



ASSESSMENT OF EPICHLOROHYDRIN USES,
OCCUPATIONAL EXPOSURE AND RELEASES

March 28, 1984

Revised May 31, 1984

Final Draft July 11, 1984

Prepared Under Contract No. 68-02-3952

Submitted to: The Economics and Technology Division TS-779
Office of Toxic Substances
U.S. Environmental Protection Agency
Washington, D.C. 20460

Submitted by: Dynamac Corporation
Enviro Control Divison
The Dynamac Building
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Rockville, MD 20852

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PREFACE

This report was prepared by Dynamac Corporation of Rockville, MD for the USEPA under Contract No. 68-02-3952. The EPA Project Officer was Mr. James Cottrell and the EPA Task Leader was Mr. George Heath.

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EXECUTIVE SUMMARY

Epichlorohydrin (ECH) is a liquid (b.p. 117°C), which is irritating and systemically toxic by oral, percutaneous, and respiratory routes of exposure (ACGIH, 1977). It is a known mutagen and there is evidence of carcinogenic potential in rats (Tassignon et al., 1983). In rats, ECH causes infertility (Milby et al., 1981). This report summarizes uses of ECH, substitutes for ECH in each use, occupational exposure to ECH and releases of ECH from plants where it is manufactured or processed.

ECH is currently produced domestically by Dow Chemical U.S.A. at Freeport, TX and Shell Chemical Company at Deer Park, TX and Norco, LA. The combined annual U.S. production capacity is 640 million pounds and the combined U.S. production in 1982 is estimated to be 336 million pounds (Cogswell et al., 1983).

Commercial production of ECH began circa 1950 when it was found that a convenient way to eliminate excess water during the manufacture of glycerin from allyl chloride was to generate ECH and isolate it from the aqueous reaction mixture before converting it to glycerin. During the 1950s and 1960s, new uses were found for ECH and the demand for synthetic glycerin decreased in the 1970s. Thus, although ECH plants are closely integrated with glycerin plants, the production of glycerin from ECH currently can probably be attributed in part to the use of the glycerin process to dispose of low grade ECH which cannot be used for other products as well as to provide synthetic glycerin when market demand warrants.

The major products produced from ECH are glycerin, epoxy resins, elastomers, wet-strength resins, water treatment polymers (coagulants), the flame retardant Fyrol 2, ion exchange resins, and alkyl glyceryl ether sulfonate surfactants (Cogswell, 1983). In each case, ECH is an intermediate that is consumed in manufacture of the product leaving only residues (usually less than 1000 ppm) in the product. Uses of ECH in which it would not be consumed in the manufacturing process are discouraged by the manufacturers.

Epoxy resins are typically manufactured by reacting ECH with a diol (usually bisphenol A). Residues of ECH in most resins are controlled to 5 ppm wt/wt by the manufacturers because it has been shown that this level of residue in the resins will not lead to violation of the atmospheric standards (5 ppm v/v) set by OSHA (Shell, 1982). Some special resins (particular those containing reactive diluents or glycidyl esters) may contain ECH residues up to the range of 1000 ppm wt/wt. The highest exposures to ECH appear to be associated with spray painting epoxy resins containing high levels of ECH under conditions of poor ventilation.

The methods used to manufacture glycerin from ECH and remove excess water suggest that the product should not have detectable levels of ECH.

Elastomers made by catalytic polymerization of ECH by itself or with ethylene oxide may have residual ECH. However, there are indications that once the elastomer is compounded, the ECH is either destroyed or immobilized (Kirk-Othmer, 1979a).

There are too few data to evaluate the residues of ECH in other products quantitatively, but in most cases the reaction conditions suggest that ECH residues will be below detectable levels (e.g., sub-ppm), although some ECH hydrolysis products may be present.

Substitutes for ECH have been examined for many of its important products. Two approaches to substitution have been considered: synthesis of the product using reactants other than ECH, and substitution of equivalent products for ECH-based products. In most cases, substitution appears to be technically feasible although cost of the alternate products or alternate synthetic routes are probably higher than the current ECH-dependent technology.

The biggest area of ECH consumption is in manufacture of epoxy resins. The most likely alternate synthetic pathway involves reaction of the diol with allyl chloride followed by peracid epoxidation or hydrochlorination-epoxidation to yield the epoxy resins. On the surface this process might be able to compete economically with ECH-epoxy resins, but the technology associated with manufacture of ECH is closely intertwined with other processes so

that major changes in the production volume of ECH could affect the economics of other material (e.g., allyl chloride, glycerin). Thus, the actual cost of implementing the alternate synthesis is quite difficult to calculate.

A series of industrial hygiene surveys for NIOSH (Bales, 1978) showed that worker exposure to ECH during manufacture and processing is rather well controlled. In these situations TWA exposures are below the OSHA standard of 5 ppm v/v. There is one reported case where workers were spray painting large structural steel sections in a poorly ventilated building and very high (e.g., up to 82 ppm TWA) exposure levels were found (Chrostek and Levin, 1981). This situation seems to be exceptional and the epoxy being used probably contained reactive diluents with high ECH levels (unlike the basic bisphenol A-ECH resins).

Dermal contact with ECH is recognized as the mode of exposure most likely to produce acute reaction. The major manufacturers attempt to educate their own employees and the employees of their customers regarding these hazards.

1.0 INTRODUCTION

1.1 Objectives

The objectives of this report are to summarize the uses, occupational exposure and environmental releases of epichlorohydrin. The health effects of epichlorohydrin (ECH) are well known and have been documented in other reports (NIOSH, 1976; EPA, 1983). The exposure and release data can be used in combination with the health effects data by EPA to evaluate the risks presented by current industrial uses of ECH. The use data will allow EPA to evaluate various options to control the risks.

1.2 Scope

This review was limited to approximately 1,300 hours of professional labor over a 4-month period. The health effects of ECH have been discussed elsewhere (NIOSH, 1976; EPA, 1983) and are not considered here. The occupational exposure to ECH has been studied by NIOSH (Bales, 1978 and supporting documents; Lewis, 1980; Chrostek and Levine, 1981); and the EPA Office of Air Quality Planning and Standards (Anderson et al., 1981; PRI, 1972; SAI, 1982) has examined atmospheric releases of ECH. Releases of ECH from manufacturing plants were also discussed by Santodonato et al. (1980). The current study does not include any field work, so our occupational exposure and environmental release discussions are limited to analysis of existing data.

In the context of this project, "use" includes the industrial uses of ECH, the economics of those uses and the potential substitutes and the economics of those substitutes for ECH in those uses. In addition, since ECH is an intermediate used to produce a variety of products, the levels of ECH residues in each type of product are an important consideration in evaluating exposure beyond the manufacturing and processing steps. Uses of ECH have been discussed by Santodonato et al. (1980) and Chen et al. (1981), but relatively little work was done on substitutes or residues in these reports.

1.3 Approach

Our approach to this project has been to absorb as much information as possible from previous reports on ECH prepared for EPA and other Federal Agencies and to conduct a search of the computerized data bases to obtain additional information to update and fill gaps in the information of particular interest here. Contacts with manufacturers, processors and users of ECH have been conducted with emphasis on determining residues of ECH in various products. Most of the original work in this project has centered on evaluation of substitutes for ECH. This area has not been investigated in depth in previous studies (Santodonato et al., 1980; Chen et al., 1981; Mathtech, 1983).

2.0 CHEMICAL AND PHYSICAL INFORMATION ON EPICHLOROHYDRIN

2.1 Identification

Name: Epichlorohydrin

Synonyms: (Chloromethyl)oxirane (9CI name)

1-Chloro-2,3-epoxypropane

3-Chloro-1,2-epoxypropane

(Chloromethyl)ethylene oxide

2-(Chloromethyl)oxirane

Chloropropylene oxide

3-Chloro-1,2-propylene oxide

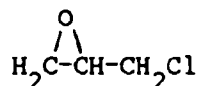
2,3-Epoxypropyl chloride

CAS No.: 106-89-8

NIOSH No.: TX4900000

Empirical Formula: C₃H₅ClO

Structural Formula:



Molecular Weight: 92.53

2.2 Physical Properties

Description: Epichlorohydrin is a colorless liquid with a characteristic chloroform-like odor (Dow, 1980). Its odor index is 160 and its average threshold odor concentration is about 10 ppm with a range of 0.08 to 100 ppm (Verschuere, 1977).

Freezing Point: -57.1°C (Dow, 1980).

Boiling Point: 116.1°C at 760 mmHg (Dow, 1980)
117.9°C at 760 mmHg (Merck, 1976)

Vapor Pressure: 17.25 mmHg at 25°C (Dow, 1980)

Specific Gravity: 1.173 at 25/25°C (Dow, 1980)

Solubility in Water: 6.6 g/100 g H₂O at 20°C (Dow, 1980)

Water Solubility in ECH: 1.47 g/100 g ECH at 20°C (Dow, 1980)

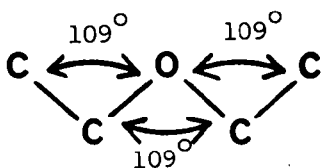
Solubility in Organic Solvents: Miscible with polar (e.g., methanol) and nonpolar (e.g., heptane) organic solvents (Dow, 1980)

Log Octanol/Water Partition Coefficient: 0.30 (Chen et al., 1981)

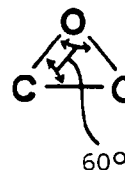
2.3 Chemical Properties

2.3.1 Hydrolysis and Other Ring-Opening Reactions

Epoxides are much more reactive than ordinary ethers because the carbon and oxygen bond angles are forced to be about 60° rather than the preferred angles of about 109° normally adopted by non-cyclic aliphatic compounds (Flippen-Anderson and Gilardi, 1981).



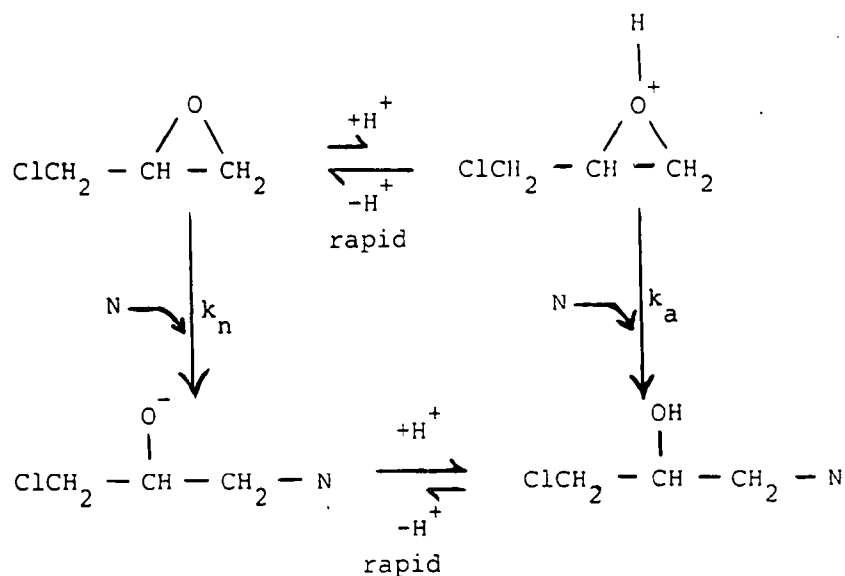
Normal Ether Bonds



Epoxide Bonds

The "abnormal" bond angles found in epoxides result in lower bond energies for the C-O and C-C bonds in the three-membered ring and the difference between the normal and abnormal bond energies can be interpreted as "strain energy" associated with the ring. Reactions that lead to opening of the epoxy ring are enhanced because they allow the C-C-O and C-O-C bond angles to change to their preferred dimensions.

The main reactions of commercial interest involve opening the epoxide ring by displacing the oxygen from one of the carbons by a nucleophile. The mechanisms for this reaction have been discussed by a number of authors. In the case of epichlorohydrin (ECH) reacting in normal solvent media (i.e., excluding the possibility of highly acidic media), the ring opening reaction can be described as shown below (Prichard and Siddiqui, 1973):



In this scheme, ECH is subject to a rapid, reversible protonation reaction. The extent of protonation depends upon the pH of the medium. Both the unprotonated and protonated forms of ECH can be attacked by nucleophiles (N) causing displacement of the oxygen from a carbon and opening the ring. In general, the rate constant k_a is much greater than k_n ; protonation of the epoxide ring catalyzes ring opening. Because nucleophilic attack with concurrent displacement of the leaving group (S_N2) generally is now rapid at the carbon with fewer substituents, the nucleophile will usually attach to the terminal carbon of the propyl group.

The overall ring-opening rate (R) is equal to the sum of the rates of the uncatalyzed (R_n) and catalyzed (R_a) process (Mabey and Mill, 1978):

$$R_n = k_n [\text{ECH}] [\text{N}]$$

$$R_a = k_a [\text{ECH-H}^+] [\text{N}]$$

$$R = (k_n [\text{ECH}] + k_a [\text{ECH-H}^+]) [\text{N}]$$

The concentration of "ECH-H+" is dependent upon the equilibrium constant (K) for the protonation reaction:

$$[\text{ECH-H}^+] = K [\text{ECH}] [\text{H}^+]$$

Thus,

$$R = (k_n + k_a K [\text{H}^+]) [\text{ECH}] [\text{N}].$$

When water (H_2O) is the nucleophile N in water solvent at 298°C , the values of k_n and $k_a K$ are as follows (Mabey and Mill, 1978):

$$k_n = \frac{9.8 \times 10^{-7} \text{ s}^{-1}}{55.6 \text{ M}} = 1.76 \times 10^{-8} \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$k_a K = \frac{8.0 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}}{55.6 \text{ M}} = 1.44 \times 10^{-5} \text{ M}^{-2} \cdot \text{s}^{-1}$$

Thus, above pH 3 (i.e., $[\text{H}^+] = 10^{-3}$) the uncatalyzed reaction (k_n) is the most important contribution to hydrolysis. It should be noted that above pH 7, the concentration of OH^- (hydroxyl anion) starts to become significant and the reaction of this nucleophile with ECH starts to become an important contribution to the overall hydrolysis rate. Mabey and Mill (1978) calculate the pseudo-first order half-life for ECH in water at pH 7 and 25°C as 197 hours. More recently, Piringer (1980) calculated half-lives of ECH in water at 20°C with the following results:

<u>pH</u>	<u>half-life of ECH</u>
pH 2.5	79 hours
pH 7	148 hours
pH 12	62 hours

At pH 2.5, the half-life is determined by reaction between both protonated and unprotonated ECH and H_2O . At pH 7, the half-life is determined by reaction between unprotonated ECH and H_2O and at pH 12, by reaction between unprotonated ECH and both H_2O and OH^- .

Piringer (1980) also tabulated the rate constants (k_n) for reaction of a variety of nucleophiles with unprotonated ECH in water at 20°C . The rate constants are listed in Table 2.3.1A.

Table 2.3.1A. Rate Constants for Reaction of Nucleophiles with Epichlorohydrin in Water at 20°C.

Nucleophile	Rate Constant (k_n) $M^{-1} \cdot s^{-1}$
H_2O	2.3×10^{-8}
NO_3^-	1.9×10^{-7}
HCO_3^-	2.9×10^{-6}
$CH_3CO_2^-$	6.2×10^{-6}
Cl^-	1.2×10^{-5}
Br^-	6.2×10^{-5}
CO_3^{2-}	1.0×10^{-4}
OH^-	1.8×10^{-4}
CNS^-	6.3×10^{-4}
I^-	1.0×10^{-3}

Adapted from Piringer (1980).

The relative order of reaction rates of nucleophiles with ECH in water listed in Table 2.3.1A is typical of these nucleophiles in protic solvents. Note that hydroxyl anion (HO^-) is about 10,000 times more reactive than water (H_2O).

The phenoxide ion (PhO^-), which is relevant to formation of bisphenol A propylchlorohydrin ether as an intermediate for epoxy resins, usually has about the same reactivity as bromide (Br^-) anion (March, 1968). Enikolopyan et al. (1982) have discussed the kinetics of the reaction of bisphenol A with ECH. The reactions are complex but follow the same principles discussed above.

The data cited above can be used to predict the half-life of ECH in water under a variety of conditions. Unfortunately, the rates of ring-opening reactions have not been studied in nonaqueous media such as glycerol or solvents which would simulate epoxy resins. Thus, although epichlorohydrin should react with glycerin and hydroxyl groups in epoxy resins, we can not accurately predict the rate of these reactions.

2.3.2 Other Reactions of Epichlorohydrin

Direct nucleophilic displacement of the chlorine from ECH is not an important process relative to the rate of opening the epoxy ring.

Free radicals can abstract hydrogens from ECH (Santodonato et al., 1980), but no commercial users of these reactions are known. Dilling et al. (1976) examined the atmospheric chemistry of ECH. From these results, the estimated half-life of ECH in bright sunlight in the southern U.S. is 42 hours. The main mode of degradation under these conditions is hydroxyl radical oxidation. Direct photolysis of ECH should not be important at the wavelengths of light reaching the earth's surface (i.e., ECH does not have a chromophore that absorbs energy at the relatively long wavelengths of light reaching the earth's surface).

3.0 MANUFACTURERS AND PRODUCTS

Over 350 million pounds of epichlorohydrin (ECH) is produced annually in the United States. All ECH is produced by two companies, Dow Chemical, U.S.A. and Shell Chemical Company.

Approximately 75 percent of the ECH produced is used captively to produce epoxy resins, synthetic glycerin and miscellaneous lower volume products. Approximately 15 percent is used by other chemical companies to produce the major end product, epoxy resins, and other lower volume products including elastomers, wet-strength and anion exchange resins and water treatment polymers. The remaining 10 percent is exported.

As shown in Table 3.1 these ECH-derived materials are in turn used to manufacture products for a variety of uses in the automotive, construction, drug, food products, and pulp and paper industries.

3.1 Production Volume and Supply

Since ECH is now produced domestically by only two companies, recent ECH production data are unavailable from the United States Department of Commerce or the United States International Trade Commission. Estimates of the production volume of crude ECH are made from published data and trade estimates of production of unmodified epoxy resins and glycerin (Chemical Purchasing, June 1982). For the years 1978-1982 the production estimates were as follows:

<u>Year</u>	Crude-ECH* <u>Production</u> (million lbs)
1978	347
1979	412
1980	397
1981	397
1982	375 (est.)

* Yield refined ECH is 97 percent crude ECH; all ECH is refined prior to use.

Source: 1978-81, U.S. Department of Commerce, Bureau of Census; 1982 estimate, Chemical Purchasing (June 1982).

Table 3.1. Epichlorohydrin Products, United States Consumption and Product End-uses.

Product	Annual ECH consumption (1982) (million lbs.)	Percent (%)	Major uses
Epoxy Resins	172-175	56	surface coatings, laminates/composites castings/molding, flooring
Bisphenol A (DGEBCA)			
Aliphatic			
Polyether			
Epoxy Novolac			adhesives
Phenoxy Epoxy and other Epoxy			
Synthetic Glycerin	87-90	29	ingredient for food/beverage, cosmetics, drugs; humectant in tobacco; plasterizer for cellophane and reactant in alkyd resin, urethane polymers, triacetin explosives production
Wet-Strength Resins	10-15	5	paper industry, for paper sizing
Water Treatment Polymers	12	4	water clarification, waste water treatment flocculating agents
Elastomers	7-9	3	seals, gaskets, jackets for wire and cable, hoses, belts, rubberized fabrics
Anion Exchange Resins	<1	0.2	
Alkyl Glyceryl Ether Sulfonates	3-5	1	surfactants; shampoos, liquid detergents
Glycidyl Ethers	3	1	reactive diluents for
Glycidyl Esters	<1	0.2	epoxy resins
Fyrol FR-2	2	0.6	flame retardant
Total (approximate)	311		

Source: Arnold (1984b), Cogswell (1983).

The decrease in production since 1979 is attributed primarily to the recessionary economy and the resulting decline in demand for ECH-derived end products. For 1983, analysts projected gains of 5 to 8 percent over 1982 levels for the large volume end products; however, even with these anticipated increases, production requirements would still be below the record high of 1979.

3.1.1 Manufacturers and Production Volume

ECH is produced domestically by Dow Chemical, U.S.A. and Shell Chemical Company. Dow has a production facility at Freeport, Texas. Shell has two plants in operable condition, but has consolidated its ECH production at one facility. The plant locations shown below have a combined annual capacity of 640 million pounds (SRI, 1983; Chemical Purchasing, June 1982).

<u>Company</u>	<u>Plant Location</u>	<u>Annual Capacity</u>
Dow Chemical, U.S.A.	Freeport, TX	420
Shell Chemical Co.	Deer Park, TX	220
	Norco, LA	

In recent years, capacity utilization has ranged from 60 to 65 percent. Trade forecasts indicate that the present rated capacity will be adequate to meet projected ECH demand until the late 1980s (Chemical Purchasing, 1982).

3.1.2. Imports and Importers

Imports of ECH contribute little to the domestic supply. ECH imports shown below for 1978 to 1983 represent less than one percent of the domestic production.

<u>Year</u>	<u>Imports</u> (million lbs.)
1978	3.4
1979	2.4
1980	1.9
1981	3.0
1982	2.1
1983	1.8 (January through September)

Source: Cogswell et al. (1983); U.S. Department of Commerce (1983)

The primary country of origin is Japan. In 1981 and 1982 over 98 percent of imported ECH came from Japan. Importers of ECH identified in the TSCA Inventory are Marubeni America Corporation, Shell Oil Company, Mitsubishi International Corporation, Nichimen Company, Inc. and Hercules Inc. (Math Tech, 1983).

3.1.3 Exports and Exporters

Exports of ECH typically amount to 10 to 15 percent of United States output. Total quantities exported have declined from a high of almost 52 million pounds in 1979, as shown below.

<u>Year</u>	<u>Exports</u> (million lbs.)
1978	21.8
1979	51.9
1980	47.3
1981	37.4
1982	26.7
1983	12.1 (January to September only)

Source: U.S. Department of Commerce, Bureau of Census (1983)

The growth in exports through 1979 has been attributed in part to the lower domestic price of raw materials and the greater efficiency of the large United States ECH plants; the decline since 1979 has been attributed to the world recession and the strong dollar, which hurts the competitiveness of U.S. ECH abroad.

A number of countries import ECH from the United States as shown in Table 3.2. Major importing nations are Japan, Mexico, Canada, Brazil, and India. A cursory examination of the quantities imported by several countries, including Brazil, Netherlands, Australia, and the Republic of South Africa, show that their imports have declined sharply since 1981. However, other countries are now importing ECH. Reasons for these individual trends have not been investigated.

3.1.4 Net Domestic Supply

The net domestic supply of ECH is summarized in Table 3.3. The net domestic supply has remained fairly constant at about 350 million pounds since 1979.

3.2 Markets

Currently for all uses, crude ECH is first refined. Of the total U.S. production of ECH, epoxy resins typically consume 50-55 percent, synthetic glycerin 25-30 percent, and miscellaneous derivatives and exports 10 percent each (MCP, 1982).

3.2.1. Epoxy resins

Approximately 50 percent of total ECH production is consumed for the manufacture of epoxy resins. In 1982 an estimated 172-175 million pounds of ECH was consumed to produce the following epoxy resins:

Bisphenol A (DGEBCA)
(25068-38-6, 25036-25-3)
Aliphatic (31921-70-7, 25038-04-4, etc.)
Polyether (39443-66-8, etc.)
Epoxy Novolac (29690-82-2, etc.)
Phenoxy Epoxy and other Epoxy

Table 3.2. U.S. Exports of Epichlorohydrin, by Country of Destination,
1981-1983

Country of destination	1981	1982	1983 <u>1/</u>
	----- (thousand pounds) -----		
Canada	4,392	954	1,010
Mexico	4,345	3,542	2,715
Haiti	154	--	--
Columbia	219	263	68
Venezuela	572	780	210
Brazil	7,630	10,978	2,645
Argentina	1,326	1,531	574
Netherlands	7,406	3,307	--
India	446	1,311	795
Japan	5,455	3,628	1,767
Australia	2,706	216	216
Republic of South Africa	2,670	--	*
Republic of Korea	--	--	375
China - Mainland	--	--	1,428
China - Taiwan	--	--	219
Saudi Arabia	--	--	2
New Zealand	--	--	36
Hong Kong	--	--	*
Guatemala	--	--	11
Other	<u>102</u>	<u>179</u>	<u>--</u>
Total	37,425	26,691	12,072

1/ January through September only.

Due to rounding these totals may not add.

* Less than 500 pounds.

Source: U.S. Department of Commerce, Bureau of Census (1983)

Table 3.3. U.S. Epichlorohydrin Production, Exports, Imports, and Net Domestic Supply, 1978-1983

Year	Production	Exports	Imports	Net domestic supply
	----- (million lbs.) -----			
1978	346.8	21.8	3.4	328.4
1979	411.9	51.9	2.4	362.4
1980	397.3	47.3	1.9	351.9
1981	397.4	37.4	3.0	363.0
1982	375 <u>a,b/</u>	26.7	2.1	350
1983 <u>c/</u>	<u>a/</u>	12.1	1.8	--

a/ Information confidential; only two producers.

b/ Estimated (Chemical Purchasing, June, 1982).

c/ January through September only.

Source: U.S. Department of Commerce, Bureau of Census (1983); Chemical Purchasing (June 1982).

Large volume markets for ECH-derived materials are the automotive and construction industries. Growth of ECH is tied directly to expansion in these markets and the relative price and performance characteristics of ECH-derived materials and possible substitutes.

Projected growth rate for the period 1982-1987 for ECH consumed for epoxy resins is 5 to 7 percent (Cogswell, 1983).

3.2.2 Glycerin

ECH is produced and used captively for the production of synthetic glycerin. The estimated consumption of ECH for synthetic glycerin in 1982 was 87-90 million pounds (Arnold, 1984b; Cogswell, 1983). The consumption of ECH for production of synthetic glycerin varies somewhat from year to year depending on the competition from natural glycerin.

Although government sources no longer report synthetic glycerin production separately, approximately one-third of the total 1982 U.S. glycerin production (synthetic and natural) of 232 million pounds (77 million pounds) was estimated to be synthetic glycerin. All synthetic glycerin is now produced by Dow from ECH (Kovats, 1983). Dow's synthetic glycerin capacity at the Freeport, Texas facility is rated at 115 million pounds (CMR, 1981). FMC previously produced synthetic glycerin from propylene oxide at its Bayport, Texas facility, but ceased production on July 1, 1982. The plant capacity was 40 million pounds, but an industry source reported that the plant was operating at only about 50 percent for the year prior to its closing. Thus, its closing had relatively little impact on the overall glycerin market (Kovats, 1983). An FMC representative (Fisher, 1983) indicated the plant closure was due primarily to the combined effects of decreased demand for glycerin and increased energy costs for this energy intensive process.

In recent years, natural glycerin has taken over a larger share of the total glycerin supply (Fisher, 1983). The natural glycerin producers have an estimated total capacity of 200-260 million pounds. In addition, Emery

Industries, Inc., a subsidiary of National Distillers and Chemical Corp., has announced a \$50 million expansion at its Cincinnati, Ohio production complex that is scheduled to be completed in early 1984 (SRI, 1983).

From 1962 to 1980 the United States was a net exporter of glycerin. However, this situation has changed and since 1981 imports have become more important in overall glycerin availability as shown in Table 3.4 (The Soap and Detergent Association, 1983).

Future demand for ECH for synthetic glycerin is difficult to predict because of its dependence on the somewhat erratic availability and economics of natural glycerin that are in turn dependent on the demand for fatty acids produced from natural glycerides. SRI (Cogswell et al., 1983) has, projected slow growth, averaging less than 1 percent annually through 1987, in the consumption of glycerin and thus of ECH for glycerin.

3.2.3 Miscellaneous derivatives

Other important uses of refined ECH include elastomers, water treatment polymers, wet-strength and anion exchange resins, alkyl glyceryl ether sulfonates and glycidyl ethers and esters. The estimated annual consumption of refined ECH in 1982 for each of these materials is shown below.

	<u>ECH Consumption (1982)</u>
	million pounds
Elastomers (24969-06-0, etc.)	9
Wet-Strength Resins (25212-19-5, etc.)	15
Water Treatment Polymers	12
Anion Exchange Resins (25014-13-5, etc.)	<1
Alkyl Glyceryl Ether Sulfonates	3
Glycidyl Ethers (2426-08-6, etc.)	3
Glycidyl Esters (106-90-1, 106-91-2, etc.)	<1
Fyrol FR-2 (13674-87-8)	2

Markets include the paper industry and a variety of industries that require high performance materials for marine applications, appliances,

Table 3.4. U.S. Natural and Synthetic Glycerin Production Exports and Imports, 1978-83.

Year	Crude natural & synthetic production	Exports	Imports
	----- (million lbs.) -----		
1978	302.6	41.5	7.7
1979	345.7	53.7	0.6
1980	301.1	57.1	19.3
1981	280	30.1	40.4
1982	232	14.1	32.3
1983*	--	7.4	23.9

* January through October. U.S. Department of Commerce, Bureau of Census (1983).

Source: The Soap and Detergent Association, Statistics, Glycerin GL-3b, April 12, 1983.

coil steel, pipe, electrical parts, circuit boards, and water treatment. Growth of ECH is tied directly to expansion in these markets and the relative price and performance characteristics of ECH-derived materials and their possible substitutes. SRI (Cogswell et al., 1983) recently published projected growth rates for the period 1982-1987 for ECH consumed in products for these markets:

Elastomers	6 to 8 percent
Other Domestic Users	3.5 to 6.5 percent

3.2.4 Exported Epichlorohydrin

Approximately 10 percent of the total U.S. ECH production is currently exported as ECH. SRI (Cogswell et al., 1983) projected an increase in demand for ECH by 1987 of 22 to 66 million pounds in Europe; the current European ECH capacity is just sufficient to meet that demand. The current Japanese capacity is about 120 million pounds per year and their current production is about 105 million pounds per year. Since the U.S. capacity is 640 million pounds per year and projected U.S. 1987 domestic consumption is under 430 million pounds, U.S. exports could increase. Based on ECH supply and demand data for Western Europe and Japan (Cogswell, 1983), Dynamac projects U.S. exports (especially to Japan) could increase at a rate of up to 10 percent per year, if the foreign market continues to grow.

In addition to direct ECH exports, annual United States exports of ECH-derived epoxy resins total about 35 million pounds (USITC, 1983). By contrast, imports of epoxy resins were 5.0 and 4.6 million pounds in 1981 and 1982, respectively.

3.3 End-Use Products Derived From Or Incorporating ECH

The primary end uses of ECH are for production of synthetic glycerin and epoxy resins. Other lower volume end uses are wet-strength resins, wastewater treatment polymers, elastomers, and a variety of miscellaneous uses. These products, quantities of ECH consumed, and their uses, summarized in Table 3.1, are described in detail below.

3.3.1 Epoxy Resins

The most important epoxy resins are produced from ECH and bisphenol A. The resins vary in properties depending on the ratio of ECH and bisphenol A. Epoxy resins are not finished products but are reactive materials that are combined with other materials to yield products that can be converted to a predetermined thermoset structure. Annual ECH consumption for these materials is approximately 175 million pounds.

Epoxy resins are cured by crosslinking agents. Cured epoxies are generally characterized by outstanding mechanical and electrical properties, dimensional stability, resistance to heat and chemicals, and adhesive to a wide range of materials.

The two major epoxy producers, Dow and Shell, have over 75 percent of the total epoxy capacity of 647 million pounds. Both produce ECH captively. Epoxy resins producers, their plant locations and capacities are listed in Table 3.5.

The epoxy total capacity, production and exports are shown in Table 3.6 for 1979-1983. Estimates are given for 1984. Imports during this period amounted to less than 2 percent of production. In 1981 and 1982, for example, imports were 5.0 and 4.6 million pounds, respectively.

Although the effective capacity is considerably below the nameplate capacity shown above because of complications in switching production of different grades, the producers have sufficient capacity for increased production. If the projected 1984 production of 340 million pounds is attained, the operating rate will be approximately 60 percent.

For the past decade premium quality thermoset epoxies have been projected to benefit from quality improvement campaigns in the automotive, electronic and other durable markets. In practice, however, these gains have been intermittent and have been noticeably impacted by recessions. Even though epoxy resin production dropped 21 percent during the 1979-83

Table 3.5. Epoxy Resin Producers, Plant Locations and Capacities.

Company	Plant location	Product name	Annual capacity	Remarks
			(million lbs)	
Celanese Corp.				
Celanese Plastics and Specialties Co., Specialty Resins	Louisville, KY	(Epi-Rez)	25	
Ciba-Geigy Corp.				
Plastics & Additives Div. Resins Dept.	Toms River, NJ	(Araldite)	60*	
Dow Chemical U.S.A.	Freeport, TX	(D.E.R.)	230	
Reichhold Chemicals, Inc.	Andover, MA Azusa, CA Detroit, MI Houston, TX	(Epotuf)	32	
Shell Chemical Co.	Deer Park, TX	(Epon)	270	
Union Carbide Corp.				
Coatings Materials Div. Specialty Chems. & Plastics Div.	Bound Brook, NJ Taft, LA	(Bakelite)	10 20	Phenoxy resins Cycloaliphatic epoxy resins
Total			647	

* Ciba-Geigy is closing this 60 million pound plant at Toms River, New Jersey and adding 100 million pound capacity at McIntosh, Alabama. Epoxies, C&EN November 21, 1983, p. 10.

