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GLYCIDYL ETHERS & POLYETHERS OF BISPHENOL-A, TETRACHLOROBISPHENOL-A & HYDROLYZED AROCLOR 1262

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PLASTICS DIVISION RESEARCH DEPARTMENT

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I. INTRODUCTION:

The market for epoxy resins has been projected to substantial quantities by 1960 (Ref. 1). Monsanto has a basic position in bisphenol-A and other polyhydric phenols which are used in these products. Considerable capital is invested in manufacturing facilities for thermosetting resins which may be threatened somewhat by epoxies or which might be advantageously supplemented by a line of epoxy resins.

The manufacture of epoxy resins has been considered previously and the opportunity to enter the field as a licensee rejected. As the use of epoxy resins has grown, the question of their manufacture periodically recurred. Up to the present time no thorough patent search, process study or economic evaluation has been made and these form the only sound basis for defining Monsanto's interest in these products.

This report reviews the research contribution to the several projects listed above - a study of the chemistry of epoxy resins with emphasis on the use of Monsanto polyhydroaromatics, the development of laboratory processes for commercial epoxies and a search for technological advantage which might result through the use of new chlorinated diphenols (hydrolyzed Aroclors and tetrachlorobisphenol-A) (Ref. 2 & 3). It also includes the results of economic analyses by Division Engineering.

This work was supplemented by a thorough patent survey concerning the epoxy resins, made with the cooperation of the Springfield Patent Department. The initial intent of this work was to explore the chemistry of epoxy resins based on bis-phenol-A (BPA) and other Monsanto dihydricphenols as it pertained to the use of these products in thermosetting resin systems. It developed, however, that these raw materials might be better exploited by entry into the epoxy resin field. It was recognized, that although chlorinated polyhydric phenols might find a place in the epoxy market, entry into the resin field would be determined principally by the economics based on bis-phenol-A.

II. SUMMARY:

An economic analysis was made of the manufacture of the three basic epoxy resin types in use today:

- Epon 828* - based on bis-phenol-A and epichlorohydrin; liquid, high epoxy content, used as an industrial adhesive.
- Epon 1001*- based on bis-phenol-A and epichlorohydrin; solid, low epoxy content, used in surface coatings.
- Epon 562* - based on glycerol and epichlorohydrin; liquid, high epoxy content, used as an adhesive and in textile treating.

*Shell Chemical

The studies were based on laboratory procedures developed for the products based on bis-phenol and on a patent procedure for the glycerol based product.

A recommendation to enter the epoxy field as a resin manufacturer can not be made based on the following results of this economic analysis:

	Selling Price	Return on Investment After 50% Tax: Market BPA	Integrated BPA
Epon 1001 type			
*3,000,000 lbs/yr.	$0.605/lb.	6.0%	9.0%
*5,000,000 lbs/yr.		6.7%	10.7%
Epon 828 type			
*1,000,000 lbs/yr.	$0.90/lb.	9.6%	
*3,000,000 lbs/yr.		26.6%	22.0%
Epon 562 type			
*1,000,000 lbs/yr.	$1.10/lb.	8.6%	
*3,000,000 lbs/yr.		21.0%	

*Monsanto Sales.

The most profitable products and those with the greatest growth potential are those which do not allow Monsanto to take full advantage of its raw material position. Epon 828 uses an excess of epichlorohydrin which contributes most to raw material costs. Epon 562 uses no Monsanto products. Without a basic position in epichlorohydrin, the economics are not sufficiently attractive to encourage capital investment.

Laboratory procedures were developed for the synthesis of liquid and solid epoxy resins based on bis-phenol-A (BPA) in good yields. The diglycidylether of tetrachlorobisphenol-A (TCBPA) was prepared in quantitative yields, and a patent application on the process was filed. A series of polymeric epoxies were synthesized in moderate to high yields by reacting epichlorohydrin with TCBPA and mixtures of TCBPA and BPA. Tetrachlorobisphenol-A gives epoxy resins of high epoxy content which are solid, fast curing and of good color. This raw material should definitely be exploited in the resin field.

Hydrolyzed Aroclors (chlorinated bi-phenyls) form another series of dihydric aromatics. A laboratory procedure for the preparation of the diglycidyl ether of hydrolyzed Aroclor 1262 was developed and a patent application filed. The initial samples of hydrolyzed 1262 were not homogeneous with regard to dihydroxy content; they were as much as 24% mono-hydroxy. This contributed markedly to the poor performance of the resins. It is suggested

that a new hydrolysis procedure be established which will furnish all dihydroxy components. This raw material should then become attractive as another building block for epoxy resins.

A fairly complete patent survey of the epoxy field was made concerning manufacture, curing and use in other thermosetting systems, including a search in the Washington Patent office. It is concluded that a competitive line of epoxy resins based on BPA can not be developed without infringement. More patent possibilities exist with systems based on phenolic lump resins, TCBPA and mixtures of BPA and TCBPA. Epoxy resins can be used in combination with many thermosetting systems. Those of principal interest to Monsanto are phenolic-protein adhesives, melamine, urea and phenol formaldehyde resins, polyurethane, nylons, polyacrylonitriles and sulfonated polystyrene. In the curing of epoxy resins, most of the coverage is specific and covers a broad range of materials.

III. CONCLUSIONS:

Monsanto's potential sales in the epoxy resins field would be reasonable at the following levels:

Epon 828 type	3,000,000 lbs/yr.
Epon 1001 type	5,000,000
Epon 562 type	1,000,000

At current prices, using market priced raw materials, only Epon 828 shows a return on investment sufficiently attractive for capital investment. As this product is used in greater quantities resulting in lower price, the return quickly becomes marginal. Integration of the bis-phenol-A facilities has little effect on these returns due to the relatively low proportion of BPA compared to Epichlorohydrin. Epon 562 does not use BPA and the profitability of Epon 1001 is not effected markedly by integration of BPA facilities. Epichlorohydrin is common to all of the materials, however, and only through integrated manufacture of epichlorohydrin can this line of products become interesting economically and there is little else to warrant the manufacture of epichlorohydrin.

Epoxy resins of the types described can be manufactured in conventional processing equipment similar to that now employed for the synthesis of solid and heavy viscosity thermosetting products. Monsanto is thoroughly experienced with the techniques involved. Good yields of high quality products have been synthesized in the laboratory from bis-phenol-A, tetrachlorobisphenol-A and hydrolyzed Aroclors.

It would be most difficult to enter the epoxy resin field without infringement of patents as reaction products of bis-phenol-A and epichlorohydrin are well covered. Resins based on TCBPA, mixtures of TCBPA with BPA and hydrolyzed Aroclors are relatively free of infringement as are products based on phenol-formaldehyde

resins. These products, however, are specialty items and it is questionable whether the volume will reach major proportions.

The use of epoxy resins as modifiers for Monsanto's line of thermosetting products is definitely the most promising immediate means of utilizing the properties of epoxies. These modifications are essentially patent free and in certain areas viz. phenolic-protein adhesives, offer interesting products.

IV. RECOMMENDATIONS:

1. Monsanto should not enter the field of epoxies as a resin producer.

2. Tetrachloro-bis-phenol-A, hydrolyzed Aroclors and similar dihydric aromatics are definitely attractive raw materials for epoxies and the program now in effect at Organic and Dayton for developing these products should be encouraged.

3. The use of epoxy resins and epoxy chemistry in thermosetting systems based on phenol, melamine, etc., is worthy of detailed study.

4. If manufacture of epichlorohydrin and its related by-products is ever considered, the manufacture of epoxy resins will warrant re-examination.

V. PATENT STATUS:

A patent application is pending on the process for the production of the diglycidyl ether of tetrachlorobisphenol-A and the ether.

A patent disclosure claiming the process for the preparation of the glycidyl ether mixture of hydrolyzed Aroclor 1262 has been filed.

The results of a fairly complete patent search are summarized below:

Manufacture:
Monsanto can - manufacture epoxy resins based on phenolic lump resins, tetrachlorobisphenol-A, and mixtures of TCBPA with BPA within certain limits.

Monsanto can not - develop a competitive line of epoxy resins based on BPA without infringement.

Use:
Monsanto can - incorporate epoxy resins in phenolic-protein adhesive mixtures and probably prepare resins by reacting epichlorohydrin with water solutions of the sodium salts of methylol phenols (highly alkaline, liquid phenolic resins).

Blend epoxy resins with melamine, urea and phenolic resins within certain limits. Ternary blends are mostly free of infringement. Blend epoxy resins with polyurethanes, nylons, acrylonitrile, acrylamide, furans, rubber, sulfonated or carboxylated styrenes.

Curing:
Monsanto can - develop specific curing systems and obtain patents.

Monsanto can not - cure with well known curing agents including carboxylic acids, anhydrides, sulfonic acids (and their chlorides), isocyanates, isothiocyanates, poly alcohols, phenolic hydroxyl groups or phosphoric acid. Many specific curing agents are covered which include amines, polyamides, amides, etc.

It may be concluded that the most fruitful area for circumventing existing patents is the synthesis of epoxy resins based on phenolic lump resins and from mixtures of BPA and TCBPA.

Approved by: _____
F.M.Dickey, Patent Dept.

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VII. EXPERIMENTAL:

The syntheses of epoxy resins involve straight forward techniques of reaction, neutralization, extraction and distillation. Common laboratory equipment designed for these purposes are satisfactory.

All of these resins are synthesized according to similar procedures:

1. Reaction of epichlorohydrin with a polyhydric compound. This is generally exothermic and careful control is required. The initial reaction products are chlorohydrin ethers.

2. Where an excess of epichlorohydrin is used, viz., in high epoxy containing products, the excess is recovered by vacuum distillation.

3. The crude product is treated with excess base and dehydrohalogenated to form the epoxy compounds.

4. Usually, several water washings are required to remove the inorganic salt and unreacted base.

5. The final product is dehydrated under vacuum to a relatively high end temperature.

6. The products are characterized by analysis for epoxy oxygen, hydrolyzable chloride and ash. The results are translated into percents of diglycidyl ether and ether chlorohydrins.

Detailed experimental procedures are given below for the preparation of all products synthesized in this study.

A. Apparatus

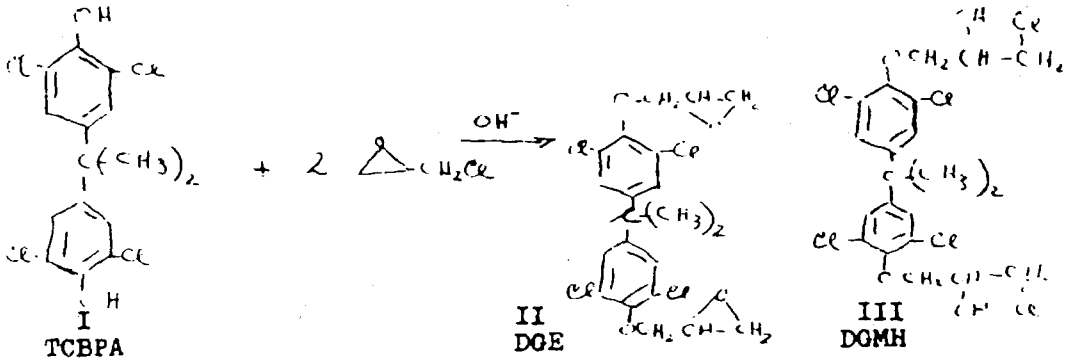
The reactions were carried out in standard laboratory equipment except as indicated under separate procedures. This consisted of a 3-necked flask fitted with a stirrer and two U-shaped adapters. The latter were fitted with two Friedrichs condensers, a thermometer dipping into the reaction mixture and a stopper. The falsk was heated by a Glas-Col mantle. For the synthesis of the high epoxy containing products, an ice bath was always included in the experimental

set up.

B. Procedure

(1) Tetrachlorobisphenol-A (TCBPA)

(a) Preparation of the diglycidyl ether of TCBPA



I TCBPA

II DGE

III DGMH

The initial condensation of TCBPA with ECH is highly exothermic: it is absolutely necessary to have an ice-H_2O bath ready when running this action.

TCBPA (1281 g, 7 eq.) and 1298 g ECH (13.8 eq, 100% XS) were mixed and heated with stirring to 84°. The procedure and observations were as follows:

Time (Min.)	Temp. (°C)	Remarks
0	84	The Glas-Col mantle was removed. 185 cc of NaOH stock soln (7.7 N) were added at once (1.42 eq).
5	99-100	The system refluxed (2 phase reflux) An ice bath was applied intermittently to contain reaction but the temperature was held above 95°.
7	99-100	Solid phase appeared (NaCl)
10	100-101	Reflux subsided
14	94°	Heat was supplied and the reaction mixture was held at 95-100° for 2.5 hours.

The excess ECH was then removed under a continually decreasing pressure and continually increasing temperature to a final pot temperature of 122° at 20-22 mm. 91.7% of the excess ECH was recovered.

To the residue from the distillation (at 110-111°) were added 819 cc NaOH stock soln. (7.7 N, 6.3 eq., 10% overall excess). The mixture cooled to 82°. The mixture was reheated to 112° and kept in the range 110-113° for 8.75 hours. The mixture was allowed to cool over approximately 2 hours. During the reaction with NaOH and cooling, samples of the aqueous phase were removed and analyzed for total alkalinity. The results are shown in Graph I.

The resin was then washed with H_2O. Hot water was added and the mixture heated to 95-102° and kept in this range for 1/2 hour. The mixture was then cooled to about 65-75° and the H_2O decanted. The first wash was with 750 ml H_2O and the succeeding 4 washes were 1000 ml each. The washes were analyzed for chloride and hydroxyl ions. The results are shown in Table I.

TABLE I

Wash No.	Total eq. Cl	Total eq. OH
1	4.97	0.35
2	1.78	0.12
3	0.22	0.013
4	0.02	0.002
5	0.01	Neutral to Litmus

The product was then dehydrated under vacuum as described below:

Time (Min.)	Temp.(Pot °C)	Pressure (MM)	Remarks
0	90	--	Vacuum applied. Variac at 80V.
5	65	ca-70-80	The mass was too viscous, the vacuum was released and the mass was reheated.
10	80	120-125	Distillation was satisfactory
15	65-70	120-125	Pressure was slowly lowered
25	75	75	--
35	104	30	Variac was set at 55V
60	125	25-30	Variac was set at 45V
75	125	25-30	Distillation was complete

The decrease in weight of the original mass was 138g (9% by weight of resin obtained).

The yield of product was 1664g. The product was odorless, slightly yellow and slightly cloudy and it crystallized slowly on standing at room temperature (m.p. 95-98°).

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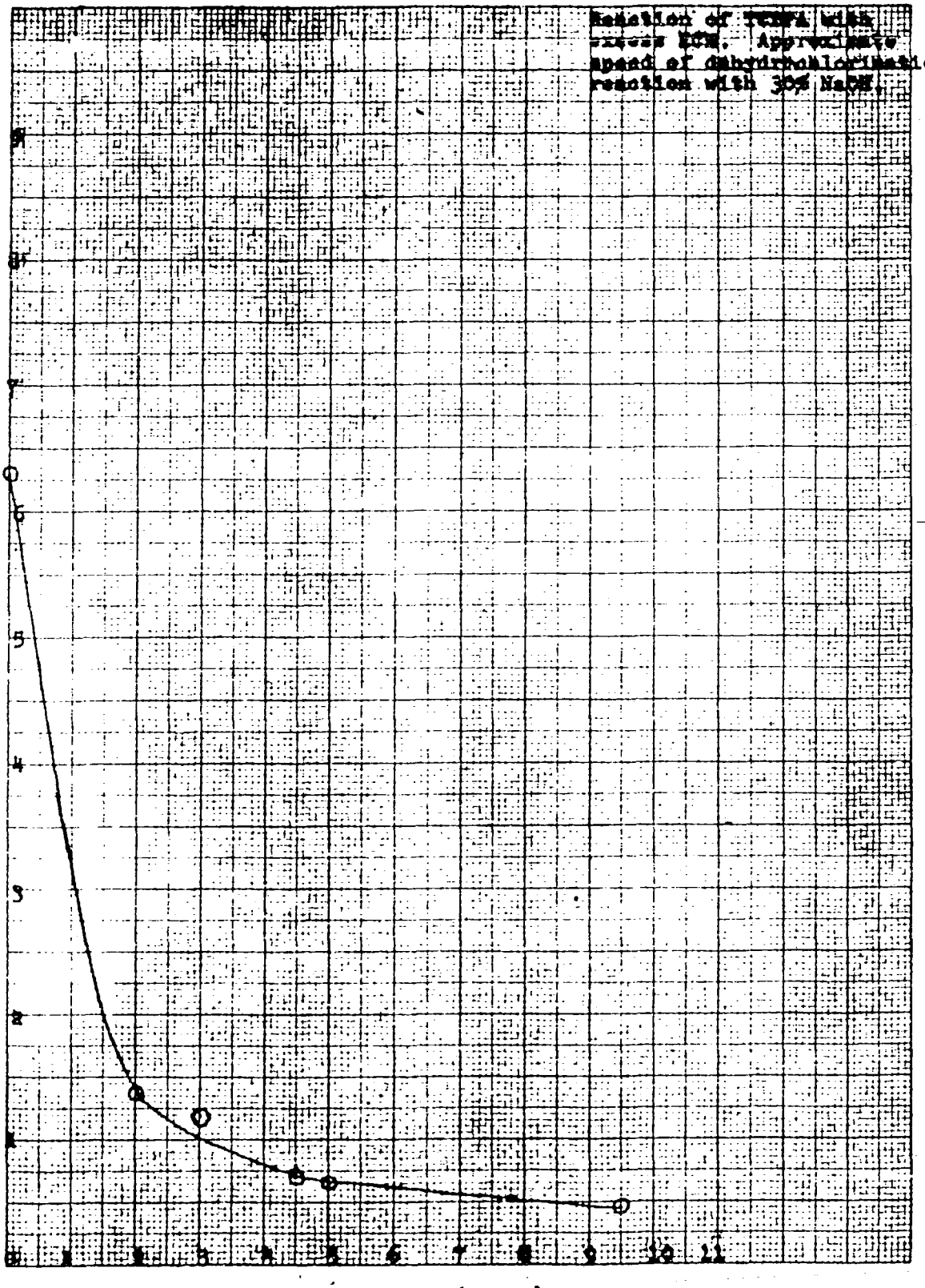
GRAPH I



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Analysis: Epoxy Oxygen: 6.39, 6.39% (95.4% DGE)
Hydrolyzable Chloride: 0.46, 0.48% (3.65% DGMH)
Ash (1600°F): 0.00

The percentage yield was 99.8%. The basis for calculating the yield is given in the Appendix.

