Appl. Biochem. Biotechnol.* **74**(2), 115–123 (1998).
254. U.S. Pat. 4,177,196 (Dec. 4, 1979), A. M. Hildon and P. F. Greenhalgh (to Interox Chemicals Limited).
255. *Hydrocarbon Process.* **64**(11), 166 (1985).
256. K. Yamagishi, O. Kageyama, H. Haruki, and Y. Numa, *Hydrocarbon Process.* **55**(11), 102–104 (1976).
257. B. K. Soni, R. L. Kelley, and V. J. Srivastava, *Appl. Biochem. Biotechnol.* **74**(2), 115–123 (1998).
258. *Chem. Eng. News* **72**(15), pp. 12–15 (1994).
259. *U.S. Code of Federal Regulations*, Title 29, Paragraph 1910.106, U.S. Government Printing Office, Washington, D.C.,
260. J. Marshall, A. Mundt, M. Hult, T. McKealvy, P. Meyers, and J. Sawyer, *Process Saf. Prog.* **14**(3), 200–211 (1995).
261. *U.S. Code of Federal Regulations*, Title 49, Parts 172, 174, 176, and 178–180, U.S. Government Printing Office, Washington, D.C., 1994.
262. J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, in J. Mitchell, Jr. et al., eds., *Organic Analysis*, Vol. **I**, Interscience Publishers, Inc., New York, 1953, pp. 127–154.
263. O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *Anal. Chem.* **23**(2), 277–282 (1951).
264. J. R. Villarreal and J. Laane, *J. Chem. Phys.* **62**(1), 303–304 (1975).
265. S. Suzuki, Y. Hori, R. C. Das, and O. Koga, *Bull. Chem. Soc. Jpn.* **53**, 1451–1452 (1980).
266. S. C. Agarwal, B. L. Van Duuren, and T. J. Kneip, *Bull. Environm. Contam. Toxicol.* **23**, 825–829 (1979).
267. H. E. Mishmash and C. E. Meloan, *Anal. Chem.* **44**(4), 835–836 (1972).
268. J. W. Russell, *Env. Sci. Tech.* **9**(13), 1175–1178 (1975).
269. T. J. Kelly, P. J. Callahan, J. Plell, and G. F. Evans, *Environ. Sci. Technol.* **27**(6), 1146–1153 (1993).
270. U.S. Pat. 5,187,287 (Feb. 16, 1993), T. T. Shih (to ARCO Chemical Technology, L.P.).
271. U.S. Pat. 4,692,535 (Sept. 8, 1987), H. V. Larson and H. D. Gillman (to Atlantic Richfield Co.).
272. U.S. Pat. 5,235,075 (Aug. 10, 1993), G. W. Bachman and R. K. Brown (to The Dow Chemical Co.).
273. U.S. Pat. 5,248,794 (Sept. 28, 1993), M. L. Chappell and C. T. Costain (to The Dow Chemical Co.).
274. U.S. Pat. 5,352,807 (Oct. 4, 1994), T. T. Shih (to ARCO Chemical Technology, L.P.).
275. Jpn. Pat. 08283253 (Oct. 29, 1996), S. Yamazaki, S. Tamura, Y. Hara, and T. Izukawa (to Mitsui Toatsu Chemicals).
276. G. H. Flores, *Chem. Eng. Prog.* **79**(3), 39–43 (1983).
277. *U.S. Code of Federal Regulations*, Title 29, paragraphs 1910.134 and 1910.1000, U.S. Government Printing Office, Washington, D.C.
278. D. Grosjean, *J. Air Waste Manage. Assoc.* **40**, 1522–1531 (1990).
279. W. Meylan, L. Papa, C. T. De Rosa, and J. F. Stara, *Toxicol. Ind. Health* **2**(3), 219–260 (1986).

280. *U.S. Code of Federal Regulations*, Title 40, Parts 302, 304, 370, and 403, U.S. Government Printing Office, Washington, D.C.
281. L. Bretherick, *Bretherick's Handbook of Reactive Chemical Hazards*, Fourth Edition, Butterworth & Co., Boston, Mass., 1990, 379–380.