Sources: SRI International estimates as of January 1, 1983; 1983 Directory of Chemical Producers, United States, pp. 816-817. (The Society of the Plastics Industry, Inc. Facts and Figures of the U.S. Plastics Industry 1982 Edition also lists Morton Industries as a producer).

Table 3.6. Annual Epoxy Resin Capacity and Production.

Year	Capacity	Production	Exports
	----- (million lbs.) -----		
1979	405*	361	36
1980	405*	315	36
1981	580	332	41
1982	580	286	40
1983	580	310 (est.)	35 (est.)
1984	600	340 (est.)	

* Liquid only.

Sources: Chemical & Engineering News, Key Chemicals, Epoxies November 21, 1983, p. 10; August 30, 1982, p. 12; September 28, 1981, p. 18; and Society of the Plastics Industry, Inc. 1982 Edition, Facts & Figures of the U.S. Plastics Industry, pp. 34-35.

period, this decline was the lowest among major thermoset resins. Even with the increase in production of 8 to 12 percent for both 1983 and 1984 that has been projected by industry analysts, the 1984 epoxy production level will be below the record 1979 production.

The major end uses of epoxies are coatings, 45 percent; laminates and composites, 25 percent; castings and molded items, 10 percent; commercial flooring, 5 percent; and adhesives 5 percent (C&EN, November 21, 1983). The largest epoxy resin coating use is for the interior of containers, particularly cans for mildly corrosive materials such as beer, soft drinks and some foods. Prospects for growth of epoxies in container coatings are low in that most of the basic market penetration has already taken place. Other major epoxy coating uses are for high performance materials for industrial maintenance, marine parts, automobile undercoats and primers, electrical products, and powder coatings of appliances and outdoor metal furniture. The second largest use of epoxies is for laminates and composites materials (i.e. products layered for high tension strength and dimensional stability) for electrical parts and electronic circuit boards. These materials are desirable in these uses because of their dielectric strength, low shrinkage upon cure, good adhesion and ability to retain properties under varying environmental conditions (Math Tech, 1983). Uses of epoxies for adhesives is divided between mature, slower growing general manufacture and consumer repair kit markets and faster growing specialty industries like aerospace. Other uses of epoxies are for commercial flooring and for tooling resins in the automobile and aerospace industry (C&EN, November 1983; August 1982).

3.3.2 Glycerin

End uses of glycerin and its products are diverse and involve many markets; the largest use (tobacco) is only 18 percent of the total (See Table 3.7). Synthetic glycerin produced from ECH is essentially interchangeable with natural glycerin (Kovats, 1983). Of the current uses of synthetic and natural glycerin shown in Table 3.7, those processes having moisture limitations and requiring 99.5-99.7 percent glycerin had

Table 3.7. Natural and Synthetic Glycerin End-use Survey, Calendar Year 1982.

	Year 1982
	(thousand pounds)
Alkyd resins (for paints)	19,823
Cellophane and meat casings	9,018
Tobacco, including triacetin	43,645
Explosives and military use	4,181
Drugs, including toothpaste	39,333
Cosmetics	20,346
Monoglycerides and foods	25,190
Urethane foams	19,789
Distributor sales	39,039
Crude consumed as crude (except for refining)	699
Miscellaneous	17,304
Total	238,367

NOTE: These data are based on reports of sales and captive uses submitted by fourteen participating companies, which are producers of refined glycerin or import brokers. While The Soap and Detergent Association believes that the statistical methods and procedures used to compile this report are reliable, it does not warrant the accuracy or completeness of the data.

Source: The Soap and Detergent Association (June 2, 1983)

been restricted to synthetic glycerin. (Natural glycerin typically is 96 percent.) Synthetic glycerin has been used exclusively for polyols and urethane foams because of its lower moisture content. However, Proctor & Gamble Company can now supply 99.5 percent minimum and Emery has 99.5 percent and 99.7 percent minimum natural glycerin (Emery Sales, 1984) which means this natural product is now suitable for most of these uses also (Kovats, 1983). The price of \$0.81 per pound, tank car delivered, for both 99.5 percent minimum kosher natural glycerin and 99.5 percent minimum synthetic glycerin (Wittwer, 1984) reflects this substitutability.

3.3.3 Elastomers

Epichlorohydrin-based elastomers or rubbers may be either the ECH homopolymer, polyepichlorohydrin, or copolymers with ethylene oxide or other simple oxiranes. Uses of these elastomers are based on their low gas permeability, retention of physical and dynamic properties over temperature range of -40 to 300°F, good tear and impact strengths and good resistance to solvents, fuels, oil, and ozone. Major uses of these elastomers are in seals, gaskets, hose, belting, wire, and cable jackets. In these uses, ECH elastomers compete with neoprene and nitrile rubbers (see Section 4.4) (Elast., January, 1983; Houston, July, 1975).

The volume of the ECH specialty engineering elastomer market in the western world was projected to grow by 66.7 percent during the period 1981-86. During that same time period the growth of the major volume engineering elastomers, nitrile rubber and neoprene, was projected to slow or decline slightly (European Rubber Journal, February 1983).

ECH consumption for elastomers was 7-9 million pounds in 1982. ECH elastomers are produced by Hercules, Inc. and the B.F. Goodrich Chemical Co. (SRI, 1983). Plant locations and capacities are shown below:

<u>Plant</u>	<u>Location</u>	<u>Product name</u>	<u>Annual capacity</u> (million lbs)
The B.F. Goodrich Co.			
B.F. Goodrich Chemical Group	Avon Lake, OH	Hydrin	9
Hercules, Inc.			
Operations Division	Hattiesburg, MS	Herclor	11

3.3.4 Wet-Strength Resins

Wet-strength resins derived from ECH are widely used in the paper industry for paper sizing (Dow, 1980). The consumption of ECH for these resins is 10-15 million pounds of ECH annually (Arnold 1984b; Cogswell, 1983). These resins are cured at neutral to alkaline pH which eliminates acid-catalyzed degradation and embrittlement of paper, provides softer, more absorbent paper and reduces machine corrosion. ECH-derived resins are also effective creping aids in absorbent papers (Kirk-Othmer, 1981). Slow growth for these wet-strength resins is predicted for the years ahead (Cogswell, 1983).

Major producers of ECH-based wet-strength resins are Hercules, Inc., and Georgia-Pacific Corporation.

3.3.5 Water Treatment Polymers

Epichlorohydrin-derived polymers are used as cationic flocculating agents by industries such as the pulp and paper industry. These water treatment polymers are used for wastewater treatment and for reclamation of materials during manufacture. Approximately 12 million pounds of ECH are consumed annually for these polymers (Arnold, 1984b).

These polymers are in competition with other polymers that may be tailor-made to predetermined specifications for treatment of specific process or waste stream conditions (Arnold, 1984c). No indication of growth trends due to this competition was found.

3.3.6 Other Uses

Each of the remaining uses of ECH consumes less than 5 million pounds of ECH annually (Arnold, 1984b):

- The production of alkyl glyceryl ether sulfonates for surfactants, primarily by Proctor & Gamble, consumes about 3-5 million pounds annually. Proctor & Gamble uses these materials in shampoos, light-duty liquids and toilet bars. Consumption is projected to decrease due to the relatively high cost of these materials (Cogswell, 1983).
- The production of glycidyl ethers and esters consumes less than 4 million pounds annually. These materials are utilized as reactive dilutents for some of the epoxy resins discussed above.
- A relatively minor use of ECH is in the flame retardent Fyrol FR-2 [tris (1,3-dichloro-2-propyl) phosphate]. Fyrol FR-2, produced by Stauffer Chemical, consumes approximately 2 million pounds of ECH annually. Fyrol FR-2 is utilized as a flame retardant in flexible foams that are used primarily for automobile and furniture cushions (Morey, 1984).
- Anion exchange resins, produced by the reaction of ECH and ethylenediamine and higher homologues by Rohm and Haas Company and Diamond Shamrock Corporation, consume less than one million pounds annually.
- In addition, ECH may have minor compounding uses including in corrosion inhibitors, asphalt improvers, and as a stabilizer in pesticide formulations (Math Tech, 1983).

4.0 SUBSTITUTES FOR EPICHLOROHYDRIN

A feasible substitute for a commercial chemical like epichlorohydrin (ECH) must be functionally equivalent, economically competitive and toxicologically/environmentally acceptable. Epichlorohydrin (ECH) is used exclusively as a chemical intermediate in industry. Thus, substitution for ECH is a matter of finding alternate processes to make the same products or alternate products for the same uses. Direct substitution of a compound like epibromohydrin for ECH would probably work for most uses, but the cost would definitely be higher and the substitute would probably retain many of the hazardous properties associated with ECH.

In this chapter some possible ways to substitute other chemicals for ECH will be discussed. However, in most cases the approaches are speculative. Almost without exception, substitution would require new capital investment, process development and more expensive raw materials. The substitutes may also cause toxicological or environmental hazards that are not evaluated here. Notes on the hazards of some chemicals mentioned as substitutes for ECH or in alternate process chemistry are listed in Table 4.1A.

4.1 Physical/Chemical Properties Required for Each Epichlorohydrin Use

Because epichlorohydrin is an intermediate rather than an end product, it is more important from the standpoint of substitutability to look at its functional equivalents rather than structural analogues.

The two main uses of ECH are manufacture of epoxy resins and manufacture of glycerin. Several alternate processes for making glycerin have been well established (Lowenheim and Moran, 1975) although the ECH process seems to be the only method of making synthetic glycerin that can compete economically with natural glycerin isolated as a byproduct of soap manufacture. Alternate methods for manufacture of bisphenol A epoxy resins do not appear to have been seriously considered, although some patents (e.g., Thigpen and Taylor, 1976) hint that alternate procedures have been considered.

Table 4.1A Hazards associated with chemicals that might substitute directly of indirectly for Epichlorohydrin or be required for alternate processes.

Chemical	LD ₅₀ (mg/kg)		LC ₅₀ (ppm) Inhalation	Comments
	Oral ^a	Dermal ^b		
acetone	9,750	20,000	--	mutagenic
acrolein	46	562	66/6h ^c	irritant, mutagenic
acrylonitrile	82	250	576/4h ^d	irritant, mutagenic carcinogenic
allene (1,2-propadiene)		no information	found	
allyl chloride	--	2,200	--	irritant mutagenic tumorigenic

^arat

^brabbit

^cmouse

^dguinea pig

Source: RTECS (1983)

In the manufacture of synthetic glycerin, the intermediate is likely to be a three carbon compound with substituents or multiple bonds that can be oxidized or hydrolyzed to the product. Examples of such compounds include:

$\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$	allyl chloride
$\text{CH}_2=\text{CH}-\text{CH}=\text{O}$	acrolein
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	acrylonitrile
$\text{CH}_2=\text{C}=\text{CH}_2$	allene
$\text{H}-\text{C}\equiv\text{C}-\text{CH}_3$	methylacetylene
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \end{array}$	acetone

The utility of acrolein (see 4.3.1) and allyl chloride (see 5.0) in manufacture of glycerin have been discussed. The other chemicals listed here are more farfetched but are possible candidates.

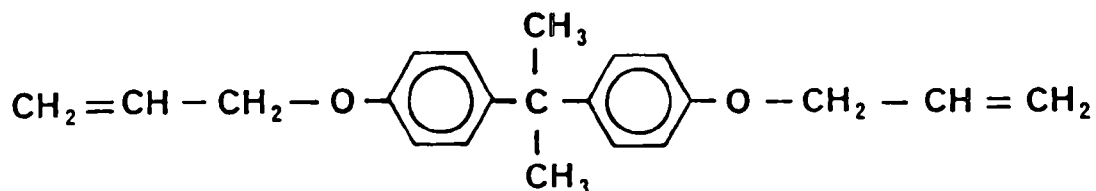
The manufacture of epoxy resins of bisphenol A and other phenols and alcohols requires a method for introducing a glycidyl ether group. Here again the intermediate should be a three carbon unit with two or more substituents (i.e., one substituent to form the ether linkage; the other substituent to form the epoxy moiety). The same compounds listed for glycerin manufacture are possible intermediates.

4.2 Alternate Processes for Synthesis of Epoxy Resins

The major commercial use of epichlorohydrin (ECH) is manufacture of epoxy resins (i.e., monomeric and oligomeric glycidyl ethers). We have identified two approaches to synthesis of glycidyl ethers that do not require ECH (Figure 4.2A). These approaches appear to be technically and economically plausible. The key intermediates and reactions are discussed in patents for similar uses. Determination of the actual feasibility of these processes is beyond the scope of the current report and would require laboratory chemical and engineering research. In this section, we will discuss the process chemistry, process engineering and economics of the alternate processes in terms of the general concept. For comparison, the current methods are discussed in section 5.2.1.

4.2.1 Alternate Process Chemistry

The key intermediate in the alternate synthetic schemes shown in Figure 4.2A is the diallyl ether of bisphenol A (DAEBPA):



This compound is listed in the non-confidential TSCA Inventory under CAS No. 3739-67-1. In 1977, it was produced at a rate of 10,000 to 100,000 lb/year by 3M Corporation. In a telephone call with Dr. Bill Paterson of 3M (Sittenfield, 1984), it was found that the chemical is produced in a batch process for use as an intermediate for consumption by 3M. They would manufacture and sell the compound in lots of about 10,000 pounds at a price between \$4 and \$5 per pound. Information obtained with a sample of the product indicated that likely starting materials were bisphenol A and allyl chloride with toluene as solvent.

A search of the patent literature revealed that DAEBPA is mentioned in several patents: duPont (Fielding and Richards, 1967) reported synthesis of DAEBPA by refluxing a mixture of bisphenol A (27.9 parts) and allyl bromide (33 parts) with potassium carbonate (35 parts, to absorb acid) in acetone (45 parts) for 1 hour. The acetone was removed (by distillation) and the product was dissolved in diethyl ether. The organic solution was washed with aqueous sodium hydroxide, dried and filtered to yield 35 parts of DAEBPA (93% yield based on bisphenol A) after evaporation of the solvent. In this same patent (Fielding and Richards, 1967), the authors prepared analogous compounds by substituting 2,3-dichloropropene, 1,3-dichloro-2-butene and 1,2-dichloro-3-butene or 1-chloro-2-butene for allyl bromide. Apparently, good yields were obtained in each case. These results indicate that substituting allyl chloride for allyl bromide would probably yield the diallyl bisphenol A ether without difficulty. A Russian patent (Savoslkin et al., 1979) describes preparation

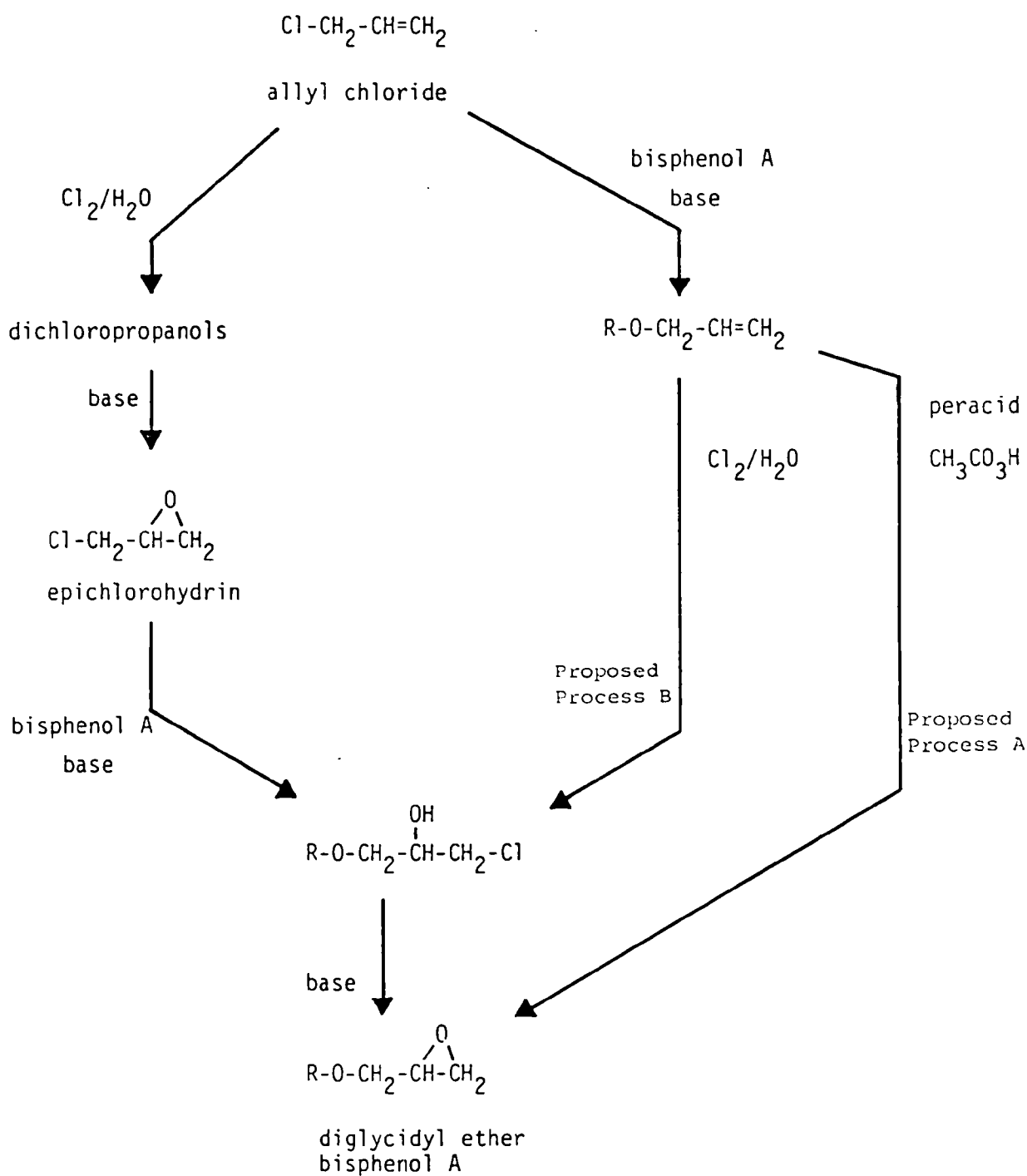


Figure 4.2A. Alternate pathways to the diglycidyl ether of bisphenol A.

of DAEBPA and other aromatic allyl ethers by the reaction of allyl chloride with the phenol in butyl alcohol at 80-90°C using KOH to make the phenolate salt as an intermediate.

Braun and Lee (1976) report that reaction of bisphenol A (115 g) with allyl chloride (38 g) in 300 mL of alcohol with sodium hydroxide (20 g) for 7 h yielded the diallyl ether (21 g) and the monoallyl ether (38 g) of bisphenol A. The mole ratio of bisphenol A to allyl chloride was 1:1 and this limited formation of the diallyl ether. Nonetheless, it is likely that reactions involving allyl chloride and sodium hydroxide in an alkyl alcohol solvent yield substantial byproduct of the allyl alkyl ether. In the experiment by Braun and Lee (1976), the bisphenol ethers only account for 55% of the allyl chloride. Brady et al. (1975) describe a similar synthesis of the diallyl ether of bisphenol A, but do not report the yield.

Reaction of a phenol with an allyl chloride has been used on a large scale to make industrial chemicals. For example, FMC Corporation reacts 2-nitrophenol with 1-chloro-2-methyl-2-propene as the first step in the synthesis of the pesticide carbofuran (Protzel, 1981). Thus, commercial preparation of DAEBPA appears to be technically feasible. The only side reactions expected to possibly lower the yield of this reaction would be the C-alkylation of the phenol that might occur if a non-polar reaction solvent were used (Roberts and Caserio, 1965). At high temperature (above 200°C), the allyl ether might rearrange to the ortho-allyl phenol (Claisen rearrangement) (Roberts and Caserio, 1965).

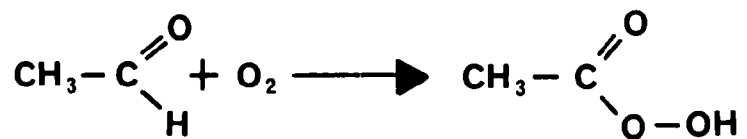
It is noteworthy that the diallyl ether of bisphenol A has potential economic applications beyond formation of epoxy resins. Fielding and Richards (1967) describe its use as a fungicide to protect sugarcane from Rhizoctonia. Brady et al. (1975) used it to prepare bis(2,3-dibromopropyl) bisphenol A ether which was found to be useful as a flame retardant. It has also been used as a crosslinking agent in photocurable lacquers (Guthrie and Rendalic, 1975) and in azo dye reactive dyeing of cotton (Wolf and Weissenborn, 1971). Heating the diallyl ether of bisphenol to about 200°C results in rearrangement to the o,o'-diallyl bisphenol A (Claisen rearrangement; Roberts and Caserio, 1965) that may have uses including formation of unsaturated epoxy resins

(Zahir and Wyler, 1977). High production of the diallyl ether of bisphenol A (as would be the case if it were used instead of ECH to make epoxy resins) would probably make it more available for these types of uses.

Two options for conversion of the diallyl ether of bisphenol A (DAEBPA) to the diglycidyl ether of bisphenol A (DGEBPA) are shown in Figure 4.2A. The practicality of the two methods will be compared in section 4.2.3. The first method involves chlorination of the diallyl ether in alkaline solution to initially produce the bis(propylchlorohydrin) ether of bisphenol A (CAS No. 4809-35-2), which is not stable under alkaline conditions and is an intermediate in the ECH method of forming epoxy resins (see Figure 5.2.1.1A). From that point, formation and isolation of the diglycidyl ether is identical to the ECH-epoxy resin process.

The second option for formation of the diglycidyl ether from the diallyl ether is reaction of the allyl groups with peracetic acid. This process has been described in a patent assigned to Celanese Corporation (Thigpen et al., 1976). Brown and Lee (1976) also used peracetic acid to convert the monoallyl ether of bisphenol A into the monoglycidyl ether.

The process described in the Celanese patent (Thigpen et al., 1976) calls for generating peracetic acid by passing acetaldehyde (bp 21°C) and oxygen (95% O₂, 5% N₂) in a mole ratio of 1:10 through an aluminum reactor at 85°C to produce peracetic acid:



A vapor mixture containing 9.9 mole % peracetic acid, 23.4 mole % acetic acid and 66.7 mole % acetaldehyde was generated and fed at a rate of 4.65 moles per hour to the bottom of a 45-plate distillation column. The column was maintained at 100°C and 250 mmHg (absolute pressure). The diallyl ether of bisphenol A was added to the top of the column at a rate of 0.325 equivalents per hour.

The diallyl ether trickled down through the column and was epoxidized by the counter current of peracetic acid. It then passed through a stripper section below the column that was heated to 150°C to remove acetic acid. The product rapidly cooled and exited the reactor at 30°C.

The crude product contained 5.7 weight % acetic acid and had an oxirane oxygen content of 4.3 weight %. The theoretical oxirane oxygen content of the diglycidyl ether of bisphenol A is 9.41 weight %; after correcting for acetic acid, the product only seems to have had about 48% of the theoretical amount of oxirane oxygen. Nonetheless, it seems likely that the reaction conditions could be optimized to obtain much higher yields of the diglycidyl ether.

Epoxidation of olefins in solution is a more common approach especially for small scale syntheses (Fieser and Fieser, 1967). Commercial solutions of peracetic acid are typically 40% peracetic acid, 5% hydrogen peroxide, 39% acetic acid, 1% sulfuric acid and 15% water (e.g., 0.77 mole peracetic acid/100 mL). Before use, the strong sulfuric acid is usually neutralized by adding 7.7 g of sodium acetate trihydrate per 100 mL of solution. The strong sulfuric acid would cause excessive hydrolysis of the epoxide moiety in the product, if it were not neutralized. The peracetic acid solution is usually added over a short period of time to a solution of the olefin in cool (20°C) methylene chloride or chloroform. The reaction mixture is usually allowed to warm slowly for about a day before washing with 5% aqueous sodium hydroxide followed by drying the organic phase and evaporating the solvent to obtain the product. Yields of purified products are usually 70-75%.

4.2.2 Alternate Process Engineering

In this section we will outline two general processes for commercial-scale manufacture of bisphenol A epoxy resins. For Proposed Process A, we envision a two-step synthesis of the diglycidyl ether of bisphenol A from allyl chloride, bisphenol A and peracetic acid via the diallyl ether of bisphenol A (Figure 4.2A). For Proposed Process B, we envision a three-step synthesis in which allyl chloride and bisphenol A are converted to the diallyl ether, the diallyl ether is converted to the chlorohydrin and the chlorohydrin is converted to the diglycidyl ether (Figure 4.2A).

The first step in the proposed alternate process is summarized in Figure 4.2.2A. The process is based on the duPont patent (Fielding and Richards, 1967) with allyl chloride replacing allyl bromide. This substitution is based on the higher availability and lower cost of allyl chloride compared to allyl bromide. The reaction with allyl chloride would probably require a longer reaction period but no reduction of yield.

A reactor equipped with a stirrer, heater and reflux condenser would be charged with:

	<u>Moles</u>	<u>Weight</u>
bisphenol A	1 mole,	1.00 part
allyl chloride	2.2 moles,	0.74 part
acetone	(solvent),	2.00 parts
potassium carbonate	4 moles,	2.42 parts

The reaction mixture would be heated and stirred at reflux temperature (about 50°C) for about 10 hours. Carbon dioxide would form from reaction of HCl on K_2CO_3 and would be vented. At the end of the reaction period, the reaction mixture would be filtered and the filter would be washed with fresh acetone. The solids would consist of a mixture of potassium chloride and potassium carbonate and would be a solid waste. The organic solution would be distilled at atmospheric pressure to remove acetone and allyl chloride, which would be recycled to the reactor. It might be possible to crudely fraction the acetone/allyl chloride mixture and use the acetone-rich fraction for filter washing while sending the allyl chloride-rich fraction back to the reactor.

The crude product, containing bisphenol A, a few percent acetone and traces of allyl chloride (and possibly some acetone condensation products), would be kept above the melting point (est. 50°C) and contacted with aqueous alkali for several hours to extract bisphenol A and convert allyl chloride to water soluble allyl alcohol.

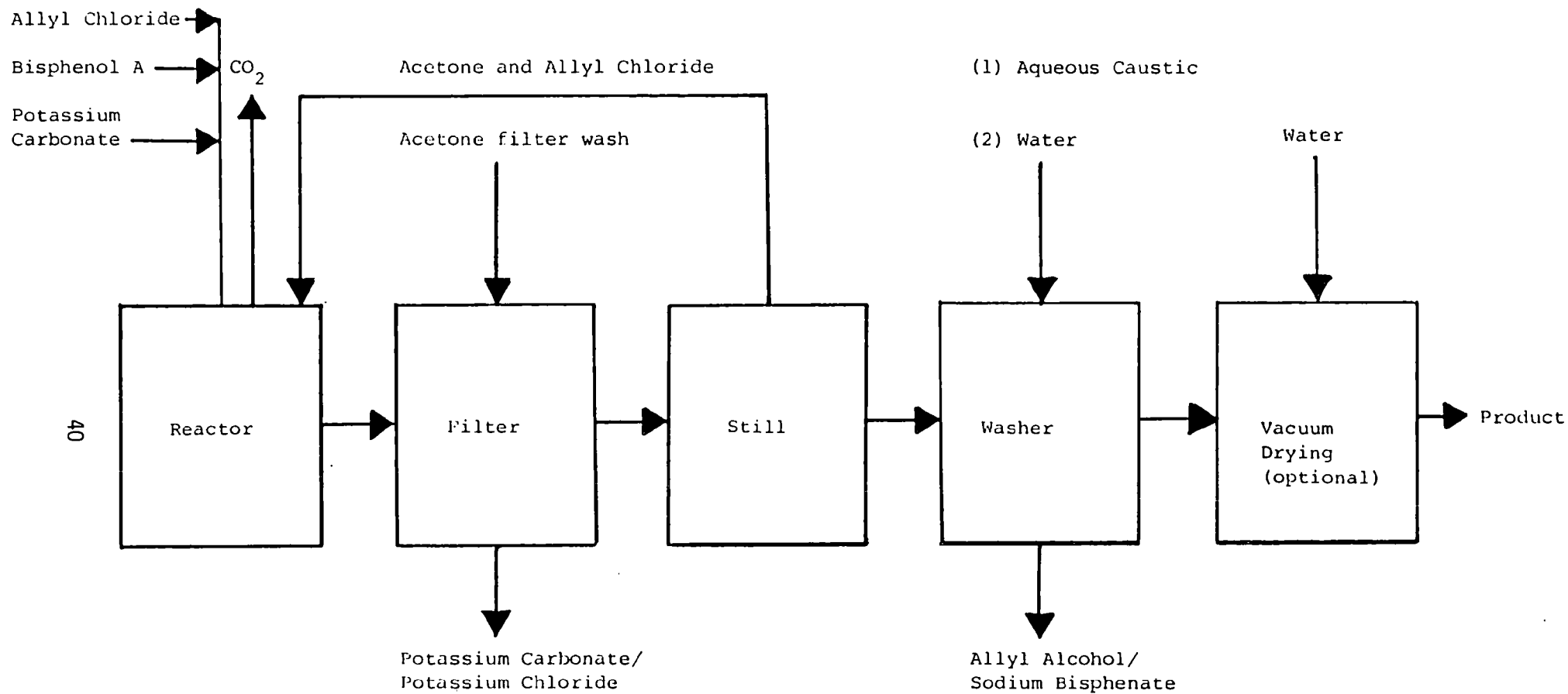


Figure 4.2.2A. Proposed Alternate Synthesis of Bisphenol A Epoxy Resin

Process A, Step 1; Synthesis of Bisphenol A Diallyl Ether.

The alkaline wash would be discarded and the product would be washed one or more times with pure water to remove base. If necessary, the product would be heated to about 100°C in vacuo (10 mmHg) to dry it. However, the subsequent epoxidation reaction does not require dry product. The yield to this point is expected to be about 90% based on bisphenol A. Also less than 5% of the starting acetone and 1% of the starting allyl chloride are expected to be lost. The product might contain traces of allyl chloride, allyl alcohol and acetone condensation products. These impurities could be effectively reduced by extending the alkaline treatment process and vacuum drying the final product.

The second step in Proposed Process A for making the diglycidyl ether of bisphenol A is peracetic acid epoxidation of the diallyl ether of bisphenol A. Celanese (Thigpen et al., 1976) discussed one approach to this epoxidation in a patent. Our hypothetical process is shown in Figure 4.2.2B. It employs the conventional solution epoxidation technique (Fieser and Fieser, 1967). The diallyl ether (obtained as described above) would be dissolved in methylene chloride in a reactor equipped for cooling (20°C), stirring and reflux. Peracetic acid (with sodium acetate) would be added over a period of about 2 hours with cooling to maintain the temperature at about 20°C and about 10% excess peracetic acid would be used. At the end of addition, the reaction mixture would be agitated for approximately 24 hours.

The product would be isolated by washing sequentially with cold 5% sodium hydroxide and cold water. The washes neutralize the acid and extract the acetate salt. The methylene chloride would be distilled at atmospheric pressure and then the diglycidyl ether of bisphenol A would be heated to about 100°C at 1 mmHg to remove the last traces of methylene chloride. The yield would be expected to be about 80% based on the diallyl ether. The product should be relatively free of low molecular weight impurities (e.g., CH_2Cl_2 or acetic acid). It might contain the diallyl ether (starting material) and a mixed allyl/glycidyl ether. There might also be some dihydroxypropyl groups and acetic esters of dihydroxypropyl group in the product resulting from ring opening reactions of the epoxide.