A portion of the product was filtered through a medium porosity fritted glass funnel at 130-145° under vacuum to give a perfectly clear, slightly yellow product. The filtration was a very slow process.

(b) Isolation of solid diglycidyl ether of TCBPA

A sample of dehydrated tacky product, 458 g, was melted and poured slowly into 1500 cc ice cooled methanol with vigorous stirring. The mixture was then stirred for 1.75 hours at room temperature. The mixture was filtered. The solid was triturated under a small portion of MeOH and filtered. The solid was dried at room temperature overnight. The filtrates were evaporated to dryness to yield a residue of 25g. (5.4%). After drying overnight, the solid was warmed at 50-60° and dried in a desiccator under vacuum for several days. The yield of white free flowing powder was 418g. (92%).

A similar result was obtained using ethanol as a solvent:
Melting point range: 93-98°C.

Analysis: Epoxy oxygen: 6.52% (97.4% DGE)
Hydrolyzable chloride: 0.16% (1.2% DGMH)
Ash (1600°F): 0.019%

The infra red spectrum of this product is shown in Appendix D.

(c) Isolation of initial condensation product

The same procedure described for the preparation of the diglycidyl ether of TCBA, through the recovery of excess ECH was followed, using 183g TCBPA (1 eq) and 185g (2 eq) ECH. Cooling was not necessary but nevertheless, an ice-H_2O bath was kept handy. A one liter flask was used for the experiment.

To the residue at about 100° were added 300 cc dioxane (purified by refluxing with solid KOH and distilling). The mixture was filtered and the dioxane filtrate distilled at 30-40 mm to a pot temperature of 120-130°. Yield: 269 g.

Analysis: Epoxy Oxygen: 1.11, 1.13%
Hydrolyzable Chloride: 10.70, 10.49%

(d) Preparation of the diglycidyl ether of TCBPA in dioxane solvent

To the product obtained as above (228g) were added 400 cc dioxane and the product dissolved by warming and then finally heated at 97-98°. To the solution were added 104cc NaOH solution (7.5 N, 31.2g NaOH, 10% excess). The temperature dropped to 76°. The two phase system was heated to reflux at 92-93° and refluxed for 9.5 hours. During refluxing NaCl precipitated. The mixture was cooled and filtered. The filtrate was poured into a separatory funnel and the lower aqueous layer withdrawn at room temperature. The upper dioxane layer was transferred to a flask and the dioxane distilled off at 30-40mm to a final pot temperature of about 125°C. Yield: 198g (97.5%).

Analysis: Epoxy Oxygen: 6.45, 6.49%
Hydrolyzable Chloride: 0.30%
Ash: 0.00 (1600°F)

(e) Preparation of Glycidyl Polyethers

This involves the reaction of ECH with TCBPA in the molar ratio 2 to 1. TCBPA (183 g, 1/2m) was mixed with ECH (92.5 g, 1m) and warmed to 100°. The mantle was removed and to the solution were added 45 cc of 7.5 N NaOH solution (13.5g, 0.336 eq). The temperature dropped to 95° and almost immediately rose to reflux at 105-106° (pot temperature). The procedure and observations were as follows:

Time (Min)	Temp (Pot, °C)	Remarks
0	105-106	Refluxing
3	- -	Mixture turned cloudy
12	95	Heat supplied to maintain the reaction mass at 95-105°
13	95	50.5cc 7.5 N NaOH solution added (15.2g, 0.38 eq). Temperature dropped to 84°. The mass was reheated to 95-105°.
61	97	50.5 cc 7.5 N NaOH solution added (10% excess). Temperature dropped to 87°. The mass was reheated to 95-105°.
136	105-110	The reaction was discontinued.

The taffy like product was washed twice with 300 cc water at 95-100°, 1/2 hour for each wash. The water washes analyzed 0.974 eq chloride ion.

The residue from the wash was dehydrated under vacuum (30-40 mm) to a final pot temperature of 138°C. The resin was a slightly yellow, slightly cloudy soft solid at room temperature. Yield 230 g (96.4%)

Analysis: Epoxy Oxygen: 5.34, 5.35%
Hydrolyzable Chloride: 0.41, 0.36%

(f) Reaction of ECH with TCBPA in the molar ratio 1.57 to 1

This reaction was carried out in a steam jacketed laboratory kettle normally used for preparation of phenol-formaldehyde resins. The speed of the anchor agitator was about 40 RPM. To the kettle were charged 1830 g (5 m) TCBPA and 3880 g of 10% (by weight) NaOH solution. The mixture was stirred and warmed to 45° by circulating 100° H_2O in the jacket. At a batch temperature of 45°, 726g (7.86m) ECH were charged rapidly to the kettle. The temperature slowly rose to 54° when a clear solution was obtained. Within five minutes the mixture turned cloudy and the temperature rose rapidly to reflux. The reflux stopped at four minutes. Steam was circulated in the jacket and the mixture brought to reflux and kept at reflux for about 80 minutes. The aqueous phase was decanted and the resin given 4 one-hour water-washes at 95-100° with 4000 cc H_2O. The washed resin was dehydrated under vacuum, first at about 310 mm and finally at about 40 mm to a final pot temperature of about 150-160°C. Yield: 2065g (about 90%).
The resin was a yellowish and almost clear brittle solid at room temperature.

Analysis: Epoxy Oxygen: 2.41, 2.38%

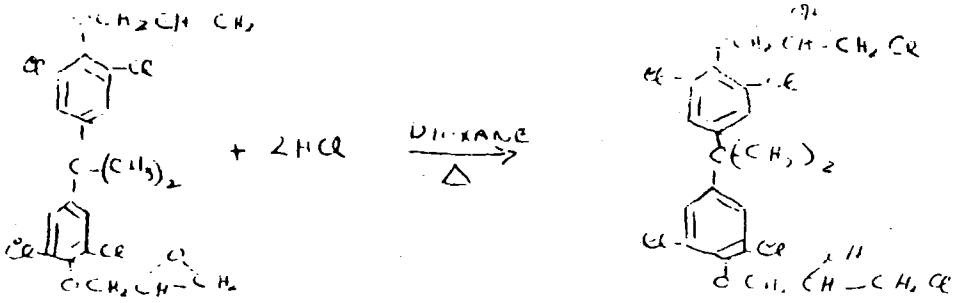
(g) Preparations of Resins from Mixtures of TCBPA and BPA

TCBPA (9.15g, 0.05 eq), BPA, (108.3g, 0.95 eq) and ECH (92.5 g, 1 eq) were mixed and heated to 40°. To the mixture were added 67cc NaOH solution (0.15 g NaOH/cc). The temperature rose rapidly and within five minutes the solution clouded. After 10 minutes stirring, 67 cc NaOH solution were added and the mixture heated to reflux (101-102°, Pot Temp). After 25 minutes at reflux, 80 cc NaOH solution (0.3g NaOH/cc) were added and the mixture heated to reflux (108-109°). After 1/2 hour, the mass was cooled to 60° and the aqueous phase was decanted. The resin was washed with H_2O at 90-100° until neutral to litmus and practically free of chloride ion. The resin was dehydrated under vacuum to a final pot temperature of 150°C at 34 mm. Yield 159 g. The product was yellowish, slightly cloudy and almost solid at room temperature.

Analysis: Epoxy Oxygen: 4.87, 4.87%

(h) Preparation of the di-α-glycerolmonochlorohydrin (DGMH) of TCBPA

This derivative was prepared from a mixture of DGMH and DGE by hydrolysis of the DGE present with aqueous HCl. The material used in the reaction is described under Run No. 3 Table XII, and is referred to as "substrate" below.



To 250 cc dioxane was added 50cc 6NHCl (2% excess over DGE present) and the mixture was warmed to 50°. To the mixture was added dropwise 100 g of substrate dissolved in 200 cc dioxane. No vigorous reaction was observed after the addition of about 15 cc. The mixture was heated to 85-92° and the rest of the substrate was added dropwise over 1.25 hours. After complete addition, the mixture was heated at 92° for 1/2 hour. Dioxane was distilled off to a pot temperature of 115° at 760 mm during 2.5 hours. The residual cloudy mixture was washed twice with 400 cc portions of H_2O at 70-90° for 0.5 hours each wash. The wash H_2O from the second wash was neutral to litmus. After decanting the wash H_2O, the residue was dehydrated to a final pot temperature of 136° at about 20 mm. Yield: 110g.

Analysis: Calcd. for $C_{21}H_{22}Cl_6O_4$:
Hydrolyzable Chloride: 12.86%

Found: Hydrolyzable Chloride, 12.48%

The infra-red spectrum of this product is given in Appendix D.

The product showed no tendency toward gellation on mixing with triethylenetetramine and heating at 160°C for 5 minutes.

The resin had a dry rubber of 15 seconds at 150°C with triethylenetetramine.

(2) Hydrolyzed Aroclor 1262

(a) Preparation of the Glycidyl Ether Mixture of Hydrolyzed Aroclor 1262 in Dioxane Solution

The addition reaction of hydrolyzed Aroclor 1262 and epichlorohydrin (ECH) is highly exothermic. An ice bath should always be handy when attempting this reaction.

To a five liter flask, adapted as already described were charged 1326g (6 eq) hydrolyzed Aroclor 1262 and 1116 g (12 eq, 100% excess) ECH. The mixture was warmed to 75°. The procedure and observations were as follows:

Time (Min.)	Temp. (Pot, °C)	Remarks
0	76	Glas-Col mantle removed; 47.6g NaOH was charged (1.19 eq) as a solution whose normality was about 7.5.
1	77°	-----
3	80	-----
5	85	-----
7	90	-----
8	92	-----
9	97-98	-----
9.5	99-100	The reaction was moderated with the ice bath in such a manner that the reaction mixture was at 95-101°.
11	100	-----
11.5	101	NaCl started precipitating.
13	99	-----
21	97	-----
38	78	The reaction was discontinued and the system adapted for vacuum distillation for recovery of excess ECH and H_2O.

The reaction mixture was subjected to distillation at 30-40 mm to a final pot temperature of 102°.

The distillate was a 2-phase system

Lower phase: 481 g.
Upper phase: 173 g.

The temperature of the distillate was 11.5°. At this temperature, the lower phase is 98.7% ECH and the upper phase is 6.5% ECH (Ref. 11). The distillate therefore contained 486g. ECH and 162 g H_2O.

The distillation was continued to a pot temperature of 105° at 1-2 mm; 43g of a single phase distillate were obtained. The total ECH recovery was 528.5 g. This was 95% of the excess used if the stoichiometric amount reacted to form the product.

The residue from the distillation was dissolved in 2003 g. dioxane (purified by refluxing with KOH pellets and distilling). The mixture was filtered and the filtrate was returned to the flask and warmed to 90-95°C. To it were added 693 cc of 7.5 N NaOH solution (5.2 eq, 10% excess). The temperature dropped to 75°. The mixture was reheated to reflux (92°) and refluxed for 3.25 hours. During this time NaCl precipitated and the system finally consisted of 2 liquid phases and a solid phase. The mixture was cooled to 51° and filtered, and the filter cake washed with 100 cc dioxane.

The filtrate was placed in a separatory funnel and the layers separated after removing an additional small amount of NaCl which precipitated as the dioxane cooled. The lower dioxane layer was withdrawn, placed in the separatory funnel and allowed to stand overnight. During this time an additional small amount of aqueous phase (upper layer) separated out. The dioxane layer was separated and the dioxane distilled off at 40-45 mm to a pot temperature of 105° and finally at 2 mm to a pot temperature of 135°C. The yield of pale yellow, slightly cloudy resin was about 1625 g. (101%).

Analysis: Epoxy Oxygen: 5.55, 5.54%
Hydrolyzable Chloride: 0.15, 0.17%

(b) Isolation of the Intermediate Reaction Product in the Reaction of Hydrolyzed Aroclor 1262 and Excess ECH.

The same procedure was used as described under (1) through the solution of the product in dioxane and filtration, using 8 equivalents of hydrolyzed Aroclor 1262 and 1.6 eq NaOH (as a 7.5 N NaOH solution).

The dioxane solution was subjected to vacuum distillation to a pot temperature of 100° at 34-37 mm and then to 127°C at 2 mm.
Yield: 2296 g.

Analysis: Epoxy Oxygen: 1.15%, 1.14%
Hydrolyzable Chloride: 9.01, 9.14%
Ash (1600°F): 0.00%

The theoretical epoxy oxygen for the glycidyl ether of hydrolyzed Aroclor 1262 is 5.76% and the theoretical hydrolyzable chloride content of the α-glycerolmonochlorohydrin is 11.3% (Appendix).

The above product therefore has a glycidyl ether equivalent percentage of $\frac{1.14}{5.76} \times 100 = 19.8\%$

and a chlorohydrin equivalent percentage of $\frac{9.07}{11.3} \times 100 = 80.2\%$, using 9.07 as the average Cl analyses.

(c) Preparation of Glycidyl Ether (GE) Mixtures of Hydrolyzed Aroclor 1262 Containing Various Percentages of the α-glycerolmonochlorohydrin (GMH) Derivatives.

To prepare these mixtures, dioxane solutions containing the initial addition product were reacted with a limited amount of NaOH, calculated to give the approximate amount of dehydrochlorination desired.

Example: To prepare a mixture composed of about 70% GMH and 30% GE.

Dioxane solution (785 g) containing 487 g. adduct (9.29% hydrolyzable chloride = 82.3% GMH) was diluted with one liter of dioxane and heated at 85-90° with 7.6 g NaOH in 15cc H_2O for 1/2 hour.

The mixture was filtered and the filtrate subjected to vacuum distillation to recover the product as previously described. Yield: 417 g

Analysis: Epoxy Oxygen: 1.50, 1.52%
Hydrolyzable Chloride: 8.32, 8.19%

By calculations described on ~~page 20~~ page 15, the product is 73% GMH and 26% GE. In the above example, the amount of NaOH to be used was calculated as follows:

$$\frac{487 \times 0.113 \times 0.12 \times 40}{35.5 \times 0.97} = 7.6 \text{ g NaOH}$$

where 487 = grams resin, 11.3% = theoretical hydrolyzable chloride for the GMH, 12% = percentage by which the chloride should be reduced, 40 = mol. weight NaOH, 35.5 = equivalent weight chloride ion and 97% = purity of NaOH.

(d) Preparation of a Glycidyl Polyether of Hydrolyzed Aroclor 1262.

To a one liter flask, adapted as already described, were charged 238.5 g (1.08 eq) hydrolyzed Aroclor 1262 and 100 g (1.08 eq) ECH. The mixture was warmed to 77° and the procedure followed and observations made are given below:

Time (Min.)	Temperature (Pot, °C)	Remarks
0	77°	Glas-Col mantle removed, 53 cc of 7.5 N NaOH solution were added.
2	90°	-----
4.5	100°	The system was refluxing
6	102°	The solution turned cloudy
12	105°	-----
17	100°	Glas-Col mantle was replaced and the mixture heated.

To the mixture at 103° were added 53 cc 7.5 N NaOH solution and the mixture was heated at 105-110° for 1/2 hour. At the end of this time 53 cc 7.5 N NaOH solution were charged (10% overall excess) and the mixture was heated at about 110° for one hour. The resin was then washed twice with 300 cc of boiling water for 35 min. each time. The water was removed by decantation. The washed resin was dehydrated to a final pot temperature of 130° at 30-40 mm. The resin was cooled slightly and dissolved in 300 cc methyl ethyl ketone. The mixture was filtered and the filtrate subjected to distillation under vacuum (30-40 mm) to a final pot temperature of about 125-130°. The resin was pale yellow, slightly cloudy and brittle at room temperature. Yield 287 g.

Analysis: Epoxy Oxygen: 3.93%
Hydrolyzable Chloride: 0.31%

(e) Reaction of a Basic Solution of Hydrolyzed Aroclor 1262 with ECH (Ref. 12).

Hydrolyzed Aroclor 1262 (662 g, 3.02 eq) was dissolved with heating in a solution of NaOH 120.8 g, (3.02 eq) dissolved in 885 cc H_2O (12% by weight) and heated to 65°. The ECH was then added dropwise and the following observations were made:

Time (Min.)	Temperature, °C	ml ECH added	Remarks
0	65	0	Heat off. Glas-Col mantle and flask. ECH addition started
5	65	9	-----
11	66	20	-----
18	67	39	Glas-Col mantle removed.
26	67	54	Mixture getting viscous
34	67	--	Mixture turned lighter in color
40	67	75	-----
55	67	100	A whitish viscous mass was obtained.
65	68	125	The mass was more viscous.
80	67-65	150	The mass solidified and could not be stirred.

The theoretical amount of ECH required for an equivalent ration was 230 cc. Therefore 65% of the required ECH was added (175.5 g, 1.9 eq). The reacting molar ratio ECH/hydrolyzed Aroclor 1262 was 1.9/1.87 = 1.02. This ratio was much too low to produce a satisfactory product.

A small portion of the product was washed by trituration under H_2O and air dried; it contained only 0.96% epoxy oxygen.

(3) Bisphenol-A (BPA)

(a) Liquid Resins (Epon 828 type)

BPA (570 g, 2.5m), 929.5 g (10.04m, 100% excess) ECH and 15 cc H_2O (1% by weight of reactants) were charged to a 5 liter flask, adapted as already described. The mixture was warmed to 75°. To the solution were added 40 g (0.97 m) NaOH pellets. The procedure and observations were as follows:

Time (Min.)	Temperature (Pot, °C)	Remarks
0	75	40g NaOH were added
12	91	Glas-Col mantle was removed
13	99-101	The mixture refluxed slightly.
19	95	-----
20	93	40g (0.97 m) NaOH were added. The temperature rose rapidly to 99-100°. The mixture was cooled with an ice bath to 91°.
22	91	The NaOH pellets were completely dissolved.
25	88	40 g (0.97 m) NaOH Pellets were added.
26	96	The mixture refluxed
27	97	The mixture refluxed
29	93	-----
31.5	88-89	40g (0.97 m) NaOH pellets were added
32.5	97	The mixture refluxed
39	89	50.5 g (1.22 m) NaOH pellets were added (2% overall excess)
43.5	98.5	The mixture refluxed. It was cooled to 95°.
46	99	The mixture refluxed
50	96.5	The mantle was replaced and the mixture was heated to reflux.