282. G. A. Pogany, *Chem. Ind.* 16–21 (1979).
283. J. Bootman, D. C. Lodge, and H. E. Whalley, *Mutat. Res.* **67**, 101–112 (1979).
284. A. K. Giri, *Mutat. Res.* **277**, 1–9 (1992).
285. R. Nilsson, B. Molholt, and E. V. Sargent, *Regulatory Toxicology Pharmacology* **14**, 229–244 (1991).
286. A. Ohnishi and Y. Murai, *Environ. Res.* **60**, 242–247 (1993).
287. C. Hine, V. K. Rowe, E. R. White, K. I. Darmer, Jr., and G. T. Youngblood, in G. D. Clayton and F. E. Clayton, ed., *Patty's Industrial Hygiene and Toxicology*, Third Revised Edition, Vol. **2A**, *Toxicology*, A Wiley-Interscience, John Wiley & Sons, Inc., New York, 1978, pp. 2148, 2157, and 2186–2191.
288. A. Ohnishi T. Yamamoto, Y. Murai, Y. Hayashida, H. Hori, and I. Tanaka *Arch. Environ. Health* **43**(5), 353–356 (1988).
289. Jpn. Pat. 01200903 (Aug. 14, 1989), S. Ando, T. Teraika, and T. Nishizumi (to Sanyo-Kokusaku Pulp Co.).
290. R. K. Jain and W. G. Glasser, *Holzforschung* **47**(4), 325–332 (1993).
291. Jpn. Pat. 61254594 (Nov. 12, 1986), M. Takamizawa, T. Ishihara, and M. Endo (to Shin-Etsu Chemical Industry Co., Ltd.).
292. Eur. Pat. 185612 (June 25, 1986), B. Mebes (to Sanitized Verwertungs A.-G.).
293. H. Sato, T. Kidaka, and M. Hori, *Int. J. Artif. Organs* **8**(2), 109–114 (1985).
294. U.S. Pat. 3,919,189 (Nov. 11, 1975), R. A. Empey and D. J. Pettitt (to Kelco Co.).
295. Jpn. Pat. 05301832 (Nov. 16, 1993), M. Fukushima, K. Ooishi, and Y. Ootoshi (to Asahi Glass Co.).
296. Jpn. Pat. 04173749 (June 22, 1992), M. Fukushima, U. Tazawa, K. Ooishi (to Asahi Glass Co.).
297. U.S. Pat. 4,108,910 (Aug. 22, 1978), M. Godfrold and R. Gerkens (to Solvay & Cie.).
298. U.S. Pat. 4,485,196 (Nov. 27, 1984), G. P. Speranza, R. A. Grigsby, Jr., and M. E. Brennan (to Texaco Inc.).
299. U.S. Pat. 4,532,304 (July 30, 1985), M. J. Fazio (to The Dow Chemical Co.).
300. U.S. Pat. 4,631,148 (Dec. 23, 1986), D. P. Braksmayer, F.-T. H. Lee, and F. R. Scholer (to FMC Corp.).
301. U.S. Pat. 4,479,010 (Oct. 23, 1984), M. Cuscurida and W. P. Krause (to Texaco Inc.).
302. U.S. Pat. 4,670,557 (June 2, 1987), W.-Y. Su (to Texaco Inc.).
303. L. I. Simandi, E. Zahonyi-Budo, and J. Bodnar, *Inorganica Chimica Acta*, **65**(5), L181–L183 (1982).
304. U.S. Pat. 4,661,589 (Apr. 28, 1987), G. L. Adams and C. D. Messelt (to The Dow Chemical Co.).
305. U.S. Pat. 4,609,729 (Sept. 2, 1986), J. L. Garner (to The Dow Chemical Co.).
306. *621 Ways to Succeed, 1993–1994 Materials Selection Guide*, Form No. 304-00286-1292X SMG, The Dow Chemical Co., Midland, Mich., 1993.
307. *A Guide to Glycols*, Form No. 117-00991-89, The Dow Chemical Co., Midland, Mich., 1981.
308. *The Polyglycol Handbook*, Form No. 118-1026-889-AMS, The Dow Chemical Co., 1988.
309. *Overview Guide to Dow Polyglycols*, Form No. 118-01163-592 AMS, The Dow Chemical Co., 1992.
310. *The Glycol Ethers Handbook*, Form No. 110-00363-290X AMS, Dow Chemical USA, 1990.

DAVID L. TRENT
The Dow Chemical Company