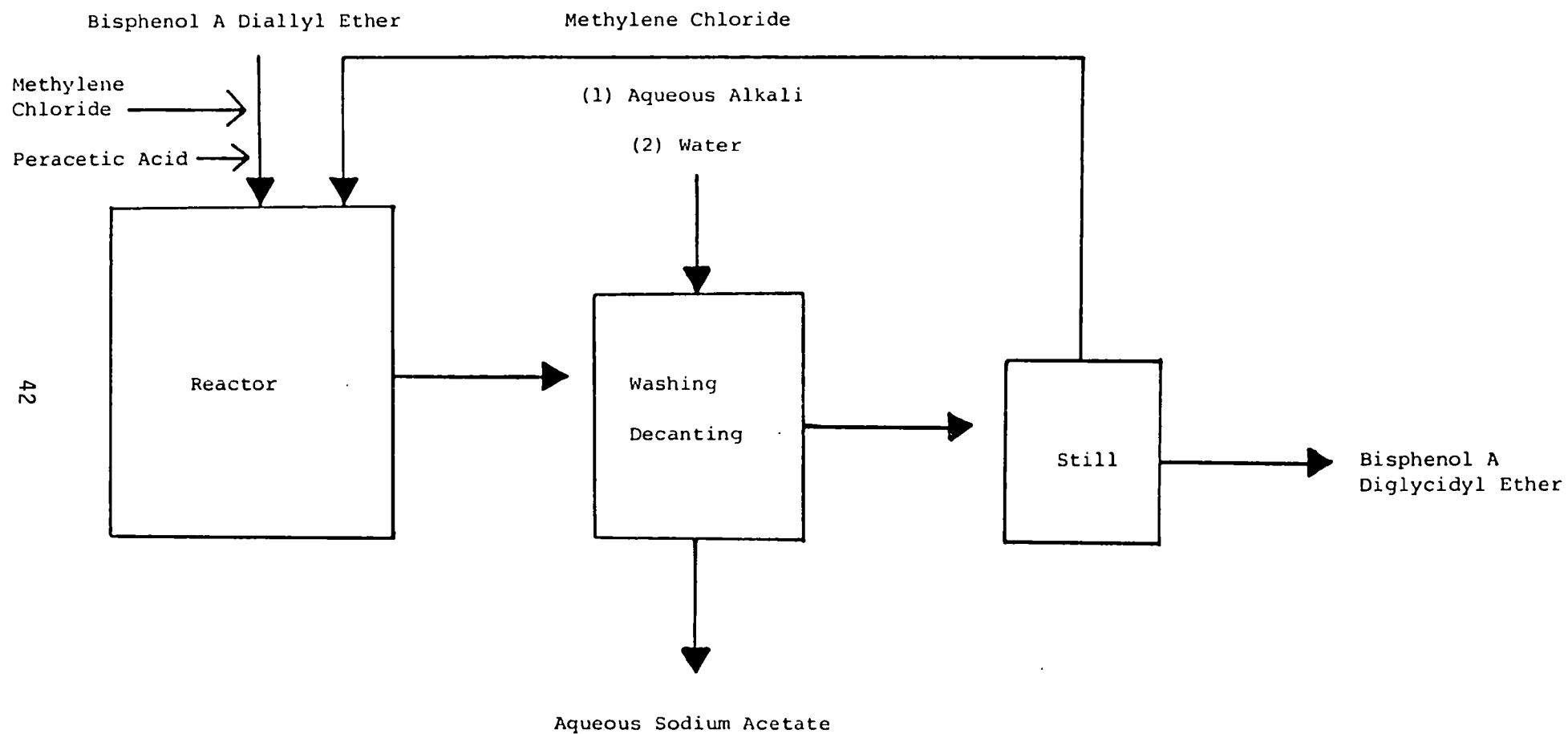
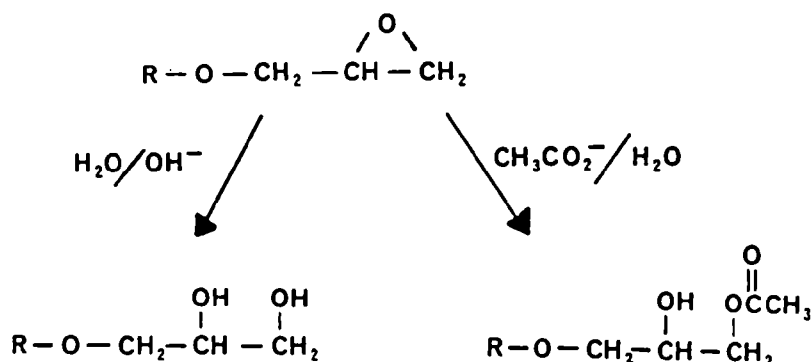


Figure 4.2.2B. Proposed Alternate Synthesis of Bisphenol A Epoxy Resin
Process A, Step 2; Peracetic Acid Epoxidation



Proposed Process B for making the diglycidyl ether of bisphenol A without using epichlorohydrin is designed to use the cheapest starting materials possible although it may have lower overall yields and produce more toxic wastes (Figure 4.2.2C).

The first step of Proposed Process B is reaction of allyl chloride with bisphenol A. It is based upon the approach of Braun and Lee (1976). A reactor equipped with a stirrer, heater and condenser would be charged with bisphenol A dissolved in an excess of allyl chloride. This solution would be heated to reflux (45°C) and 50% aqueous sodium hydroxide would be added at a rate which allows the water to distill out as an azeotrope with allyl chloride (azeotrope bp 43°C, 97% H₂O). This azeotrope should stay as a single phase. The hydroxide would form the bisphenoxide anion that would react with allyl chloride. The reaction would probably require several hours and allyl alcohol would probably be a major byproduct.

The reaction mixture would be heated to distill off most of the excess allyl chloride, which would be recovered for the next batch. The residue would consist of the product, sodium chloride salt and allyl alcohol (bp 97°C). Water would be added to dissolve the salt and extract the allyl alcohol. The aqueous salt and allyl alcohol solution would be mixed with the aqueous allyl chloride from the reactor vent and used as a feedstock for manufacture of glycerin.

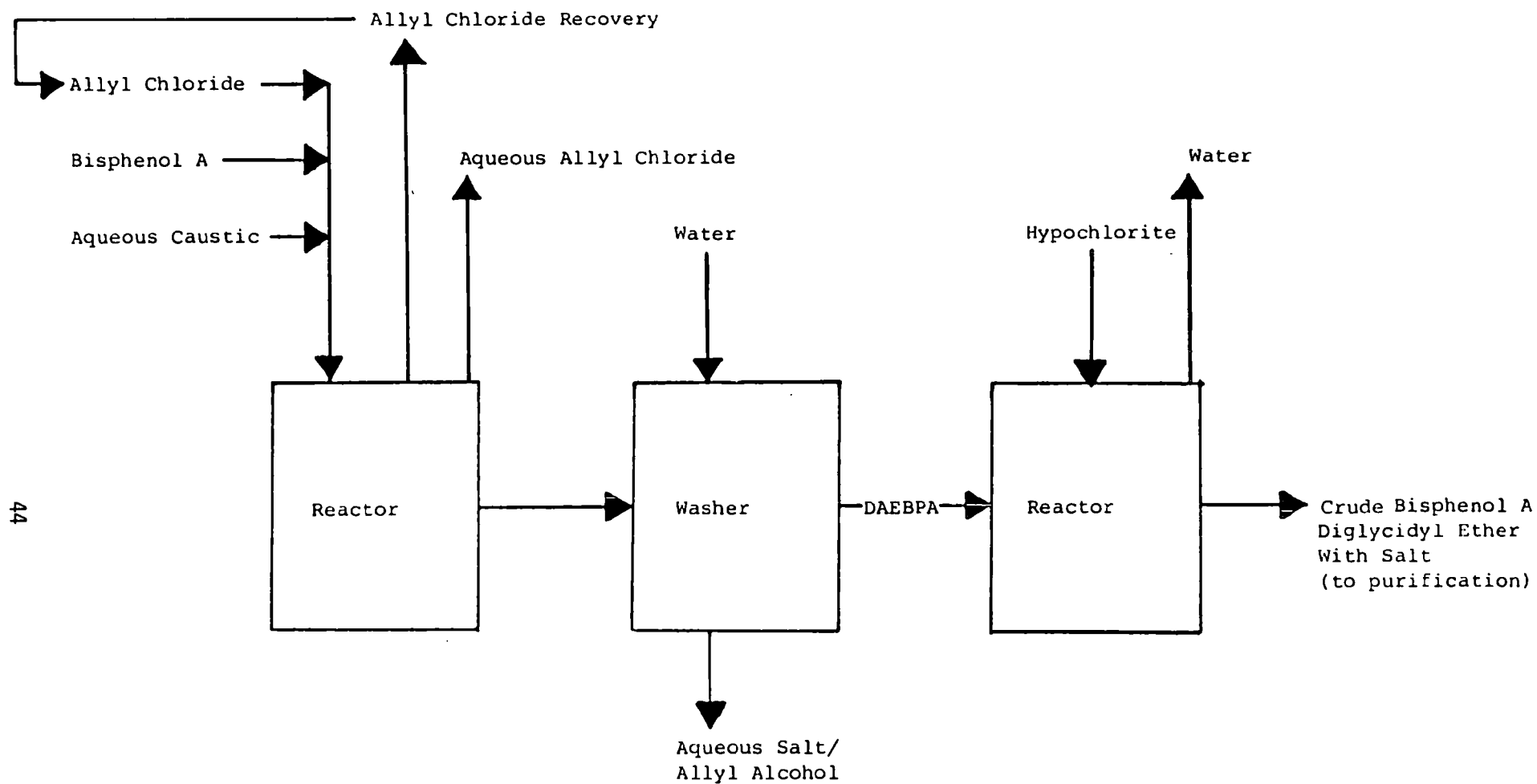


Figure 4.2.2C. Proposed Alternate Synthesis of Bisphenol A Diglycidyl Ether
 Process B, Step 1; Synthesis of the Diallyl Ether of Bisphenol A
 (DAEBPA) and the Diglycidyl Ether of Bisphenol A.

After thoroughly washing with water, the diallyl ether would be heated and stirred and aqueous hypochlorite solution would be added. Excess water would be distilled from the reaction mixture. The chlorohydrin intermediate would form and be converted to the diglycidyl ether (Figure 4.2.2C). At the end of the reaction, the reaction mixture should be similar to the crude product obtained by reacting ECH with bisphenol A and base in the conventional epoxy process (Jones and Chandy, 1974). The reaction mixture would be worked up to isolate the diglycidyl ether of bisphenol A by a procedure very similar to that described in Section 5.2.1.1.

The yield of product based on bisphenol A should be rather good (e.g., 80% overall), but as noted above an appreciable amount of allyl chloride would probably be converted to allyl alcohol in the first step.

4.2.3 Comparative Cost of Manufacturing Epoxy Resins by the Epichlorohydrin Method and the Proposed Alternate Method

For the purposes of this evaluation we are assuming that a company would have to buy all starting materials for manufacturing the diglycidyl ether of bisphenol A from other chemical companies. We also assume that the capital, labor, waste disposal and energy costs of the two processes are similar. Thus, our analysis of comparative costs are limited to the costs of raw materials and solvents to produce equivalent amounts of product.

The results are summarized in Table 4.2.3A. The cost of materials are based upon recent (late 1983, early 1984) data provided by manufacturers for large quantity purchases. We have made chemical and engineering estimates of reaction yields and recoveries of products that are reflected in the quantities of each feedstock listed.

It is apparent from Table 4.2.3A that the cost of peracetic acid and the large quantity of potassium carbonate that would probably be required make Proposed Process A very expensive even though it probably has higher yields than Process B. Production of peracetic acid onsite from acetaldehyde and oxygen as described in a Celanese patent (Thigpen et al., 1976) would probably lower the cost of this process considerably.

Table 4.2.3A. Raw Materials Needed to Produce One Pound of DGEBA

	Cost ^a \$/pound	Conventional Process		Proposed Process A		Proposed Process B	
		pounds ^b	cost(\$)	pounds ^b	cost(\$)	pounds ^b	cost(\$)
Allyl chloride (FW 75)	0.61	0.82	0.50	0.61	0.37	1.0	0.61
Chlorine (FW 71)	0.08	0.77	0.06	-	-	0.53	0.04
Caustic (50% solu.) (FW 40)	0.15	0.87	0.13	-	-	0.79	0.12
Bisphenol A (FW 228)	0.67	0.74	0.50	0.93	0.62	0.82	0.55
Peracetic acid (35%) (FW 76)	2.66	-	-	0.61	1.63	-	-
Potassium carbonate (FW 138)	0.34	-	-	2.29	0.78	-	-
Acetone	0.21	-	-	0.15	0.03	-	-
Methylene chloride	0.29	-	-	0.15	0.04	-	-
<u>Methyl Isobutyl Ketone</u>	<u>0.47</u>	<u>0.09</u>	<u>0.04</u>	<u>-</u>	<u>-</u>	<u>0.09</u>	<u>0.04</u>
DGEBA product:		1.0 pound/\$1.23		1.0 pound/\$3.47		1.0 pound/\$1.36	
Solid wastes produced: ^c		2.29 pound		3.74 pounds ^d		2.23 pounds	

^aBased on current prices for large volume purchases.

Data for peracetic acid are from FMC. Other data are from CMR (Hammaker, 1984).

^bBased on Dynamac chemical and engineering estimates.

^cDisposal cost are not considered here but could be about \$0.05/lb.

^dAbout one pound of this is CO₂ vented from the reactor.

Even with these crude figures, it seems clear that the conventional ECH process for making epoxy resins is the most inexpensive. For comparison, the price for epoxy resin currently listed in Chem. Mkt. Rptr. (1984) is \$1.31 to \$1.41 per pound (bulk liquid in tank cars). If the epoxy resin manufacturers also make many of the feedstocks and coproducts (e.g., glycerin) associated with the manufacture of epoxy resins via ECH, then the unit cost of the conventional process would be even less. It should be noted that the raw material cost of manufacturing bulk epoxy resins from DGEBA produced in any process could be less per pound than DGEBA because excess bisphenol A (\$0.67/lb) would be reacted with DGEBA to make the resins.

4.2.4 Substitutes for Epichlorohydrin-Based Epoxy Resins

In the previous sections (4.2.1-4.2.3), an alternate synthetic scheme for epoxy resin has been considered. In this section, substitutes for epoxy resins in various uses will be discussed. Because of the numerous applications of ECH-based epoxy resins, only a few of the more important areas can be considered. The major application areas for epoxy resins are listed below (Kirk-Othmer, 1980a):

Applications

- Coatings
- Laminated-composites
- Moldings-castings
- Construction
- Adhesives
- Miscellaneous

4.2.4.1 Substitutes for Epoxy Resin Coatings

Protective coatings is the largest market area for epoxy resins (Kirk-Othmer, 1980a). The features that make epoxys desirable in these applications are adhesion, toughness and chemical resistance. Various types of application include automobile primers and finishes, marine coatings, can coatings, and maintenance coatings (e.g., in oil refineries). Most epoxy

coating systems are solvent-based, but epoxy resins are adaptable to the waterborne-high solids and solventless systems. Advantages of epoxy resins in solventless coatings include the ability to apply thick coats, minimal surface defects, excellent resistance to heat and chemicals and low overall application cost. One of the main problems in using epoxy resins as solventless coating is the short "pot life" (i.e., rapid hardening).

The ability to apply thick single coats of epoxy resins is the result of the fact that epoxies do not require oxygen from the air to set (i.e., dry); epoxy resins cure by reaction of the epoxy with a curing agent. The type of curing agent affects the resin coating (Kirk-Othmer, 1979a). The main types of epoxy resin systems are described below:

- o Amine-cured epoxies
 - short pot life
 - high chemical resistance
 - brittle
 - chalk when exposed to weather
- o Polyamide-cured epoxies
 - poorer chemical resistance than amine-cured epoxy
 - better weather resistance than amine-cured epoxy
 - flexible
 - degraded by strong bacterial growth
- o Phenolic-epoxies
 - heat cured
 - most chemically resistant epoxy coatings
- o Coal tar-epoxies
 - good chemical resistance
 - reasonable weather resistance but do chalk
 - excellent resistance to water (fresh, salt, brine, acid, alkaline, anaerobic)
 - excellent durability
 - black to reddish-brown color

These epoxy coatings are compared to other resistant coatings in Table 4.2.4.1A. The cost (1977 data) of various resistant coating materials are shown in Table 4.2.4.1B.

4.2.4.2 Substitutes for Epoxy Resins in Laminates and Composites

Behind coatings, the next largest market area for epoxy resins is laminates and composites (Kirk-Othmer, 1980a). Kirk-Othmer (1981b) indicates that, in principle many polymeric resins that wet reinforcing fibers (glass, graphite) could be used to make laminates, but in practice most reinforced plastics in commerce are based on unsaturated polyester, epoxy or thermoplastic matrix materials.

Unsaturated polyesters and epoxies are both liquids that are irreversibly cured. In the case of polyester, a prepolymer (oligomer) is formed from an anhydride (usually maleic anhydride) and a diol and an inhibitor (hydroquinone) is added to prevent premature crosslinking. Then the prepolymer and styrene are mixed with the reinforcing fibers in a mold and benzoyl peroxide is added to initiate the polymerization in which styrene crosslinks the prepolymer via the maleic acid moieties. In the case of epoxy resins, the epoxy is mixed with the reinforcing fibers and a curing agent, which crosslinks via the epoxide moieties. During hardening, unsaturated polyesters shrink about 8% in volume and epoxy resins shrink about 4% in volume. Because the fibers do not shrink, internal stresses are created. The epoxies are better than the polyesters from that standpoint. Epoxies also adhere to most surfaces better than polyester, are more resistant to water and can be cured more precisely than polyesters (Kirk-Othmer, 1981b). However, polyesters are cheaper than epoxies (Kirk-Othmer, 1981b) and polyesters may have better electrical resistivity because halogen-containing moieties in epoxy resins may give rise to ions during curing.

Thermoplastics such as nylon, polycarbonate, polyester, polypropylene and SAN are also used for forming laminates. Thermoplastic laminates are particularly useful for injection molding and extrusion, where unsaturated polyester and epoxy resins cannot be used.

Table 4.2.4.1A. Properties of Resistant Coatings^a

Uses of resistant coatings	Lacquer coatings				Coreactable coatings		
	Vinyl chloride-acetate copolymer	Vinyl-acrylate copolymer	Chlorinated rubber	Coal tar-pitch (hot melt)	epoxy-amine	epoxy-polyamide	Coal tar-epoxy
Abrasion resistance	G	G	G	F	G	G	G
Bacterial and fungal resistance	E	G	G	G	G	NR	G
Chemical resistance	BSR	G	BSR	G	G	G	G
acid-oxidizing	S or F	F	S or F	NR	NR	NR	NR
-nonoxidizing	S or F	F	S or F	F	F	F	F
-organic	I fatty acid	F	dissolves in fatty acids	NR	Spillage, F	F	NR
alkali	G	D	G	G	G	G	G
salts-oxidizing	Splash, S	F or D	F or D	NR	F	F	F
-nonoxidizing	I, G	F or D	I, G	sea water G	I, G	I, G	I, G
solvent-aliphatic	E	F	G	NR	E	G	G
-aromatic	swells	dissolves	dissolves	NR	G	NR	NR
-oxygenated	dissolves	dissolves	dissolves	NR	NR	NR	NR
water	VGI	G	VGI	E	VGI	VGI	VGI
Moisture permeability	low		low	low	low	low	low
Contamination of contacting materials							
food	C		water, G	water, G	G	G	NR
chemical	VG		G		G	G	F
decontamination	VG				VG	VG	NR
Friction resistance (faying surfaces)							
Heat resistance, °C							
wet	48	38	38	48	48	48	48
dry	65	65	60	65	95	95	95
Radiation resistance, Gy ^d	10 ⁶		10 ⁶		10 ⁷	10 ⁸	5x10 ⁶
Soil resistance				E			G
Weather and light resistant	G, properly pigmented	E	G, properly pigmented	NR	heavy chalking	G	chalking
Principal hazard	solvent F	solvent F	solvent F	coal tar F	dermatitis solvent F	solvent F	dermatitis solvent F

^aG, Good; VG, Very Good; E, Excellent; NR, Not Recommended; BSR, Broad-Spectrum Resistance; I, Immersion; S, Spray; F, Fumes; D, Dusts.

^bG, primer required; critical for immersion.

^cG, odorless; tasteless; nontoxic.

^dTo convert gray to rad, multiply by 100.

Source: Kirk-Othmer (1979a)

Table 4.2.4.1B. Typical High-Performance Coating Material Costs, 1977

	Cost/m ² per 25 µm thickness (\$)	Cost/m ² per recommended thickness (\$)
4-coat water tank, vinyl	0.376	2.26
6-coat vinyl food lining	0.495	4.95
2-coat high-build vinyl (ext)	0.258	2.58
2-coat polyamine-epoxy tank lining	0.204	2.04
3-coat polyamide-epoxy (exterior)	0.247	3.44
3-coat epoxy-phenolic tank lining	0.430	5.16
2-coat coal tar-epoxy	0.118	1.93
inorganic zinc	0.398	1.18

Adopted from Kirk-Othmer (1979a).

The main applications for epoxies in the areas of laminates and composites are in electrical laminates (e.g., printed circuit boards) and filament winding (e.g., filament-wound glass-reinforced pipe). To achieve flame retardance in electrical applications, the diglycidyl ether of tetrabromobisphenol A is used as the basic epoxy building block (Kirk-Othmer, 1980a). Some specialized epoxies such as the tetraglycidyl ether of methylenedi (aniline) cured with diaminodiphenylsulfone are used in the aerospace industry for their high temperature performance in ablative materials (reentry vehicles) (Kirk-Othmer, 1980a).

The total market for reinforced polyester laminates and composites was 798,000 metric tons in 1978 while the reinforced epoxy market was relatively small at 24,000 metric tons (Kirk-Othmer, 1981b). In the electrical area, polyesters were used at a rate of 73,000 metric tons compared to 10,000 metric tons for epoxies; and only 9,000 metric tons of epoxies were used in filament windings while over 100,000 metric tons of polyesters were used in each of the following areas: marine, transportation, construction, and appliance-aerospace-consumer. It appears that polyesters dominate the laminate/composite areas except where specialized epoxies have demonstrated superior performance and cost is not important.

4.2.4.3 Substitutes for Epoxy Moldings and Castings

Epoxy resins used for molding are generally solids while liquid epoxy resins are used for casting. The uses of epoxy molding as casting materials are generally as follows (Kirk-Othmer, 1980a):

Molding

- Transfer molding - encapsulation of solid state electrical components using cresol-novolac solid epoxy resin with phenol or cresol novolac hardener.
- Compression molding - fabrication of large fiber-reinforced parts (impellers, valves, pipefittings, pump housings).

Casting

Large electrical components including post insulators, bus-bar supports, switchgear components, transformers, and encapsulated coils for indoor use and tools.

Other resins used for molding include phenolic resins, amino resins and unsaturated polyester resins. Unsaturated polyesters are used for casting.

Phenolic resins used for molding are usually novolacs in powder or pellet form cured with hexamethylene-tetramine. Transfer, compression, and injection molding techniques are used. The cured resins resist high temperature and solvents and have good electrical properties (dielectric constant ca. 5.0) and are used for auto distributor caps, relays, brake pistons, and appliance parts that are exposed to high temperature (Kirk-Othmer, 1982a).

Amino resin molding compounds are typically urea-formaldehyde or melamine-formaldehyde methylol compounds combined with alpha cellulose pulp and dried to a hard popcorn-like intermediate. Catalysts, stabilizers, colorants and mold lubricants are mixed with the intermediate to form the molding compound. Amino resin molding compounds are used for decorative products such as melamine plastic dinner plates; but the excellent electrical properties, resistance to heat, hardness and strength make them useful in industrial applications. They currently are more costly than phenolic resins and they do not resist water as well as phenolic resins (Kirk-Othmer, 1978a).

Unsaturated polyester resins with high fumarate (replacing maleate) content along with fillers (clays), thermoplastics and thickeners (metal oxides) are mixed with a high temperature polymerization initiator (t-butyl perbenzoate) and used for sheet molding. The sheet molding compound is mixed with chopped fiber glass and sandwiched between layers of polyethylene film. The sandwich is stored as a roll until the viscosity of the molding compound rises (due to crosslinking between the fumarates). The sandwich is finally cut and molded under high pressure and temperature to yield parts with smooth glossy surfaces. These parts have most application as sections of automotive exterior skin (Kirk-Othmer, 1982b).

Unsaturated polyester resins have numerous applications as cast objects including bowling balls, simulated marble, furniture parts, floor tile, buttons and electrical encapsulation (Kirk-Othmer, 1982b).

4.2.4.4 Substitutes for Epoxy Resins in Construction

Currently the only significant use for epoxy resins considered under the category of construction is in flooring (Kirk-Othmer, 1982c). Only 8,000 metric tons of epoxy resins were used for this purpose in 1979 as compared to 168,000 metric tons of calendered vinyl and 61,000 metric tons of urethane foam underlay. The epoxies are probably used in applications where chemical resistance and heat resistance are required.

4.2.4.5 Substitutes for Epoxy Adhesives

Epoxy, acrylic, urethane, silicone and unsaturated polyesters are examples of adhesives that "cure" (i.e., undergo chemical reaction) rather than "set" when applied (Kirk-Othmer, 1978b).

4.3 Alternate Processes for Synthesis of Glycerin

Glycerin is obtained as a byproduct of soap manufacture and from several synthetic processes (Lowenheim and Moran, 1975). According to Cogswell et al. (1983), natural glycerin from soap manufacture is available in adequate supply to meet most demands, although there was a period in the early 1970s when synthetic glycerin dominated the market because of excess ECH capacity (Lowenheim and Moran, 1975). At that time, three synthetic glycerin processes were used:

- glycerin from allyl chloride via ECH (see Section 5.2.2)
- glycerin from propylene via acrolein
- glycerin from propylene via propylene oxide

Prior to 1969, a fourth process involving reduction of molasses was also used.

Statistics compiled by Cogswell et al. (1983) show the impact of increased cost (e.g., production of glycerin from propylene oxide is energy intensive (Fisher, 1983)) on the manufacture of synthetic glycerin after the 1973-1974 period. The production of glycerin from each process decreased in a stepwise fashion:

Estimated U.S. Production of Synthetic Glycerin
(millions of pounds)

	<u>by Dow and Shell</u> <u>via ECH</u>	<u>by Shell</u> <u>via acrolein</u>	<u>by FMC</u> <u>via propylene oxide</u>
1973	139	40	29
1977	75	33	33
1980	99	16	26
1982	78	0	8

Shell stopped production of synthetic glycerin via acrolein in mid-1980; FMC stopped production via propylene oxide in early 1982 (Fisher, 1983).

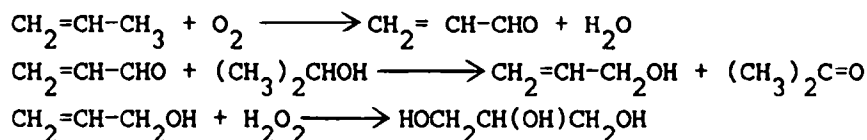
The producers of natural glycerin currently have a capacity estimated at over 200 million pounds per year, and National Distillers and Chemical Corporation has announced a \$50 million expansion at its Cincinnati, OH plant by 1984 (Hammaker, 1983).

It can be concluded that virtually all current demand for glycerin (about 290 million pounds per year, Cogswell et al., 1983) could be met by natural glycerin and synthetic glycerin from sources other than ECH. Cogswell et al. (1983) project slow growth for the glycerin market through 1987 with a demand for 300 to 305 million pounds in that year. Based on the projection that only ECH-derived synthetic glycerin will be used, Cogswell et al. (1983) predict that the 1987 demand for ECH in this use will be 107-117 million pounds (1.15 pounds of crude ECH are needed to make a pound of glycerin).

Regulatory restrictions against the use of ECH to manufacture glycerin or increased pressure to remove residual ECH from synthetic glycerin would not reduce the availability of glycerin but would probably increase its cost. The most reasonable approach to avoid potential exposure to ECH residues (if any) in synthetic glycerin would probably be to direct ECH synthetic glycerin into manufacture of products like nitroglycerin or alkyd resins in which the reaction conditions would favor hydrolysis of the oxirane ring.

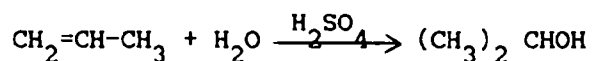
4.3.1 The Acrolein Process

Lowenheim and Moran (1975) summarize the chemistry and engineering involved in manufacture of glycerin via acrolein. The chemical reactions are as follows:



The yield of the first step is 85%; the yield of the second step is 77%; and the yield of the third step is 80 to 90%. Thus, the overall yield for the manufacture of glycerin based on propylene is 52% to 59%.

It should be noted that oxygen and propylene are the only raw materials needed in this process. Propylene can be converted to isopropyl alcohol in 70% yield:



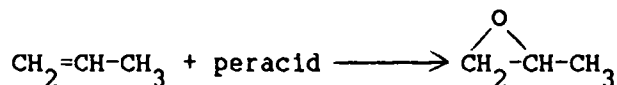
and isopropyl alcohol can be used to make hydrogen peroxide in 87% yield

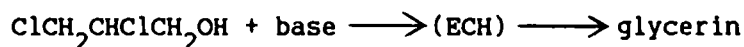
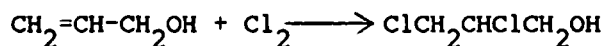
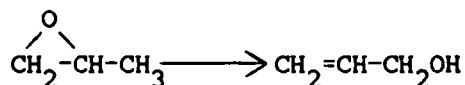


(Lowenheim and Moran, 1975). Thus, using these processes, propylene and oxygen can be used to produce glycerin with acetone as a byproduct and hydrogen peroxide and isopropyl alcohol as intermediate reactants.

4.3.2 The Propylene Oxide Process

Glycerin has also been made from propylene by the series of reactions shown below (Lowenheim and Moran, 1975):

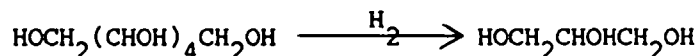




Lowenheim and Moran (1975) indicate that ECH is an intermediate in the process as shown above. However, it appears that the chlorination step could be applied in water to yield chlorodihydroxypropane, which would yield glycerin via glycidyl alcohol rather than ECH.

4.3.3 The Invert Molasses Process

A final process for making glycerin described by Lowenheim and Moran (1975) involves catalytic reduction of invert molasses to mannitol and sorbitol. The sorbitol can be split into two moles of glycerin by high temperature hydrogenolysis:



4.3.4 Comparison of Synthetic Glycerin Processes

As discussed by Lowenheim and Moran (1979), synthetic glycerin plants are integrated with the manufacture of other chemicals and cost are difficult to determine. The feasibility of manufacturing glycerin will be affected by the prices of its coproducts. For example, the markets for acrolein, isopropanol, allyl alcohol, acetone and hydrogen peroxide all affect the desirability of manufacturing glycerin from propylene via acrolein. We have not attempted to untangle these many factors, but we note that the net result was that during the mid-1970s processes used by Dow, Shell and FMC to make synthetic glycerin were competitive with natural glycerin from soap manufacture. Currently, glycerin from epichlorohydrin seems to be the only synthetic glycerin competitive with natural glycerin. This situation may continue because glycerin manufacture constitutes a method of recycle/reuse of wastes from manufacture of allyl chloride and epichlorohydrin.

4.4 Substitutes for Epichlorohydrin Elastomers

The elastomers made from epichlorohydrin have many very useful properties (Houston, 1975; Kirk-Othmer, 1979a; Scheer, 1978). In general, they have good tear resistance and impact strength, but the factors that have made them the materials of choice in certain applications are their resistance to fuels (especially partially oxidized fuels, unleaded aromatic fuels and methanol (Gummikunst, 1980)) under conditions of appreciable heat (up to 300°F) and their ability to retain flexibility at low temperatures (-70°F; CPI Mgmt, 1972). According to ML Zwickert and NC MacArthur of Hercules (cited in R & P News, 1981), the copolymer of ECH and ethylene oxide (ECO; CAS No. 24969-10-6) is subject to depolymerization with progressive formation of a lower strength, solvent-swollen material during prolonged exposure to "sour" (oxidized) gasoline containing hydroperoxides. The homopolymer of ECH (CAS No. 24969-06-0) has better resistance to oxidized gasoline and meets General Motors specification GM 6498M.

The most important limitation on applications of ECH elastomers is loss of tensile strength during service, although hardness increases less during aging than with most other elastomers (Gummikunst, 1982). The fatigue life of ECH-elastomer bonds to metal has been noted as problem in using ECH-elastomers for shock-absorbing motor mounts (Rubber Age, 1972). The price of ECH-elastomers has been a limitation to its commercial success. In 1975, the price of ECH-elastomers was about \$1.15/lb (Houston, 1975).