The reaction mixture was allowed to reflux for 0.75 hours. The system was then adapted for vacuum distillation. The H_2O and excess ECH were distilled off first at about 200 mm to pot temperature of 97° and then at about 95 mm to a pot temperature of 160°. The two phase distillate, 409.5 g lower layer and 89g upper layer, was calculated to contain 409.3 g ECH and 89.4 g H_2O. The ECH consumed in the reaction was 929.5 - 409.3 g = 520.2 g (5.62 m) and the H_2O formed was 89.4 - 15 = 74.4 g (4.15m). The apparent reacting molar ratio ECH/BPA was 5.62/2.5 = 2.24. The residue was cooled to 100° and washed as follows.

Wash No.	g. H_2O	Temp., °C.	Time (hrs.)	Method of Removing Wash H_2O and temp.	g. H_2O	Remarks
1	1161	100-102	1	Syphoned off (100°)	1359g	Clear wash H_2O
2	1016	52-74	1/2	Decanted (74°)	796	V. cloudy wash H_2O
3	1007	55	1/2	Decanted (55°)	907	V. cloudy wash H_2O
4	995	60-75	1/2	Decanted (75°)	990	Cloudy wash H_2O
5	1022	95-100	1/2	Separatory Funnel (95-100°)	1066	Practically clear wash H_2O
6	1013	95-100	1/2	Separatory Funnel (95-100°)	1214g	Clear wash H_2O

The washed resin was dehydrated under vacuum first at about 310 mm to a pot temperature of 115° and then at about 95 mm to a pot temperature of 168°.

Weight distillate: 195 g.
Yield of Resin: 827 g. (92%)
Analysis: Epoxy Oxygen: 7.24%
Hydrolyzable Chloride: 1.13%
Epoxide equivalent: 221

(b) Solid Resins (Epon 1001 type)

Small Scale

BPA, (114 g. 0.5 m) was mixed with a solution of NaOH 38.8 g (0.97 m) in 340 cc H_2O in a one liter flask, adapted as already described, and heated. The procedure and observations were as follows:

Time (Min)	Temperature (Pot °C)	Remarks
0	25	Variac was set at 50 V. A slurry was present.
8	41	Variac was set at 40 V.
10	43	72.5 g (0.784 m) ECH were charged rapidly.
12	45	-----
14	55	Practically all solids were in solution.
15	59	The solution was turning cloudy.
16	64	-----
18	72	-----
21	80	Resinous material started forming.
27	85	-----
28	87	Variac was set at 60 V.
35	95	A moderately viscous material was present.
59	97	Variac was set at 40 V.

The mixture was heated at 97-100° for an additional 80 minutes. The mixture was cooled to about 70° and the aqueous phase was decanted. Volume 319 cc. The resin was washed with 400 cc portions of H_2O each at 101-102° for 20 minutes each wash. After each wash the mixture was cooled to 70-75° and the aqueous phase was decanted. The results are as follows:

Wash No.	Vol. Decanted	OH (eq)	Cl (meq)
Original Aq phase	319	0.025	650.76
1	415	0.002	108.06
2	390	0.000	8.697
3	400	-	0.880
4	336	-	0.134
5	400	-	-

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The total chloride ion analysis was 0.77 eq. This compared with 0.78 equivalents of chloride introduced as ECH.

The washed resin was dehydrated by distilling off the H_2O at 760 mm to a pot temperature of 125° and then to 165° at 40 mm. Yield: 149g. The resin was yellowish and slightly cloudy.

Analysis: Epoxy Oxygen: 3.10, 3.12% Average 3.11%
Epoxide Equivalent: 515
Hydrolyzable Chloride: 0.24% Max.

The hydrolyzable chloride analysis was based on the fact that only 0.01 eq ECH was not accounted for in the wash H_2O. This is 35.5 x 0.01 = 0.355 g of chlorine in 149 g resin or 0.238%.

Large Scale

For this experiment a 22 liter laboratory scale reactor was used. This consisted of a 22 liter wide neck flask on which was fitted a head through the center of which passed a stirrer shaft and which was adapted for carrying a reflux condenser, a thermocouple well, and a stopper. The flask was heated by a Glas-Col mantle.

To the flask were charged 2280 g (10 m) BPA and 776 g (18.82 m) NaOH dissolved in 7756 g H_2O. The slurry was heated to 45° and 1450 g (15.69 m) ECH were charged rapidly. The mixture cleared and almost immediately started turning cloudy. Within 20 minutes the temperature rose to 100°. During this time the resin phase formed starting first as globules and gradually coalescing into a continuous mass. The mixture was held at 100-101° for an additional 1.5 hours. The resin phase was allowed to settle (about 4 minutes) and the aqueous phase was decanted. Weight, 8428 g. The resin phase was washed five times with about 8000 g portions of H_2O at about 100° for 1/2 hour each wash. The H_2O phase was in each case decanted at about 95-100°. The results of the washing are given in Table II.

TABLE II

Wash No.	H_2O Charged (g)	H_2O Decanted (g)	Analysis Cl (eq)	OH (eq)	Net H_2O Weight *1
1	8047	6934	0.832	0.180	6878
2	8206	8250	0.180	0.050	8238
3	8245	8324	0.054	0.000	8321
4	8028	7715	0.018	-	7714
5	8256	7905	0.007	-	7905
*2	-	8428 g	14.340	3.298	7458
		Totals	15 430	3 528	46514

*1 Obtained by subtracting from the gross weight of alkaline, saline H_2O its analyzed equivalent of NaCl and NaOH.
*2 Initial H_2O phase decanted from the reaction mixture.

The washed resin phase was dehydrated under vacuum first at about 400 mm to a pot temperature of 89° (1.25 hours) and finally to 170° at 85-135 mm.
Weight distillate: 1762 g
Weight Resin: 3002 g (95.2%)

Analysis: Epoxy Oxygen: 2.78%
Hydrolyzable Chloride: 0.30% maximum
Epoxide Equivalent: 575

The hydrolyzable chloride content of the resin was calculated on the basis that 15.69 - 15.43 = 0.26 eq chloride was not accounted for. This equaled 35.5 x 0.26 = 9.24 g Cl in 3002 g resin which equals 0.30%.

MATERIAL BALANCE

	Charged	Discharged	Difference	Percent Difference
Cl	15.69 eq	15.43 eq	-0.26 eq	1.66%
OH	18.82 eq*1	18.96 eq	+0.14 eq	0.74%
H_2O	48,816 g	48,276 g*2	-540 g	1.1%
Total Mass	53,044 g	52,320 g	-724 g	1.36%

*1 Calculated as 97% minimum NaOH
*2 This figure includes 278 g H_2O produced in the reaction (15.43 eq).

The loss of chlorine is probably too high and the figures given are on the assumption that the ECH used was 100% pure. The ECH used was not analyzed before use because a satisfactory method was not available.

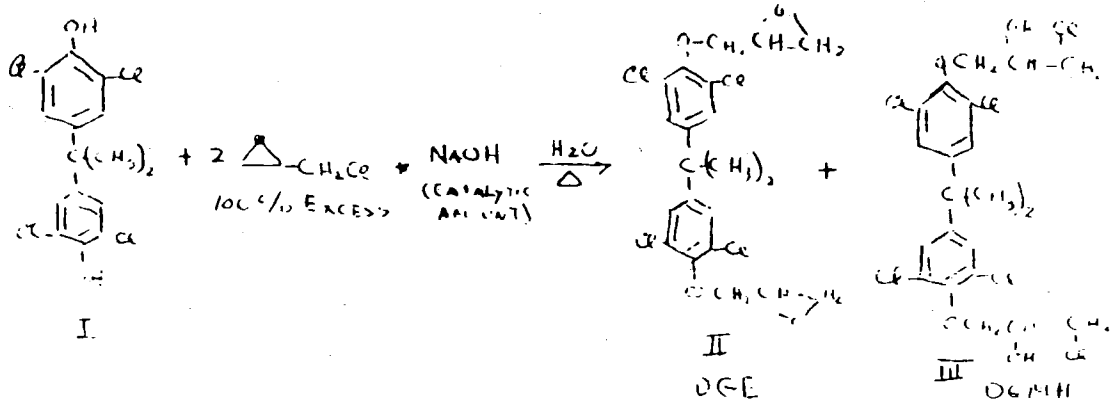
Losses taking place during manipulations (by spillage, incomplete transfers, evaporation losses) were considered the chief reasons for the lack of complete recovery of materials.

VIII. DISCUSSION:

(A) Reaction of excess ECH with (a) TCBPA, (B) hydrolyzed Aroclor 1262, (C) bisphenol-A, (D) preparation of polymeric epoxides from these phenols. (E) Additionally, although practically no work was done on the preparation of epoxies from glycerol, a section is included which notes relevant factors of this preparation. (F) Economic evaluation of (C) and (D).

(A) Reaction of Excess ECH with TCBPA

When a limited amount of aqueous NaOH was added to a solution of TCBPA in at least 100% excess ECH at temperatures above 55°, the following reaction took place exothermically:



This reaction proceeded to completion very rapidly when the equivalent ratio NaOH/TCBPA was between 0.05 - 0.20 and the relative amounts of II and III produced depended on this ratio. At the end of this initial addition reaction, excess ECH and H_2O were distilled off and the residue was dehydrochlorinated to give a high yield of II, contaminated with traces of III. Table XII (Appendix) lists the results for all the runs made.

The reactions of TCBPA or hydrolyzed Aroclor 1262 with excess ECH do not follow the same pattern as the reaction of BPA with excess ECH. The reactions of these diphenols with limited amounts of ECH are probably the same however. This will be evident from the data given in the discussion. It is therefore convenient to discuss the experimental work as follows:

For an optimum yield of II, and an optimum recovery of excess ECH, several variables were recognized: (1) ECH/TCBPA ratio, (2) NaOH/TCBPA (3) temperature and (4) concentration of NaOH.

(1) For the preparation of II the equivalent ratio ECH/TCBPA must be 2/1 or greater. At a lower ratio, polymer formation would undoubtedly take place. Higher ratios would have no effect on the nature of the product, but heat dissipation from the exothermic reaction would be much better.

(2) Graph II shows the exothermic rise of temperature of the reaction mixture when various amounts of aqueous NaOH were added to a solution of TCBPA in excess ECH at the same initial temperature. It is seen that as the ratio NaOH/TCBPA increased from 0.05 to 0.80, the reaction becomes increasingly uncontrollable because of the rapid rise in temperature. Graph III shows the effect of this increasing ratio on the total analysis of the products obtained. The inflections in the curve are considered to be meaningless; given a more accurate method of analyses, the inflections would probably disappear. This comparison was useful because the departure from 100% analysis

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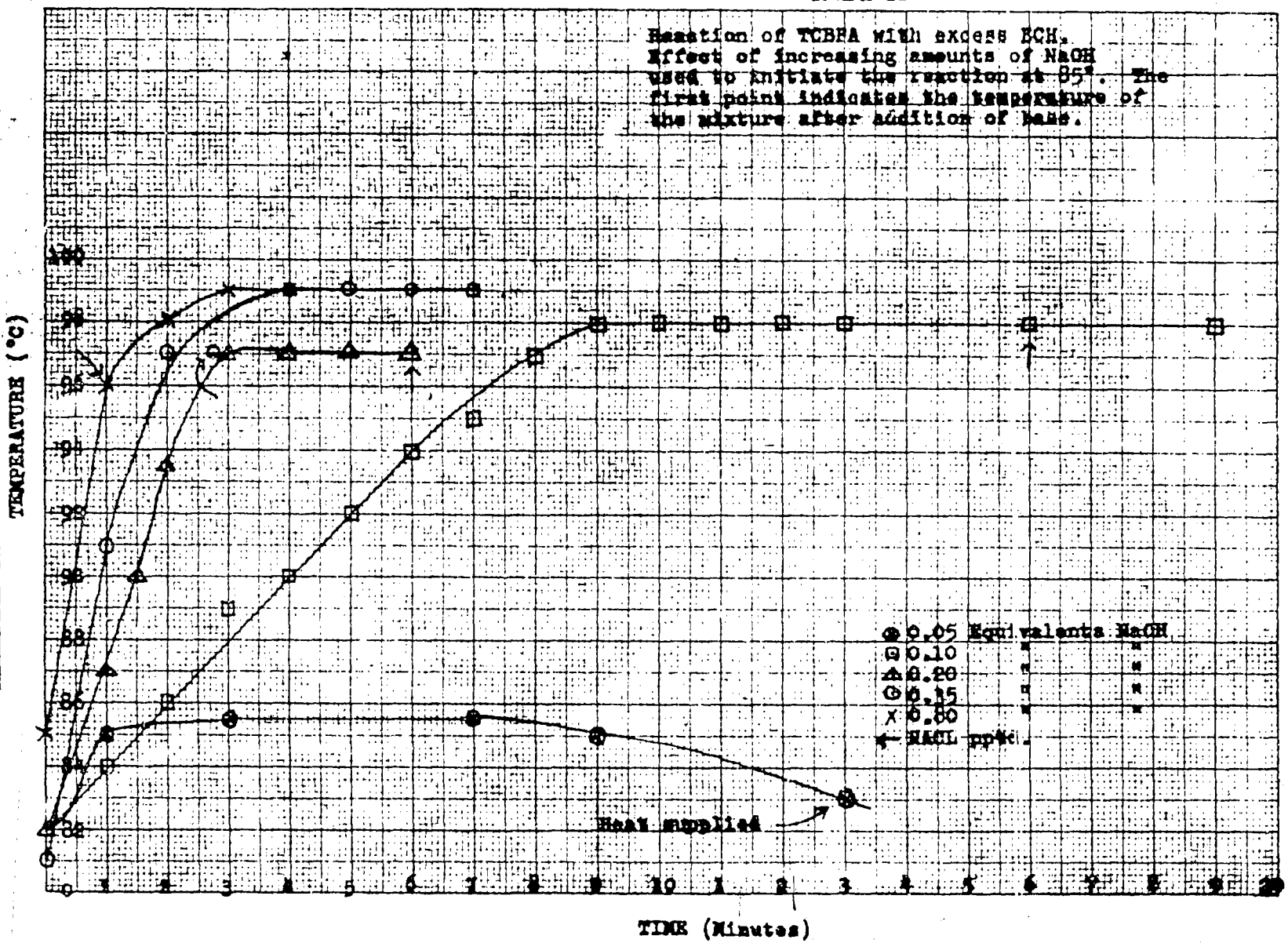
GRAPH II



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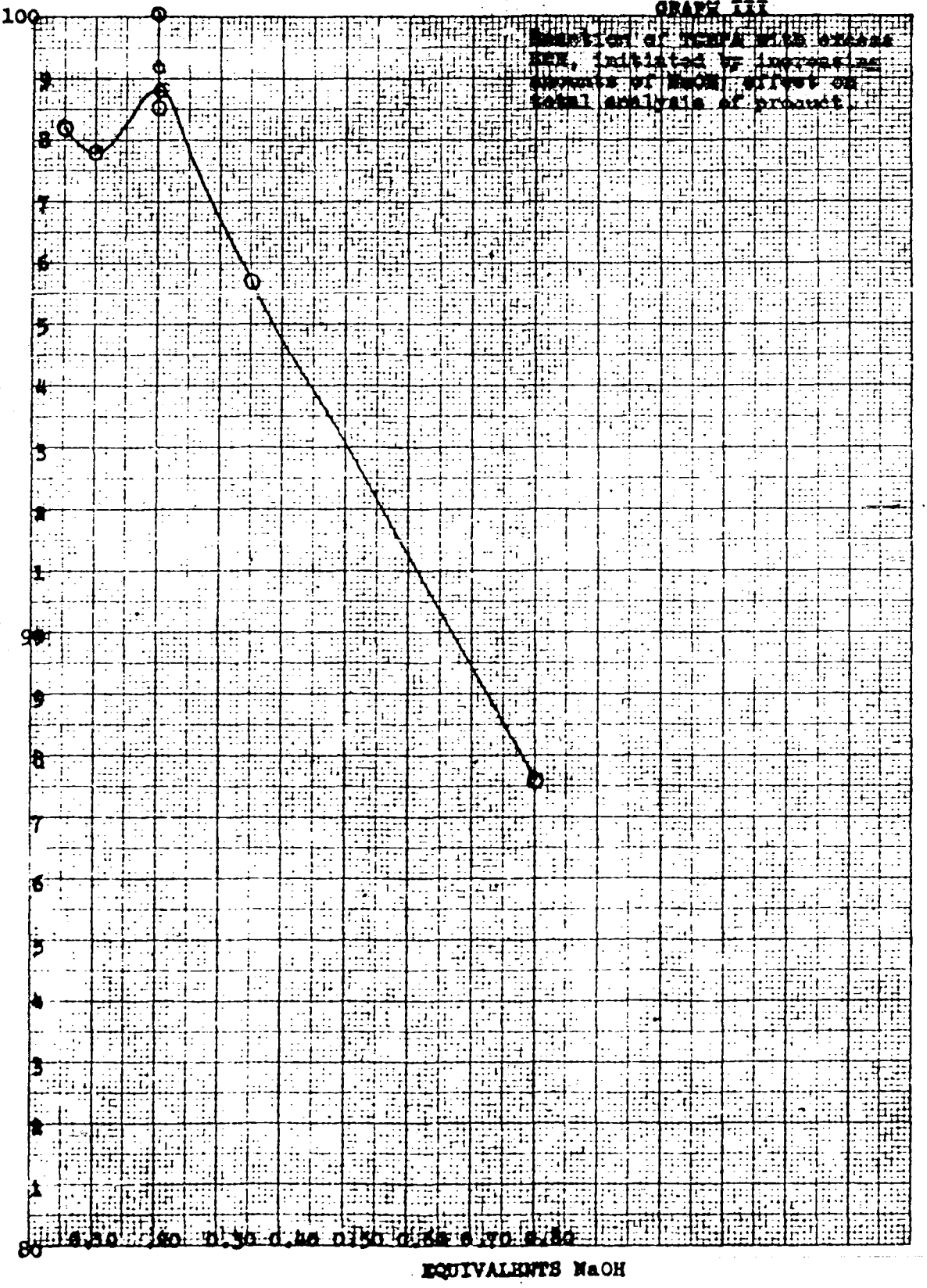
GRAPH III

Reaction of TGBA with excess HBr, initiated by increasing amounts of NaOH effect on total analysis of product



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indicated polymer formation. A very adverse effect at high NaOH/TCBPA ratios was the simultaneous destruction of ECH, as indicated by lowered recoveries of excess ECH.

(3) At a constant NaOH/TCBPA ratio of 0.2/1, the temperature at which the NaOH solution was added had very little effect, if any, on the nature of the products obtained below 100°, but does effect the Exotherm. Graph IV illustrates the latter point. For each temperature used in this set of experiments, the product had a very high percentage of II. Above about 100° however, it was noted that the recovery of excess ECH was lower, indicating that ECH was destroyed at the higher temperature.

(4) The concentration of NaOH used in the preparation procedure is important in the recovery of excess ECH from the reaction mixture. ECH is recovered by distillation of the two phase system ECH-H_2O from the reaction mixture. Since ECH is soluble in H_2O to a slight extent, the lower the concentration of NaOH, the higher is the loss of ECH to H_2O phase for a constant amount of NaOH used. From an economic standpoint, therefore, the concentration of NaOH should be high, if the aqueous phase from the distillation is to be discarded.

The second phase of the reaction, the dehydrochlorination of the adduct obtained with caustic solution after recovery of excess ECH, has not been extensively studied. The approximate speed of HCl elimination was shown in Graph I under Experimental Procedures (p 10-11). Considerable improvement in the rate could undoubtedly be obtained by an increase in the percentage of excess NaOH used or by counter-current techniques.

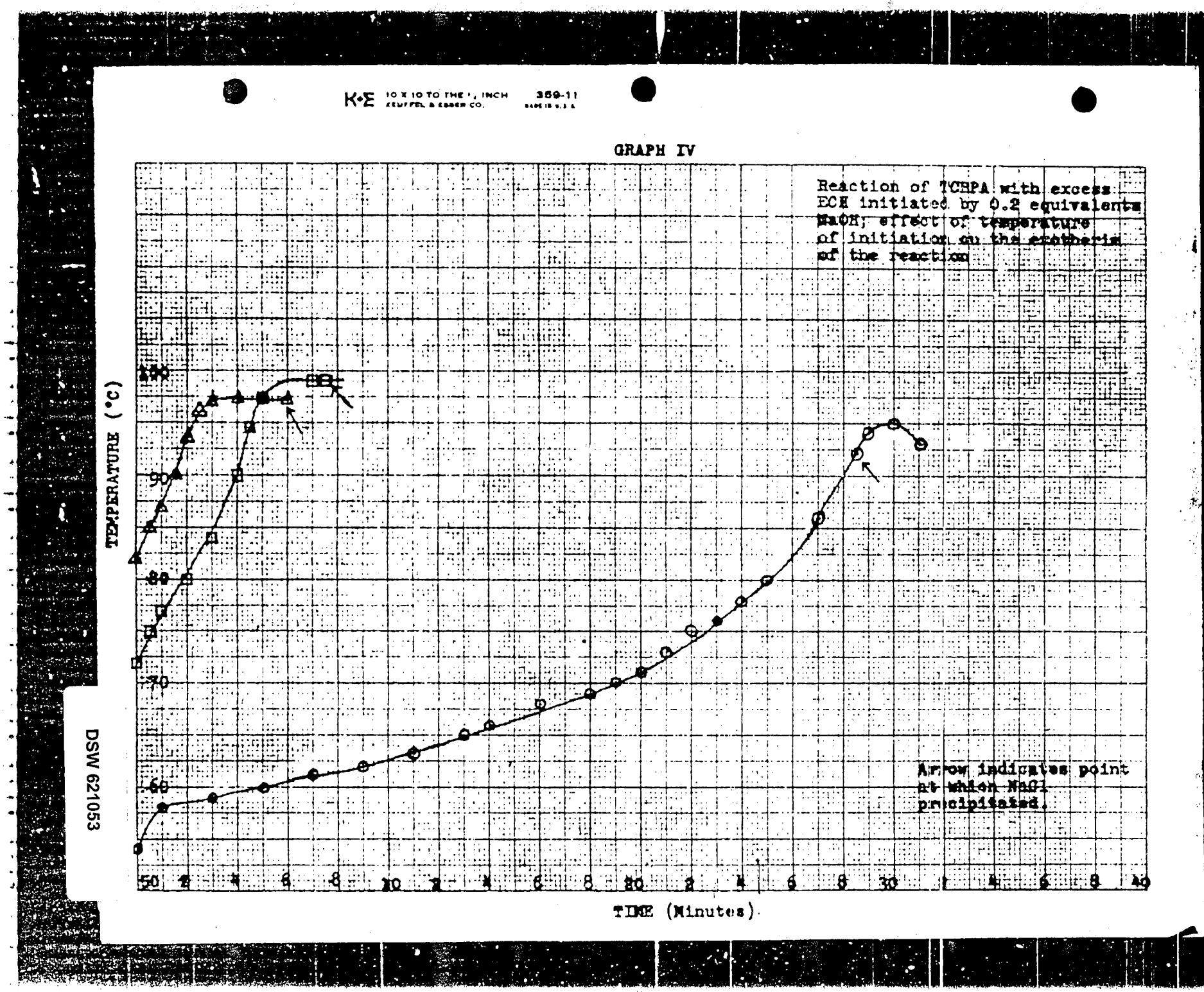
The washing of the product obtained was also a slow process, and improvements could be introduced; washing by the counter current technique would be much more efficient.

The product as obtained by dehydration was always somewhat cloudy. It is thought that this is due to the presence of traces of H_2O. Prolonged heating during dehydration would reduce the H_2O content of the product but it would appear that drying with a thin film evaporator would be more efficient.

The product could, of course, be isolated with the aid of organic solvents, such as benzene; although this would be a much more rapid process, the necessity for solvent recovery units would be disadvantageous.

(B) Reaction of Excess ECH with Hydrolyzed Aroclor 1262

The same considerations which were discussed under (A) are applicable to the preparation of the glycidyl ether mixture of hy-



VII, by reaction with the excess ECH present and additional NaOH added, may react again to yield the chlorohydrin derivative.

Thus in the case of BPA, it is not possible to perform the initial addition reaction, recover the excess ECH and then react the product obtained with caustic (as with TCBPA). An excess of ECH must be present throughout the course of addition of NaOH. If one proceeds with BPA as with TCBPA using the equivalent ratio NaOH/BPA ratio = 0.3, then the product is not a high epoxy containing material but one which has an epoxide equivalent of about 400. (The epoxide equivalent of V is 170).

The above observations were made in conjunction with experimental work being performed on TCBPA. When a program for obtaining cost estimates for the production of BPA epoxies was initiated, the processes described in the patent literature were followed. In the process for the preparation of Epon 828 type resins (Ref 13), solid caustic is added in portions to a solution of BPA in 150% excess ECH and containing about 1% H_2O. Upon completion of caustic addition the excess ECH is recovered by distillation and the product is isolated from benzene. Although the process is capable of reproduction, it was decided that in this study, the benzene system would be eliminated.

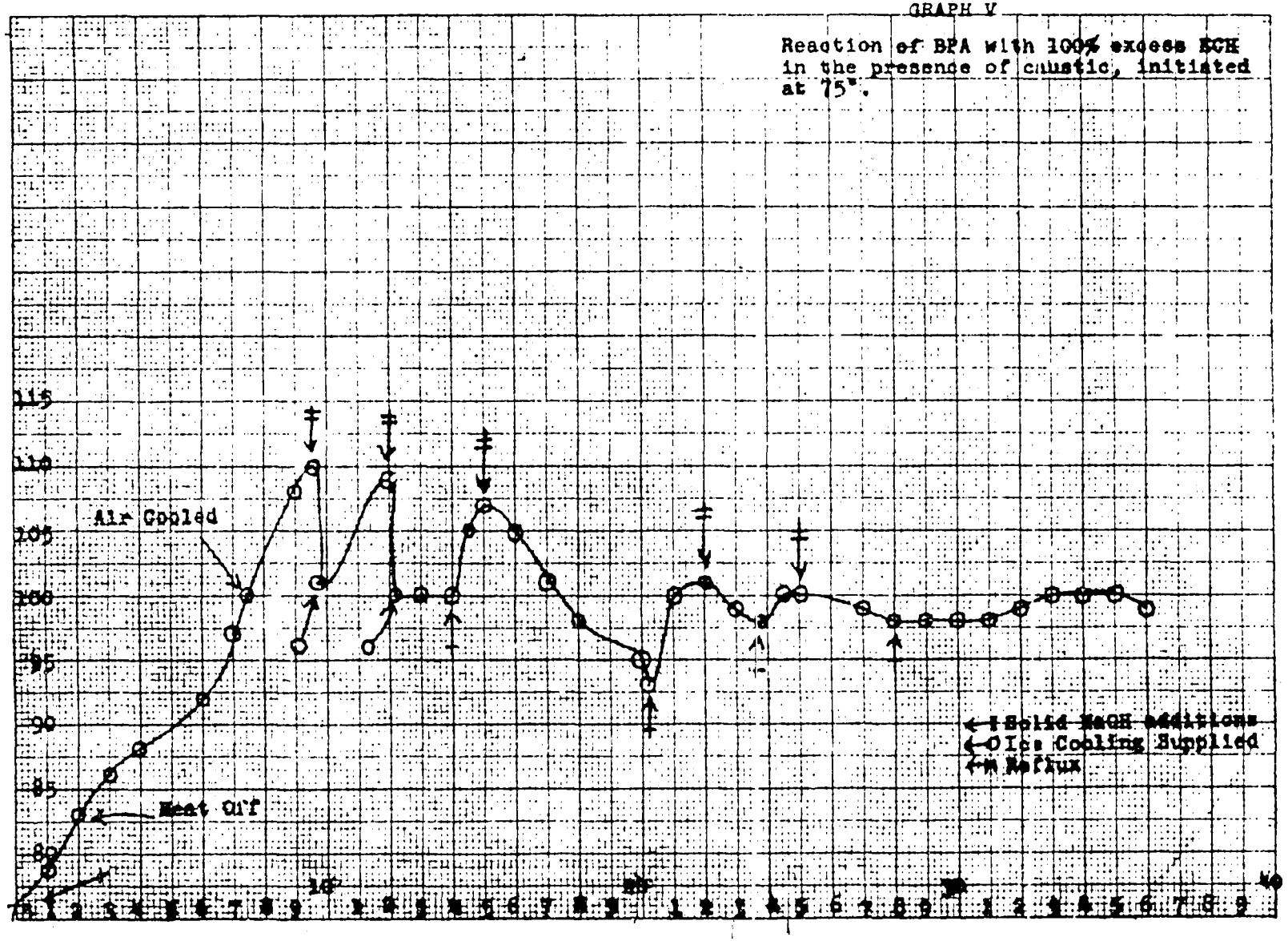
In the process which was studied during this program, BPA was dissolved in 100% excess ECH and 1% (by weight of reactants) H_2O was added. To this solution, starting at 75° NaOH pellets were added in 5 portions in the equivalent ratio NaOH/BPA = 0.194 for four additions, and a final portion of 0.244 (2% overall excess). During the additions, the mixture was cooled with an ice-H_2O bath in order to maintain the reaction mixture at about 95-100. The excess ECH was recovered by distillation, the residue was washed with H_2O and the washed resin dehydrated under vacuum. The product obtained by this process was an amber colored fluid resin whose hydrolyzable chloride content was about twice that of the commercial product (1.1% vs. 0.5%). From the analytical data it was shown that by further dehydrochlorination of this product (X to 0.5% Cl), Epon 828 would result. In one experiment, an attempt was made to reduce this content by introducing caustic (5% excess) into the first H_2O wash but the attempt was unsuccessful since a part of the product gelled during the washing cycle.

Because of limited time spent on this process and because the data obtained were somewhat inconclusive, future work should incorporate the following ideas.

(a) It is believed that 100% excess of ECH is sufficient for obtaining the proper product but that for better heat control it may be necessary to go as high as 150%. Graph V illustrates the temperature variations during the reaction cycle using 100% excess ECH.

GRAPH V

Reaction of BPA with 100% excess ECH in the presence of caustic, initiated at 75°.



(b) The method of caustic addition is probably satisfactory, but it may be necessary to increase the time between additions in order to effect better dehydrochlorination.

(c) The recovery of excess ECH by distillation is considered satisfactory.

(d) The washing and removal of wash waters should be conducted at about 90-100°C. Some additional work may be desirable with respect to addition of caustic to the first wash (a smaller excess than in the case given above) with the idea of effecting a part of the dehydrochlorination here.

(e) Since the products obtained by dehydration were slightly cloudy, i.e. H_2O may have been present, it may be necessary to prolong the dehydration or to revert to a thin film evaporator.

(f) The analysis should be expanded to include hydroxyl determination and molecular weight determination. The former would especially be useful in obtaining a more precise determination of the ECH requirements of the process.

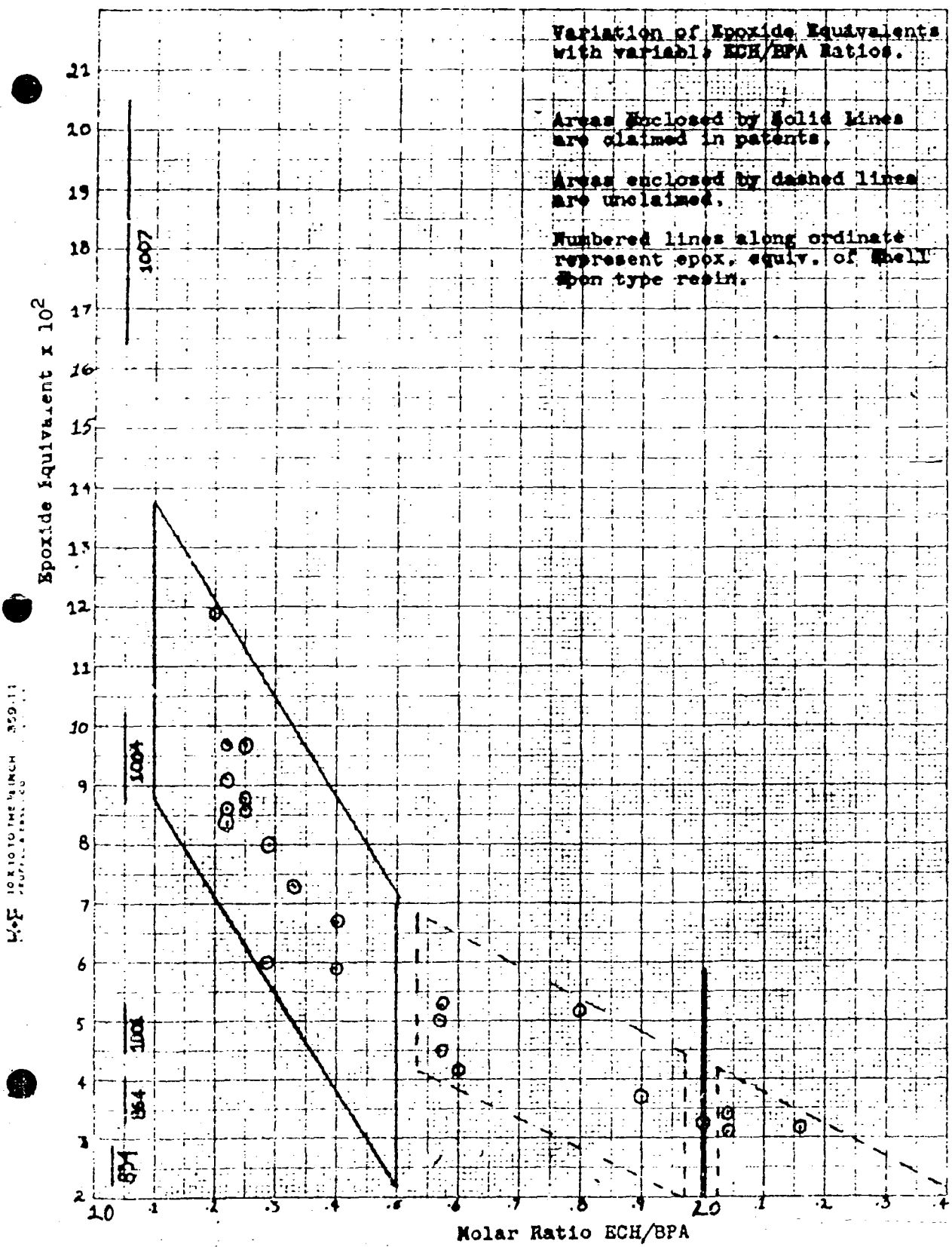
(D) Preparation of Polymeric Epoxides

The processes followed for the preparation of polymeric epoxides were those described in the patent literature (Ref 14). In these processes the nature of the product is determined predominently by the molar ratios ECH/BPA and NaOH/ECH, and the manner of addition of the caustic. Graphs VI and VII illustrate the variation of epoxide equivalents and softening points of resins with the variable ratio ECH/BPA.

For the preparation of solid type resins from BPA the synthesis of Epon 1001 was undertaken. For the preparation of this resin the molar ECH/BPA ratio was 1.57 and the NaOH/ECH ratio was about 1.25. The preparation procedure consisted of dispersing BPA in the caustic (10%), heating to about 45°, and charging the ECH rapidly to BPA-caustic mixture. The temperature was allowed to rise to about 95-100 (heat supplied) and kept at this range for about 80 minutes. The product was washed with hot water, dehydrated under vacuum and discharged from the flask while hot. In this procedure, the following variables were recognized: (a) ECH/BPA ratio, and NaOH/ECH ratio, (b) rate of addition of ECH, and rate of stirring, (c) heating period, (d) washing cycle (e) dehydration and (f) yield. Additionally, (g) concentration of caustic must be considered because this factor determines the capacity of the charge. These variables are treated separately below.