Overall, the uses of ECH homopolymer seem to be in applications where resistance to heat and fuel are most important, whereas the uses of ECH-ethylene oxide copolymer seems to be in applications where resistance to fuel and low temperature flexibility are most important. Some examples found in the trade literature are as follows:

ECH Homopolymer (CAS No. 24969-06-0)

Automotive seals and gaskets	(R & P News, 1982; Elast., 1977)
Automotive hoses and tubes	(R & P News, 1981; Chem. Mkt. R., 1979)
Liners for hazardous waste ponds (0 to +325°F)	(Hercules, 1983a)

ECH-Ethylene Oxide Copolymer (CAS No. 24969-10-6)

Wellhead seals for arctic oil production	(World Oil, 1976)
Arctic-weather petroleum hose ("Blue Arctic Flexwing")	(CPI Mgmt., 1972)
Liners for hazardous waste ponds (-40 to 300°F)	(Hercules, 1983a)

The other ECH elastomers found in the TSCA Inventory seem to have few, if any, commercial uses. These elastomers include:

<u>ECH-Polymer</u>	<u>CAS No.</u>
ECH polymer with propylene oxide	24969-08-2
ECH polymer with ethylene oxide and propylene oxide	25931-44-6
ECH polymer with allyl glycidyl ether	24969-09-3
ECH polymer with ethylene oxide and allyl glycidyl ether	26587-37-1

A Japanese company has a patent to use the last polymer listed above (CAS No. 26587-37-1) as a cover for rubber pipes and hoses. It is composed of 35 to 80 mole % ECH, 15 to 50 mole % ethylene oxide and 5 to 15 mole % unsaturated epoxide (allyl glycidyl ether). It is vulcanized with a di- or tri-mercapto-s-triazine (Fukushima et al., 1980). This ECH terpolymer (ETER) can also be crosslinked with peroxides (Gummikunst, 1981). It is believed that B.F. Goodrich calls this polymer Hydrin 400 (Scheer, 1978).

Mohan (1977) summarized the properties and costs of elastomers that are competing for uses similar to those of polyepichlorohydrin (Table 4.4A). It can be concluded from the data in Table 4.4A that the polyepichlorohydrin elastomers do not appear to be essential for any use, but they offer good properties at moderate prices. For low temperature, fuel-contact applications, only silicones and ethylene acrylic rubbers offer similar properties and both of these are much more expensive than the polyepichlorohydrin rubber.

Table 4.4A. Synthetic Rubbers Uses in Hot/Oil Automotive Applications

Type	Tradenames	Producer	Properties	Typical Uses	Typical Cost (1977) (\$/lb)
Polyepichlorohydrin	Herclor Hydrin	Hercules B.F. Goodrich	Resistant to heat (325°F), oil, fuel, ozone; good low temperature flexibility (-40°F)	Hose & tubing, molded products, diaphragms	\$1.20-1.40
Polychloroprene	Neoprene (generic)	Denka Chemical DuPont	Resistant to heat (250°F), oil, weathering; good dynamic properties	Hose, tubes and covers, V-belts, molded parts, sponge seals	\$0.60-0.80
Ethylene Propylene (EPDM)	EPCAR Epsyn Nordel Royalene Vistalon	B.F. Goodrich Copolymer Corp. DuPont Uniroyal Exxon Chem.	Resistant to heat (275°F), marginal oil resistance, good electrical properties, ozone and weather resistant	Door & window seals, wire insulation, sight shields	\$0.45-0.63
Fluoroelastomer	Fluorel Viton	Minnesota Mining DuPont	Resistant to heat 400°F constantly, 600°F intermittently, excellent resistance to fuels and oils	O-ring seals, shaft seals, carburetor, tips, diaphragms	\$12.00
Silicone	Silastic Rhodorsil	General Electric Dow Corning SWS Silicones Co. Rhodia, Inc.	Resistant to heat (500°F), oil, solvents, good electrical properties, low compression set, low temperature flexibility (-150°F)	Seals, wire insulation, spark plug boots	\$3.00-5.20
Polyacrylate	Cyanacryl Hycar	Amer. Cyanamid B.F. Goodrich	Resistant to heat (350°F), oil resistant	Oil seals, valve stem seals	\$1.35-1.60
Ethylene Acrylic	Vamac	DuPont	Resistant to heat (375°F), oil resistant; vibration damping, low temperature flexibility	Seals, body mounts	\$1.50
Butadiene Acrylonitrile (nitrile rubber, NBR)	Chemigum FR-N Hycar Krynac Nysyn Paracril	Goodyear Firestone B.F. Goodrich Polysar, Ltd. Copolymer Corp. Uniroyal	Resistant to heat (250-300°F) transmission fluids, oil, oxidation and ozone	Transmission, valve stem and crankshaft seals hose tubes	\$0.60-0.80
Chlorosulfonated Polyethylene	Hypalon	DuPont	Resistant to heat (300°F), oil and complete ozone resistance, weather resistant	Hose tubes and covers, ignition cable jacket, spark plug boots	\$0.73-0.83

Adapted from Mohan (1977), Hawley (1977).

4.5 Substitutes for Epichlorohydrin Wet-Strength Resins

There are two general classes of ECH wet-strength resins; one group is based on aminopolyamide resin, the other group is based on polymeric amines (Kirk-Othmer, 1981a). The newer polymeric amines include polymers of diallylmethylamine, which contain only tertiary amines and form "perepiquat" resins with ECH (Van Eenam, 1980). The polyamine resins do not appear to be very important commercially (Kirk-Othmer, 1981a). The technology associated with manufacture and use of these resins is discussed in Section 5.2.4.

The aminopolyamide resins were introduced in 1958 by Hercules, Inc. and the polyamine resins were introduced in the 1970s (Kirk-Othmer, 1981a). They cost more than urea-formaldehyde and melamine-formaldehyde resins but they are more efficient and are cured at neutral or alkaline pH, which avoids embrittlement of the paper, reduces corrosion of the paper making equipment and provides a softer, more absorbent product (Kirk-Othmer, 1981a).

Kirk-Othmer (1981a) discusses four types of resins that might be used as substitutes for ECH wet-strength resins:

- urea-formaldehyde resins
- melamine-formaldehyde resins
- aldehyde-modified resins
- polymeric amines

As noted above, the formaldehyde resins are functional and cheaper than the epichlorohydrin resins, but they have undesirable characteristics. Resins containing free aldehyde moieties can also be used as wet-strength resins (probably by forming hemi-acetals). However, the wet-strength provided by these resins decreases upon soaking (probably due to hydrolysis of hemi-acetals). This property makes these resins suitable for treatment of sanitary tissues (Kirk-Othmer, 1981a), which can break down to pulp in sewer systems. Polymeric amines, like polyethyleneimine and chitosan (a polysaccharide based on glucosamine obtained from the exoskeleton of insects, crabs, etc.) have been considered but polyethyleneimine is more expensive and less efficient than other resins. Chitosan is not available on a large scale although it is cheap and potentially abundant.

Some of the ECH wet-strength resins might be accessible via alternate synthetic schemes. For example, treatment of an aminopolyamide or polyamine (like polydiallylmethylamine) (see Section 5.2.4) with allyl chloride would produce a cationic resin with quaternary ammonium sites. This resin could be activated prior to treatment of paper either by addition of hypochlorite at pH 11 or peracetic acid. If hypochlorite were used the process should yield very similar results compared to the current wet-strength resins. A major advantage of the "perallylquats" compared to "perepiquats" would be complete absence of a tendency to gel during production or storage. Moreover, the presence of allyl groups as well as chlorohydrin (incipient glycidyl) groups in the hypochlorite-activated "perallylquat" resins would give the interesting property of being able to crosslink cellulose or wool with unsaturated polyester. Since allyl chloride and hypochlorite are used to make epichlorohydrin, the cost of obtaining wet-strength resins by this route should be similar to the usual process. The only limitation on this approach would be that the allyl-treated polymer should have few unquaternized amino moieties because these would tend to be oxidized by hypochlorite or peracetic acid.

4.6 Substitutes for Epichlorohydrin-Based Water Treatment Chemicals

There are several hundred synthetic flocculants currently available commercially, but these are composed of a relatively few types of chemicals (Kirk-Othmer, 1980c). These agents are used to flocculate and coagulate suspended solids and allow their removal from water by sedimentation or filtration. Flocculants can be classified according to the source as inorganic (e.g., alum), synthetic organic or natural (e.g., starch, protein), but these classifications do not reveal much about their applications, which will be discussed below. The trends in flocculant useage discussed in Kirk-Othmer (1980c) seem to indicate that alum and natural products (starch and protein celloids) are being replaced by synthetic organic polymers. In 1977, the projected annual growth rate for synthetic organic flocculants was 8 to 10% per year through 1985 (W.J. Storch, Chem. Eng. News 56(4):9 (1978) cited in Kirk-Othmer, 1980c). General economic data for major classes of flocculants is listed in Table 4.6A.

Table 4.6A. Economic Data for General Classes of Flocculants

Chemical	U.S. Consumption as Flocculant	Price
Alum	0.4×10^6 t in 1978	16¢/kg in 1979
Lime	2.0×10^6 t in 1978	3.4¢/kg in 1979
Ferric Chloride	0.06×10^6 t in 1975	9.9¢/kg in 1975
Synthetic Organics	0.02×10^6 t in 1977	\$2.75 to \$5.00 in 1977

Source: Kirk-Othmer (1980c).

Selection of flocculants is always based on cost and performance factors (Kirk-Othmer, 1980c). The performance of a flocculant is affected by factors such as pH, temperature and ionic strength of the turbid stream and the concentration and nature of the solids to be flocculated. The most important performance factor in municipal water treatment may be clarity of the final product, although in mineral recovery settling, rate may be more important. Kirk-Othmer (1980c) provides a lengthy table of typical uses for various flocculants. For synthetic organics, the factors that are important in determining uses are the molecular weight (low = 10^3 to 10^5 , medium = 10^5 to 10^6 , high = 1 to 5×10^6 , very high = greater than 5×10^6), the charge density (percentage of monomer units that contribute charge) (low = 1 to 10%, medium = 10 to 40%, high = 40 to 80%, very high = 80 to 100%), the nature of the charge (cationic or anionic), and whether or not the charge is constant or varies with pH.

Cationic synthetic organic polymers listed in Kirk-Othmer as commercial products are presented in Table 4.6B. Two of these are polymers of ECH with methyl- or dimethyl-amine. Based on comments in Kirk-Othmer (1980c), the most important commercial compounds are the poly[N-(dimethylaminomethyl)-acrylamide] and poly(2-hydroxypropyl-1-N,N-dimethylammonium chloride). These polymers are expected to be used for municipal and industrial water supply clarification, thickening iron ore concentrates and tails, and sewage sludge dewatering. Alum, lime and ferric chloride are all applied for these same uses. Thus, there are many potential substitutes for ECH-based water-treatment chemicals.

Table 4.68. Principal Commercial Synthetic Organic Polymers Used as Cationic Flocculants

	CAS No.	Structure	Comments
poly(ethyleneamine)	26913-06-4	$\text{-(CH}_2\text{CH}_2\text{NH)}_n$	charge density varies with pH
^a poly(2-hydroxypropyl-1-N-methylammonium-chloride)	31568-35-1	$\text{-(CH}_2\text{CH(OH)CH}_2\text{-NH(CH}_3\text{)}^+\text{)}_n$	charge density varies with pH
^a poly(2-hydroxypropyl-1-N,N-dimethylammonium chloride)	39660-17-8 ^b	$\text{-(CH}_2\text{CH(OH)CH}_2\text{-N(CH}_3\text{)}_2^+\text{)}_n$	strongly cationic, pH-insensitive, chlorine-resistant
poly[N-(dimethylamino-methyl)acrylamide]	25765-48-4	$\text{-(CH}_2\text{CH(O}=\text{C-NHCH}_2\text{N(CH}_3\text{)}_2\text{))}_n$	charge density varies with pH
poly(2-vinylimidazolium bisulfate)	—	$\text{-(CH}_2\text{CH(NH-CH}_2\text{-NH)}^+\text{)}_n$	charge density varies with pH
poly(diallyldimethylammonium chloride)	26062-79-3	$\text{-(CH}_2\text{CH(CH}_2\text{N(CH}_3\text{)}_2^+\text{CH}_2\text{))}_n$	strong cationic, pH-insensitive, chlorine-resistant
poly(N,N-dimethylaminoethyl methacrylate)	25145-86-3	$\text{-(CH}_2\text{C(CH}_3\text{)(OCH}_2\text{CH}_2\text{N(CH}_3\text{)}_2\text{))}_n$	charge density varies with pH
poly[N-(dimethylaminopropyl)-methacrylamide]	64080-86-0	$\text{-(CH}_2\text{C(CH}_3\text{)(O}=\text{C-NHCH}_2\text{CH}_2\text{CH}_2\text{N(CH}_3\text{)}_2\text{))}_n$	charge density varies with pH

^aBased on epichlorohydrin

^bListed in TSCA Inventory under 25988-97-0 "ECH polymer with N-methylmethaneamine"

Source: Kirk-Othmer (1980c).

4.7 Substitutes for Alkyl Glyceryl Ether Sulfonates

The Proctor and Gamble Company has several patents on various uses of alkyl glyceryl ether sulfonates (AGES):

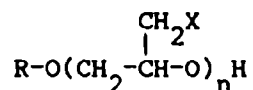
<u>Use</u>	<u>U.S. Patent</u>
Ternary synergistic sudsing detergent composition	3,332,879
Detergent composition having superior sudsing characteristics (synergistic mixture)	3,332,874
Detergent tablets	3,318,817
Unbuilt, high-sudsing, light-duty liquid detergent having special utility under acid conditions	3,179,599
Personal use lotion	2,999,068
Granular detergent bath composition	3,798,179
Nonsmearing detergent bar	2,979,511
Cream shampoo	2,979,465
Opaque liquid detergent composition	2,970,964 and 2,970,963
Liquid detergent composition (single-phase, liquid, heavy duty)	2,877,185
Clear liquid detergent composition	2,877,185
Fabric softener (absorbent sheet)	3,843,395

Other companies have patented uses outside the household/cosmetic detergent field:

<u>Use</u>	<u>Patent</u>	<u>Company</u>
Fabric softener in clothes dryer	4,170,678	A.R. Stanley Mfg. Co.
Photographic coating	3,824,102	Konishiroku Photo Ind.
Foaming agent for removing material from well bore holes	3,773,110	Conoco, Inc.

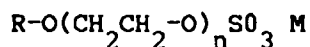
No information was found on the essentiality of AGES for these uses. It can be noted that the composition of AGES is fairly unique among the surfactants commonly employed. Its structure is compared to other surfactants below:

Alkyl glyceryl ether sulfonates (AGES)



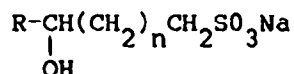
Where R is an alkyl radical containing 8 to 22 carbon atoms, n=1 to 4 and X=Cl, -OH, or -SO₃H and at least one X in each compound of the mixture is a sulfonic acid salt (Whyte and Korpi, 1962).

Alcohol Ethoxy Sulfates (AES)

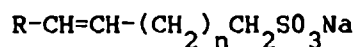


Where R is typically an alkyl radical with 10 to 18 carbon atoms, n=1 to over 12, and M is usually a sodium cation.

Alpha Olefin Sulfonates (AOS)



and



Compounds with 2 or more sulfonates where R is an alkyl group and n=0, 1, 2, 3, etc.

It seems likely that AES or AOS could substitute for AGES in some or all uses. AES are known for their immunity to the negative effects of water hardness, their high foaming capabilities and their "softness" to skin. AOS are said to give a "soft feeling" to washed fabrics. AOS also has detergency and foam properties similar to linear alkylbenzenesulfonates (LAS) and may be superior to LAS in hard water. AOS also has good water solubility (ADL, 1977).

According to Whyte (1976), AGES is inherently more expensive than "workhorse" surfactants (e.g., linear alkylbenzenesulfonates (LAS) and tallow alkyl sulfates) and is not expected to enter the large-volume, heavy-duty laundry product market. AGES can be used in specialty areas where its foam-boosting ability and other performance attributes will compensate for higher cost. It should be noted that Parran et al. (cited in Whyte, 1976) found that a mixture of 70% sarcosinate and 30% AGES provided a voluminous, stable lather for shampoos, but hair oils have a negative affect on the foaming of AGES making it unsuitable as the sole or major surfactant in shampoos.

4.8 Substitute for Epichlorohydrin-Based Anion Exchange Resins

A very small percentage of ECH goes into ion exchange resins. No information was found on application of these resins. However, Rohm and Haas Company (Meteyer and Fries, 1980) claims that ion exchange resins made by reacting alkylpolyamines (e.g., triethylenetetraamine) with ECH followed by alkylation of secondary amines with formaldehyde have enhanced stability with respect to oxidation in test with oxidation by copper/hydrogen peroxide. These ion exchange resins are described as "weakly basic" ion exchange resins and probably could be replaced by other weakly basic ion exchange resins such as Amberlyst A-21 (Rohm and Haas Co.) 4 kg/\$96 (Aldrich, 1982).

4.9 Substitutes for Fyrol 2

Fyrol 2 (tris(1,3-dichloro-2-propyl) phosphate, CAS. No. 13674-87-8) is a flame retardant manufactured by the Stauffer Chemical Company. Parris et al. (1983) classify Fyrol 2 as a plasticizing additive flame retardant and identified several commercial flame retardants that have similar properties. These are summarized in Table 4.9A. Fyrol 2, Antiblaze 78 and Thermolin 101 are all liquids at 30°C and have low vapor pressures. They are used principally in urethane foams (e.g., seat cushions). Tris(monochloroalkyl) phosphates such as

tris(1-chloro-2-propyl) phosphate Stauffer, Fyrol PCF Mobile, Antiblaze 80	(CAS No. 13674-84-5)
tris(2-chloro-1-propyl) phosphate Pelron, 9338	(CAS No. 6145-73-9)
tris(2-chloroethyl) phosphate Pelron, 9500	(CAS No. 115-96-8)

are inferior because they have higher vapor pressures (Parris et al., 1983).

Fyrol 2 could be synthesized from 1,3-dichloro-2-propanol and POCl_3 , but removal of the HCl byproduct might be a problem. It might also be possible to refine the crude dichloropropanol stream from ECH manufacture (waste stream 3B in Figure 5.1.2.B, Saletan. et al., 1977) and react it with POCl_3 to make a flame retardant mixture that would be similar to Fyrol 2.

Table 4.9A. Substitutes for Fyrol 2

Trade name	Manufacturer	Chemical Name/Structure/CAS No.	Comments
Fyrol 2	Stauffer	Tris(1,3-dichloro-2-propyl)phosphate $[(\text{ClCH}_2)_2\text{CHO}]_3\text{PO}$ CAS No. 13674-87-8	Melting point 26.7°C Vapor Pressure 10^{-4} mmHg Solubility in water 100 mg/L
Antiblaze 78	Mobile	Bis(2-chloroethyl) 2-chloroethyl- phosphonate (CAS No. 6294-34-4) and 1,2-Bis(bis(2-chloroethyl)phosphono) -ethane (CAS No. 58823-09-9) $\begin{array}{c} \text{O} \quad \text{O} \\ (\text{ClCH}_2\text{CH}_2\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_2 \end{array}$	Melting point 28°C
Thermolin 101	Olin	Tetrakis(2-chloroethyl) ethylene diphosphates $\begin{array}{c} \text{O} \quad \text{O} \\ (\text{ClCH}_2\text{CH}_2\text{O})_2\text{P}-\text{OCH}_2\text{CH}_2\text{O}-\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_2 \end{array}$ CAS No. 33125-86-9	Pour point -62°C Vapor pressure 0.85 mmHg at 25°C Solubility in water 2 g/L

Source: Parris et al. (1983).

5.0 EPICHLOROHYDRIN MANUFACTURING AND PROCESSING

The history of the manufacture of epichlorohydrin is relevant to the current form of the industry. In the 1940s, there was a demand for glycerin which opened the market for synthetic glycerin. It was known that glycerin could be obtained from allyl chloride by several pathways (Chem. Eng. Progress, 1948). Tymstra (1952) mentions two methods which seem to have been used at the time:

- (1) In the first method, allyl chloride was chlorinated to 1,2,3-trichloropropane, which was hydrolyzed to glycerin.
- (2) In the second method, allyl chloride was hydrolyzed to allyl alcohol, which was hydrochlorinated to chloropropylene glycol (monochlorohydrin), which was subsequently hydrolyzed to glycerin.

Shell Development (Tymstra, 1952) patented a method for conversion of allyl chloride to the dichlorohydrins (i.e., dichloropropanols) via hydrochlorination (i.e., chlorohydrination) followed by hydrolysis to glycerin. This process required dilute solutions because allyl chloride is not very soluble in water (0.36% in water by weight at 20°C; Riddick and Bunger, 1970). The main feature of Tymstra's patent was an idea for reducing the amount of water (and salt) in the final crude glycerin solution by diverting 20 to 75% (preferably 35 to 65%) of the aqueous dichloropropanol solution through a heated (150-210°F) reactor where epichlorohydrin (ECH) was formed. The ECH was distilled from the reactor and recombined with the remaining dichloropropanol stream before final hydrolysis to glycerin.

Another problem that was encountered in this process was the formation of chloroethers as a byproduct during the hydrochlorination of allyl chloride. The only way to avoid the formation of chloroethers was to use dilute solutions. The advantages of forming ECH, which could be easily distilled from water and byproducts, as an intermediate in glycerin production was noted by

Olin Mathieson Chemical Corporation (Thomas, 1958). Olin Mathieson (Thomas, 1958) patented the idea of subjecting the crude dichloropropanol solution to distillation to obtain about 5 to 15% dichloropropanol/water azeotrope (free of chloroethers) and using the undistilled aqueous fraction to generate ECH. As in the Shell Development patent (Tymstra, 1952), the ECH was recombined with the distilled dichloropropanol before hydrolysis to glycerin. The trends in manufacture of glycerin, thus, were to convert chloropropanols to ECH as a convenient method of removing byproducts and minimizing water in the final crude glycerin product. The current process is discussed in Section 5.2.2.

The first epoxy resins were developed in Germany in the late 1930s (Kirk-Othmer, 1980a). In the late 1940s, a series of US patents were assigned to the large US paint manufacturer Devoe and Reynolds. About this time, Shell Development was looking for new markets for ECH, which they were isolating during glycerin manufacture (Jones and Chandy, 1974). Thus, ECH changed from being just an intermediate for glycerin into an important commercial chemical on its own. ECH-epoxy resins are discussed in Section 5.2.1.

In the late 1950s, Hercules, Inc. patented polyether elastomers made from ECH (Vandenberg, 1983). These elastomers are discussed in Section 5.2.3. Hercules also found use for ECH in manufacture of wet-strength resins from aminopolyamides in the late 1950s (Kirk-Othmer, 1981a). These compounds are discussed in Section 5.2.4.

In the mean time, other methods of manufacturing synthetic glycerin were developed (see Section 4.3) and the demand for synthetic glycerin has recently declined. Even though other synthetic glycerin processes have been forced out of the market, the demand for ECH for glycerin is only a small part of the overall demand for ECH. Thus, ECH was once produced incidental to synthetic glycerin, but now synthetic glycerin is produced incidental to ECH.

5.1 Manufacture of Epichlorohydrin

Manufacture of ECH has historically been tied to manufacture of glycerin

(Tymstra, 1952). Moreover, since the same companies make allyl chloride from propylene, the complete propylene to glycerin process is tied together (Lowenheim and Moran, 1975; Chem. Eng. Progress, 1948).

5.1.1 Process Chemistry

The first reaction of interest is the chlorination of propene (propylene) to yield allyl chloride (Fairbairn et al., 1947; Groggins, 1963). Chlorine can react with propene by addition to the double bond to yield 1,2-dichloropropane or substitution for the allylic hydrogen to yield allyl chloride. The addition reaction could involve an electrophilic mechanism but it and the substitution reaction both probably involve free radicals since the industrial reaction is normally conducted at high temperature in the gas phase. Under these conditions chlorine (Cl_2) undergoes homolysis to yield free radical chlorine atoms which add to double bonds or abstract hydrogen. The total concentration of reactants and their relative ratios affect the product ratios.

In Figure 5.1.1A we show the principal reactions expected in situations where the total pressure of gaseous reactants is moderate and the ratio of chlorine to propene is such that propyl radicals have similar probabilities of reacting with Cl_2 or propene (Pilorez, 1962; Goldfarb et al., 1980, Sittenfield et al., 1980).

The most favored reaction is abstraction of the allyl hydrogen which leads to formation of allyl chloride. As the concentration of allyl chloride builds up, it reacts with chlorine radicals. A variety of reactions leading to "heavy" (high boiling) byproducts are not shown in Figure 5.1.1A. These products result from coupling of the propyl radicals with one another and addition of these radicals to propene to form chloro-hexanes, -hexenes, etc. Also at higher temperatures (e.g., 600°C) benzene (C_6H_6) starts to become an important byproduct. Benzene probably comes from the propene coupling products by elimination of HCl and ring closure. The product ratios achieved are summarized in Figure 5.1.1B (Fairbairn et al., 1947). Under normal

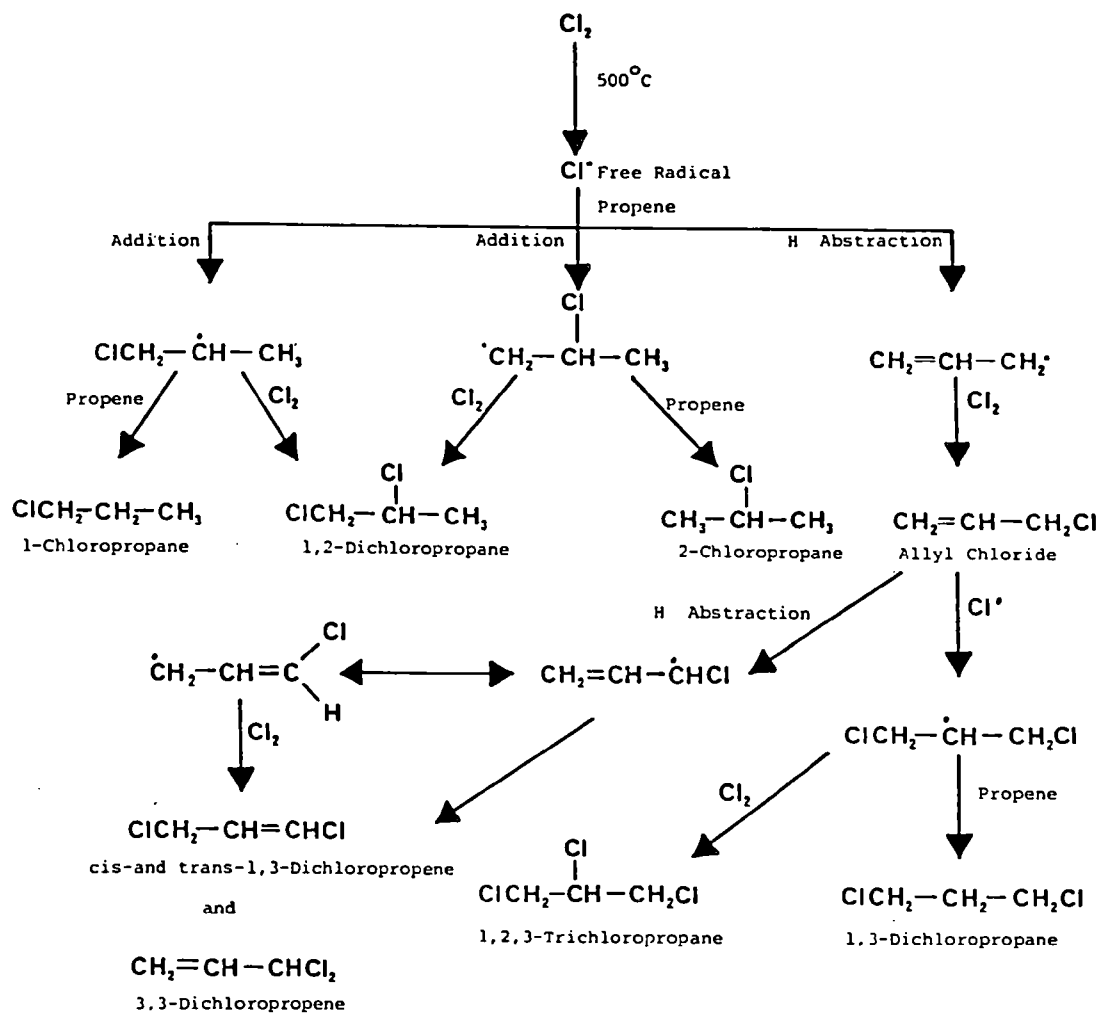


Figure 5.1.1A. Some significant free radical reactions involving propene and chlorine.

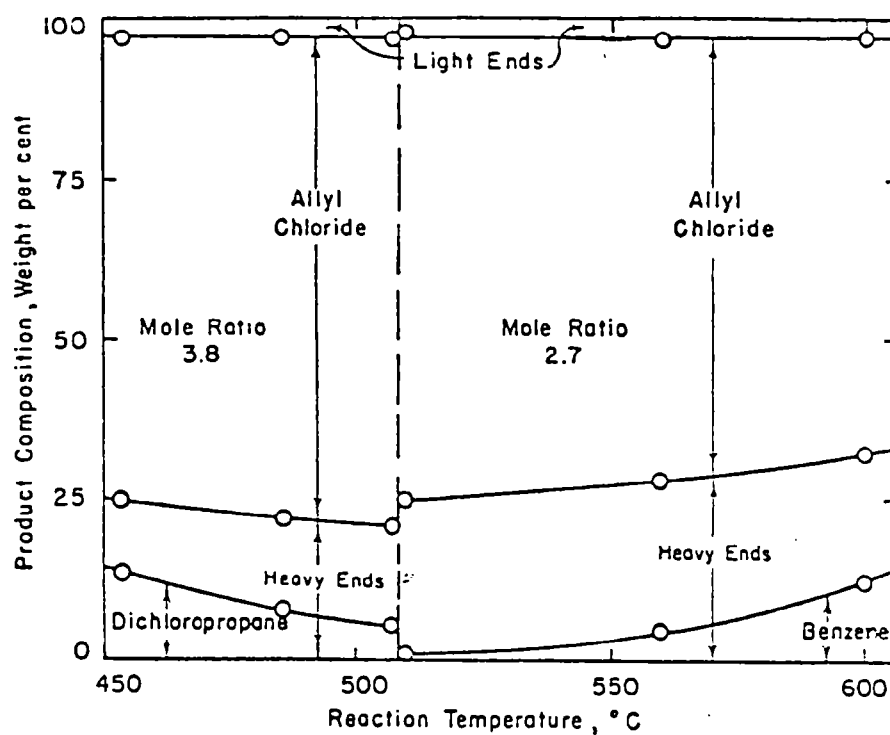


Figure 5.1.1.B Effect of reactant ratio and temperature on products from chlorination of propene. (Note that propene is present in 3 to 4 times the concentration of chlorine.) This graph shows the optimum condition for manufacture of allyl chloride and relative amounts of byproducts and products. Source: Fairbairn et al. (1947).

operating conditions 1,2-dichloropropane and 1,3-dichloropropene are the principal byproducts accounting for about 15% of the propene consumed (Lowenheim and Moran, 1975). They are isolated and used as a soil fumigant (Telone®, Dowfume N®).

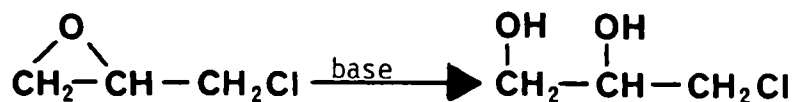
After a series of distillations allyl chloride (b.p. 45°C, yield 80%, Lowenheim and Moran, 1975) with small amounts of byproducts is isolated and passed on to manufacture of epichlorohydrin.

The formation of epichlorohydrin (ECH) involves two steps. The first is reaction with hypochlorite to yield a mixture of 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol with 1,2,3-trichloropropane, chloroether and allyl alcohol byproducts (Figure 5.1.1C). This is an electrophilic addition to the double bond and it is conducted in an aqueous solution. According to Thomas (1958), the final concentration of dichloropropanols (dichlorohydrins) in the aqueous solution must be kept below 5% by weight to avoid excessive formation of chloroethers. This requires that fairly dilute solutions be used. Formation of allyl alcohol from allyl chloride results in a series of byproducts analogous to those shown in Figure 5.1.1C in which a chlorine is replaced by a hydroxyl group. For example, reaction of allyl alcohol with hypochlorite yields dihydroxychloropropanes (monochlorohydrins).

The second step involves ring closure of the dichlorohydrin intermediates which is catalyzed by base. Santodonato et al. (1980) estimated that the rate constant for epoxide formation from dichloropropanol at ambient temperature can be calculated from

$$k_c = 1.3 \times 10^{-6} \text{ s}^{-1} + 3.3 \times 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1} [\text{OH}^-].$$

Both of the dichloropropanol isomers yield epichlorohydrin. The ECH is usually distilled from the reaction mixture to avoid subsequent hydrolysis to monochlorohydrin.



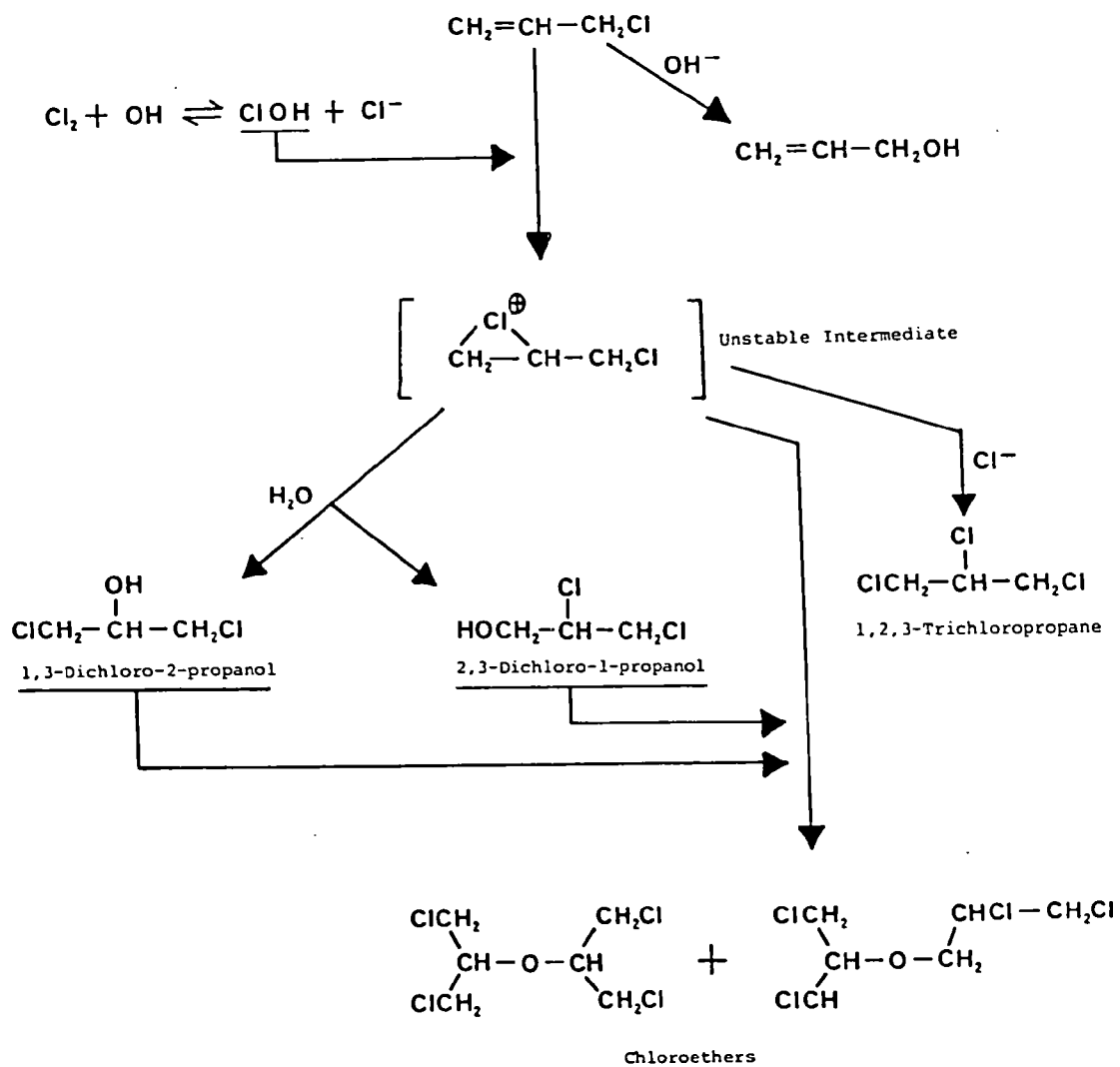


Figure 5.1.1C. Reaction of allyl chloride with hypochlorite.

The epichlorohydrin azeotrope (b.p. 86°C, 75% ECH; Lichtenwalter and Riesser, 1964) boils near the dichloropropanol azeotrope (b.p. 99°C, 23% dichloropropanol, Thomas, 1958) and crude ECH contains dichloropropanols. This material is purified by distillation to obtain 98% pure ECH (Lowenheim and Moran, 1975).

5.1.2 Process Engineering

The process flow for the manufacture of allyl chloride is given in Figure 5.1.2A (Pilorez, 1962). Wet propylene from storage is chilled by passage through a bayonet type cooler immersed in dry propylene. The chilling causes condensation of water which is subsequently removed in a coalescer. The separated water is drawn off periodically. The propylene then passes through a dryer packed with activated alumina where residual water is removed. The dried propylene then flows to the dry propylene storage tank.

The propylene is vaporized in the dry storage tank providing refrigeration for chilling the wet propylene feed. The dry, gaseous propylene flows through a heater prior to mixing with gaseous chlorine and entering the reactor. Normally the feed will contain about 4 moles of propylene per mole of chlorine. The reaction temperature is maintained at between 500 and 510°C and the pressure in the reactor is about 1 atmosphere gauge pressure. Residence time is a few seconds. It is important to keep residence time short to minimize the formation of side products (Fairbairn et al., 1947).

Because carbonaceous material accumulates in the reactor, it is necessary to clean the reactor about once every two weeks. Therefore two reactors are commonly provided so that one is in operation while the other is being cleaned.

The reaction product is cooled rapidly and fed directly to a prefractionator where excess propylene and byproduct hydrogen chloride is separated as an overhead product from the organic chlorides. Liquid propylene, cooled to -40°C by self-vaporization in a propylene flash drum, is

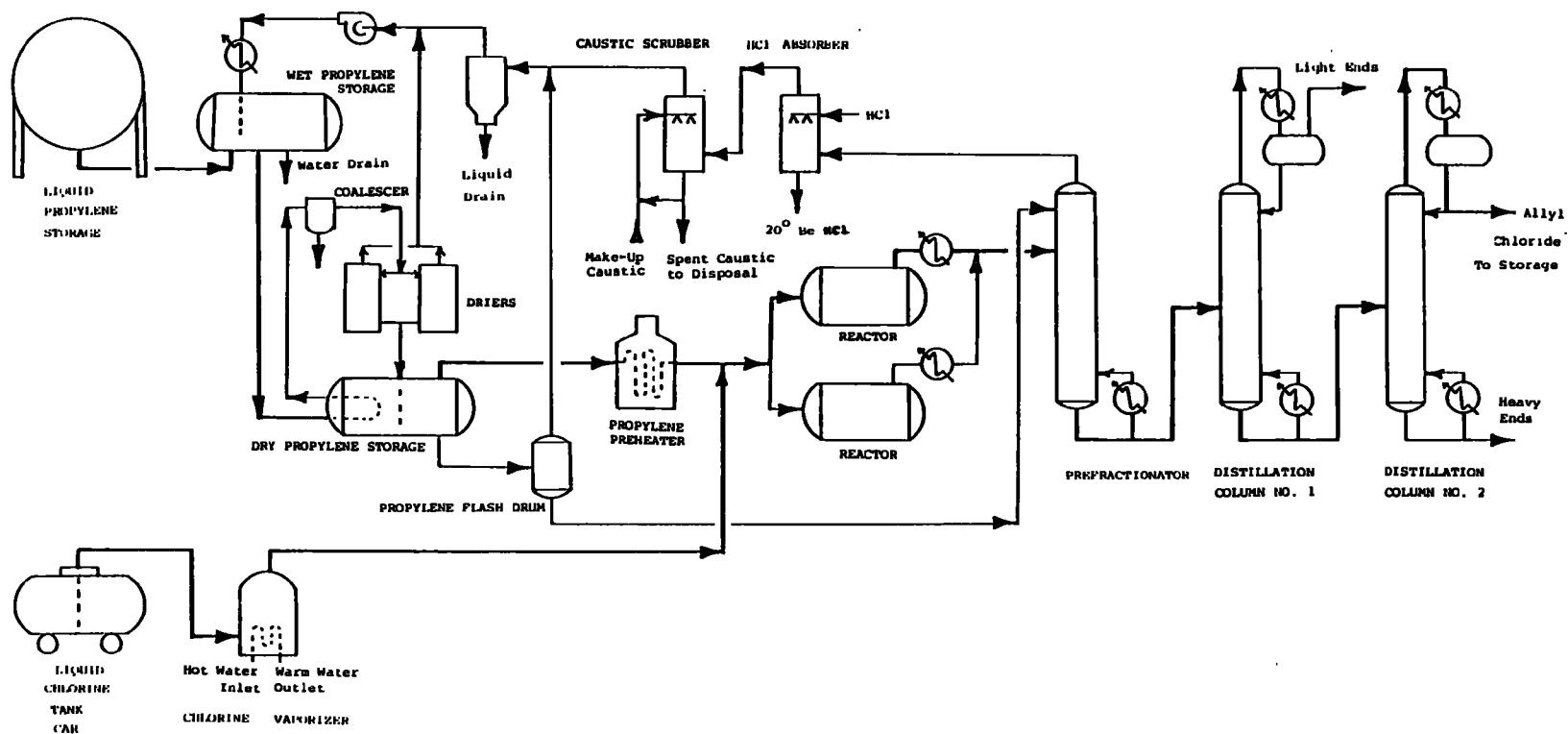


Figure 5.1.2A Chlorination Process for the Manufacture of Allyl Chloride from Propylene

used as reflux in the prefractionator and to cool the reaction products and to scavenge unreacted chlorine.

The propylene and hydrogen chloride mixture overhead from the pre-fractionator flows through an absorber where commercial strength hydrochloric acid is produced. Additional liquid propylene is used to remove the heat of absorption in this process and also to extract any residual organic chlorides. The propylene leaving the absorber is scrubbed with caustic to remove residual hydrogen chloride, passes through a liquid knockout pot to remove entrained water before being compressed, liquified, and returned to wet propylene storage. Gaseous propylene (generated in the propylene flash drum and during regeneration of the dryers) is also recycled through the compressor to wet propylene storage.

The organic chlorides from the bottom of the prefractionator have the following approximate composition:

<u>Compound</u>	<u>%</u>
mono chloropropenes allyl chloride.	80 - 85
dichloropropenes	10 - 15
trichloropropanes and propenes tetrachloropropanes and propenes telomers	5

The organic chlorides are separated by fractional distillation in two columns. In the first, light ends such as 2-chloropropene, and very small amounts of chloropropanes are removed overhead (see boiling point data in Table 5.1.2A).

The bottoms from the first column are fractionated in the second column where allyl chloride of 97% purity is obtained. The 3% impurities are trans-1-chloropropene and di-chloropropenes such as 1,2-dichloropropene and perhaps traces of trichloropropanes.

Table 5.1.2A. Boiling Point Data

Compound	Boiling Point (°C)
2-chloropropene	22.65
cis-1-chloropropene	32.8
trans-1-chloropropene	37.4
allyl chloride	44.6
1,2-dichloro-1-propene	76.8
1,2,2-trichloropropane	122
1,1,3-trichloropropane	147
1,1,2,3-tetrachloropropane	156.85
1,1,2,3-tetrachloropropane	180

The still bottoms would contain some allyl chloride together with substantially all the heavier chlorinated hydrocarbons formed in the reaction.

A typical process flow diagram for conversion of allyl chloride to ECH based on Lowenheim and Moran (1975) and other sources cited in this section is shown in Figure 5.1.2B. Allyl chloride is fed continuously into a reactor containing a solution of hypochlorous acid at 30-40°C. Hypochlorous acid is formed in a counter-current absorber column by contacting chlorine and water. The chlorination reactor effluent is fed to a separator; the upper (aqueous) layer is recycled to the chlorine absorber; then is fed to a second agitated reactor.

In the second reactor, trichloropropane is added to form a two-phase system in which the chlorohydrins are efficiently converted to ECH by reaction with lime (CaO) slurry or dilute sodium hydroxide solution. The effluent from the second reactor is steam stripped to distill ECH as the water azeotrope. The crude product contains water and small amounts of dichloropropanols (Lowenheim and Moran, 1975).

According to Saletan et al. (1977), the organic byproduct distillation bottoms from this process (waste stream 3B, Figure 5.1.2.B) contain the following components (weight %):

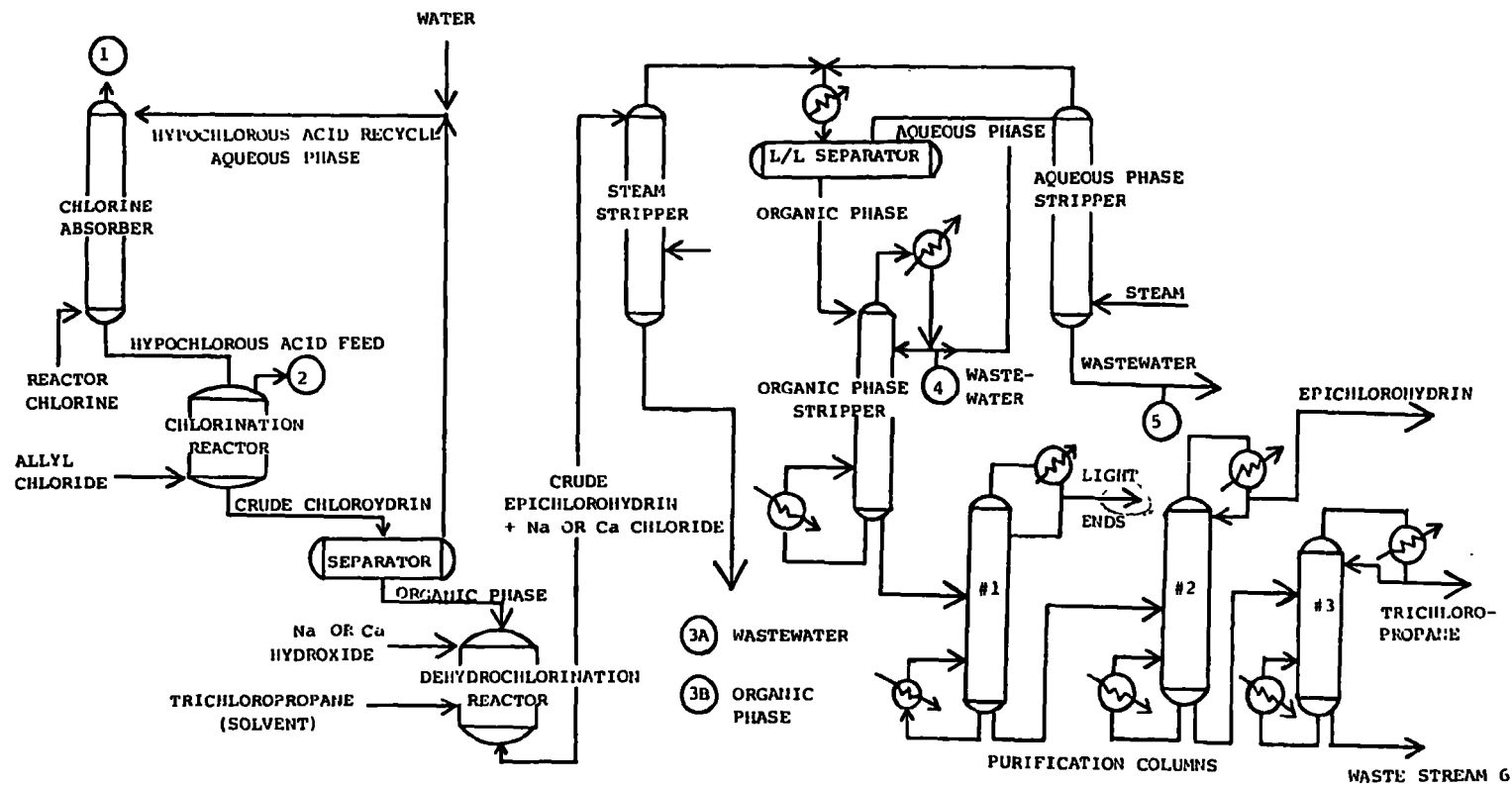


Figure 5.1.2B. Epichlorohydrin from allyl chloride via dehydrochlorination of dichlorohydrins.

1,2,3-Trichloropropane	51%
2,3-Dichloro-1-propanol	19%
1,3-Dichloro-2-propanol	7%
Chlorodihydroxypropane	11%
Epichlorohydrin	1%

The chlorodihydroxypropane content can be up to 45% and ECH can be up to 10%. According to Pervier et al. (1974, cited in Santodonato et al., 1980), the trichloropropane waste stream was stored. It is likely that it has been used to recover trichloropropane as a specialty chemical and disposed of as a hazardous waste. More recently, Saletan et al. (1977) proposed using this organic phase as a solvent for ECH in the production of glycerin by hydrolysis in a two-phase system. In the Saletan method, the excess water from manufacture of dichloropropanol is separated by preparing ECH and collecting the organic bottoms, then the ECH and organic bottoms are fed into the glycerin process and most of the components of the organic bottoms except the 1,2,3-trichloropropane are converted to glycerin. Thus, more product (glycerin) is obtained and the volume of the trichloropropane waste/byproduct is minimized.

The crude ECH-water azeotrope separates into two phases and the aqueous phase is sent to a stripper to remove volatile organics. The remaining water becomes waste stream 5 in Figure 5.1.2B. The organic ECH phase is sent to a stripper where it is dehydrated and the water that is removed as an overhead stream becomes waste stream 4 in Figure 5.1.2B. These aqueous waste streams are likely to contain allyl alcohol and dichloropropanols.

The dehydrated organic ECH layer flows to a series of distillation columns where allyl chloride and byproducts are separated. The waste streams from manufacture of ECH from allyl chloride are listed in Table 5.1.2B. The composition and production rates are based on engineering estimates. The yield of pure ECH based on allyl chloride is 85 to 90%. Halasa (1976) has reported the composition of several samples of ECH from various sources. The results for ECH prepared from propene are listed in Table 5.1.2C.

Table 5.1.2B. Waste Streams for Epichlorohydrin Manufacture^a

Waste Stream	Type	Chemical Compounds	Amount lb/lb Epichlorohydrin
1	Tail Gas Absorber Vent-Gas to Air	chlorine hydrogen chloride allyl chloride	0.0000005 0.0000005 0.002
2	Reactor Vent-Gas to Air	allyl chloride chlorine trichloropropane hydrogen chloride epichlorohydrin	0.002 0.0000005 0.0005 0.0000005 0.0015
3	Waste Water	calcium chloride chlorohydrins allyl alcohol glycerine	0.598 0.003 trace 0.12
4	Waste Water	dichlorohydrins allyl alcohol	0.004 trace
5	Waste Water	dichlorohydrins allyl alcohol	0.003 trace
6	Still Bottoms	trichloropropane chloroethers dichlorohydrins	0.0371 0.0074 0.0047

^aThese waste streams correspond to Figure 5.1.2B and represent refined ECH. Crude ECH for glycerin manufacture would be the same except for waste-stream "6" which would be carried along as part of the ECH.

Table 5.1.2C. Composition of Epichlorohydrin from various sources^a

<u>Compound</u>	<u>Percent Composition</u>		
	<u>ZSSR</u>	<u>Solvay</u>	<u>Shell</u>
Epichlorohydrin (ECH)	98.4	98.85	>98.
Allyl chloride	0.037	-	0.012
Chloroform	0.078	-	-
2,3-Dichloro-1-propene	0.862	0.246	0.312
1,2,3-Trichloropropane	0.398	0.112	0.26
Dichloropropanols	0.225	0.237	0.218
"Związki niezidentyfikowane"	-	0.57	-

^a This table is based on a partial translation of an article in an eastern European language.

Source: Halasa (1976).

5.1.3 Alternate Process for Manufacture of Epichlorohydrin

Although it is unlikely that any process can be cheaper than the current approach used to make ECH, it is interesting that Interlox Chemicals Ltd. (London) has patented a process for continuous epoxidation of allyl chloride with perpropionic acid (Hildon and Greenhalgh, 1979).

5.2 Processing Methods for Epichlorohydrin

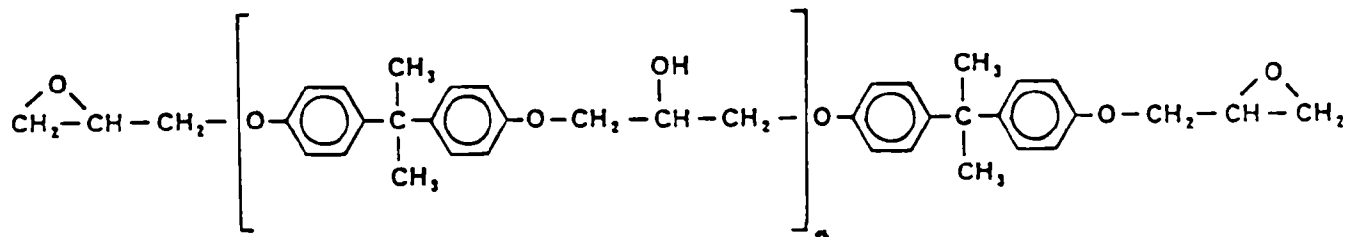
5.2.1 Manufacture of Epoxy Resins from Epichlorohydrin

There are several types of epoxy resins.

The resins can be grouped as follows (Kirk-Othmer, 1980a):

- o liquid, unmodified epoxy resins are almost pure diglycidyl ether of bisphenol A (DGEBA) and are used in coatings, castings, tooling, flooring and reinforced pipe.
- o liquid, modified epoxy resins are usually small to moderate oligomers of DGEBA diluted with various glycidyl ethers or esters and are used in coatings, impregnation and flooring.
- o solid epoxy resins are usually moderate to high molecular weight oligomers of DGEBA and are used in fiberglass sizing and various powder coating systems.
- o solution of epoxy resins are usually moderate to high oligomers of DGEBA dissolved in xylene, methyl isobutyl ketone, toluene or brominated acetone (55 to 80% solids) and are used as coatings and for printed circuited boards.
- o specialty epoxy resins include (1) epoxy-phenol novolacs and epoxy-cresol novolacs used for laboratory bench tops, adhesives and various types of moldings; (2) polyfunctional epoxides used in the aerospace industry; and (3) cycloaliphatic epoxies used for electrical casting.

The most important resins are based on bisphenol A and the diglycidyl ether of bisphenol A. The product has the general formula



and can be identified by two CAS numbers both of which are listed in the TSCA Inventory. The CAS No. 25068-38-6 is defined as the epichlorohydrin polymer with bisphenol A. This definition seems to imply a one-step synthesis of the polymer from the starting materials. This appears to include epoxy resins produced by the "Taffy Process". The CAS No. 25036-25-3 is defined as the polymer of the diglycidyl ether of bisphenol A (CAS No. 1675-54-3) with bisphenol A. This polymer appears to be produced in two steps from ECH and bisphenol A by the "Advancement Process".

These two processes are discussed below.

5.2.1.1 The Advancement Process

The advancement process for manufacture of bisphenol A epoxy resins (Figure 5.2.1.1A) seems to be more versatile and yield more consistent products than the taffy process. The advancement process can be used to produce resins with a wide variety of average n-values (0.1 to 16.0) and physical property data is summarized below (Kirk-Othmer, 1980a). However, it should be noted that the actual polymers have only even n-values (n=0, 2,4,6...). This is because a diphenol is being added to a diglycidyl ether (Kirk-Othmer, 1980a).

Properties of Commercial Epoxy Resins Made by the Advancement Process			
Average n value	Epoxy equiv wt	mp(Durran's), °C	Approx mol wt
0.1	185	liquid	360-380
0.3	210	liquid	390-450
0.6	255	liquid	360-560
2.2	487	65-75	805-1100
5.5	950	95-105	1750-2050
14.4	2250	125-135	4000-5000
16.0	3250	145-155	5000-8000

The pure diglycidyl ether of bisphenol A (n = 0.0) melts at 43°C (Kirk-Othmer, 1980a).

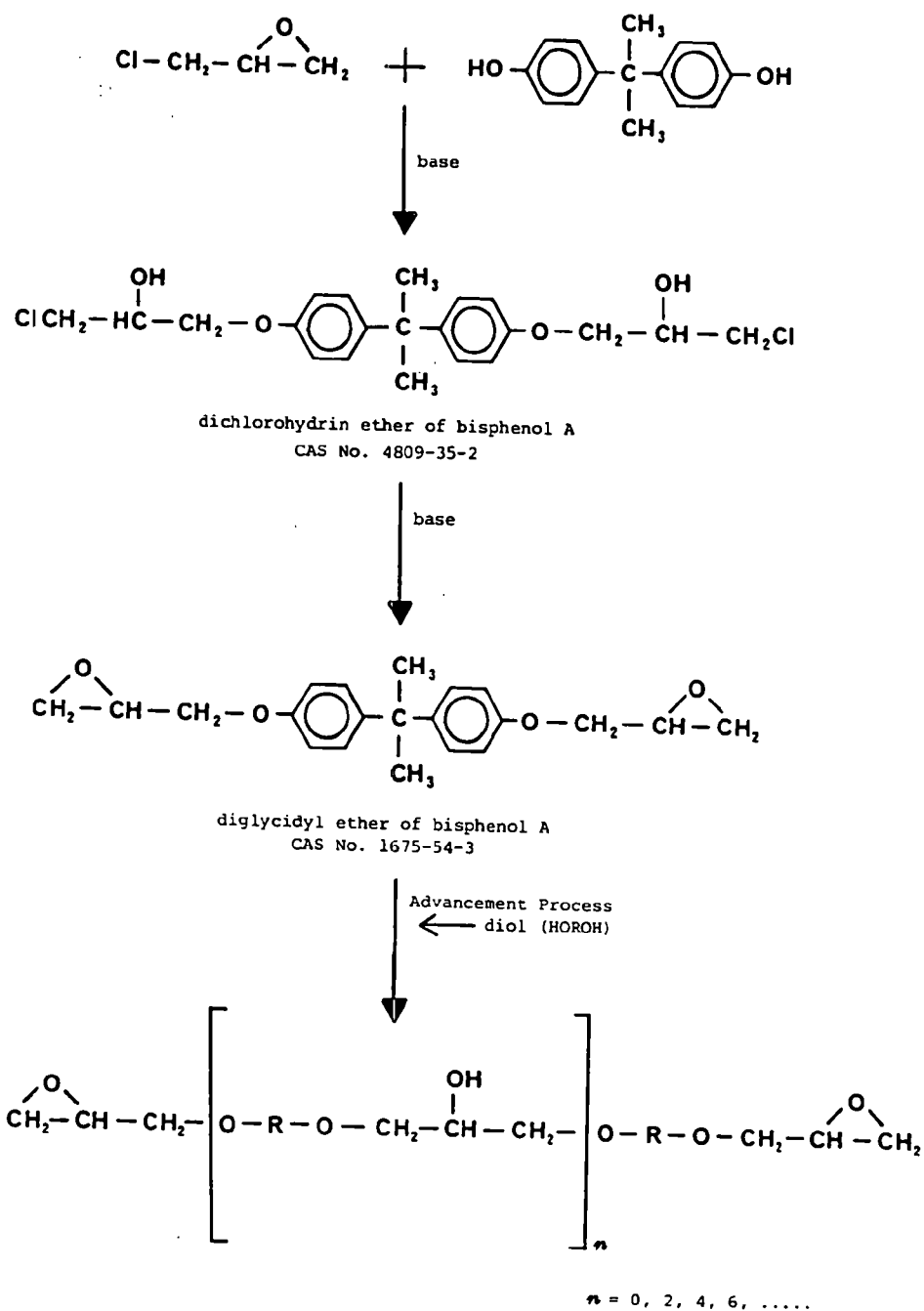
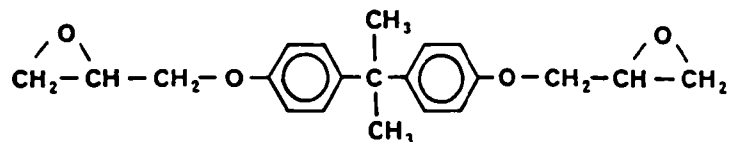


Figure 5.2.1.1A. The advancement process for making epoxy resins of Bisphenol A. Note: HOROH represents bisphenol A.

The first step in the advancement process is manufacture of the diglycidyl ether of bisphenol A (DGEBA, CAS No. 1675-54-3).



The commercial process used to make DGEBA is probably similar to the method patented by Shell Development in 1958 (Jones and Chandy, 1974).

The reaction is carried out in a vessel fitted with a heater, stirrer, thermometer and distilling head. The distilling head is equipped with a liquid separator which allows the lower layer to be returned to the reaction mixture. The vessel is charged with a solution of bisphenol A in ECH (10 moles of ECH per mole of bisphenol A).

The reaction mixture is heated to about 100°C (ECH boils at 116°C at 760 mmHg) and maintained at that temperature during addition of a 40% aqueous solution of sodium hydroxide. A total of 1.90 moles of sodium hydroxide per mole of bisphenol A is added. The water introduced with the caustic distills as an azeotrope with ECH (75% ECH, 25% H₂O, bp 86°C; Lichtenwalter and Riesser, 1964). The azeotrope condenses and separates into two layers. The lower layer is ECH containing about 1.5% H₂O and the upper layer is water containing about 6.6% ECH (Dow, 1980). The lower layer is returned to the reaction mixture. The addition of the aqueous caustic solution is kept at a rate such that the water is removed and does not build up in the reaction mixture above the 1.5% level. The addition takes about 2 h.

When all the caustic has been added, the bulk of excess ECH is distilled and the reaction mixture is heated to 160°C at 1 mmHg to remove residual ECH. At this point, the reaction mixture consists mainly of the diglycidyl ether of bisphenol A (mp 43°C) and sodium chloride (salt).

Jones and Chandy (1974) describe two methods of isolation of pure DGEbPA from the reaction mixture. In one procedure, methyl isobutyl ketone and water are added and two phases form. The aqueous salt solution is removed and the organic phase is contacted with a solution of aqueous base (5% NaOH) to complete the epoxidation of the halohydrin intermediate. The organic phase is again separated and washed with aqueous sodium dihydrogen phosphate. Finally, the organic phase is distilled up to a temperature of 160°C at atmospheric pressure and then the pressure is reduced to 1 mmHg to remove the solvent. The product from this isolation process is DGEbPA in the form of a pale yellow liquid containing 0.25% chlorine and 0.521 epoxy equivalents per 100 g and a molecular weight of 355. Hagnauer (1979) recrystallized DGEbPA from a commercial product and purified the compound to a chlorine content of 0.051% and an average molecular weight of 339. The second method of isolating DGEbPA described by Jones and Chandy (1974) involves filtering the hot reaction mixture and washing the NaCl filter cake with isopropyl alcohol to recover the product. The isopropyl alcohol is distilled from the filter cake wash and the DGEbPA is mixed with the portion that came through the filter. No data are available on the product from this isolation process.

Once relatively pure DGEbPA has been isolated, a variety of products can be obtained by the advancement process. For example, the TSCA Inventory lists these polymers of DGEbPA (CAS No. 1675-54-3):

<u>Diol reacted with DGEbPA</u>	<u>Epoxy Resin CAS No.</u>
bisphenol A	25036-25-3
tetrabromobisphenol A	31942-06-0

The TSCA Inventory also lists the polymer of the diglycidyl ether of tetrabromobisphenol A with tetrabromobisphenol A (polymer CAS No. 68928-70-1).

5.2.1.2 The Taffy Process

The taffy process for manufacturing epoxy resin is employed to make resins with n=1 to 4 (Kirk-Othmer, 1980a). The polymerization process involves

reacting similar amounts of epichlorohydrin, bisphenol A and base. The crude product is a highly viscous emulsion of salt water and resin. The product is isolated by separating the phases and washing the taffy resin with water (Jones and Chandy, 1974; Kirk-Othmer, 1980a). Kirk-Othmer (1980a) gives the following data that indicate the nature of the product obtained with various ratios of epichlorohydrin to bisphenol A in the taffy process (Figure 5.2.1.2A).

<u>Mole ratio epichlorohydrin-bisphenol A</u>	<u>Epoxy equiv wt</u>
2.6	249
2.15	345
1.57	516
1.4	582
1.33	730
1.25	862
1.2	1180

5.2.1.3 Engineering Considerations in Epoxy Resin Manufacture

The plants used for manufacturing bisphenol A epoxy resins by the advancement process and taffy process are probably similar. The main differences are associated with the initial ratio of reactants (10 moles of ECH/mole bisphenol A in the advancement process versus 2.6 to 1.2 moles ECH/mole bisphenol A in the taffy process) and method of isolating the product. Here we will outline a typical taffy process plant and identify its waste streams and vents (Figure 5.2.1.3A). The process described here is based on a plant designed by M. Sittenfield for a chemical company.

Bisphenol and an excess of ECH are charged into the reactor. An excess of sodium hydroxide is added as a 50% aqueous solution over a period of about 3 h while the reactor is maintained at about 110°C. Water and ECH distill as an azeotrope that separates into a dense ECH phase and light water phase. The ECH phase (containing about 1.5% H₂O) is returned to the reactor. Upon completion of the reaction, the excess ECH is vacuum stripped at 50 mmHg and a maximum temperature of 150°C.