(a) Molar ratio ECH/BPA and Molar ratio NaOH/ECH

The ratio ECH/BPA = 1.57 and the ratio NaOH/ECH = 1.25 was chosen



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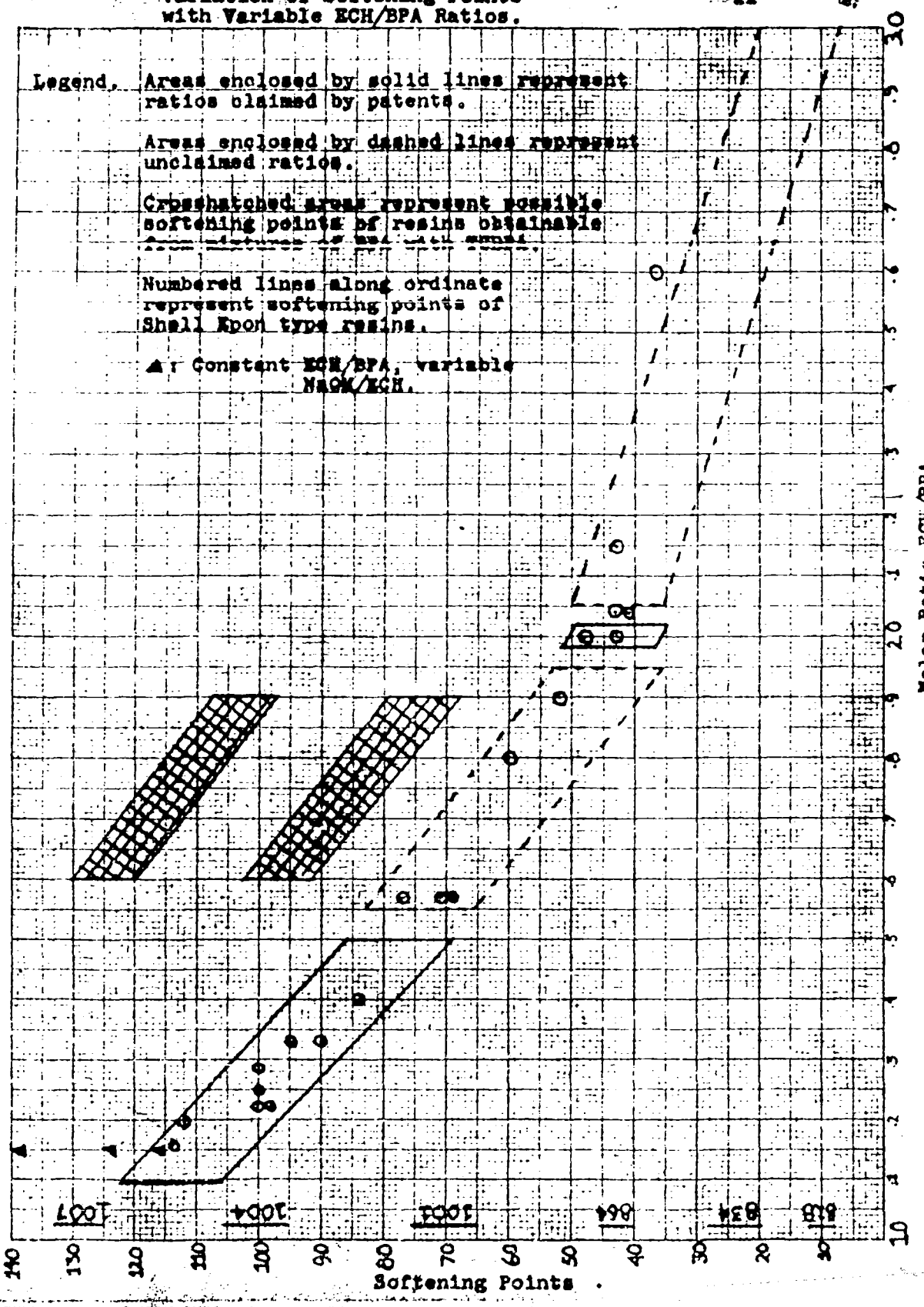
Variation of Softening Points with Variable ECH/BPA Ratios.



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by comparison of the published properties of Epon 1001 and the preparative procedures and properties given in the patent literature. Additionally, the approximate molar ratio ECH/BPA, contained in the resin, was found by calculations from the specifications of Epon 1001. (Appendix B, page 49).

(b) Rate of addition of ECH and rate of stirring

For the preparation of the correct epoxide equivalent resin, the ECH must be charged rapidly and the stirring should be very efficient. The reactions which are probably "balanced" in the whole process are (a) addition reaction of ECH with BPA and the polymers formed and (b) the addition reaction of BPA with the BPA glycidyl ethers formed. It is thought that slow addition of ECH or inefficient stirring would emphasize reaction (b) and lead to a product whose epoxide equivalent is too high. This is somewhat borne out by the scale up to a laboratory kettle of the BPA charge from 1/2 m to 10 m, to a kettle, where in the last two cases the stirring was not as efficient as in the 1/2 m runs. The epoxide equivalent for those runs was higher than in the 1/2 m runs, where the correct equivalent was obtained.

Table III shows the results from these runs.

TABLE III

Scale and Equipment	% Epoxy Oxygen (average)	Epoxide Equivalent
1/2 m, Common lab	3.22	493
1/2 m, Common lab	3.11	515
10 m, 22 l reactor	2.87	557
10 m, 22 l reactor	2.78	575
5 m, 3 gal. lab kettle	2.60	615
5 m, 3 gal. lab kettle	2.48	645

(c) The heating period

A heating period of 80 minutes was found to be satisfactory for obtaining a product whose hydrolyzable chloride content was very low and comparable to the commercial product. No attempts were made to reduce this ~~time~~ VALUE.

(d) Washing cycle

The factors considered in the washing cycle were (1) temperature of washing and at decantation and (2) volume of wash water used and (3) time of washing; (2) and (3) were important from the standpoint of capacity.

(1) It was found by trial and error that the most efficient process was in washing at a temperature of 95-100° and decanting as

as soon as the resin settled. Very clear wash waters could be decanted using this procedure in contrast to considerable cloudiness when decantation was carried out at lower temperature.

(2) No study was made of the efficiency of washing with respect to volume of water used per wash. It was found however that the volume could be reduced from 8000 cc to 4000 cc on the basis of a 10 m BPA run for a resin yield of about 3000 g.

(3) The time factor was not studied either. Washes of one-half hour each were chosen arbitrarily. This element could easily be determined by removing aliquots of wash at various time intervals and analyzing for chloride and hydride ions. From these data a time limit for most efficient washing could be chosen.

(e) Dehydration

The washed resin retained about 50% H_2O by weight of resin obtained. It is thought that the dehydration as carried out under reduced pressure (the latter was determined by the softening point of the resin, about 75°) represents the limit available with this process. A significant improvement could be introduced however by the use of a thin film evaporator from the standpoint of continuous operation and perhaps obtainment of a clearer product.

(f) Yield

This factor is difficult to evaluate properly and no attempts were made in this study to determine the reasons for the approximately 95% yields obtained; it would appear that the yields should be almost quantitative. Some resin was definitely lost to the wash waters (as suspended material, probably not greater than 1%). The best guess would be that the loss in yield is in the BPA, by virtue of its contaminants (e.g. phenol, but only a small percent) and by its incomplete reaction and removal as the sodium salt in the wash waters. The latter could certainly be quantitatively ascertained by analysis of the wash waters for BPA.

(g) Concentration of Caustic

It is easily seen that the use of 10% caustic limits the capacity of this process severely. Since this is the concentration used in the patent processes, it was used in this study. A few "spot" experiments using 30 and 20% caustic were unsuccessful, the reaction mass being unstirrable. It appeared from these experiments that about 14-16% caustic may be the workable limit with the present process. Although the effect of concentrated caustic on the resin is not known it would appear to be small since in the preparation of Epon 828 type resins, very concentrated caustic is present in the preparation mixture without any drastic loss of epoxy groups.

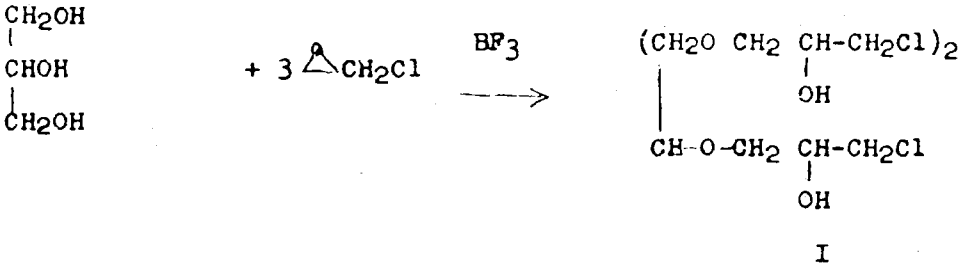
(E) Preparation of Epoxides from Glycerol

Work on the preparation of these epoxides has been carried out at Seattle by R. G. Neville (Ref 15).

In this laboratory no study was made. It appeared desirable to include a section in this report on the chemistry of this preparation since an economic survey was made on this basis. The chemistry in turn was to a good extent deduced from data given in the patent literature (Ref 16).

Epoxides from glycerol have reached only the developmental stage; the resin available from Shell is Epon 562. This resin is prepared by the bulk reaction of ECH and glycerol in the presence of about 1% by weight of reactants of BF_3ET_2O (Ref 17) followed by dehydrochlorination by salts such as $NaAlO_2$, $NaZnO_2$, Na_2SiO_3 in an organic solvent such as dioxane. The inorganic salts are filtered off and the solvent is distilled to recover the resin.

The theoretical reactions are as follows:



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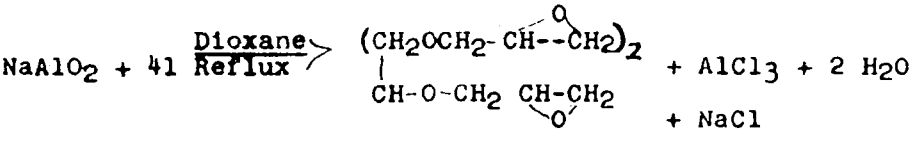

II

$$AlCl_3 + 3\ H_2O \dashrightarrow Al(OH)_3 + 3HCl$$

$$NaAlO_2 + H_2O + HCl \dashrightarrow NaCl + Al(OH)_3$$

The last two reactions show that H_2O must be added to the dioxane, as indicated in the patent literature. The $NaAlO_2$ is recovered from the reaction:

$$Al(OH)_3 + NaOH \dashrightarrow NaAlO_2 + 2\ H_2O,$$

The process in effect consumes NaOH in the dehydrochlorination reaction.

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The above reactions are complicated by interfering reactions, such as polymerization of ECH by BF_3, further reaction of I with ECH, hydrolysis of II by H_2O, and by products arising from the incomplete reaction of glycerol and ECH.

It is interesting to compare the properties of Epon 562 with the stoichiometry of this preparation. The reaction of equivalent quantities of ECH and glycerol followed by reaction with excess $NaAlO_2$ should yield approximately equivalent quantities of epoxy oxygen in the product, i.e., the epoxide equivalent of the product should be about 87. The commercial product has an epoxide equivalent of about 145 indicating that undoubtedly the resin contains a large percentage chlorine. This may be due to an incomplete reaction of $NaAlO_2$ with the chlorohydrins or the fact that chlorine atoms are present whose functionality is not like that of the chlorohydrin, i.e., they are not as easily removed as HCl (Ref 18). These views must be taken into consideration if any additional work for the preparation of glycidyl ethers of polyols is undertaken by Monsanto.

(F) Economic Evaluation of the Production of Epon 562, 828 and 1001 Type Resins

This section contains a summary of the work performed by J. Chunga of Division Engineering (Ref 4, 5), M. F. Drumm and the writer. It includes;

(a) Production of Epons 562, 828 and 1001. (Mr. J. Chunga)
(b) Flow diagrams for the production of these resins. (Mr. J. Chunga)
(c) Monographs showing variable returns on investment for variable cost of BIA and ECH and variable selling prices of resins. (Dr. M. F. Drumm and Dr. S. E. Gebura)

Production of Epons 562, 828 and 1001.

Table IV - Facility A. 1,000,000 lbs/yr Epon 828 and 3,000,000 lbs/yr Epon 1001.
Table V - Facility B. 3,000,000 lbs/yr Epon 828 and 5,000,000 lbs/yr Epon 1001.
Table VI - Facility C and D. 1,000,000 and 3,000,000 lbs/yr Epon 562.
Table VII- Facility E, F and G 20,000,000 lbs/yr Epon 828, 20,000,000 lbs/yr Epon 1001 and 20,000,000 lbs/yr Epon 562.

TABLE IV

ANNUAL PROFIT AND LOSS STATEMENT
FACILITY "A"

(In Thousands of Dollars)

	Epon 828 Production	Epon 1001 Production
1. Annual Net Sales		
Quantity, lbs.	1,000,000	3,000,000
Unit price, list, $/lb.	0.80	0.605
Freight charge, $/lb.	0.01	0.010
Net Price, $/lb.	0.79	0.595
Amount ANS	790.00	1785.00
2. Cost of Goods Sold		
Manufacturing		
Raw Materials	425.60	1179.90
Direct Conversion	91.01	133.11
Depreciation	17.21	26.82
Indirect Conversion	24.63	38.10
Packaging & Shipping	20.00	30.00
Royalties of 5% AGS	40.00	90.75
Total Cost Goods Sold	618.45	1498.68
3. Gross Profit	171.55	286.32
4. Deduct SARE at 10% ANS	79.00	178.50
5. Net Income Before Taxes	92.55	107.82
6. Income Taxes at 50% Net Income Before Taxes	46.28	53.91
7. Earnings After Taxes	46.27	53.91

CAPITAL ESTIMATE SUMMARY
FACILITY "A"
(In Thousands of Dollars)

A. New Property to be Installed:		
Building	26.4	26.4
M & E	202.0	322.0
New Fixed Capital	228.4	348.4
B. Share Existing Property: at 30% NFC	68.5	104.6
C. Total Fixed Capital	296.9	453.0
D. Working Capital		
Inventory	66.8	173.0
All Others at 15% ANS	118.5	267.8
Total Working Capital	185.3	440.8
E. Total Operating Investment	482.2	893.8
F. Return on Investment	9.6%	6.0%

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TABLE V

ANNUAL PROFIT AND LOSS STATEMENT
FACILITY "B"

(In Thousands of Dollars)

	Epon 828 Production	Epon 1001 Production
1. Annual Net Sales		
Quantity, lbs.	3,000,000	5,000,000
Unit price, list, $/lb.	0.800	0.605
Freight Charge, $/lb.	0.010	0.010
Net price, $/lb.	0.790	0.595
Amount ANS	2370.00	2975.00
2. Cost of Goods Sold		
Manufacturing		
Raw Materials	1276.80	1966.50
Direct conversion	149.22	216.15
Depreciation	20.49	41.40
Indirect conversion	41.43	59.00
Packaging and Shipping	60.00	50.00
Royalties at 5% AGS	120.00	151.25
Total Cost Goods Sold	1667.94	2484.30
3. Gross Profit	702.06	490.70
4. Deduct SARE at 10% ANS	237.00	297.50
5. Net Income Before Taxes	465.06	193.20
6. Income Taxes at 50% Net Income Before Taxes	232.53	96.60
7. Earnings after Taxes	232.53	96.60

CAPITAL ESTIMATE SUMMARY
FACILITY "B"

A. New Property to be Installed:	44.6	44.6
Building	44.6	44.6
M & E	234.5	495.0
New Fixed Capital	279.1	539.6
B. Share Existing Property at 30% NFC	83.6	161.9
C. Total Fixed Capital	362.7	701.5
D. Working Capital		
Inventory	189.2	289.2
All others at 15% ANS	355.5	446.0
Total Working Capital	544.7	735.2
E. Total Operating Investment		
F. Return on Investment	25.6%	6.7%

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Epon 562

Since the product is not marketed in commercial quantities at the present time (small quantities are sold by Shell at a "development" price reported at about $1.50 per lb.), the estimates at both production levels have been made at three product prices.

Case A: $0.90/lb., list
Case B: $1.00/lb., list
Case C: $1.10/lb., list

As was anticipated, the price range chosen was sufficient to indicate the sales conditions for poor and good returns on investment.

ANNUAL PROFIT AND LOSS STATEMENT

Facility C: 1,000,000 lb/yr Epon 562 type resin
Facility D: 3,000,000 lb/yr Epon 562 type resin

(In Thousands of Dollars)

		Facility C	Facility D
1. Annual Net Sales			
Quantity, lbs.		1,000,000	3,000,000
Unit price, list $/lb	Case A:	0.90	0.90
	Case B:	1.00	1.00
	Case C:	1.10	1.10
Freight charge, $/lb		0.01	0.01
Net price, $/lb	Case A:	0.89	0.89
	Case B:	0.99	0.99
	Case C:	1.09	1.09
Amount ANS	Case A:	890.00	2670.00
	Case B:	990.00	2970.00
	Case C:	1090.00	3270.00
2. Cost of Goods Sold			
Manufacturing			
Raw materials		617.70	1853.10
Direct conversion		109.89	172.38
Depreciation		27.05	39.96
Indirect conversion			
	Case A:	27.66	52.44
	Case B:	27.84	53.01
	Case C:	28.02	53.55
Packaging & Shipping		20.00	60.00
Royalties at 5% AGS			
	Case A:	45.00	135.00
	Case B:	50.00	150.00
	Case C:	55.00	165.00
Total Cost Goods Sold			
	Case A:	847.30	2312.88
	Case B:	852.48	2328.45
	Case C:	857.66	2343.99
3. Gross Profit			
	Case A:	42.70	357.12
	Case B:	137.52	641.55
	Case C:	232.34	926.01
4. Deduct SARE at 10% ANS			
	Case A:	89.00	267.00
	Case B:	99.00	297.00
	Case C:	109.00	327.00

ANNUAL PROFIT AND LOSS STATEMENT
(Continued)

		Facility C	Facility D
5. Net Income Before Taxes			
	Case A:	None	90.12
	Case B:	38.52	344.55
	Case C:	123.34	599.01
6. Income Taxes at 50% Net Income Before Taxes:			
	Case A:	---	45.06
	Case B:	19.26	172.28
	Case C:	61.67	299.51
7. Earnings After Taxes			
	Case A:	---	45.06
	Case B:	19.26	172.27
	Case C:	61.67	299.50

CAPITAL ESTIMATE SUMMARY

Facility C: 1,000,000 lb/yr Epon 562 type resin
Facility D: 3,000,000 lb/yr Epon 562 type resin

(In Thousands of Dollars)

		Facility C	Facility D
A.	New Property to be Installed:		
	Building	60.0	97.0
	M & E	308.5	452.0
	New Fixed Capital	368.5	549.0
B.	Share Existing Property: at 30% NFC	110.6	164.7
C.	Total Fixed Capital	479.1	713.7
D.	Working Capital		
	Inventory	75.7	222.6
	All Others at 15% ANS		
	Case A:	133.5	400.5
	Case B:	148.5	445.5
	Case C:	163.5	490.5
	Total Working Capital		
	Case A:	209.2	623.1
	Case B:	224.2	668.1
	Case C:	239.2	713.1
E.	Total Operating Investment		
	Case A:	688.3	1336.8
	Case B:	703.3	1381.8
	Case C:	718.3	1426.8
F.	Return on Investment*		
	Case A:	no return	3.4%
	Case B:	2.7%	12.5%
	Case C:	8.6%	21.0%

*By extrapolation, at a selling price of $1.20 per pound, the returns would be

for Facility C: 14%
for Facility D: 29%

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TABLE VII

ANNUAL PROFIT AND LOSS STATEMENT
(In Thousands of Dollars)