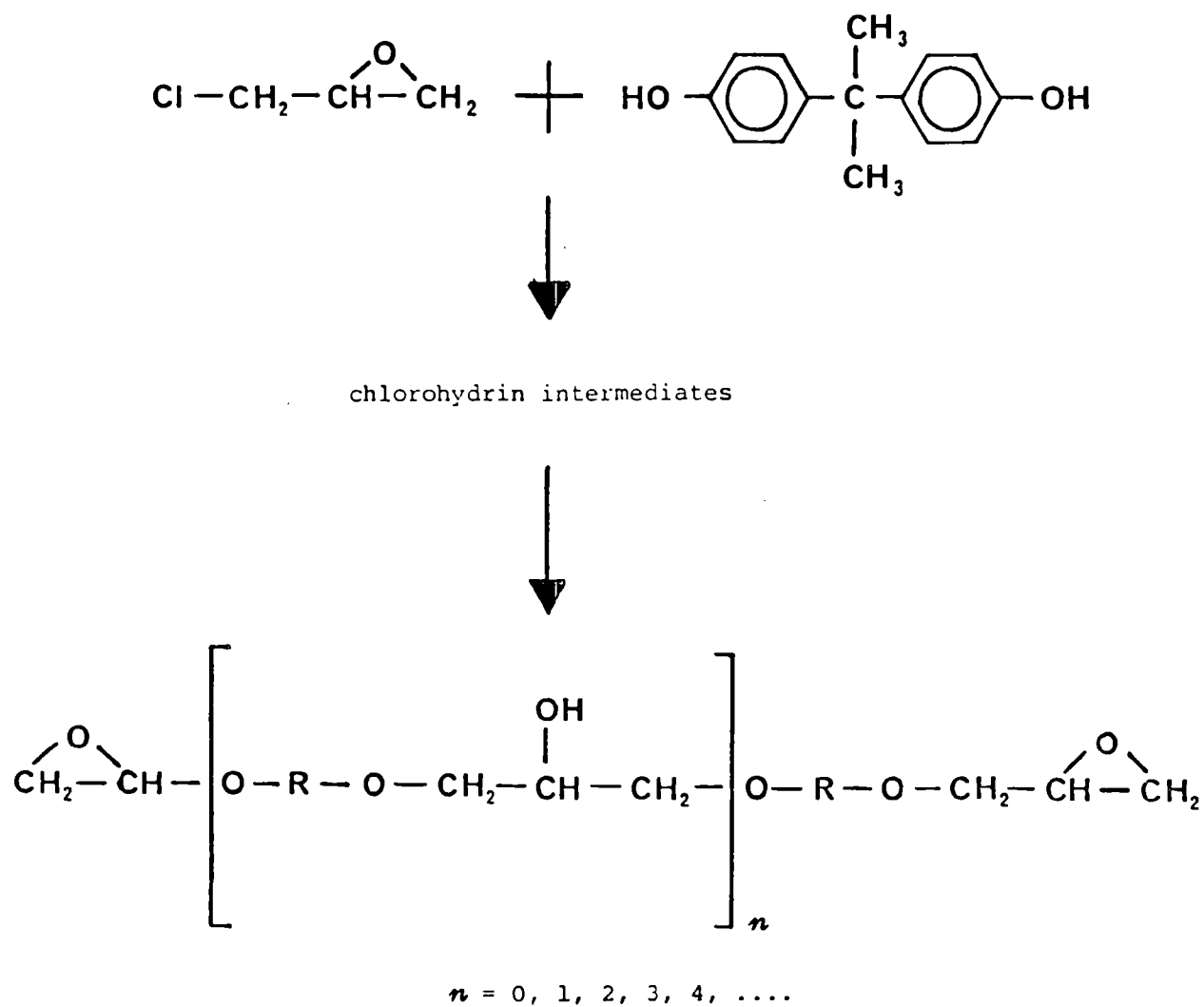


Figure 5.2.1.2A. Process Chemistry of Taffy Method of Forming Epoxy Resins.

Figure 5.2.1.3A. Typical epoxy resin manufacturing plant.

The reaction product consists of the epoxy resin (liquid or solid depending upon initial ratio of ECH to bisphenol A) and sodium chloride salt. The mixture is cooled to 90°C and a solvent (usually toluene) is mixed with the reaction product. The mixture is passed to a centrifuge to separate the salt. The epoxy resin solution from the centrifuge is clarified by filtration and then vacuum stripped at about 70 mmHg and 150°C to remove toluene and residual ECH. If desired, the epoxy resin solution can be washed with sodium hydroxide to reduce ECH residues.

Much of the plant operation is concerned with recovery of solvents and reactants and disposal of wastes.

- The azeotropic aqueous phase containing about 1.5% ECH from the reactor is stripped and the ECH mixed with ECH recovered from the reactor for recycle. The aqueous waste stream can contain up to about 0.3% ECH.
- There is a vent from the reactor vacuum pump that produces atmospheric discharge of ECH.
- There are vents on the feed tank and surge tank for the ECH recovery column.
- There is a centrifuge vapor vent and a vent on the salt disposal unit.
- The salt itself is a major solid waste.
- The filter cake from the clarifier is a solid waste.
- There is a vent on the toluene stripper vacuum pump.
- The toluene stripper wash water is a liquid waste.

The compositions and production volumes of the liquid and solid waste streams are described in Table 5.2.1.3A.

5.2.1.4 Manufacture of Epoxy Resins, Reactive Diluents and Related Compounds That Are Not Based on Bisphenol A.

Glycidyl Ethers

Epoxy resins can be prepared from ECH and various diols other than

Table 5.2.1.3A. Solid and Liquid Waste Streams from Manufacture of Bisphenol A Epoxy Resins.

Waste Stream	Component	lb/lb of resin product
Epichlorohydrin stripping column bottoms	water	0.36
	ECH	0.0011
salt byproduct waste	sodium chloride	0.35
	Toluene	0.35
	ECH	0.00068
	Resin	0.0106
	Sodium hydroxide	0.0113
Filter cake from clarifier	Filter aid	0.00163
	Toluene	0.00326
	Resin	0.00326
	ECH	neglibile
Toluene stripper wash water	Sodium hydroxide	(variable, no data available)

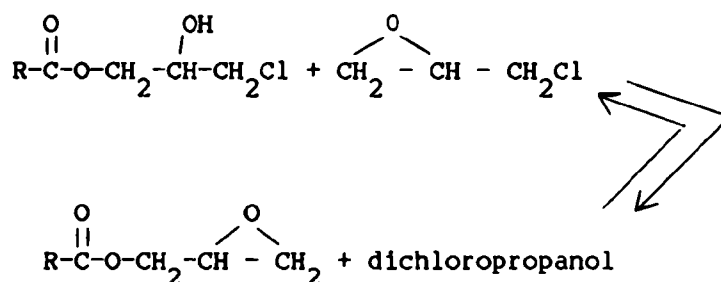
Source: M. Sittenfield, private files.

bisphenol A. The public TSCA Inventory includes epoxy resins based on aliphatic diols (31921-70-7, 25038-04-4, etc), polyether diols (39443-66-8, etc.) and phenol-formaldehyde resins (novolac, 29690-82-2, etc). Aryl glycidyl ethers are probably prepared by base-catalyzed addition of ECH followed by epoxidation of the chlorohydrin with alkali (see 5.2.1.1). Alkyl glycidyl ethers are probably prepared by acid-catalyzed addition of ECH to the alcohol followed by epoxidation of the chlorohydrin with alkali (see 5.2.7).

Glycidyl Esters

Glycidyl esters are more difficult to prepare than glycidyl ethers. Dukes and Welch (1975) discuss the processes for manufacturing glycidyl esters. The methods include:

- (1) reaction of glycidol with an acid chloride
- (2) epoxidation of allyl esters
- (3) reaction of ECH with carboxylic acid (catalytically) followed by disproportionation of the resulting chlorohydrin ester with excess ECH.



- (4) reaction of ECH with dry potassium salts of carboxylic acids.
- (5) reaction of ECH with carboxylic acid (catalytically) followed by dehydrochlorination of the chlorohydrin ester with alkali.

In a patent assigned to Celanese Coatings and Specialties, Dukes and Welch (1975) describe a method similar to the last listed above. Their key improvement seems to be careful control of temperature (at or below 200°F for the first step and between 90°F and 130°F for the second step).

Dukes and Welch (1975) describe a typical reaction as follows:

A reactor was charged with adipic acid (400 parts), ECH (2533 parts) and tetramethylammonium catalyst (8 parts). The mixture was agitated and heated up to 175°F (80°C) where it was held for 90 minutes at which time all the acid was completely esterified.

The reaction mixture was cooled to 105°F and the reactor was evacuated to a pressure of 10 mmHg before beginning the epoxidation. Aqueous 50% sodium hydroxide solution (438 parts) was added over a period of 315 minutes at this temperature. ECH-water azeotrope distilled during the addition and the ECH layer that formed as the azeotrope condensed was returned to the reactor. At the completion of the reaction, the vacuum was released and water (500 parts) was added to the reactor to dissolve the byproduct salt. The brine layer was allowed to separate and was drawn off.

To complete the epoxidation, the organic phase was returned to 100 to 110°F in the reactor at 10 mmHg. An additional 176 parts of 50% sodium hydroxide solution was added during a period of 115 minutes and ECH that distilled was returned to the reactor as described above. As in the first phase of epoxidation, the byproduct salt was dissolved in 1,000 parts of water and withdrawn from the reactor.

The excess ECH was removed from the product (diglycidyl ester of adipic acid) by distillation at a pot temperature of 305°F (152°C) and 10 mmHg. The yield of product was 540 parts (98%) with an epoxide equivalent weight of 144 (theoretical 129) and total chlorine content of 2.12%.

Dukes and Welch (1975) described similar reactions using isophthalic acid, terephthalic acid, azelaic acid and dimer acids of linseed fatty acids. They also mentioned other suitable acids including oxalic, sebacic, succinic, pimelic, phthalic, trimellitic and chlorendic.

Non-Glycidyl Epoxides

ECH is used to prepare glycidyl epoxy resins. However, there are some commercial epoxides that do not contain the glycidyl group. Most of these are made by epoxidation olefins. The process may involve peracid epoxidations or halohydrin epoxidations.

Reactive Diluents

Many of the non-bisphenol A epoxy compounds in commerce are reactive diluents for epoxy resins. These compounds are usually simple glycidyl ethers or esters or epoxy cycloaliphatics (Pilny and Mleziva, 1977).

5.2.1.5 Residues of Epichlorohydrin in Epoxy Resins

Direct data on residues of ECH in epoxy resins has been relatively difficult to find. While there have been studies of the gross composition of epoxy resins (Hagnauer, 1979; Braun and Lee, 1976), data on ECH residues have not been found. The only information on ECH residues is product specifications published by manufacturers. We have also not found any distinction between the residues found in resins made by the advancement process and taffy process.

In Shell's Technical Bulletin SC:106-82 (Shell, 1982), the company notes that epoxy resins and reactive diluents produced from ECH contain trace amounts of three relatively volatile impurities:

- epichlorohydrin
- phenyl glycidyl ether
- diglycidyl ether

Shell lists a number of its Epon resins that are sold under a release specification that the residual ECH content cannot be greater than 5 ppm (Table 5.2.1.5A). According to Shell (1982), it is more common for these resins to have ECH residue levels of 1 to 2 ppm. Eponol resins contain lower residue levels.

Table 5.2.1.5A. Epon Resins with ECH Content of 5 ppm, wt, max

Epon Resin	Epon Resin
825	1004 F
826	1007 F
828	1009 F
829	2002
830	2002-FC-5
834	2004
836	2014
1001 F	2024
1002 F	8280

Source: Shell (1982)

Obviously, solutions made by diluting these resins in an inert solvent will have even lower ECH levels. However, Shell (1982) stipulates that resins with reactive diluents (e.g., phenyl glycidyl ether) are not covered by these specifications. Some specialty resins and reactive diluents have substantially higher ECH residue levels. For example, the data in Table 5.2.1.5B was gleaned from Shell material safety data sheets. Chemische Fabriek Zaitbommel of the Netherlands makes n-butyl and 2-ethylhexyl glycidyl ethers containing 25 ppm ECH residue (Farbe & Lack, 1982).

Table 5.2.1.5B. Residues of ECH in Specialty Resins and Reactive Diluents

<u>Tradename</u>	<u>Chemical Family</u>	<u>ECH level</u>
Epon 871	flexible epoxy resin	1400 ppm
Epon 815	modified epoxy resin (contains 13.5% butyl glycidyl ether)	15 ppm max
--	100% butyl glycidyl ether	10 ppm

Source: Shell Material Safety Data Sheets (1983).

Shell's ECH residue standard for their main line resins (Table 5.2.1.4B) appears to be based on an evaluation of the ECH residue levels that will produce vapor concentrations exceeding the OSHA standards. (The regulatory limits for ECH exposure in the workplace are summarized in Table 6.0A.) Through experimental work Shell determined the equilibrium concentration of ECH vapor that can be achieved (i.e., the maximum ECH concentration that can be achieved) in air in contact with epoxy resins at various temperatures. The results are shown in Table 5.2.1.5C. Shell (1982) argues that a 5 ppm (wt/wt) concentration of ECH in the bulk resin will not give rise to a vapor concentration above the OSHA limit (5 ppm, v/v) except at the maximum recommended handling temperature (i.e., 200°F, 93°C). It should be noted that the equilibrium concentrations are independent of the method of application of the resin (pouring, spreading, spraying); but the rate at which the equilibrium (i.e., maximum) air concentrations are reached will depend upon the surface area of resin in contact with air.

These data appear to apply to uncured liquid resins. It should not be assumed that the solubility of ECH in the cured solid resin is the same as in the uncured liquid. If ECH is less soluble in the solid cured resin, it would

tend to be forced out of the solid (into the air) during curing. The result would be higher air levels of ECH than expected on the basis of Table 5.2.1.5C. The reaction of ECH residues with the curing agent is a mitigating factor.

We asked the Dow Chemical Company to comment on levels of residual ECH in various products (Hammaker, 1983) and Dow responded with the data summarized in Table 5.2.1.5D (Arnold, 1984b).

Table 5.2.1.5C ECH Vapor Concentrations above Epoxy Resins at Various Temperatures Under Static Equilibrium Conditions.

ECH levels in resin, ppm, wt.			
10			
5			
1			
Temperature, °C(°F)			
ECH level in vapor, ppm, v/v			
27 (80)	0.6	0.3	0.06
49 (120)	2	1	0.2
Note: 140°F Recommended handling temperature			
71 (160)	5	2.6	0.5
93 (200)	12	6	1.2
Note: 200°F Recommended maximum handling temperature			
116 (240)	26	13	2.6
138 (280)	50	23	5.0
149 (300)	64	32	6.4

Source: Shell (1982).

Table 5.2.1.5D. Levels of Epichlorohydrin Residues in Typical Epoxy Resins and Reactive Diluents.

Epoxy Resin	ECH Residue (ppm)
Bisphenol A (DGEBCA) (25068-38-6, 25036-25-3)	5 max.
Aliphatic (31921-70-7, 25038-04-4, etc.)	50 max.
Polyether (39443-66-8, etc.)	10 max.
Epoxy Novolac (29690-82-2, etc.)	10 max.
Glycidyl ethers (2426-08-6, etc.)	10
Glycidyl esters (106-90-1, 106-91-2, etc.)	1,000

Source: Arnold (1984b).

5.2.1.6 Reduction of Residual Epichlorohydrin Levels in Epoxy Resins

As a result of concern about the health effects of ECH and other volatile epoxy compounds like glycidyl ether, various methods have been considered for reducing their levels in epoxy resins. Vacuum stripping and washing with aqueous caustic solution have been used as routine methods for reducing residues in bisphenol A epoxy resins. Bisphenol A epoxy resin is relatively insensitive to heat and hydrolysis. Other types of epoxy resins are more readily destroyed by heat and caustic treatment. Thus, Ciba-Geigy Corporation (Sury, 1983) has patented a process for reducing ECH residues in heat sensitive epoxy resins. The method also works for bisphenol A epoxy resins and probably would work for other types of ECH derivatives.

The method involves heating the product in vacuo as it trickles through a packed column against a counter current of inert gas (e.g., nitrogen). A variety of factors (e.g., temperature, vacuum, resin flow rate, N₂ flow rate, length of column) can be varied to achieve the most economical stripping with respect to achieving a desired final ECH residue level. Results that were achieved using a laboratory-scale apparatus are presented in Table 5.2.1.6A.

Table 5.2.1.6A. Epichlorohydrin Concentrations (ppm) vs. Number of Passes Through Column.

Resins or Product ^a	A	B	C	D
Temperature °C	130	120	120	120
Ratio (g/g) N ₂ /Resin (product)	0.10	0.15	0.10	0.1
Resin Rate g/minute	8.9	8.1	11.3	6.3
Passes Through Column				
0	5176	2882	3500	2269
1	1637	1548	1840	1025
2	529	747	1270	502
3	173	410	940	325
4	95	262	515	250
5	35	104	522	63
6	23	53	381	79
7	4	31	285	50
8	0	18	240	40
9		13	167	21
10		9	93	31
11		9	90	
12			58	
13			42	
14			30	
15			17	
16			5	

^aA is 2,2-bis(4-glycidyoxyphenyl)propane, ARALDITE 6010.

B is N,N-diglycidyl-5,5-pentamethylenehydantoin.

C is N,N,O-triglycidyl-p-aminophenol.

D is N,N,N',N'-tetraglycidyl-4,4'-methylenedianiline.

Because a relatively small packed column (0.5 x 18 inches) was used the product was repeatedly passed through (up to 16 times in one case). It is not clear whether the starting ECH concentrations were typical of ECH residues in the various resins or whether the ECH was "spiked" into the resin. However, no mention of fortifying (spiking) the resins with ECH was mentioned by the author. In addition to the materials listed in Table 5.2.1.5A, the author also experimented with triglycidyl isocyanurate with similar results.

Under the conditions employed, no adverse changes in the resins were noted. The epoxy value and chromatographic properties were unchanged but the viscosity increased and hydrolyzable chlorine content decreased (Sury, 1983).

It seems likely that other approaches for stripping residual ECH from products (including epoxy resin, elastomers and wet-strength resins) could be employed successfully. The main factors preventing stripping of ECH are probably viscosity of the product, low vapor pressure of ECH and affinity of ECH for the product. These factors can be overcome by dissolving or melting the product and exposing a large surface area, lowering the overhead pressure (applying a vacuum), and introducing an innocuous solvent with more affinity for the product than ECH. We envision, for example, dissolving an ECH-contaminated product in dimethyl ether, methylene chloride, a freon or similar solvent and passing it through a heated, packed column in which the solvent is evaporated and entrains the residual ECH in the vapor.

5.2.1.7 Other Impurities in Epoxy Resins

There are potentially hazardous impurities in epoxy resins other than ECH. Two of the most important are diglycidyl ether (DGE) and phenyl glycidyl ether (PGE) (Shell, 1982). According to Shell, DGE has been found in random samples of Epon resins at levels up to 31 ppm, but it rarely exceeds 5 ppm. The concentration of PGE in undiluted bisphenol A-ECH Epon resins is typically 5 to 40 ppm with occasional findings as high as 2000 ppm. (Epon resins 1031 and 1030-B-80 have PGE at about 2% by weight as a reactive diluent.) Hagnauer (1979) also suggests that glycidyl alcohol may be a common impurity.

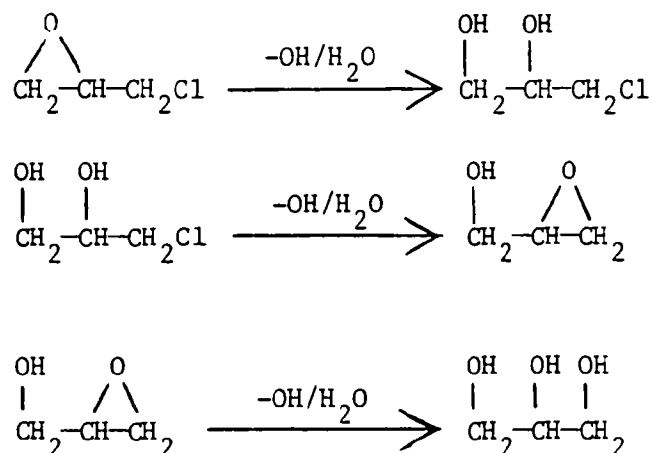
Glycidyl alcohol and diglycidyl ether are produced by base hydrolysis and condensation of ECH. Phenyl glycidyl ether is produced by reaction of ECH with phenol impurity in the bisphenol A. Hagnauer (1979) mentioned that phenol is usually present at less than 0.1 wt% in bisphenol A. Halasa (1976) reported analyses of various bisphenol A samples with findings of 0.01 to 0.07% phenol. Hagnauer (1979) and Halasa (1976) also discuss other bisphenol A impurities that effect the performance of the resin, but which are not volatile enough to be a hazard.

5.2.2 Manufacture of Glycerin from Epichlorohydrin

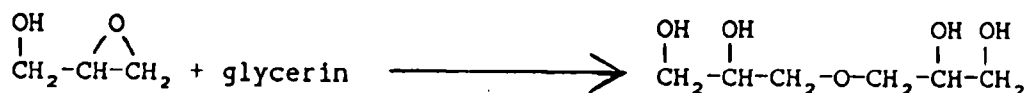
5.2.2.1. Process Chemistry

Early processes for manufacturing glycerin from allyl chloride involved (a) chlorination of the allyl chloride to 1,2,3-trichloropropane or (b) hydrolysis of allyl chloride to allyl alcohol followed by hydrochlorination (chlorohydrination) to dihydroxychloropropanes (monochlorohydrins) followed in each case by hydrolysis to glycerin (Tymstra, 1952). The method patented by Shell Development (Tymstra, 1952) involves the hydrochlorination of allyl chloride followed by hydrolysis of the dichlorohydrins to glycerin. This process suffers from the fact that dilute solutions must be used because of the low solubility of allyl chloride in water and because bis(dichloropropyl) ethers are formed if the intermediate dichlorohydrins are allowed to build up (Thomas and Dannels, 1958). This excess water and accompanying salts are difficult to remove from the product glycerin.

Conversion of part or all of the dichlorohydrins to ECH which can be readily distilled away from excess water, salt and bis(chloropropyl) ethers became an efficient method of making the isolation of pure glycerin more economical. The final reaction is a three-step hydrolysis of ECH as shown below:



Some polyglycerols can be formed by reactions among the intermediates. For example,



5.2.2.2 Process Engineering

Shell pioneered the propylene-allyl chloride-epichlorohydrin-glycerin process. Discussions of the early developments are provided by Fairbairn et al. (1947) and Chem. Eng. Progress (1948). This work culminated in a patent by Tymstra (1952). The key engineering problem in manufacture of glycerin is separation of glycerin from excess water, salt and impurities. Isolation of ECH was mainly a method for reducing water in the crude glycerin (Tymstra, 1952). Literature descriptions of the actual final purification of glycerin (Lowenheim and Moran, 1975; Petrol. Refiner, 1955) are vague. However, since glycerin is very high boiling (182°C at 2 mmHg), virtually all the impurities except polyglycerols and salt are removed in the light overhead streams.

A process flow diagram is provided in Figure 5.2.2.2A. Crude epichlorohydrin is reacted with caustic soda at 157-180°C and 1.14 mPa (11.2 atm, 150 psig) in a stirred vessel for up to 30 minutes (minimum 10 min). The crude diluted glycerin is neutralized with hydrochloric acid and concentrated to about 80% glycerin in multiple-effect evaporators. The resultant sodium

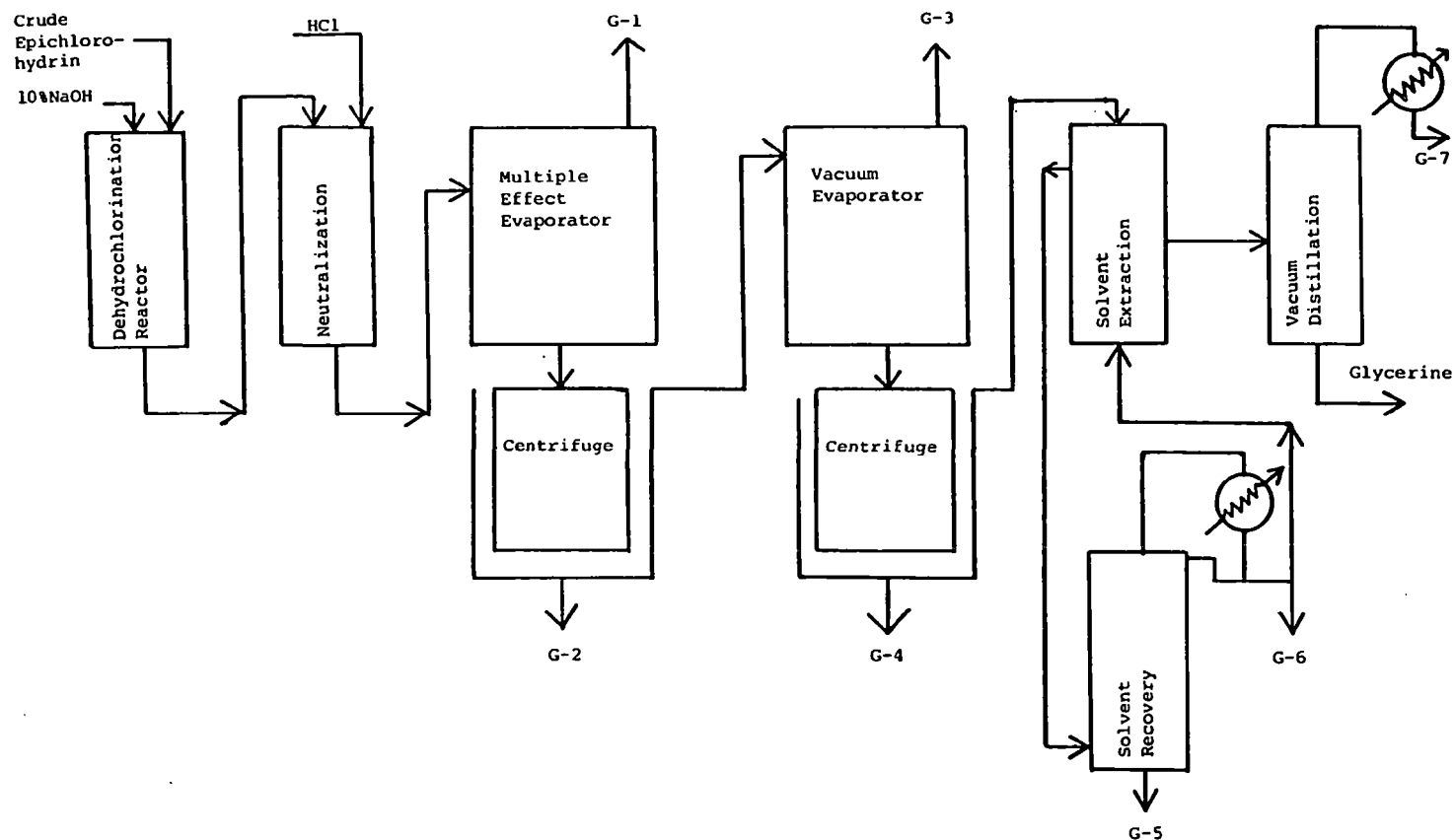


Fig. 5.2.2.2A

Glycerine From Epichlorohydrin

Source: Industrial Process Profiles
 Lowenheim & Moran (1975) and
 Private Files M. Sittenfield.

Table 5.2.2.2A. Summary Waste Streams

Waste Description	Designation Fig. 5.2.2.2A	kg waste/ kg product ^a	Composition	Total* Estimated Generation 10 ⁶ kg/yr
Water Condensate from multiple effect evaporators	G-1	4.5×10^{-3}	Glycerin	0.17
Water Condensate from multiple effect evaporators	G-3	9.5×10^{-3} 61.0×10^{-3}	Glycerin Misc. Impurities	0.37 2.4
Solid sodium chloride	G-2	431×10^{-3}	Sodium chloride	16.6
Solid sodium chloride	G-4	82.5×10^{-3}	Sodium chloride	3.18
Toluene recovery still bottoms	G-5	n.d.	Toluene and heavy impurities	
Toluene recovery overhead	G-6	4.5×10^{-3}	Toluene	0.17
Overhead final purification col'n	G-7 G-7	0.95×10^{-3} 1.55×10^{-3}	Glycerin Toluene	0.04 0.06

^aInd Process Profiles, Chapter 6, EPA 600/2-77-023 (1977).

*Based upon estimated U.S. production glycerin from ECH at 85×10^6 lb/yr (38.6×10^6 kg/yr).

chloride-glycerin slurry is centrifuged to remove salt and then further concentrated in vacuum multiple-effect evaporators to 98 to 99% glycerin. Additional salt is removed by centrifugation. Color may be removed from the glycerin by extraction with toluene at this stage. Finally, the product is steam-vacuum distilled to produce 99+ % pure glycerin.

The waste streams from the process are summarized in Table 5.2.2.2A.

5.2.2.3 Residues of Epichlorohydrin in Glycerin

Dow (Arnold, 1984b) states that no ECH residues were detected in their synthetic glycerin (detection limit 1.5 ppm). This is not surprising considering the rate of base hydrolysis of ECH and the condition of manufacturing glycerin.

According to Piringer (1980), the rate constant (k) for base hydrolysis of ECH is given by

$$k = A \exp (-E/RT)$$

where

$$A = 1.8 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1},$$

$$E = 68,000 \text{ J/mole},$$

$$R = 4.18 \times 1.99 \text{ J/mole deg},$$

and T is the absolute temperature (°K)

Under the condition of manufacturing glycerin, the minimum process temperature is 157°C (sec. 5.2.2.2) this corresponds to 430°K. Thus,

$$k = 1.8 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1} \exp \left[\frac{-68,000 \text{ J/mole}}{4.18 \times 1.99 \text{ J/mole deg}} \right] 430 \text{ deg}$$

$$k = 1.8 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1} \times 5.54 \times 10^{-9}$$

$$k = 1.00 \text{ M}^{-1} \cdot \text{s}^{-1}$$

The solution into which the ECH is mixed is probably at least 1.0 M in base.

$$\begin{aligned}\text{Rate} &= k[\text{base}] [\text{ECH}] \\ &= (1.0 \text{ M}^{-1} \cdot \text{s}^{-1})(1.0 \text{ M}) [\text{ECH}] \\ &= 1.0 \text{ s}^{-1} [\text{ECH}]\end{aligned}$$

The pseudo-first order rate constant for the reaction under these conditions (157°C, 1 molar base) is 1.0 s^{-1} . Thus, the pseudo-first order half-life is

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{1.0 \text{ s}^{-1}} = 0.693 \text{ s}$$

Since the minimum contact time is believed to be at least 10 minutes (600s), it would be very conservative to estimate that, even with problems of mixing, the minimum contact of ECH with the base solution could be 30 s. This is equivalent to 43 half-lives. Thus, the concentration of ECH remaining in the crude product should be no more than

$$\text{ECH residue} = \frac{\text{original concentration}}{(2)^{43}} = \frac{\text{original concentration}}{9 \times 10^{12}}$$

If it is assumed that the original concentration is about 10 M, then

$$\begin{aligned}\text{ECH residue} &= \frac{10\text{M}}{9 \times 10^{12}} = 1.1 \times 10^{-12} \text{M} \\ &= \frac{(92.5 \text{ g ECH/mole}) (1.1 \times 10^{-12} \text{ mole/L})}{(1.26 \times 10^3 \text{ g glycerin/L})} \\ &= 8 \times 10^{-14} \text{ g ECH/g glycerin} \\ \text{ECH residue} &= \text{less than 1 part per trillion}\end{aligned}$$

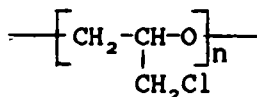
It is clear from these calculations that if any ECH residues occur in crude glycerin it is probably because of poor mixing in the reactor rather than resistance of ECH to hydrolysis. Because of the several high temperature distillations that must be used to concentrate and purify crude glycerin (Figure 5.2.2.2A), ECH residue expected in the final product would be even less than the level calculated above.

5.2.3 Manufacture of Epichlorohydrin Elastomers

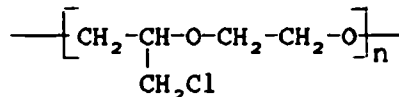
In 1957, EJ Vandenberg of Hercules, Inc. discovered catalysts for obtaining high polymers of epichlorohydrin (i.e., amorphous polyepichlorohydrin) (Vandenberg, 1983). Because Hercules was not a rubber company, there was little initial interest in marketing the material and some production rights were licensed to B.F. Goodrich Chemical Company. In 1963, copolymers of epichlorohydrin and ethylene oxide were prepared. Goodrich began production of the copolymer in 1965 at its plant in Avon, OH under the tradename Hydrin. The copolymer had a variety of desirable properties and Hercules began its own production in 1966 under the tradename Herclor. However, it was not until 1968 that Hercules began construction of a commercial plant, which began operating in March 1970. Recently, Hercules and Goodrich have each expanded their capacities to 24 million pounds per year (Vandenberg, 1983).

The motivation for Vandenberg's experimentation described above (Vandenberg, 1983) seems to have been partly due to the expectation among polymer chemist that poly(ethylene oxide)-type polyethers would have better elastomeric behavior than the polyolefin materials available in the 1950s. However, until Vandenberg's discovery, only low-molecular-weight, liquid polyethers had been obtained (Kirk-Othmer, 1979a).

The idealized structures of ECH homopolymer (abbreviated CO by ASTM) and the ECH-ethylene oxide copolymer (abbreviated ECO) are shown below:



ECH Homopolymer
(CAS No. 24969-06-0)



ECH-Ethylene Oxide
Copolymer
(CAS No. 24969-10-6)

It has been shown that the ECH homopolymer has more than 97% head-to-tail ECH units as shown. Although the 1:1 ECH to ethylene oxide composition is preferred for the copolymer, there appears to be irregularities in which strings of ethylene oxide units occur. The end groups of the polymer chains are normally $-\text{CH}_2\text{OH}$ units (Vandenberg, 1967), but these may be crosslink with the $-\text{CH}_2\text{Cl}$ side chains during curing.

The properties of the polymers are summarized in Table 5.2.3A. the homopolymer has good low temperature flexibility, and excellent resistance to oils, but is not very rubbery (poor rebound). The copolymer has less resistance to oils, but excellent low temperature flexibility and good elasticity. Both polymer have good heat-aging, ozone, and flame resistance (Kirk-Othmer, 1979a).

5.2.3.1. Process Chemistry

Much attention has been given to the development of the catalysts for conducting these polymerizations (e.g., Vandenberg, 1983). The catalyst is prepared by reacting a trialkylaluminum compound such as triisobutylaluminum with less than a stoichiometric amount of water (0.6 moles of water per mole of aluminum alkyl) to form a compound with an empirical formula $\text{R}_2\text{AlOAlR}_2$ where R is an alkyl group. Addition of acetylacetone (one mole per mole of aluminum) to the product yields a more effective catalyst. The formula usually given for this catalyst is shown below.

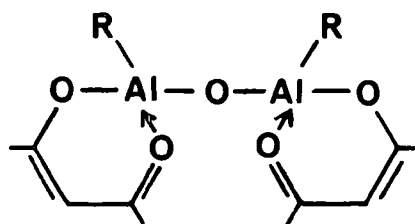


Table 5.2.3A. Properties of Vulcanized Epichlorohydrin Elastomers.

Property	ECH-Homopolymer	ECH-EO Copolymer
Tensile strength (MPa) ^a	15.9	15.0
Ultimate elongation (%)	230	320
Shore A hardness	82	74
Low temperature brittleness (T _b °C)	-18	-40
Lupke rebound (%)		
at 23°C	26	67
at 100°C	75	63
Volume change after immersion (%)		
at 70 hours		
in No. 3 oil at 150°C	4	8
in fuel A at 23°C	0	1
in fuel B at 23°C	8	11
in water at 23°C	0	5

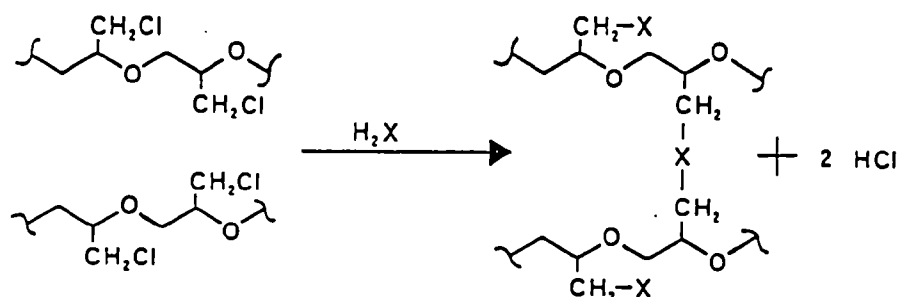
^aTo convert MPa to psi, multiply by 145.
Source: Kirk-Othmer (1979a).

Shih et al. (1982) discussed preparation of similar initiators and noted that their catalysts preparations were not homogeneous. Moreover, more rapid polymerization was achieved when some of the solid was included in the polymerizing mixture.

Both the homopolymer and copolymer are produced by solution polymerization processes in benzene, toluene or methylene chloride solvent (Kirk-Othmer, 1979a). Bulk polymerization and use of aliphatic solvents have been considered, but do not appear to be in commercial application. In the commercial processes the catalysts and solvent are selected to give the highest portion of amorphous polymer. The commercial products do not require separation of crystalline polymer, but this can be achieved on a laboratory scale by dissolving the amorphous polymer in acetone, in which the crystalline form has lower solubility. Because ethylene oxide is more reactive with the catalysts than ECH, an initial composition of 94% ECH and 6% ethylene oxide is required to obtain the desired 1:1 copolymer. Molecular weight of the polymer is controlled by use of a carbonium ion precursor.

Vandenberg (Kirk-Othmer, 1979a) notes that a phenolic antioxidant is added to the polymer solution before solvent is removed. This antioxidant appears to be B.F. Goodrich's "Good-rite 3125", which is a trifunctional hindered phenol in finely divided crystalline form (Elast, 1978).

The ECH elastomers are vulcanized (crosslinked) by difunctional nucleophilic reagents that react with the chloromethyl groups releasing HCl as a byproduct (Kirk-Othmer, 1979a). Crosslinking agents such as



hexamethylenediamine, 2-mercaptoimidazoline and trimethylthiourea have been used. An acid acceptor (such as a stearate salt) must be used to absorb the HCl. Fillers (such as carbon black) are used to increase the tensile strength and plasticizers (such as di(n-octyl) phthalate) are used to improve low temperature flexibility in compounded rubber (Kirk-Othmer, 1979a). Typical vulcanization formulations are listed in Table 5.2.3.B.

5.2.3.2. Process Engineering

The current commercial plant processes have not been published, but based on recent comments by Vandenberg (Kirk-Othmer, 1979a), they seem to vary from the methods described in early patents (Vandenberg 1964a,b,c; 1965; Robinson, 1962; Robinson and Willis, 1967). The current commercial plants appear to be designed for continuous solution polymerization usually employing aromatic hydrocarbon solvents (toluene). A simple process flow diagram is shown in Figure 5.2.3A. Because ethylene oxide is about seven times more reactive than ECH (Kirk-Othmer, 1979a) the initial monomer composition for forming the 1:1 copolymer must be 96% ECH and 4% ethylene oxide. Thus, a considerable amount of excess ECH must be recovered along with the solvent when the copolymer is isolated. Steam stripping is used to remove traces of solvent and ECH monomer from the crude elastomer. According to Vandenberg (Kirk-Othmer, 1979a), proper selection of the solvent and catalyst allows production of a polymer that is mainly amorphous so that separation of crystalline polymer is not required in commercial processes.

Table 5.2.3B. Vulcanizate Formulations.

Ingredient	ECH Homopolymer (parts by wt.)	ECH Ethylene oxide (parts by wt.)
polymer	100	100
carbon black	50	50
stearic acid	1.0	0.75
red lead	5.0	5.0
nickel dibutyldithiocarbamate	1.0	1.0
2-mercaptoimidazoline (NA-22)	1.5	1.5

Source: Kirk-Othmer (1979a).

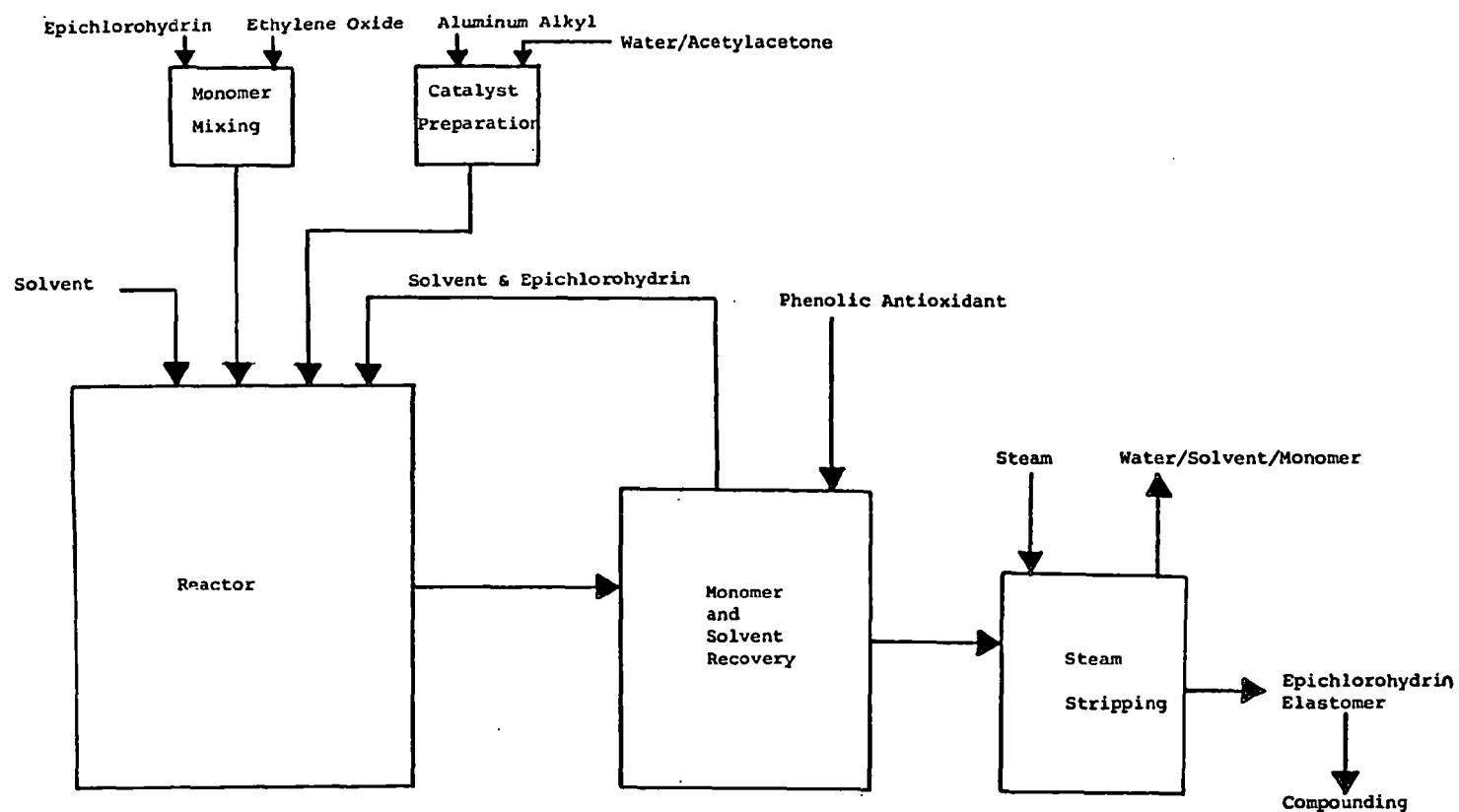


Figure 5.2.3A. Likely Epichlorohydrin Elastomer Process Based on Description of Commercial Process by E.J. Vandenberg (Kirk-Othmer, 1979).

5.2.3.3. Residues of Epichlorohydrin in Elastomers

There is potential for significant residue of ECH monomer in the crude ECH elastomers especially the copolymer, which must be prepared with a large excess of ECH. Reaction of residual ECH with vulcanizing agents (i.e., nucleophiles) or stabilizer additives and adsorption of residual ECH by carbon black filler are credited by Vandenberg (Kirk-Othmer, 1979a) with preventing excessive airborne ECH concentration during storage and processing. The actual ECH residue levels in the elastomers were not stated.

5.2.4. Epichlorohydrin-based Wet-Strength Resins

Natural polymers such as carbohydrate (cellulose/paper) and protein (hair/wool) often are not highly crosslinked. When exposed to water, which hydrates the hydrophilic polymer strands, the fibers can change position (resulting in changes in the size or shape of the object they compose) or they may become completely separated (Kirk-Othmer, 1981a; Britt, 1970). Thus, wet-strength resins are used to form a stable polymeric web among the natural fibers and the web is covalently linked to the natural fibers to give a permanent organization to the natural fibers without changing their desirable properties.

Wet-strength resins containing glycidyl groups or incipient glycidyl groups (i.e., halohydrins) have been prepared by reacting epichlorohydrin with various polymers containing amino groups (Van Eenam, 1980; Kirk-Othmer, 1981a). The ECH wet-strength resins that have had the most commercial importance are based on amino polyamides. Typical examples found in the TSCA Inventory include the following:

<u>Amino polyamide modified by ECH</u>	<u>Wet-strength resin</u> <u>CAS No.</u>
N-(2-aminoethyl)-1,2-ethanediamine with hexanedioic acid	25212-19-5

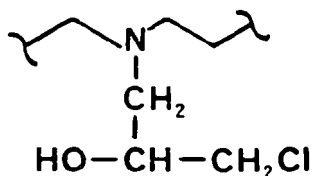
with pentanedioic acid	52470-29-8
with methylenebutanedioic acid	52404-84-9
N,N'-bis(2-aminoethyl)-1,2-ethanediamine with hexanedioic acid	26568-79-6

<u>Polyamine modified by ECH</u>	<u>Wet-strength resin CAS No.</u>
N-methyldiallylamine polymer	37890-28-1
N-(2-aminoethyl)-N'-[2-(2-amino-ethyl)amino]ethyl-1,2-ethanediamine	26658-42-4
N-(6-aminohexyl)-1,6-hexanediamine (hydrochloride salt)	67953-56-4 68239-30-5

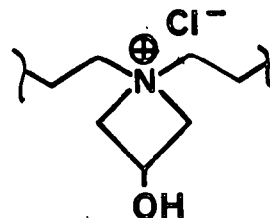
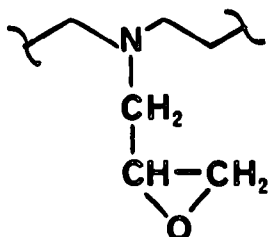
The ECH-modified diethylenetriamine hexanedioic acid polymer (CAS No. 25212-19-5) is the most important compound in this group. Its major producer is Pacific Resins & Chemicals, which produced 13 to 80 million pounds of the resin in 1977 according to the non-confidential portion of the TSCA Inventory. Other producers include Hercules, Inc. and Georgia-Pacific Corporation. Diamond Shamrock and Monsanto were manufacturers of the polyamine resins. Kirk-Othmer (1981a) mentions that use of byproduct still bottoms from hexamethylenediamine production to make wet-strength resins. Some of these resins appear to be in the TSCA Inventory (CAS No. 68784-97-4, 68958-56-4).

5.2.4.1 Manufacture of Wet-Strength Resins

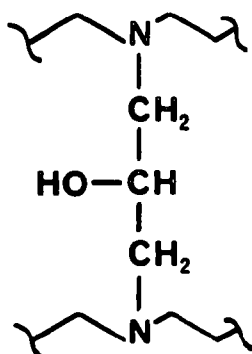
The conventional method of forming wet-strength resins involves reacting polyamines with ECH in alkaline solution and monitoring the viscosity of the reaction mixture (Van Eenam, 1980). The initial reaction between the polyamine and ECH forms ECH adducts of the type shown below:



But some conversion of these intermediates to glycidyl amines and quarternary ammonium compounds occurs under the reaction conditions:

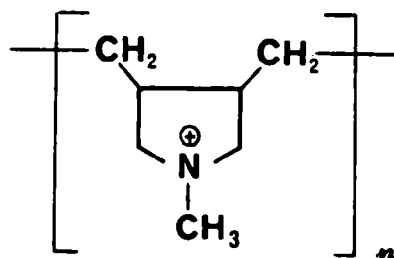


The glycidyl groups begin crosslinking the polyamine resins forming bridges like the one shown below:

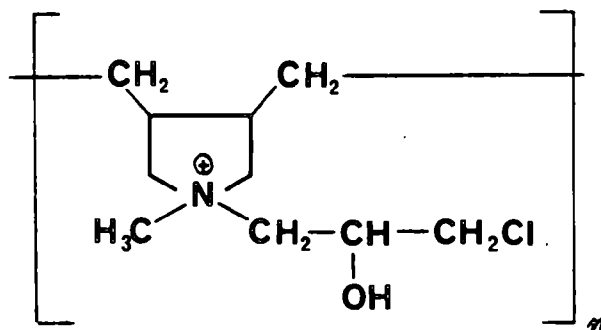


As a result, the viscosity of the reaction mixture begins to rise and unless acid is added to reduce the pH (and stop formation of glycidyl amine groups) the mixture will form a gel, which precipitates. Sulfuric acid is used to stop gel formation in commercial practice (Bales, 1977c). Conventional wet-strength resins are prepared as acidified solutions that are reactivated by adding base just before use. Guise and Smith (1982) have studied the composition of Hercosett 125 (adipic acid-diethylenetriamine-ECH, CAS No. 25212-19-5) and found it to have a number-average molecular weight of 2,100.

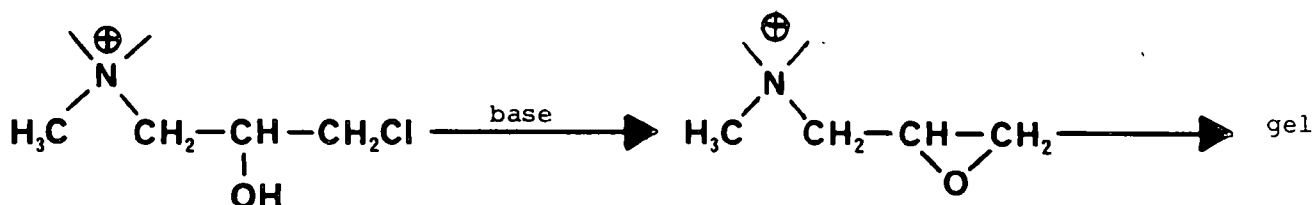
Monsanto (Van Eenam, 1980) patented a process for forming "perepiquat" polymers. The perepiquats are based on polyamines containing only tertiary amino groups. A typical polymer can be formed from diallylmethylamine. The polymer has the structure shown below:



Van Eenam (1980) lists a variety of other polymers and copolymers which contain only tertiary amines and are suitable for forming perepiguats. In each case, the perepiguats are formed by reacting the tertiary amine polymer in a partially protonated cationic form with ECH at 20°C or below. Under these conditions, almost all the amine groups are quaternized to yield structures such as shown below:



Because there are no free amine groups in the polymer, the polymer gels very slowly after activation with base:



The perepiguat polymers readily crosslink cellulose when applied and cured at elevated temperature.

Monsanto (Van Eenam, 1980) compared their perepiguat polymer with a leading commercial ECH-aminopolyamide "S-2064" produced by Hercules, Inc. by the conventional method. Both resin solutions (3 to 10% solids) were activated by adding 7.0 meq of 25% aqueous sodium hydroxide per gram of resin solid over a period of 15 seconds. The activated resin solutions were stirred and diluted to 1.2% solids.

The wet-strength resin solutions were added to a wood pulp slurry at a rate of 5 kg solution/metric ton of pulp slurry. The slurry was allowed to stand at room temperature for 10 minutes before it was formed into sheets and dried at 96°C for 2 minutes. The perepiquat resins (which had longer gel times than the conventional resin) produced stronger paper sheets. Similar tests comparing the Monsanto products with other Hercules products (kymene 557 H and kymene 557 M (see Section 6.5)) gave similar results. Monsanto (Van Eenam, 1980) seemed to be building an argument that the perepiquat resins could be used at lower treatment levels than conventional resins to achieve the same results.

5.2.4.2 Application of Wet-Strength Resins

The wet-strength resins are added at the "wet end" of paper machines (Figure 5.2.4.2A). They are reactivated by adding base just before or during application to the pulp. According to Britt (1970) "The pH of the head box stock system must be maintained at the proper level for the resin being used. The flow of resin solution, in proportion to the quantity of fiber must be closely controlled (in order to meet the wet tensile test required) without using an excess of resin. The percent resin on basis of fiber varies considerably, depending on the grade of paper and the wet strength requirement. Normally the range is from 0.5 to about 1.0% although for special purposes it may go as high as 5%.

The paper at the reel normally has not received sufficient exposure to heat to effect complete cure of resin. For test purposes, a paper sample is heated at about 125°C for 3 to 5 min and then tested for wet tensile strength. Natural aging will develop wet-strength in the product after a few days or weeks. The relationship between the accelerated test and natural aging must be determined experimentally for each mill and product."

5.2.4.3. Release of Epichlorohydrin from Wet-Strength Resins

Wet-strength resins are prepared and used as aqueous solutions. Because of the tendency of conventional resins to form gels, the conversion of ECH is

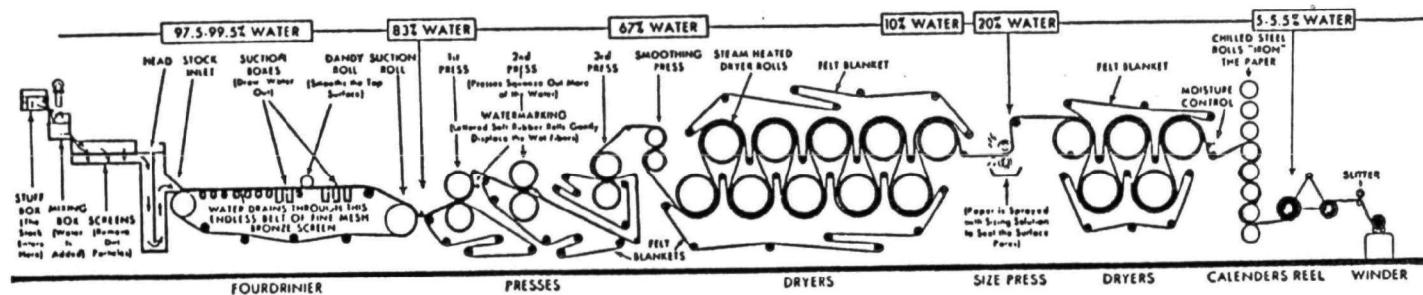


Figure 5.2.4.2A. Diagram of Fourdrinier paper machine.
Source: Riegel's Handbook of Industrial Chemistry.

poor and the aqueous solutions probably have considerable amounts of free ECH. The residual ECH hydrolyzes (see Section 2.3.1) with a half-life of less than 150 hours in aqueous solution, but because of the gel problem, the wet-strength resins are probably used before the ECH levels can greatly dissipate.

It is important to note that sulfuric acid (and not hydrochloric acid) is used to prevent gel formation in conventional wet-strength resins (Bates, 1977c). If hydrochloric acid were used, the excess ECH would be converted to dichloropropanols which would be carried with the resin in aqueous solution. When base is added to activate the resin, the dichloropropanols would be converted to ECH in situ. The amount of ECH potentially introduced by this route would be much greater than the expected levels of residual ECH.

5.2.5 Epichlorohydrin-Based Ion Exchange Resins

Little information was found on ECH-based ion exchange resins. Reactions of epichlorohydrin with ethylenediamine or higher homologues of ethylenediamine produced water-insoluble materials that can be used as anion exchange resins (Dow, 1980). The TSCA Inventory lists a number of these materials including:

<u>ECH Polymer with Amine</u>	<u>Cas No.</u>
1,2-ethanediamine	25014-13-5
N-(2-aminoethyl)-1,2-ethanediamine	25085-17-0
N-(2-aminoethyl)-N'-[2-(2-aminoethyl)amino]ethyl-1,2-ethanediamine	26658-42-4
N,N'-bis(2-aminoethyl)-1,2-ethanediamine	27754-94-5
N,N'-dimethyl-1,3-propanediamine	27029-41-0
1,2-ethanediamine and dimethylamine	42751-79-1

Rohm and Hass Co. and Diamond Shamrock are manufacturers of ion exchange resins.

Rohm and Haas Company (Meteyer and Fries, 1980) has patented a weakly basic ion exchange resin made from ECH and the process for making it. The typical process involves preparing a solution of ECH (about 200 g/L) and a suspending agent such as polybutenylsuccinimide polyamines (about 5 g/L) in chlorobenzene or similar solvent in which the polyamine is not soluble. The solution is heated to about 35°C with stirring and a solution of an amine like triethylenetetramine in water (about 50% solution) is added dropwise. The exothermic nature of the reaction raises the temperature and the reaction is completed by refluxing for up to about 12 hours.

ECH is used in ratios of 2/3 to 1 1/2 times the stoichiometric amount of amine where each amine hydrogen is assumed to react with 1/2 of a mole of ECH (e.g., one mole of triethylenetetramine is equivalent to three moles of ECH). If less than 2/3 of the stoichiometric amount of ECH is used, the final ion exchange resin is too weak for commercial use. On the other hand, if more than 1 1/2 times the stoichiometric amount of ECH is used the final resin is extensively crosslinked and it is too fragile and the rate of ion exchange is too slow for commercial use.

After the reaction is complete, the organic solvent is distilled off and replaced by water at a rate needed to maintain a fluid slurry. The resulting ECH-polyamine condensation product is alkylated to improve the oxidation stability of the final resin. Reductive alkylation can be applied by treatment with formaldehyde/formic acid or exhaustive alkylation can be applied by treatment with any appropriate alkylating agent (e.g., methyl bromide, allyl chloride). In either case, a molar excess of alkylating agent is used to assure conversion of primary and secondary amines to tertiary or quaternary forms.

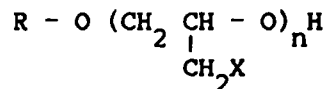
A typical alkylation with formaldehyde is achieved by adding formaldehyde solution to the crude condensate slurry at 55°C and allowing it to react for about 2 hours before adding formic acid to the mixture. About 2 moles of formaldehyde and formic acid are added for each mole of primary or secondary amine in the crude condensate slurry. When alkylation is complete, the resin is isolated, washed and dried and is then ready for packing into an ion exchange column.

5.2.6 Fyrol 2

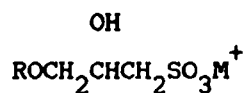
No details have been found concerning the manufacture of tris(1,3-dichloro-2-propyl) phosphate (CAS No. 13674-87-8) from ECH and POCl_3 . The process probably involves reacting POCl_3 with an excess of ECH (ECH may be used as solvent) followed by distillation of ECH/solvent. The resulting product is probably rather pure and may be passed over a solid base to neutralize any acid and remove any monoalkyl and dialkyl phosphate esters. If aqueous alkaline washing is used, a significant amount of Fyrol 2 will dissolve in the wash water and the Fyrol 2 probably has to be dried.

5.2.7 Alkyl Glycidyl Ether Sulfonates

Proctor and Gamble Co. (Whyte, 1976) have been the leaders in development of alkyl glycidyl ether sulfonates (AGES), which are specialty surfactants that appear to be used in cosmetic and personal hygiene applications. The composition of AGES is summarized in this structure

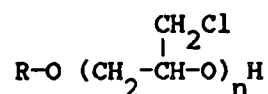


Where R is an alkyl group containing 8 to 22 carbon atoms, $n=1$ to 4 and $\text{X} = -\text{Cl}$, $-\text{OH}$ or $-\text{SO}_3\text{H}$ (Whyte and Korpi, 1963). Some examples found in the public TSCA Inventory include:



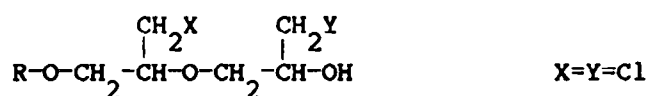
<u>R=</u>	<u>M=</u>	<u>CAS No.</u>
2-ethylhexyl	sodium	58965-18-7
isooctyl	sodium	68072-33-3
6-methylheptyl	sodium	68959-45-5
octyl	sodium	51946-14-6

AGES are made in two steps (Whyte, 1976; Whyte and Korpi, 1962). In the first step, an alcohol (e.g., the C₁₂ cut from reduction of coconut oil) is reacted with excess ECH and an acid (H₂SO₄) or Lewis acid (SnCl₄) catalyst. This "condensation" reaction produces alcohol-polychlorohydrin ethers:



Typically, the mole ratio of alcohol to ECH used in the condensation is about 1:1.4 to ensure that all the alcohol is converted without building excessively long polychlorohydrin chains (n=1 to 4). The reaction time is about 15 minutes at 220°F using 1.5% SnCl₄ catalyst.

The second step is the sulfonation and can be accomplished by the Strecker reaction of the chlorohydrin ether with sodium sulfite, or by conversion to an intermediate glycidyl ether followed by reaction with sodium bisulfite. The direct Strecker reaction produces a water-soluble product that is difficult to separate from the sodium chloride (salt) and the insoluble, finely-divided basic tin chloride (SnCl₂O). The Strecker reaction of



yields

50%	X=Y=	-SO ₃ ⁻
35%	X= -OH , Y=	-SO ₃ ⁻
15%	X= -Cl , Y=	-SO ₃ ⁻

If the manufacturer prefers a salt-free product, the alkyl glycidyl ether can be formed as an intermediate that can be washed free of salt and catalyst before reaction with bisulfite (Whyte, 1976).

5.2.8 Epichlorohydrin-Based Water-Treatment Chemicals

Two ECH-based flocculants for water treatment were identified by Kirk-Othmer (1980b). They are polymers of ECH with methylamine and dimethylamine.

poly(2-hydroxypropyl-1-N-methylammonium chloride) CAS No. 31568-35-1

poly(2-hydroxypropyl-1-N,N-dimethylammonium chloride) CAS No. 25988-97-0

They are both cationic resins, but the polymer with dimethylamine is more important commercially because it has only quaternary ammonium ions which make it insensitive to pH and chlorine-resistant (Kirk-Othmer, 1980b).

A request to Nalco Chemical Company for product bulletins on their ECH-based water treatment resins was answered by data sheets on Nalcolyte 8105, 7135, 8101, and 8100 each of which is described as an aqueous solution of polyquaternary ammonium chloride (Nalco, 1984). They are light yellow liquids with slight ammoniacal odor and their pHs vary from 3 to 8. Nalcolyte 8105, 8108, and 8100 are approved by the EPA for treatment of potable water at an application rate of up to 20 ppm. For Nalcolyte 8100, the manufacturer recommends (Nalco, 1984):

<u>Application Program</u>	<u>Application Rate</u>	<u>Use</u>
Conventional clarification or lime softening	1 to 10 ppm	primary coagulant to partially or completely remove inorganic salts

Clay polymer clarification	1 to 10 ppm	primary coagulant in a total replacement for alum or iron coagulants
direct filtration	0.2 to 2.0 ppm	primary coagulant for low turbidity and colored water
filter aid	0.05 to 1.0 ppm	secondary coagulant to improve filter effluent quality

6.0 OCCUPATIONAL EXPOSURE TO EPICHLOROHYDRIN

There has been considerable interest in occupational exposure to epichlorohydrin as a result of fear of adverse health effects. A summary of occupational standards for ECH is presented in Table 6.0A. Tracor Jitco, Inc. conducted a broad survey of ECH exposure at manufacturing and user sites for NIOSH (Bales, 1978). In this chapter, we summarize the NIOSH studies and supplemental data that we have found in the literature.

Dermal exposure to ECH is not a routine occurrence and there are no standards for dermal contact. In section 6.6, we discuss some aspects of the problem of dermal exposure.

6.1 Exposure Associated with Manufacture of Epichlorohydrin and Glycerin

Tracor Jitco (Bales, 1977d; Doyle and Bales, 1977) conducted industrial hygiene surveys at the epichlorohydrin-glycerin complexes run by Dow Chemical at Freeport, TX (July, 1976) and Shell Chemical at Deer Park, TX (August, 1976). Shell's glycerin production has recently closed down, but they still make ECH for epoxy resins and sales. Because of the relevance of these plants to this report, they will be discussed in some detail.

6.1.1 Dow's Epichlorohydrin-Glycerin Plant

Dow's ECH-glycerin plant occupies a block in their large (1,000 acre) petrochemical complex on the Brazos River near the Gulf of Mexico. The ECH-glycerin plant has been in operation since 1956 and has a design capacity of 260 million pounds of ECH per year.

Dow's process follows the steps discussed in Sections 5.1 and 5.2.2. Allyl chloride is produced from propene in an adjacent block and delivered to the ECH-glycerin plant by pipeline.

Table 6.0A. Exposure Limits for Epichlorohydrin

	TWA ^a		STEL ^b	
	ppm, v/v	mg/m ³	ppm, v/v	mg/m ³
PEL ^c (OSHA), 1981	5	19	-	-
TLV ^d (ACGIH), 1981	2	10	5	20
RES ^e (NIOSH), (1978)	0.5 ^f	2 ^f	5	19
Shell Internal Standard (1978)	1	5	3	15

^aTime-weighted average, 8-hour day/40-hour week, unless otherwise noted.

^bShort Term Exposure Limit, 15 minutes, max.

^cPermissible Exposure Limit (Occupational Safety and Health Administration), updated 1981.

^dThreshold Limit Value, (American Conference of Governmental Industrial Hygienists).

^eRecommended Exposure Standard (National Institute for Occupational Safety and Health).

^fTime Weighted Average, 10-hr day/40-hour week.

Source: Shell (1982).