	Epon 828 Production	Epon 1001 Production	Epon 562 Production
A. Annual Net Sales			
Quantity, lbs.	20,000,000	20,000,000	20,000,000
Unit price, list, $/lb.	0.80	0.605	1.00
Freight charge, $/lb.	0.01	0.010	0.01
Net price, $/lb.	0.79	0.595	0.99
Amount ANS	15,800	11,900	19,800
B. Cost of Goods Sold			
Manufacturing			
Raw Materials	8,512	7,866	12,354
Direct Conversion	460	440	580
Depreciation	64	96	98
Indirect Conversion	126	120	160
Packaging and Shipping	400	200	400
Royalties at 5% AGS	800	605	1,000
Total Cost Goods Sold	10,362	9,327	14,592
C. Gross Profit	5,438	2,573	5,208
D. Deduct SARE at 10% ANS	1,580	1,190	1,980
E. Net Income Before Taxes	3,858	1,383	3,228
F. Income Taxes at 50%	1,929	692	1,614
Net Income Before Taxes			
G. Earnings After Taxes	1,929	691	1,614

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CAPITAL ESTIMATE SUMMARY

(In Thousands of Dollars)

		20,000,000 pounds per year		
		Epon 828 Production	Epon 1001 Production	Epon 562 Production
A.	New Property to be Installed:			
	Building	83	61	302
	M & E	732	1,140	1,410
	New Fixed Capital	815	1,201	1,712
B.	Share Existing Property:			
	at 30% NPC	244	360	514
C.	Total Fixed Capital:	1,059	1,561	2,226
D.	Working Capital:			
	Inventory	1,241	1,157	1,484
	All Others at 15% ANS	2,368	1,788	2,970
	Total Working Capital	3,609	2,945	4,454
E.	Total Operating Investment:	4,668	4,506	6,680
F.	Return on Investment:	41%	15%	24%

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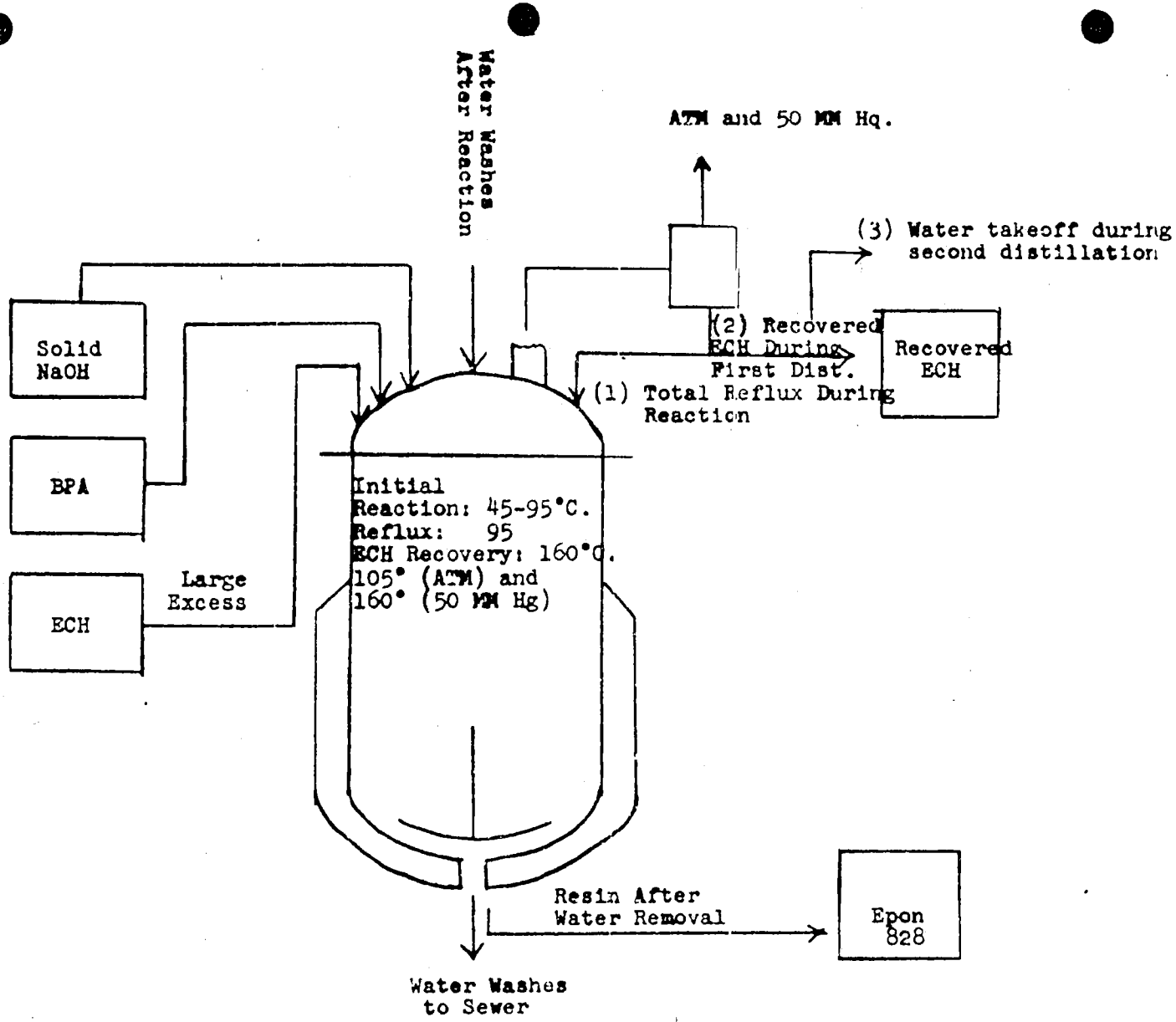

Epon 828 Production Process Flow

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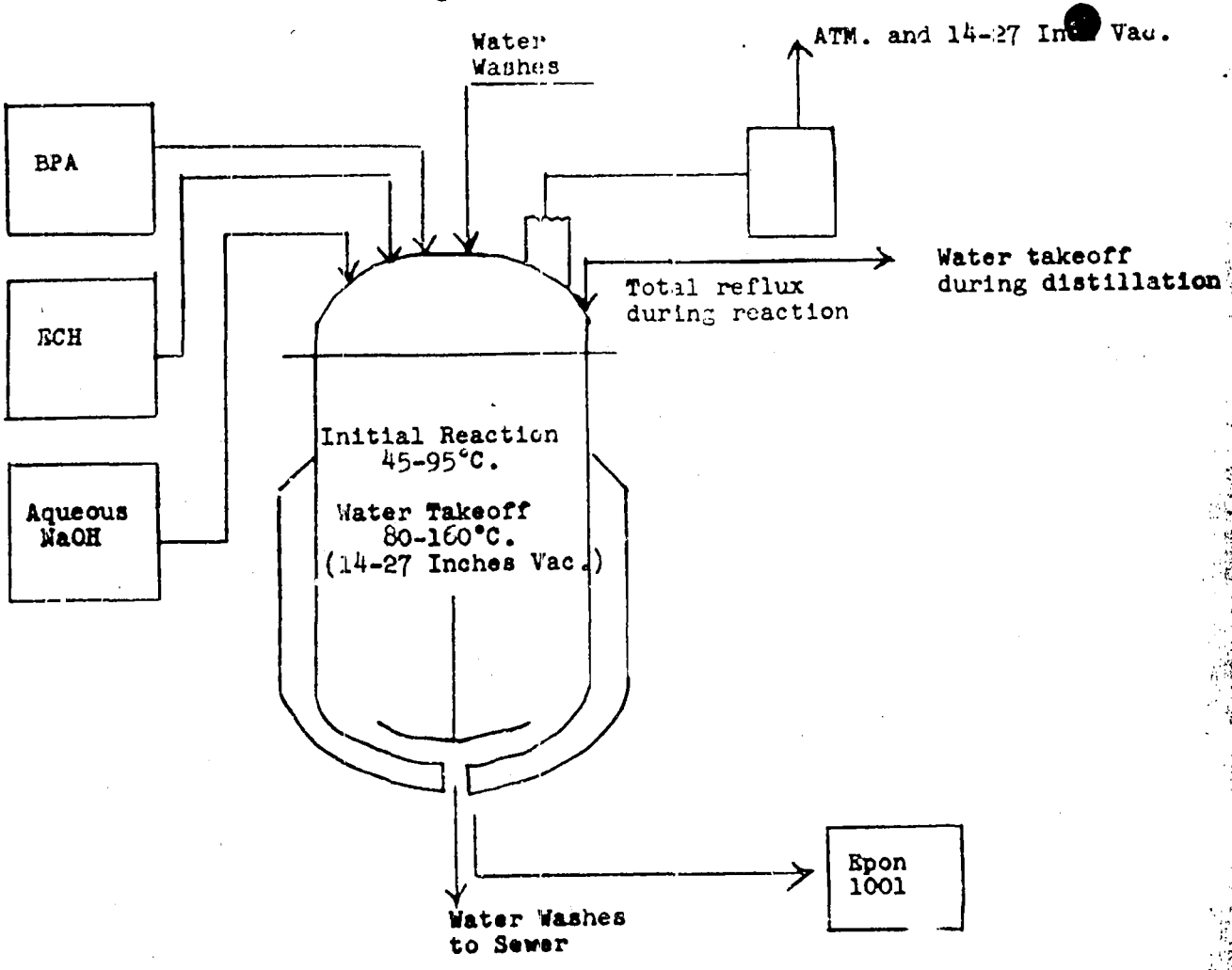


DSW 621072

Epon 1001 Production Process Flow

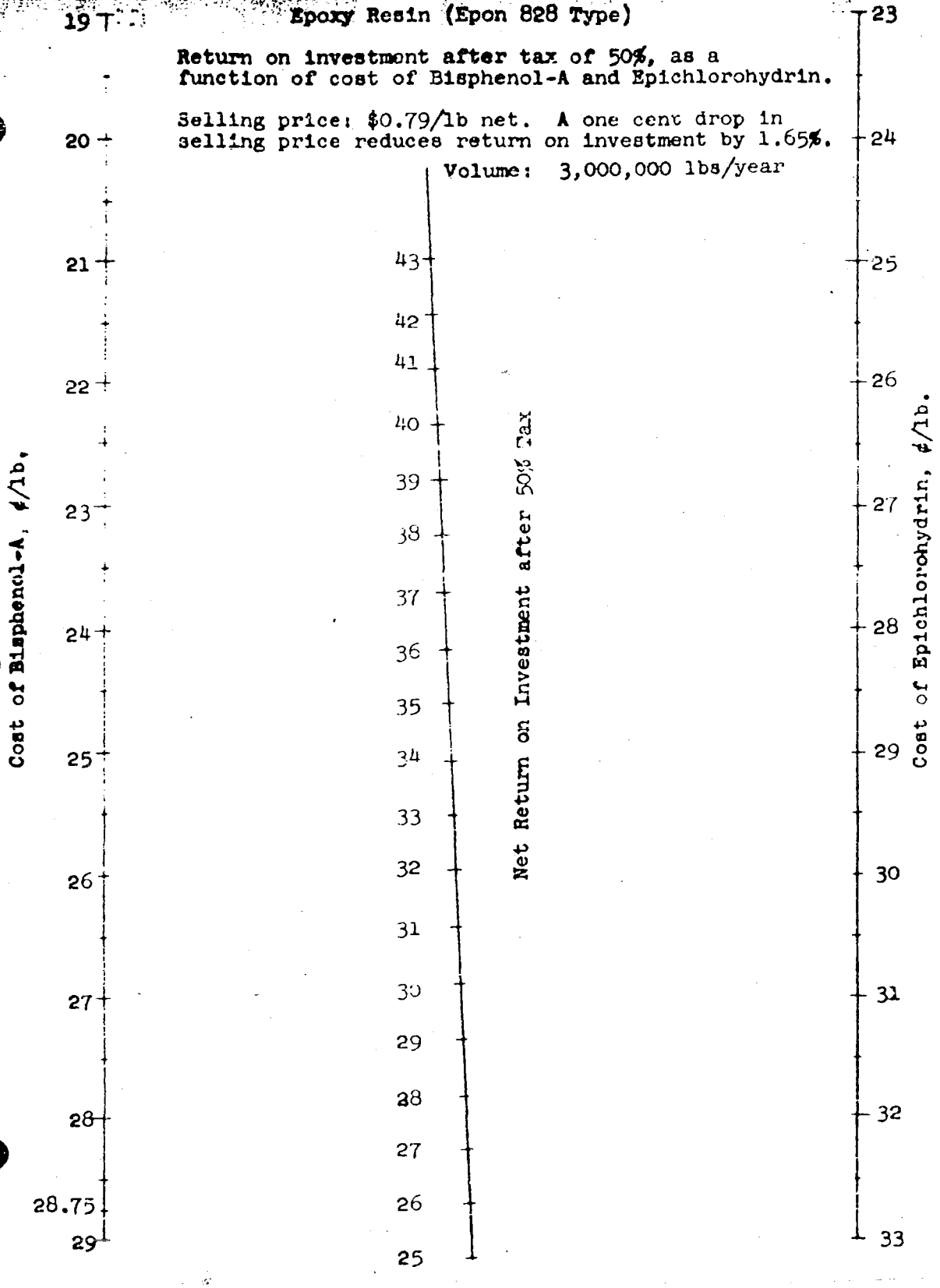
19

Epoxy Resin (Epon 828 Type)

Return on investment after tax of 50%, as a function of cost of Bisphenol-A and Epichlorohydrin.

Selling price: $0.79/lb net. A one cent drop in selling price reduces return on investment by 1.65%.

Volume: 3,000,000 lbs/year



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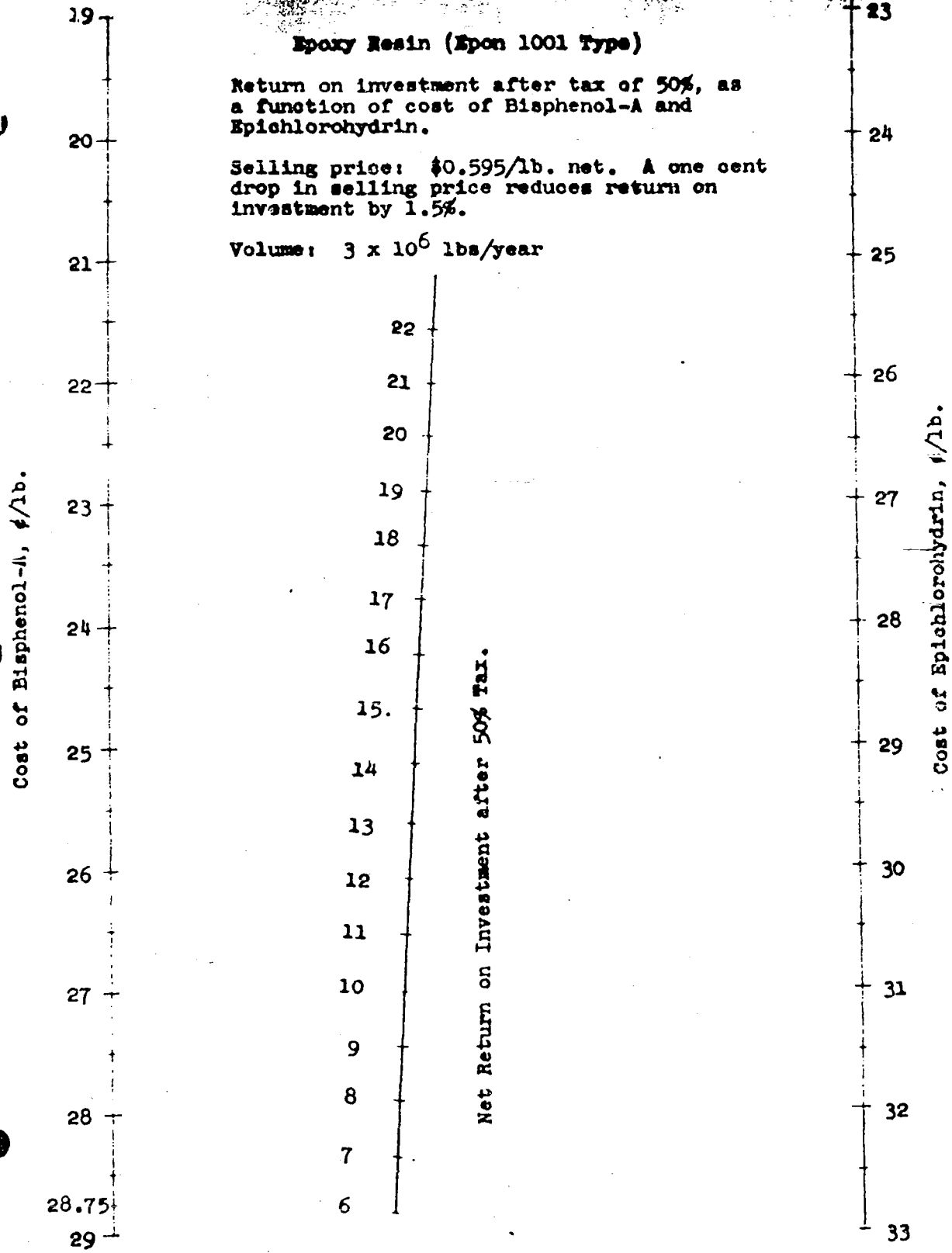
Epoxy Resin (Epon 1001 Type)

Return on investment after tax of 50%, as a function of cost of Bisphenol-A and Epichlorohydrin.

Selling price: $0.595/lb. net. A one cent drop in selling price reduces return on investment by 1.5%.