The allyl chloride is reacted with hypochlorous acid to produce dichloropropanols and the dichloropropanols are reacted with base to yield ECH. The product is isolated and purified by distillation. ECH is converted to glycerin by hydrolysis with base.

Dow's ECH-glycerin plant employs 50 persons (Doyle and Bales, 1977):

<u>Supervisory and Technical Staff</u>		<u>Production Staff</u>	
Superintendent	1	Production Foreman	2
Engineers	4	Shift Foreman	4
Laboratory	9	Operators	13
Secretary	1	Maintenance	11
Totals	15		35

- o The supervisory and technical staff and production foremen have little opportunity for exposure to ECH. Shift foremen may spend 50% to 100% of their time in the production area.
- o There are two classes of operators: Control A and Control C. Control A is the senior operator and is responsible for monitoring control instruments and making necessary adjustments to maintain production. They spend more than 80% of the work shift in the control room.
- o The Control C Operator spends about 50% of the work shift in the production area; one of his major duties is the collecting and analysis of the process samples. During the sampling operation he is required to wear an organic vapor respirator. At the time of the study (1976), automatic sampling and analysis equipment was being installed which will relieve the Control C Operator of the sampling responsibility.
- o Maintenance personnel are primarily mechanics and pipe-fitters. Their exposure to epichlorohydrin is a function of the time spent in repairing and servicing epichlorohydrin units.
- o There is one Head Packaging Operator and four general operators. The Head Packaging Operator spends most of his time in supervisory and administrative duties. The four general operators are responsible for loading epichlorohydrin into railroad tank cars, tank trucks, and drums. In addition, they maintain the warehouse and load trucks with filled drums.

The results of the analyses are summarized in Table 6.1.1A.

6.1.2 Shell's Epichlorohydrin-Glycerin Plant

Shell ECH-glycerin plant is part of a large petrorefining and petrochemical complex located adjacent to the Houston Ship Channel. Manufacture of ECH began at this site in 1945. The ECH-glycerin plant ("G-plant") began production in 1948. Some ECH was delivered to the Deer Park complex by barge from the Shell plant in Louisiana, but with the end of Shell's synthetic glycerin production, this has probably stopped.

Shell's ECH-glycerin plant includes the following operators (Bales, 1977d).

<u>Job</u>	<u>Number</u>
Production of allyl chloride (G100)	3
Production of ECH and crude glycerin (G200-300 and HTH)	2
Production of refined glycerin (C-plant)	1
Tank farm operator	1

A summary of the analytical results for these operators and other employees is presented in Table 6.1.2A.

6.1.3 Dermal Exposure to Epichlorohydrin at Epichlorohydrin - Glycerin Plant

No information was found on frequency, duration or intensity of dermal exposures to ECH during its manufacture or the manufacture of glycerin. It is clear from reading the manufacturers literature that such incidents would be considered to be a major failure of proper handling procedures. Maintenance of pumps, valves and fittings and filling of drums appear to be the activities with the most potential for exposure.

6.2 Exposure Associated with Manufacture of ECH-Epoxy Resins

Bales (1977a,b,d) and Doyle and Bales (1977) conducted industrial hygiene surveys at several plants where epoxy resins were manufactured from ECH:

Table 6.1.1A. Summary of Atmospheric Samples for Epichlorohydrin and Allyl Chloride at Dow's Epichlorohydrin-Glycerin Plant (July, 1976)

Shift	Worker Sampled	Type or Duration of Sample	Atmospheric Concentration (ppm)	
			Epichlorohydrin	Allyl Chloride
1	Control A Operator	TWA	0.38	0.24
2	" " "	TWA	N.D.*	N.D.
3	" " "	TWA	0.23	N.D.
1	Control C Operator	TWA	0.33	0.68
2	" " "	TWA	N.D.	N.D.
3	" " "	TWA	0.39	0.11
1	Control C Trainee	TWA	0.41	0.11
2	" " "	TWA	N.D.	0.26
1	Shift Foreman	TWA	0.17	0.3
2	" "	TWA	0.1	0.17
3	" "	TWA	0.14	N.D.
1	Pipefitter 1	5 hrs	N.D.	N.D.
1	" 2	5 hrs	N.D.	N.D.
1	" 3	5 hrs	N.D.	N.D.
1	Packing Op. 1 - Drum	4 hrs, 20 min	N.D.	
1	" " 2 - "	4 hrs, 20 min	N.D.	
1	Packing Op. 1 - Tank Car	3 hrs, 10 min	0.28	

*Not detectable based on the limit of the analytical method (0.05 ppm for ECH and 0.1 ppm for allyl chloride) according to Bales, 1978.

Source: Doyle and Bales (1977).

Table 6.1.2.A Summary of Epichlorohydrin Exposure Levels at Shell's ECH-Glycerin Plant, C Plant and Shipping (1976).

Job Types	No. Samples	Epichlorohydrin TWA Exposure Levels ^a	
		Median (ppm)	High (ppm)
<u>Glycerine Plant Area</u>			
G 100 Operator	6	N.D.	0.26
G 300 Operator	5	N.D.	2.1
G 300 Foreman	6	N.D.	0.31
HTH Operator	4	0.30	0.92
G 300 Control Room	5	N.D.	0.50
Maintenance Foreman	2	0.29	0.50
G 300 Area	1	N.D.	N.D.
<u>C Plant Area</u>			
C Plant Operator	6	0.18	0.34
C Operations Control Room	1	0.37	0.37
<u>Shipping</u>			
Tank Loading Operator	1	0.27	0.27

^aDetection limit 0.05 ppm according to Bales (1978).

Source: Bales (1977d).

Dow Chemical, Freeport, Texas, July, 1976

Shell Chemical Co., Houston, Texas, August, 1976

Celanese Coatings and Specialties Co., Louisville, Kentucky,
February, 1976

Ciba-Geigy Corp., Toms River, New Jersey, May, 1976

In all cases, 1976 exposures were below 1 ppm TWA. Dow had some data from 1975 that showed some cases of potential exposure to about 3 ppm, but these exposures were mitigated by protective equipment.

6.2.1 Dow's Epoxy Resin Plant

The epoxy resin unit at Dow's Freeport complex is about a mile from the ECH-glycerin plant. ECH is pumped to the epoxy plant and stored in closed tanks. Bisphenol A and Novolac resins are prepared by conventional techniques, the excess ECH is stripped and the resins (in solvent) are pumped to the resin finishing area. When operators are in the production area, they are required to wear long-sleeve jackets, gloves, and eye shields and must carry an organic vapor respirator for emergency use. During normal operations there are only two operators in the epoxy resin area. They spend about 80% of their time in the control room and 20% in the production area.

Dow provided Doyle and Bales (1977) with some monitoring data for 1973 and 1974. Most of the personnel samples were below 0.03 ppm. In 1974 the highest level for an operator was 0.90 ppm. Some grab samples, presumably of areas where leaks or spills were expected, had concentrations up to 15 ppm. In the study by Doyle and Bales (1977), no detectable levels of ECH were found (Based on other work by these worker, the detection limit appears to be 0.05 ppm (Bales, 1978)).

6.2.2 Shell's Epoxy Resin Plant

Shell's epoxy resin plant is similar to Dow's and employs conventional technology. There are about 9 operators per shift; altogether about 60 people are routinely employed in the epoxy plant area. Some key jobs include:

- | | |
|----------------------------|---|
| 2A Kettle Operator | - includes process control of manufacture of a solid epoxy resin. |
| 3A Kettle Operator | - includes process control of the manufacture of a liquid epoxy resin. |
| 3A Utility Kettle Operator | - includes process control in manufacture of liquid epoxy resin. |
| Resin Train Operator | - includes process control of liquid epoxy resins. |
| Feed and Recovery Operator | - includes process control in liquid epoxy resin manufacture of feed materials and recycling or recovery. |
| .Shift Foremen | - supervises the epoxy resin processes. |

The results of ECH monitoring is summarized in Table 6.2.2A.

6.2.3. Celanese's Epoxy Resin Plant

The Celanese epoxy resin plant studied by Bales (1977b) is located in the city of Louisville, KY. Epoxy resin production began here in 1952. The plant was operated by Devoe and Raynolds until 1965. ECH is received in railroad tank cars and stored in outdoor tanks. As needed, it is pumped to weighing tanks on the fourth floor of the plant. It is then allowed to flow by gravity into the reaction kettles where bisphenol A and caustic are added also via piped connections. Apparently, after the reaction is complete, water and solvent are added and the aqueous brine is removed. The resin in solvent is removed and the solvent is distilled. Liquid resins are shipped out in railroad tank cars and solid resins are shipped in bags.

About 35 employees are directly involved in manufacture of epoxy resins at this plant. Monitoring data are summarized in Table 6.2.3A.

6.2.4 Ciba-Geigy's Epoxy Resin Plant

In the period 1960 - 1966 Ciba-Geigy produced ECH and epoxy resins at their Toms River, NJ plant. Now ECH is purchased and received in railroad tank cars. The ECH facility and process seem to be similar to the Celanese

Table 6.2.2.A Summary of Epichlorohydrin Exposure Levels at Shell's Epoxy Plant, August, 1976.

Job Type	Epichlorohydrin TWA Exposure Levels		
	No. Samples	Median (ppm)	High (ppm)
Shift Foreman	6	N.D.	0.60
2A Kettle Operator	5	N.D.	0.10
3A Kettle Operator	4	N.D.	0.56
Resin Train Operator	6	0.23	0.83
Feed and Recovery Operator	4	0.26	0.52
3A Utility Operator	2	N.D.	N.D.
Maintenance Foreman	1	N.D.	N.D.
Finishing Operator	2	0.45	0.80

According to Bales (1978) the detection limit is 0.05 ppm ECH.

Source: Bales (1977d).

Table 6.2.3A Results of Air Sampling Analyses at Celanese's Epoxy Resin Plant in Louisville, KY, February, 1976.

Sample Location/Description	Operation	Epichlorohydrin Air Concentration ppm
Resin Kettle Area - 3rd level. Side of Kettle (weight scale)	Charge ECH - Draw off	0.35
Resin Kettle Area - 3rd level. Top of Kettle (Catwalk)	Charge EPI - Draw off	0.59
Wet Tank Room	Normal	1.5
Control Room - 3rd level	Normal	N.D. ^a
Resin Kettle and Weight Scale Area - 3rd level	Charge Bisphenol A	0.05
Resin Kettle and Weight Scale Area - 3rd level	Charge ECH	0.07
-----	-----	nil
Resin Kettle and Weigh Scale Area - 3rd level	Pressure on Kettle-Draw off	0.13
Resin Kettle and Weigh Scale Area - 3rd level	Charge Solvent and Draw down	0.05

^aNot detectable based on an analytical limit of 0.05 ppm ECH.
Source: Bales (1977b).

plant discussed above. About 60 people are involved with epoxy resin production. In 1976, Bales (1977a) did not find any detectable exposures to ECH at this site. The detection limit appears to be 0.05 ppm based on other reports by this author (Bales, 1978).

6.2.5 Dermal Exposure to Epichlorohydrin during Manufacture of Epoxy Resins

There appears to be little opportunity for dermal exposure to pure ECH during manufacture of epoxy resins. No information on frequency, intensity or duration of dermal exposures to ECH during the manufacture of epoxy resins was found.

6.3 Exposure Associated with the Use of Epoxy Resins

6.3.1 Inhalation Exposure

We have found one report of very high exposures of employees to ECH during use of ECH epoxy resins (Chrostek and Levine, 1981). In this case, large structural steel members were being coated with a two-part epoxy paint by hand spraying in a large enclosed building with poor ventilation. High levels of ECH and glycidyl ether of bisphenol A were found (Table 6.3A and 6.3B).

Shell (1982) provided some monitoring data that they consider to be typical of ECH exposure during use of epoxy resins (Table 6.3C). Other monitoring data have been collected by OSHA. The positive findings from the OSHA National Inspection Summary Report for June 1, 1979 to March 31, 1983 are summarized in Table 6.3D. The numerous negative findings are probably similar to the report by Lewis (1980) who studied workmen who were using epoxy resin to encapsulate instruments for measuring water flow in a pipe. In this process, the epoxy resin and curing agent were mixed using a hand-held mixer and then poured into a water pipe where the instruments were attached. No ECH or phenyl glycidyl ether were found in any time-weighted-average air sample (detection limits 0.1 mg/sample and 0.04 mg/sample, respectively).

Table 6.3A Results of Sampling for Epichlorohydrin Vapor, Palmer Industrial Coatings, Williamsport, PA

Date	Job Description	Sample Period	Airborne Concentrations*	Remarks
Sept. 9	Foreman	08:35-15:00	45.5	Operator's Exposure
	Sprayer	07:15-10:05	88.2	Operator's Breathing Zone
	Sprayer	10:05-15:18	76.7	Operator's Breathing Zone
	TWA		80.7	
	Sprayer	07:20-15:30	2.4	Operator's Breathing Zone
Sept. 10	Sprayer	07:29-15:25	138.9	Operator's Breathing Zone
	Sprayer	07:10-12:10	83.3	Operator's Breathing Zone
	Sprayer	12:10-15:25	82.1	Operator's Breathing Zone
	TWA		82.8	
	Sprayer	07:10-12:00	56.9	Operator's Breathing Zone
	Sprayer	13:25-15:00	104.7	Operator's Breathing Zone
	TWA		68.2	
	Sprayer	07:10-12:00	43.9	Operator's Breathing Zone
	Sprayer	13:25-15:30	42.0	Operator's Breathing Zone
	TWA		43.3	
	Foreman	07:25-12:00	36.3	Operator's Exposure
	Foreman	12:30-14:55	42.6	Operator's Exposure
	TWA		37.8	

*Denotes milligrams of contaminant per cubic meter of air sampled, detection limit 0.05 mg.

Source: Chrostek and Levin (1981).

5.2 →

Table 6.3B Results of Sampling for Bisphenol A and Glycidyl Ethers of Bisphenol A at Plamer Industrial Coatings, Williamsport, PA

Date	Worker	Time Period	Bisphenol A	Glycidyl Ethers* of Bisphenol A	Remarks
09/09	Painter	07:15-10-05	0.6**	0.6	OBZ***
	Painter	10:05-15:18	0.6	24.18	
	Painter	07:29-15:25	0.6	4.86	OBZ
	Painter	07:20-15:30	0.6	2.27	OBZ
	Foreman	08:30-15:00	0.6	2.72	OE****
09/10	Painter	07:10-15:30	0.6	28.61	OBZ
	Painter	07:10-15:25	0.6	8.19	OBZ
	Painter	07:10-15:39	0.6	11.85	OBZ
	Foreman	07:25-14:25	0.6	5.38	OE

* Denotes micrograms of contaminant per cubic meter of air sampled.

** Denotes lower limit of detection, 6 micrograms per sample.

*** Denotes operator's breathing zone.

**** Denotes operator's exposure.

Source: Chrostek and Levine (1981).

Table 6.3C. ECH Exposures During Industrial Use of Epon Resins

Type of application	ECH content of resin (ppm)	Airborne ECH (ppm)
Filament winding of pipe	1	N.D.* (0.05)
Coatings manufacture	1, 1.6	N.D. (0.05)
Encapsulation	1	N.D. (0.05)
Filament winding - pipe	10	N.D. (0.05)-0.1
Filament winding - pipe	10	0.1
Filament winding - tape	1	N.D. (0.05)-0.1
Bow mfg.	10 max.	N.D. (0.05)
Adhesives mfg.	15-88.1	N.D. (0.05)-1.6
Epoxy tank spraying	1	N.D. (0.05)
Epoxy grout application	16	0.6-1.1
Simulated field application	1100 (spiked)	N.D. (0.05)-0.15
Resins formulation	--	N.D. (0.05)

*N.D. - None detected, 0.05 ppm detection limit.

Source: Shell (1982)

Comment: These results are actual monitoring dates that Shell (1982) consider to be typical of ECH exposure during use epoxy resins. The data in Table 5.2.1.5C represent equilibrium (i.e., maximum) concentration of ECH achieved in static laboratory tests (using various concentrations of ECH in the resin and various working temperatures). The data in Table 6.3D are the results of investigations of worker complaints and represent the positive findings culled from 39 investigations involving 300 workers (73 personally sampled).

**Table 6.3D Summary of Positive Epichlorohydrin Findings from OSHA Surveys^a
June 1977 - March 1983.**

Area	SIC	Type of Business	Number of Exposed Workers	ECH Levels (ppm)
Boston	3832	Optical Instr. & Lenses PTR Optics Corp.	2	TWA 3.8
-	2821	Plastic Materials, etc. Wilmington Chem. Corp.	1	TWA 0.71
Tampa	3612	Power, Distr. & Spec. Trans. Instrument and Transformer Co.	18	TWA 0.14
Appleton	3991	Brooms and Brushes Besh Roller Inc.	0 6 0	TWA 2.66 TWA 3.38 TWA 3.02
Milwaukee	3079	Misc. Plastic Products Lewis Systems Mensha Corp.	2	TWA 0.01
Lubbock	3479	Coating, Engraving, etc. Spincote Plastic Coatings	2 2	TWA 3.70 TWA 3.70

^aDuring this time period OSHA conducted 39 plant surveys and monitored 79 workers out of 300 potentially exposed. No exposures in excess of the 5 ppm PEL were observed.

Source: OSHA (1983)

6.3.2 Dermal Exposure

Dermal exposure to ECH during use of epoxy resins is possible mainly for coating, casting, molding, adhesive and patching applications. In most cases the ECH levels in the resin are probably below 10 ppm and dermal contact would be brief. Except for some coating applications, dermal contact should be limited to the hands and gloves would probably be worn. One report of dermatitis due to penetration of gloves by one or more components of Araldite MY 750 (a coal tar epoxy resin with glycidyl ether reactive diluent made by Ciba-Geigy) was found (Pegum, 1979). Any residual ECH in this product would probably be the most mobile component, but the reactive diluent might also penetrate gloves so it cannot be assumed that ECH caused the dermatitis. No data on the frequency, intensity or duration of dermal exposure during use of epoxy resins were found.

6.4 Exposure Associated with the Manufacture and Use of ECH-Elastomers

6.4.1 Inhalation Exposure

According to Hercules product information cited by Vandenberg (Kirk-Othmer, 1979a), ECH levels in air have been monitored during manufacture, storage and processing (at three customer plants). The levels were generally found to be less than 0.1 ppm, well below the Federal standard of 0.5 ppm. Data from the Hercules plant collected in July 1977 using the NIOSH method showed that the time-weighted-average exposure of most workers (including operators, helpers, mechanics and laborers) was below the detection limit (i.e., 0.1 ppm). In three cases, operators working around the polymerization vessel (including such tasks as changing ECH pump check valves) had TWA exposures of 0.2 ppm (Hercules, 1983b). At processing plants, no detectable TWA exposures were found. The processing plants included elastomer weighting, extrusion, two-roll mill mixing, and molding (Hercules, 1983b).

6.4.2 Dermal Exposure

Dermal contact with uncured ECH elastomers may occur, but no data were found on the frequency, intensity or duration of contact. Cured (compounded and vulcanized) ECH elastomer is not expected to contain significant ECH residue.

6.5 Exposure Associated with Wet-Strength Resins

6.5.1 Manufacturing

Tracor Jitco (Bales, 1977c) surveyed the Hercules, Inc. plant at Savannah, GA on June 17, 1976. Wet-strength resins of the ECH-aminopolyamide type have been manufactured here in a two-story semi-enclosed building continuously since 1952. They are sold under the tradename kymene.

ECH is brought in by tank trucks and transferred to a storage tank several hundred yards from the kymene plant. The ECH is pumped as needed to the kymene plant for batch operations. The manufacturing process is carried out in closed reaction vessels. First the aminopolyamide resin is formed in one vessel and the polymer is fed into a second reactor where it is diluted with water. ECH is pumped into the second reactor and the reaction begins as described in Section 5.2. The reaction is stopped before the crosslinking becomes too great by adding sulfuric acid, diluting the solution with a large amount of water and cooling. The aqueous solution of wet-strength resin is pumped to tank cars, tank trucks or drums for shipping (Bales, 1977c).

The kymene process employs 2 to 5 operators and one supervisor over three shifts. It was estimated that 50 workers had worked in the kymene facility at various times between 1952 and 1976. The results of air sampling are summarized in Table 6.5A (Bales, 1977c). Occupational exposure during manufacture of wet-strength resins is very minor.

Table 6.5A Results of Air Sample Analyses at a Hercules, Inc.
Wet-Strength Resin Plant (1976).

Sample location	Sample type	Job/sample description	Shift	Epichlorohydrin air concentration (ppm)
Kymene Building 2nd level	GA	Kettle area Batch 557 H	1	0.36
Kymene Building	TWA	Kymene operator	1	0.15
Kymene Building 1st level	GA	Adj. to polymer kettle pump	1	N.D.
Kymene Building 1st level	GA	Kymene kettle	1	N.D.
Kymene Building 2nd level	OP BZ	(Total EPI reaction period) Add EPA to reaction kill	1	N.D.
Kymene Building 2nd level	TWA	Kymene operator	2	0.05
Kymene Building 2nd level	GA	Kettle area Batch 557 H	2	0.42

N.D. - non-detectable based on an analytical limit of 0.05 ppm.

OP BZ - operators breathing zone (near head).

TWA - time-weighted-average personnel sampler.

GA - general area.

Source: Bales (1977c).

Bales (1977c) makes the statement that there are no ECH residues in the product, but no data are given. If residues of ECH do remain in the product (or if dichloropropanols in the product are converted to ECH when the resins are activated by base prior to use, see 5.2.4.3), then there might be ECH exposure during application of wet-strength resins to paper.

6.5.2 Possible Exposure during Use

If residues of ECH are contained in the aqueous wet strength resin solutions, some exposure to ECH may occur during manufacture of paper. Dermal exposure to the resin solution is possible but probably slight. The most likely type of exposure would be to ECH vapor released during the dewatering and drying steps. It is very unlikely that free ECH residues remain in finished paper.

6.6 Dermal Exposure to Epichlorohydrin

Both Dow (1980) and Shell (1969) emphasize avoidance of dermal contact with ECH in their industrial hygiene programs. A specimen label for ECH is shown in Figure 6.6A. In particular, it makes the following admonition:

"Wear chemical goggles, rubber gloves, and protective clothing when handling. Medium or heavy thickness rubber protective equipment is preferred. Polyethylene, polyvinyl chloride, and thin rubber give protection for minor liquid contact only. Epichlorohydrin in continuous liquid contact penetrates these materials in a relatively short time. Do not use leather articles, such as shoes or gloves, as they cannot be decontaminated."

Similarly, Shell (1969) states:

"Keep the liquid off the skin and clothes. The greatest hazard results from spilling epichlorohydrin on the skin or clothing. Consequently, when danger of spillage on the body exists, workers should wear protective clothing and face splash guards. Furthermore, since epichlorohydrin slowly penetrates rubber, rubber clothing that has been in contact with the liquid should be discarded."



EPICHLOROHYDRIN

A HIGHLY REACTIVE CHEMICAL INTERMEDIATE

DANGER POISON

MAY BE FATAL IF SWALLOWED • CAUSES IRRITATION • PROLONGED CONTACT CAUSES BURNS • HARMFUL IF INHALED • HARMFUL IF ABSORBED THROUGH SKIN • VAPOR IRRITATING TO EYES, NOSE, AND THROAT • MAY CAUSE ALLERGIC SKIN REACTION • FLAMMABLE

Do Not Take Internally • Do Not Get in Eyes, on Skin, on Clothing • Do Not Breathe Vapor • Use Only with Adequate Ventilation • Keep Container Closed • Wash Thoroughly After Handling • Keep Away From Heat, Sparks, and Open Flame • Do Not Cut or Weld Container

FIRST AID: If swallowed, induce vomiting immediately by giving two glasses of water and sticking finger down throat. Get medical attention. Never give anything by mouth to an unconscious person.

If inhaled, remove patient to fresh air, keep him warm and quiet. Call a physician immediately. If not breathing, give artificial respiration, preferably mouth-to-mouth. If breathing is difficult, give oxygen.

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before reuse. Discard contaminated leather articles.

NOTE TO PHYSICIAN: Consult standard literature.

HANDLING PRECAUTIONS

Wear chemical goggles, rubber gloves, and protective clothing when handling. Medium or heavy thickness rubber protective equipment is preferred. Polyethylene, polyvinyl chloride, and thin rubber give protection for minor liquid contact only. Epichlorohydrin in continuous liquid contact penetrates these materials in a relatively short time. Do not use leather articles, such as shoes or gloves, as they cannot be decontaminated.

HIGHLY REACTIVE COMPOUND

Epichlorohydrin and its derivatives which contain the epoxide group are generally unstable in the presence of acidic or basic substances. Epichlorohydrin, glycidol and glycidyl ethers may react vigorously to explosively with strong sulfuric acid and with anhydrous metal halides. These materials should be handled with due precautions by experienced and competent personnel.

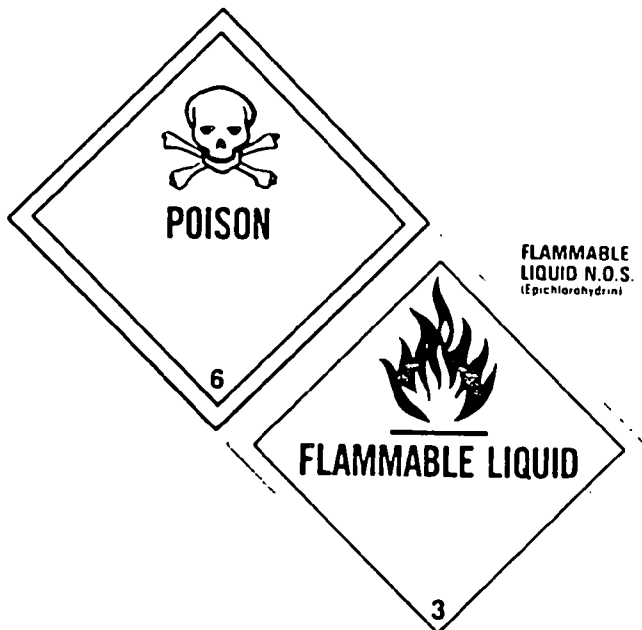
THE DOW CHEMICAL COMPANY

AND SUBSIDIARIES

MIDLAND, MICHIGAN 48640 USA HÖRGEN, SWITZERLAND HONG KONG
CORAL GABLES, FLORIDA 33134 USA SARNIA, ONTARIO, CANADA

* Trademark of THE DOW CHEMICAL COMPANY

18.93 L / 5 GAL



E378

Figure 6.6A. Specimen Label for Epichlorohydrin.

Dow's product bulletin for ECH devotes 4 of its 12 pages to handling procedures for ECH. Dow (1980) also notes:

"Short contact with epichlorohydrin may result in slight irritation. Prolonged contact may result in severe irritation and a superficial burn. These effects may be delayed, appearing some time after contact. Human experience has also indicated that a small percentage of persons may develop hypersensitivity from repeated contacts.

Epichlorohydrin is readily absorbed through intact skin in acutely toxic amounts (The LD₅₀ for rabbits is in the range of 0.5 gm/kg.). Reports in the literature indicate an appreciable hazard of systemic intoxication from repeated slight contacts. There is little doubt that one of the greatest hazards associated with the handling and use of epichlorohydrin is from contact with the skin.

Proper protective equipment and garments should be worn to prevent the material from contacting the skin or clothing. Do not use leather shoes; use rubber shoes or overlays when working in an area where epichlorohydrin may be contacted. It is recommended that workers bathe with soap and water after each work day and wear freshly laundered clothing each morning (Note: Because epichlorohydrin slowly permeates rubber, any gloves or rubber garments should be worn only for a limited time when in gross contact with epichlorohydrin). It is desirable to wash rubber gloves with soap and water each day, and dry them in a moving stream of air. Discard gloves if they show any sign of deterioration."

First Aid: If exposure should occur, immediately irrigate skin with copious amounts of water. Remove all contaminated clothing while continuing decontamination with copious amounts of water for 15 minutes. Obtain medical attention immediately."

According to ACGIH (1971), there were no reported instances of serious injury to industrial workers during the production or handling of epichlorohydrin through 1971 although several cases of skin burns from contact with the liquid had occurred. Dermal contact appears to be most likely during transfers and maintenance operations. Dow and Shell have made efforts to minimize the risk of such accidents and mitigate their effects if they occur for their employees and customers.

It is possible to make estimates of the amount of ECH that would penetrate intact skin in a spill situation. The calculations that are presented below do not take into consideration the damage that concentrated ECH does to skin and so the results probably underestimate the actual exposure that would occur. As described by Scheuplein (1965) the flux (J) of a chemical through skin can be calculated as follows:

$$\text{Flux} = J = k_p C \quad (1)$$

where

J = the amount of solute that penetrates a unit of skin per unit time
 $\text{mg/cm}^2 \cdot \text{s}$,

k_p = the permeability constant (cm/h), and

C = the difference in concentration between outside and inside mg/cm^3 .

It has been found that k_p is a function of temperature and can be related to the activation energy for diffusion (Blank et al., 1967). The activation energy for diffusion of polar alcohols through human skin is about 16.5 kcal/mole and the activation energy for non-polar alcohols is about 10.0 kcal/mole above 23°C.

If k_p is available for the substance of interest, J can easily be calculated using equation (1) for any particular concentration of the substance applied to the skin surface. However, since k_p is seldom known, it is useful to look at a more detailed equation (Idson, 1971):

$$J = \frac{K_m D \Delta C}{\delta} \quad (2)$$

where

K_m = the partition coefficient of solute between skin and the solvent
 D = the diffusion coefficient of solute in skin (cm^2/s)
 C = the concentration difference of solute across skin (mg/cm^3)
 δ = thickness of skin (i.e., stratum corneum) in cm.

Overall, the skin seems to have lipophilic character, and since the solvent for the substance is often water, linear relationships between K_m and the octanol/water partition coefficient (P) have been suggested (Roberts et al., 1977):

$$\log K_m = 0.57 \log P - 0.1 \quad (3)$$

The diffusion coefficient (D) is also related to molecular properties of the substance. The molecular size is the only feature generally recognized to be related to diffusion coefficients, and larger molecules are generally expected to diffuse more slowly than small ones (Calvert and Billingham, 1979; Scheuplein and Blank, 1973). Scheuplein (1965) notes that the diffusion constant is inversely proportional to the cube root of the molecular volume (i.e., changing the volume by a factor of 4 changes D by a factor of 1.6).

In practice, it is probably most reasonable to assume that chemicals with similar octanol/water partition coefficients and similar molecular size will penetrate the skin at similar rates at the same temperature. In Table 6.6A the permeability constants (k_p) through human skin and the octanol/water partition coefficients are listed for a series of alcohols. We noted that the log octanol partition coefficient for ECH is 0.30 (Chem et al, 1981), which is similar to log P for propanol. Using the k_p for propanol from Table 6.6A and the density of ECH 1.17 g/cc as the maximum possible concentration of ECH (Dow, 1980):

$$\begin{aligned}
 J = \text{flux} &= (0.004 \text{ cm/h}) (1.17 \text{ g}/\text{cm}^3) \\
 &= 4.7 \text{ mg}/\text{cm}^2 \cdot \text{h}
 \end{aligned}$$

Table 6.6A. Permeability Constants and Octanol/Water Partition Coefficients for Alcohols.

Alcohol	Permeability constant ^a for human skin, 40°C (cm/h)	Log P (octanol/water) ^b
ethanol	0.001 (-3) ^c	-0.32
propanol	0.004 (-2.4)	0.34
butanol	0.007 (-2.2)	0.88
pentanol	0.040 (-1.4)	1.40
hexanol	0.073 (-1.1)	2.03
heptanol	0.096 (-1.0)	2.41 (est.)
octanol	0.11 (-0.95)	3.15

^aExtrapolated and interpolated from Figure 2 of Blank et al. (1967). Roberts et al. (1977) provided similar data for several phenols. If the data from Roberts et al. (1977) Table 1 are corrected from 25°C to 40°C using the log P-dependent extrapolation of Blank et al. (1967), the results would be similar to these. In general, changing the temperature from 25°C to 40°C increases the k_p for polar compounds by a factor of about 10 and nonpolar compounds by a factor of 2.

^bLeo et al. (1971).

^clog (k_p) in parentheses.

If we assume a spill might involve 100 cm² of skin and would be washed off within 0.1 h (6 minutes)

$$\text{estimated dose} = (4.7 \text{ mg/cm}^2 \cdot \text{h})(100 \text{ cm}^2)(0.1 \text{ h})$$

estimated dose = 47 mg of ECH absorbed in spill of neat liquid onto 100 cm² of skin followed by decontamination in 6 minutes.

Because the k_p used here assumes steady state diffusion, immediately cleaning the skin (e.g., with 30 seconds) probably stops exposures before penetration is achieved (Scheuplein, 1967). At longer exposure times, damage to the skin probably results in faster permeation. Both these factors point to the need for immediate decontamination of ECH spills on skin or clothing.

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