Volume: 3×10^6 lbs/year



DSW 621074

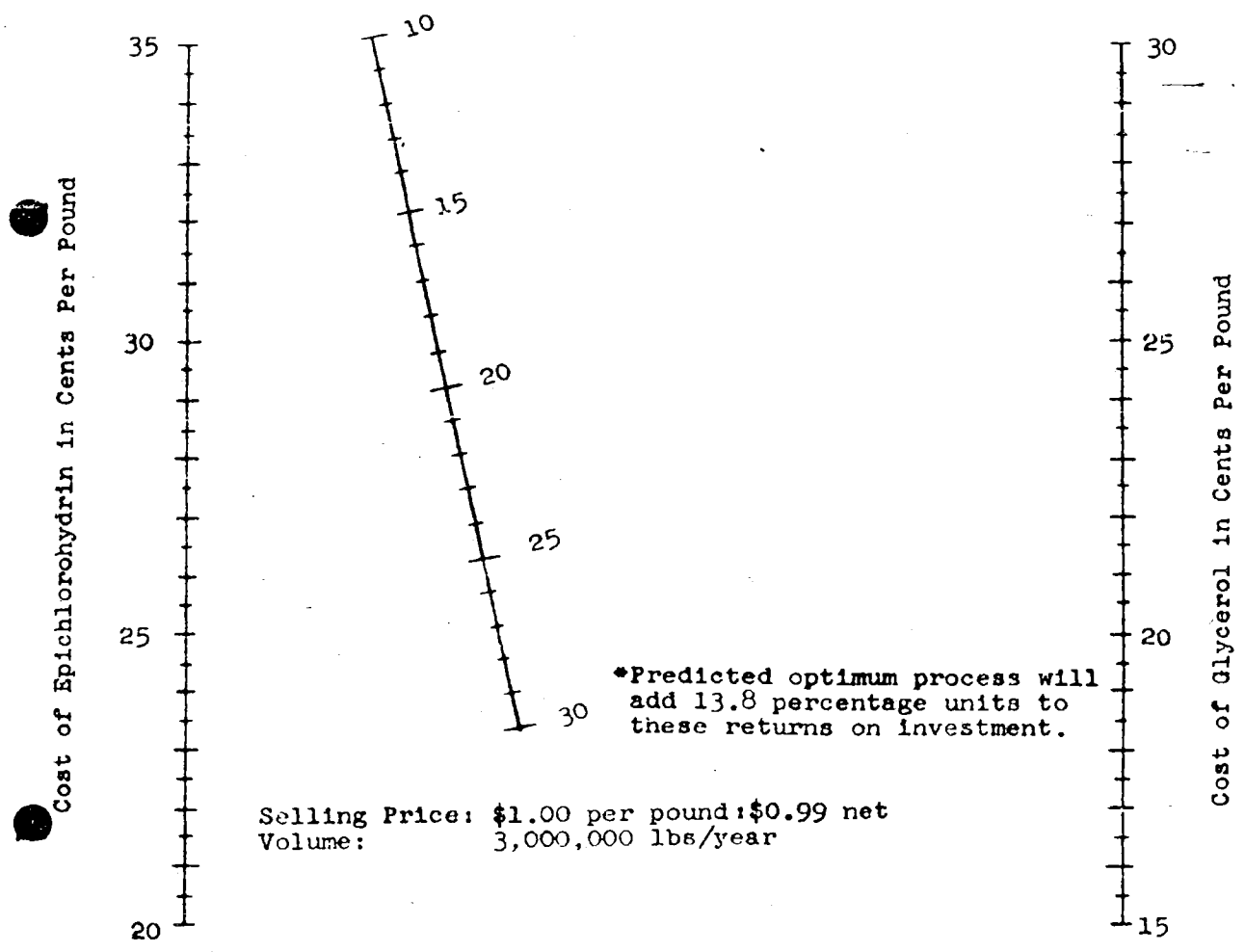
Epoxy Resin (Epon 562 Type)

Return on Investment - After Tax 50%

As a Function of Cost of Epichlorohydrin and Glycerol

(*Described in patent literature)

A one-cent drop in selling price reduces return on investment by 0.6 percentage points.



*Predicted optimum process will add 13.8 percentage units to these returns on investment.

Selling Price: $1.00 per pound : $0.99 net
Volume: 3,000,000 lbs/year

DSW 621075

XI. MATERIAL SPECIFICATIONS, ANALYTICAL PROCEDURE:

Source of Materials:

Hydrolyzed Aroclor 1262. This material was prepared from Aroclor 1262 which is a chlorinated biphenyl. Flash distilled hydrolyzed Aroclor 1262 (Monsanto, St. Louis) was used. The typical material was a glass at room temperature which analyzed 48.83% chlorine and which had an equivalent weight of 221.

Tetrachlorobisphenol-A. Monsanto, St. Louis, Lot No. 22046.
Bisphenol-A. Monsanto, St. Louis.

Epichlorohydrin. Shell Development Corporation, 98% min. NaOH. Mallinckrodt, Analytical Reagent, 97% min.

Product specifications. The development of laboratory processes for epoxy resins from BPA was directed to producing products with the following specifications.

Liquid resins (Epon 828 type)	Epoxide Equivalent: 190-210 Hydrolyzable Chloride: 0.5%
Solid Resins (Epon 1001 type)	Epoxide equivalent: 450-525 Hydrolyzable Chloride: 0.2% Max.
Liquid Resins from Glycerol (Epon 562 type)	Epoxide Equivalent: 140-165

Aromatic Chlorine - The aromatic chlorine content of the products obtained from hydrolyzed Aroclor 1262 was determined at Dayton under the direction of Dr. John Dazzi.

Epoxy Oxygen - The procedure followed for epoxy oxygen determination was the standard pyridine hydrochloride method (Ref. 19).

Apparatus - 100 ml single neck RB flasks, reflux condensers.

Reagents - About 0.2 N pyridine hydrochloride solution prepared by diluting 16cc cond HCl 1 kl to 1000 ml volume with Fischer certified Reagent pyridine; about 0.1N standard NaOH, phenolphthalein indicator.

Reactions

$$\underset{\text{I}}{ROCH_2CH\text{-}CH_2} + \underset{\text{II (Excess)}}{\text{(C}_6\text{H}_5\text{)}\cdot HCl} \xrightarrow[\text{Reflux}]{\text{Pyridine}} ROCH_2\underset{\displaystyle OH}{\underset{|}{CH}} - CH_2$$

$$\text{II (Excess)} + NaOH \longrightarrow NaCl + H_2O$$

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Procedure

The pyridine hydrochloride was compared with standard NaOH using phenolphthalein indicator. The volume of NaOH required for 25cc of reagent was recorded. (A)

The sample to be analyzed was weighed directly into a flask. To the flask were added boiling chips and 25 cc reagent. The flask was warmed slowly and swirled occasionally to dissolve the sample. The solution was refluxed for 1/2 hour. The flask was cooled in an ice - H_2O bath. Four drops of phenolphthalein were added and the solution was titrated with standard NaOH to the pink end point. During the titration the flask was kept in an ice H_2O bath. The volume of NaOH used was recorded (B). The percent epoxy oxygen was calculated from the equation

$$\% \text{ Epoxy Oxygen} = \frac{(A-B)\ N \times 0.016 \times 100}{\text{Weight Sample (g)}}$$

where N is the normality of the NaOH

Hydrolyzable Chloride

The procedure described here was not applicable to solid resins from BPA because of their insolubility in ethanol.

Hydrolyzable chloride was determined by converting the organic chloride into soluble inorganic chloride and analyzing by the Volhard method (Ref 20).

Apparatus - The equipment used for epoxy oxygen analysis was also used here.

Reagents - Standard $AgNO_3$ and KSCN, $FeSO_4$, HNO_3 (6N), nitrobenzene and approximately 0.5 N ethanolic KOH.

Reactions -

$$\begin{array}{l} ROCH_2CH - CH_2 \\ \quad\quad\ |\quad\quad\ | \\ \quad\quad OH \quad Cl \end{array} + KOH \xrightarrow[\text{Excess}]{} KCl + H_2O \pm \text{Organic products}$$

$$\begin{array}{l} ROCH_2CH - CH_2Cl \\ \quad\quad\ | \\ \quad\quad O - OCH_2R \end{array}$$

$$KOH\ (\text{Excess}) + HNO_3 \rightarrow H_2O + KNO_3$$

$$KCl + AgNO_3\ (\text{Excess}) \longrightarrow AgCl + KNO_3$$

$$AgNO_3\ (\text{Excess}) + KSCN \longrightarrow KSCN + KNO_3$$

Procedure

The sample was weighed out into a flask and to it were added 10 ml ethanolic KOH. Boiling chips were added and the mixture was

heated and swirled occasionally to affect solution. The mixture was then refluxed for one hour. During the reflux the mixture was swirled occasionally in order to keep the mass well dispersed in the ethanolic solution. The mixture was cooled, diluted with 10-15 cc distilled H_2O and acidified with HNO_3. The soluble chloride was analyzed by the Volhard method.

$$\% \text{ Hydrolyzable Chloride} = \frac{(C-D) \times 0.03546 \times 100}{\text{weight sample (g)}}$$

where C = ml $AgNO_3$ used x its normality

and D = ml KSCN used x its normality

XII. TOXICITY AND HAZARDS:

(1) Epichlorohydrin (ECH)

Epichlorohydrin may polymerize violently in the presence of acidi catalysts. Caution must be observed in order that large volumes of ECH do not come in contact with these catalysts (Ref 21).

Bisphenol-A

Bisphenol-A is moderately irritating to the skin and eyes. It should be removed from the skin with soap and water and flushed from the eyes with clean water, if contact occurs. Oral LD_{50} to rats is 6.5 g per kilo. The chemical is not considered hazardous to handle, but contact should be avoided or promptly remedied as above (Ref 23).

Tetrachlorobisphenol-A and Hydrolyzed Aroclor 1262

The toxicity of these new materials is unknown. It may be assumed that the precautions used for working with phenol itself can be applied here. For phenol, the liquid or solutions are very corrosive to the skin. Phenol is readily absorbed through the skin and mucous membranes. It can also be absorbed through the lungs as gastrointestinal treact. After absorption the toxic effects are exerted primarily upon the central nervous system but following sufficient exposure, there can be edema of the lungs, kidney, liver, pancreas and spleen. Exposure to toxic amounts usually results in death in a few hours (Ref 24).

Bisphenol-A Epoxides

Studies to determine acute toxicity have shown that the resins (Epon type) are practically non toxic. The oral administration of more than 6cc liquid resin (Epon 834 type) per kilo of body weight was tolerated by white mice without symptoms. There was no hazard from vapor exposure. The solid resins (Epon 1001 type) present no hazard whatever in ordinary industrial use.

Cases of dermatitis among workers handling liquid resins (Epons 828, 834, 562) have established that the latter will cause skin irritation in hypersensitive individuals. In the normal individual, handling methods which minimize skin contact would ordinarily suffice as a precautionary measure. The latter includes gloves, heavy aprons and full face shields. In case of contact protective creams, such products as Merphenex, Acid Mantle and Kerodex have been found beneficial (Ref 25).

Tetrachlorobisphenol-A and Hydrolyzed Aroclor 1262 Epoxides

The toxicity of these new materials is unknown. It may be assumed that the precautions necessary for handling bisphenol-A epoxide resins are applicable here also.

BF_3 - Etherate

This material is flammable and can cause explosions. It is easily inhaled because it is volatile. It is toxic. The fluoride content of this material renders it an irritant to the skin, eyes and mucous membranes. The material should be used in closed systems, if possible. Personnel exposed to it should wear protective clothing, safety goggles and a respirator. The material should be stored in a cool place out of direct rays of the sun away from areas regarded as acute fire hazards (Ref 26).

Glycerol

A combustible liquid and a moderate fire hazard. It is considered relatively non toxic. It can cause iritis, slight internal congestion and slight necrosis. Personnel who handle large quantities should protect the eyes with chemical safety goggles. To fight fires of this aterial, water (fog or spray), carbon dioxide, carbon tetrachloride and dry chemical may be used (Ref 27).

Dioxane

A flammable liquid and dangerous fire hazard. The liquid is dangerous to the eyes and can cause lackrymation. One of the earliest symptoms of intoxication is misty vision. It also produces irritation of the lungs and prolonged exposure can cause narcosis. It has insidious long range effects and prolonged exposure can produce damage to the liver and kidneys. Toxic amounts may be absorbed through the skin. It is capable of forming peroxides and it can explode when distilled.

Dioxane should be used in closed systems or with adequate exhaust ventilation. For protection of the eyes personnel should wear chemical safety goggles. If the concentration is over 50 ppm, a respirator should be worn. It should be stored in a cool, well ventilated place away from acute fire hazard or powerful oxidizing agents. To fight fires of this material carbon dioxide, carbon tetrachloride and dry chemical may be used (Ref 28).

XIII. ACKNOWLEDGMENT:

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Dayton: J. Dazzi and J. Herbig

St. Louis: M. Terpstra and R. Cass

Witnessed by: Janet M. Webster S. E. Gebura

S. E. Gebura, Chemist

Date: January 29, 1959

M. F. Drumm, Group Leader

/jw

XIV: APPENDIX:

The conclusions drawn from the U.S. patent survey concerning epoxy resins are given below. The report on this survey will be issued separately.

It should be noted that purchase of epoxide resins permits their curing or blending without patent infringement.

Manufacture of Resins

Monsanto can manufacture, without patent infringement, resins from bisphenol-A (BPA) by reactions where the molar ratio of epichlorohydrin (ECH) to BPA is 1.6 - 1.9 to 2.1 to 3.9. These ratios give products whose properties are such that they would not provide a competitive line of epoxide resins and result in a narrow range of properties. Patents prevent the manufacture of resins from BPA by reactions where the molar ratio of ECH to BPA is 1.1 - 1.5, 2.0 or 4.0 or greater. A variety of resins from tetrachlorobisphenol-A (TCBP-A) or mixtures of TCBPA and BPA can be manufactured which could very well be competitive in the epoxide resin field.

Patents prevent the manufacture of monomeric glycidyl ethers from polyhydric phenols where the molar ratio of ECH to polyhydric phenol is 4.0 or greater. Resins of high molecular weight cannot be pro-

duced from low molecular weight resins or monomeric glycidyl ethers by further reaction with dihydric phenols without patent infringement. The production of the adduct of glycerol and ECH in the presence of fluorine containing catalysts is claimed by patents. Monsanto can produce this adduct however, in the presence of other acid acting catalysts, eg. $FeCl_3$, H_2SO_4 etc.

Monsanto cannot produce the epoxide resin derived from this adduct by hydrochlorinating it with sodium aluminate, zincate or silicate in an organic solvent. It may be possible to prepare this resin by other dehydrochlorinating processes, whether a particular process infringes the patent literature will be determined by the nature of the product obtained, i.e. its chloride content and type of chloride.

No patents were found which claim the processes or products of the epoxidation of phenol aldehyde novolacs. Since this is being done commercially in England, British patents may exist and may be copending in the U. S.

Although the epoxidation of the alkali salts of methylol phenols is covered by only a single patent, it is thought that this patent could be troublesome. The claims would tend to include the Monsanto West Coast resins which have a high content of monomeric methylol phenols. The claims do not include the polymeric one stage phenol formaldehyde resins.

Curing

The patent literature describes a large number of curing reagents. For the most part these are specific reagents for which specific advantages are claimed. Monsanto could, therefore, easily enter into the field of utilization of hardeners by developing new curing systems or specific curing reagents possessing superior properties to those disclosed so far. The functional groups which are not completely blocked by the patent literature include amino, carboxylic acid, mercaptan, amide aldehyde, ketone, and various combinations of these functional groups or their derivatives. Patents prevent the use of hardeners which contain in general one to three of the functional groups carboxylic acid anhydride, sulfuric acids or their chlorides, isocyanate, isothiocyanate, polyol (containing at least two primary OH), phenolic hydroxyl, phosphoric acids and derivatives. In addition Monsanto may not use the specific curing reagents which are listed in Table VIII.

Blends of Epoxide Resins

(a) Phenol, melamine or urea aldehyde condensates. The patent situation concerning the blending of epoxide resins with aldehyde condensates of phenol, melamine or urea is extremely complex. It is not possible to state any definite conclusions with respect to these blends until a thorough examination of the situation by the patent department is made. With this reservation, it is

possible to reach the following conclusions: (a) Monsanto can formulate ternary or higher blends which may be improvements on the binary systems covered in the patents; (b) in a limited number of cases, it may be possible to formulate binary blends which fall outside the patented limits of components; (c) patents prevent the formulation of higher blends of epoxides with these condensates which are listed in Table IX.

(b) Other polymeric systems - Monsanto cannot utilize those blends of epoxies with other polymeric systems which are listed in Table X.

The blends of polymeric systems with epoxies which have not been uncovered in the patent survey include polyurethane, Nylon type, acrylonitrile, acrylamide, furan, thiokol, rubber, vinylidene cyanide sulfonated or carboxylated styrene, terephthalic and isophthalic acid types and various copolymeric systems which are not listed in the tables.

KEY TO TABLES:

N. S.	Not stated in broadest claim
A	Aliphatic polyepoxide
DHP	Dihydric phenol epoxide
PHP	Polyhydric phenol epoxide
DGE	Diglycidyl ether
BPA	Bisphenol-A

TABLE VIII.

U.S.Patent No.	Date	Number of Claims	Curing Reagent	Range	Type of Epoxide	Application
2,324,483	7/20/43	10	Partially polymerized adipic acid	N.S.	Phenolic	Molded articles varnishes
2,444,333	6/29/48	1	Alkaline organic or inorganic reagent	0.1-5%	Phenolic - two moles ECH per mole di-hydric phenol	Molded articles varnishes
2,500,449	3/14/50	11	Oxalic Acid	5-300%	Phenolic polyol	Varnishes, enamels, adhesives, moldings
2,500,600	3/14/50	15	Sat aliphatic amine $C_nH_{2n}(NH_2)2$ n = 4; one NH_2 attached to tertiary C atom	5-300%	Phenolic polyol	Enamels, adhesives
2,553,718	5/22/51	12	 CH_2NMe_2	7-25%	Phenolic	Cold setting adhesive
2,569,920	10/2/51	22	Citric acid Tricarballylic acid aconitic itaconic citraconic malic diglycollic	N.S.	Not. clear	Glass Coatings
2,575,558	11/20/51	10	ET_3N	5-25%	Phenolic	Cold setting adhesive
2,585,115	2/12/52	2	polyethylene polyamines	0.25 1.7 equiv.	Phenolic	Varnishes Coatings

U.S. Patent No.	Date	Number of Claims	Curing Reagent	Range	Type of Epoxide	Application
2,640,037	5/26/53	14	Fatty acid salt of reaction product of sec. amine and a polyepoxide	N.S.	Phenolic	Molding adhesives varnishes enamels
2,642,412	6/16/53	8	N,N-dialkyl- 1,3 propanediame alkyl = 1 or 2 C atoms	0.05-1 mole per exox equiv.	Phenolic polyol	Potting coatings adhesives
2,643,239	6/23/53	6	Reaction product of sec. amine and polyepoxide	N.S.	Phenolic polyol	Potting adhesives baked surface coating
2,651,589	9/8/53	21	Reaction prod. of poly-epoxide and a hardening reagent containing a plurality of neutralizable H atoms	50-150%	Phenolic polyol	Surface coatings adhesives
2,681,901	6/22/54	5	2-ethylhexoic acid salt of 2,4,6-tri (dimethylaminamethyl) phenol	0.05-0.85 N atoms per epox group	Phenolic polyol	Moldings Adhesives
2,683,131	7/6/54	15	Acidic low mol. wgt. polyester having acid no. above 200	N.S.	Phenolic polyol	Coating, Casting, Laminating, Adhesives
2,712,535	7/5/55	15	X-R-X R= at least 14 C atoms; X= group capable reacting with epoxide group	N.S.	Phenolic polyol	Elastic products

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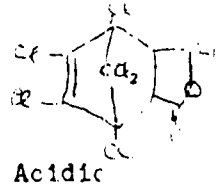
U.S. Patent No.	Date	Number of Claims	Curing Reagent	Range	Type of Epoxide	Application
2,717,885	9/13/55	4	BF_3 salt of amines	N.S.	Phenolic	—
2, 723,924	11/15/55	6	Neutral salt of alkylene polyamine with a sat aliphatic monocarboxylic acid of 2-5 C atoms	N.S.	Phenolic	Wool treatment
2,744,845	5/8/56	10		0.8-1.2 equiv.per each epox equiv.	Phenolic polyol	Fire retardance
2,752,269	6/26/56	13	Acidic H_2O-ETOH soln. or emulsion of epoxide A	N.S.	Polyol	Cotton and rayon treatment (crease & wrinkle resistance)
2,753,323	7/3/56	18	A-A'N(CH_2CH_2N)x-$CH_2CH_2NA'A$ x= 0-3 AA'=H or $-CH_2CH_2CN$ at least one N is non tertiary	N.S.	Phenolic Polyol	Greater fluidity and longer pot life
2,510,885	6/6/50	12	Amine--polyhydric phenol	Amine or amide active H plus phenolic OH are more than 1/2 epox. equiv.	Phenolic polyol	Coatings, moldings, adhesives
2,510,886	6/6/50	12	Amide--polyhydric phenol		Phenolic	" "
2,589,245	3/18/52	7	Carboxylic acid amide	N.S.	Phenolic	" "
2,713,559	7/19/55	6	Urea	N.S.	Phenolic	" "
2,712,001	6/28/55	10	Aromatic sulfonamides	N_2H is substantially 1# of epox gps.	Phenolic	" " (N.S.-Not stated)

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R= alkyl, phenyl - X= OH, alkoxy
m= 1-2 - n= 0.01-3 - m + n < 4
(b) terephthalic or iso phthalic acids or lower alkyl esters
(c) glycerin

64 68 R3

TABLE IX

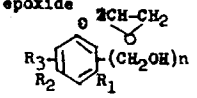
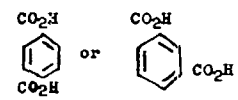
U.S. Patent No.	Date / No. of Claims	Type of Epoxide	Blend of Epoxide with	Range
2,528,360	10/31/50 21	PHP	Alkylated condensate of aldehyde and amines or amides polyhydric phenol	N.S. N.S.
2,521,911	9/12/50 13	PHP	Phenol-aldehyde condensate alkaline catalyst	Equal parts to 3-1/3 parts epoxide to condensate "substantial percentage"
2,521,912	9/12/50 7	A	Phenol-aldehyde condensate alkaline catalyst	Ratio of epoxide groups to phenolic OH is 1.8-1 to 1-1.4 "substantial amount"
2,687,397	8/24/54 9	PHP	Urea-CH_2O condensate Neutral salt of amine and a sulfonic acid amine: Et_2NH, Et_3N, i-Pr_2NH, aniline, pyridine, morpholine, cetyldimethylamine	N.S. Small amount
2,730,467	1/10/56 3	A PHP	Urea-CH_2O condensate epoxide  Z=$(CH_2)x$ n=1-3 $R_1R_2R_3$=H, alkyl, aryl Solvent	7-15% by weight 10-17% " " 60-80%
2,703,765	3/8/55 14	BPA	Butylated urea-CH_2O, melamine-CH_2O, or propylated urea - CH_2O condensates Salicylic acid, 5-chloro salicylic acid, acetyl salicylic acid	N.S. N.S.
2,631,138	3/10/53 12	BPP	Alkylated urea - CH_2O condensate Hydrocarbon containing 1-3 SO_3H or SO_2CL groups	N.S. N.S.
2,687,396	8/24/54 2	BPA	1. A phenol -CH_2O resin reaction product of 2. (a) $R_mS_1X_xO_{4-\left(\frac{m+n}{2}\right)}$ R= alkyl or phenyl X= OH, alkoxy m= 1-2, n= 0.01-3 (b)  or lower esters (c) glycerin	5-20% 60-80% (10-30% epoxide)
2,637,716	5/5/53 10	PHP	Polybasic carboxyic acid or anhydride; polyamine alkyl ether of CH_2O condensate of phenol, urea, melamine or dicyandiamides	1/8 - 6/5 equivalent N.S.
2,637,715	5/5/53 15	PHP	Polybasic acid or anhydride dicyandiamide alkyl ether of CH_2O condensate of phenol, urea, melamine or dicyandiamide	1/8 - 6/5 equivalent 0.06 - 0.6 m. N.S.
2,458,796	1/11/49 21	PHP	Dicyandiamide; ether of CH_2O condensate of urea, phenol, melamine or dicyandiamide	

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TABLE X

U.S. Patent No.	Date / No. of Claims	Type of Epoxide	Blend of Epoxide with	Range
2,511,913	6/20/50 14	PHP	Aldehyde-aromatic amine condensate	N.S.
2,494,295	1/10/50 6	PHP	Aldehyde-aromatic sulfonamide condensate	N.S.
2,707,177	4/26/55 20	A PHP	Triallylcyanurate Triallylcyanurate Plastisol of a vinyl halide resin or vinyl copolymers	N.S. N.S. N.S.
2,705,223	3/29/55 12	A PHP	Polymeric polyamide containing free amine and carboxyl groups	N.S.
2,699,413	1/11/55 8	DHP	Alkaline condensation product of CH_2O and a mono or dialkyl phenol or mixtures H_3PO_4 Solvent	50-50 to 80% epoxide to 20% condensate 5-20%
2,602,785	7/8/52 11	DHP	Polyvinyl ester of a fatty acid	minor proportion (1-10%)
2,596,737	5/13/52 8	Unsat fatty acid ester of an epoxide of a DHP	Styrene	Containing 10-75% by weight of polymerized styrene
2,591,539	4/1/52 2	PHP	Monobasic acid modified alkyd aldehyde-amide or amine condensate	25-75% 10-25% 5-50% epoxide
2,542,664	2/20/51 6	A	Phenol-vegetable oil condensate (2:1) containing at least 2 phenolic OH	20 parts/18 epoxide 166 parts/16 epoxide
2,502,145	8/28/50 8	PHP	Phenol-vegetable oil condensate (2:1) containing at least 2 phenolic OH	50-50 3 parts epoxide to 1 of condensate
2,604,464	7/22/52 10	DGE of BPA	Styrene-acrylic acid o methacrylic acid from at least 50 parts styrene and at least 5 parts acid Amine or quartenary ammonium compound	1 mole DGE for every two CO_2H groups 0.5 by weight of copolymer
2,662,870	12/15/53 10	DHP	Copolymer of (a) styrene (50 parts) (b) acrylic or methacrylic acid (at least 5 parts) (c) vinyl pyridine (0.05-1.0 parts/100 parts (a b)	One epoxide group for each CO_2H group
2,736,717	2/28/56	Nat. drying oil acid ester of an epoxide of a DHP	(a) styrene or alkyl or halogen subst. styrenes (b) drying or semi-drying oil	N.S. N.S.
2,713,565	7/19/55 8	PHP	Polyvinylacetal resin 2 alkenyloxybenzene containing 1-3 CH_2OH groups	0.2-3% N.S.
2,689,834	9/21/54 2	Epoxy ester (castor oil dehydrated acids)	Styrene	Containing 7-35% polymerized styrene
2,626,223	1/20/53 14	PHP	Polyester-amide	Reacted in ratios to give specified softening points
2,742,448	4/17/56 4	BPA	Alkyl orthotitanate B-hydroxyamine or polyamine	N.S. N.S.
2,687,398	8/24/54 1	BPA	Reaction product of (a) $R_mSiXO_{\frac{4-(m+n)}{2}}$ R= alkyl, phenyl - X= OH, alkoxy m= 1-2 - n= 0.01-3 - m + n < 4 (b) terephthalic or iso phthalic acids or lower alkyl esters (c) glycerin	70-90%

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ght of an epoxy
16g (one equivalent)
viding 16 by the
ltiplying by 100.

h of resin required
C18 fatty acid is

dyl ethers of TCBPA
ric resins are com-
n calculating the

percent of phenol

zed Aroclor 1262 it
d that its conversion

o the diglycidyl
rivatives was deter-
zable chloride. The
al yield.

the procedure given

lysis were 6.39% and
ly monomeric products
= 0.954 conversion

on to the chlorohydrin

ce the equivalent
ponding chlorohydrin
e expected yield for
ther expected
hlorohydrin expected
yield

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68
RS

TABLE X - con't

U.S. Patent No.	Date No. of Claims	Type of Epoxide	Blend of Epoxide with	Range
2,695,276	11/23/54 5	DHP	Polymeric silanol	25-75%
2,709,664	5/31/55 23	PHP	Metal coating 1st coat - A polyvinyl acetal 2nd coat - Pigmented epoxide resin 3rd coat - Epoxide resin	—
2,528,417	10/31/50 6	A PHP	Phenolic pitch	appreciable proportion
2,731,437	1/17/56 16	DGE of a bisphenol	$(CH_2\overset{O}{\diagdown\diagup}CH-CH_2)_2S-R$ R= $-(C_2H_4OCH_2OC_2H_4S)_n-$ $C_2H_4OCH_2OC_2H_4-$	N.S.
2,555,169	5/29/51 8	A	Halogen containing organic substance, M.W.>2000	N.S.
2,559,333	7/3/51 15	Mixture of A and PHP	Halogen containing organic substance, M.W.>2000	N.S.
2,564,194	8/14/51 10	PHP	Organic material containing halogen, M.W.>162	0.2-5%
2,590,059	3/18/52 9	A PHP	Organic matter containing 10-75% halogen, M.W.>2000 Cadmium or alkaline earth salt of a carboxylic acid	0.1-10%
2,595,619	5/6/52 15	A PHP	Halogen contining polymer diamides of carbonic acid and derivatives	—
2,609,355	9/2/52 12	A	Vinyl chloride copolymers containing at least 70% PVC ester of unsat alcohol and a dicarboxylic acid containing an olefinic bond Salt of a carboxylic acid whose ionization constant is less than that of phthalic acid	—

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Appendix B:

Definitions

Epoxide Equivalent. The epoxide equivalent weight of an epoxy resin is the weight of resin required to yield 16g (one equivalent) of oxirane oxygen. The value os obtained by dividing 16 by the analyzed percent of epoxy oxygen (E.O.) and multiplying by 100.

$$\text{Epoxide Equivalent} = \frac{16 \times 100}{\% \text{ E.O.}}$$

Equivalent weight to esterification. The weight of resin required to completely esterify 60g acetic acid or 280g C18 fatty acid is the equivalent weight to esterification.

Calculations

Yield - The yield calculations for the diglycidyl ethers of TCBPA and hydrolyzed Aroclor 1262 and for the polymeric resins are complex. The factors which were not considered in calculating the yields are:

(a) Composition of the dihydric phenols - i.e. percent of phenol or phenolic derivatives present.
(b) The purity of the epichlorohydrin
(c) The H_2O content of the resins
(d) The hydroxyl analysis of the products

For the diglycidyl ethers of TCBPA and hydrolyzed Aroclor 1262 it was assumed that the material was 100% pure and that its conversion in the reaction was omplete.

The extent of the conversion of the material to the diglycidyl ether and to the corresponding chlorohydrin derivatives was determined by analysis for epoxy oxygen and hydrolyzable chloride. The expected yield was then compared with the actual yield.

Example - Referring to the product obtained by the procedure given on page (10).

The epoxy oxygen and hydrolyzable chloride analysis were 6.39% and 0.47% (average) respectively. Assuming that only monomeric products were formed, these values represent $\frac{6.39}{6.70} \times 100 = 0.954$ conversion to diglycidyl ether and $\frac{0.47}{12.86} = 0.0365$ conversion to the chlorohydrin derivative.

Since seven equivalents TCBPA were used and since the equivalent weights of the diglycidyl ether and the corresponding chlorohydrin derivatives are 239 and 275.5 respectively, the expected yield for 100% conversion of TCBPA was

7 x 239 x 0.954 = 1596 g weight ether expected
7 x 275.5 x 0.0365 = 70g weight chlorohydrin expected
1666g expected yield

The actual yield was 1664g. The percentage yield was

$$\frac{1664}{1666} \times 100 = 99.8\%$$

For the polymeric solid resins, it was assumed that the materials were 100% pure were completely incorporated into the product and that the molar amount of ECH used represented the molar amount of HCl split off.

Example: Referring to the product obtained by the procedure described on page (~~i.e. described on page~~ 20)

Expected Yield = 2280g (BPA) + 1450g (15.69m) ECH

$$- (36.5 \times 15.69)\text{ g HCl} = 3157\text{g}.$$

The actual yield was 3002g. The percentage yield was

$$\frac{3002}{3157} \times 100 = 95.2\%$$

For the liquid resins from BPA, it was again assumed that 100% pure reactants were used and that BPA was completely converted. It was also assumed that the ECH consumed in the reaction was incorporated into the product.

Example: Referring to the product obtained by the procedure described on page (17 ex. 3).

The amount of ECH incorporated into the product was 520.2g (5.62M). Of this amount $\frac{827 \times .0113}{35.4} = 0.264\text{m}$ appeared as ECH in the product (827g) by virtue of its hydrolyzable chloride analysis. The amount of HCl to be split off was therefore 5.62 - 0.26 = 5.36m = 190g HCl.

The expected yield was therefore 570g BPA + 520g ECH - 190g HCl = 900g. The actual yield was 827g. The percentage yield was therefore $\frac{827}{900} \times 100 = 92\%$.

Calculations for the Recovery of excess ECH.

The excess ECH was recovered by distillation from the reaction mixture of the two phase system ECH-H_2O. The system was allowed to separate and its temperature was adjusted by warming under the hot water tap. The separate layers were then removed and weighed. The ECH and H_2O contents of the phases were calculated on the basis of the table reproduced on following page (Ref 11).

Temperature (°C)	Weight % ECH Lower Layer	Upper Layer
0.0	98.91	6.48
10.0	98.74	6.52
20.0	98.53	6.58
25.0	98.48	-
30.2	-	6.60

Calculations for the composition of Epon 828, 1001 and 1004 in terms of BPA and ECH.

By using the epoxide equivalent weight of resin and the equivalent weight to esterification, it was possible to approximate the ratio ECH/BPA contained in the resin. For these calculations the following constants were used.

Epon Resin	Epoxide Equivalent	Average	Ester Equivalent
828	190-210	200	85
1001	450-525	488	145
1004	870-1025	947	190

The equivalent weight of ECH incorporated into the resins is 92.5 - 36.5 = 56g.

(a) Epon 828

Calculate the epoxy equivalence for the esterification equivalent (85g) from the epoxide equivalent of 200:

$$\frac{85}{200} = 0.42 \text{ equivalents opoxy oxygen}$$

This value is equivalent to 0.84 equivalents of hydroxyl to esterification. Therefore in the esterification equivalent 1-0.84 = 0.16 equivalents of hydroxyl is present from ECH incorporated into the polymeric chain and chlorohydrin portion of the resin. The total equivalents ECH incorporated is therefore 0.42 + 0.16 = 0.58 equivalents. Since 56 is the equivalent weight of ECH incorporated into the resin 56 x 0.58 = 32.48g ECH equivalent in the resin

In 85g of resin, therefore, 85-32.5 = 52.5g (0.23m) BPA is incorporated.

The molar ratio ECH/BPA in the resin is therefore $\frac{0.58}{0.23} = 2.4$

Proceeding in the same manner for Epons 1001 and 1004 the ECH/BPA ratio is found to be 1.52 and 1.25 respectively.

Notebook pages containing the experimental data.

209264 - 209300
217251 - 217282
217293 - 217300
218901 - 218950
221151 - 221200
223601 - 223650
226401 - 226450
229001 - 229050
231551 - 231600
238401 - 238450
239401 - 239450
244401 - 244450
249451 - 249500

Physical Properties of Materials.

Bisphenol-A (Ref 23).

Emperical Formula:	$C_{15}H_{16}O_2$
Molecular Weight:	228.28
Appearance:	White flakes
Melting Range:	150-155° (Solidification Range)
Solubility:	H_2O - insoluble ETOH - soluble CCl_4 - slightly soluble $(CH_3)_2CO$ - soluble

Tetrachlorobisphenol-A.

Emperical Formula:	$C_{15}H_{12}Cl_4O_2$
Molecular Weight:	366
Appearance:	White crystalline powder

Hydrolyzed Aroclor 1262 (Ref 29).

Appearance:	Clear, light brown glass
Equivalent Weight:	219-221

Epichlorohydrin (Ref 11).

Emperical Formula:	C_3H_5OCl
Molecular Weight:	92.53
Boiling Point:	116.1
Specific Gravity (20°):	1.18066
Refractive Index (20°):	1.43805

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Epon 828 (Ref 30).

Appearance:	Light brown clear liquid
Epoxide Equivalent:	190-210
Esterification Equivalent:	85
Gardner Viscosity:	50-150 poises

Epon 1001 (Ref 30).

Appearance:	Light yellow clear solid
Softening Point:	64-76°C (Durrans)
Epoxide Equivalent:	450-525
Esterification Equivalent:	145

Epon 562 (Ref 30).

Appearance:	Very pale yellow clear liquid
Epoxide Equivalent:	140-165
Esterification Equivalent:	65
Gardner Viscosity:	C-F

Dioxane.

Molecular Weight:	88.1
Specific Gravity:	1.033 $20°/4$
Melting Point:	9.5 - 10.5°
Boiling Point:	101.1
Solubility:	H_2O - infinite ETOH - soluble ET_2O - soluble

TABLE XI

REACTION PRODUCTS OF POLYHYDRIC PHENOLS AND EPICHLOROHYDRIN

Polyhydric Phenol	Epichlorohydrin/ Polyhydric Phenol Ratio	Physical Rate	Percent Epoxy Oxygen	Percent Hydrolyzable Chloride	Epoxide Equivalent
TCBPA	100% Excess	tacky solid white pdr.	6.39 6.52	0.47 0.16	250 246
TCBPA	2:1	semi solid	5.34	0.38	300
TCBPA	1.57:1	brittle solid	2.39		670
Hydrolyzed Aroclor 1262	100% Excess	Gloss	5.54	0.16	288
Hydrolyzed Aroclor 1262	100% Excess	Gloss	1.51	8.26	1060
Hydrolyzed Aroclor 1262	2:1	brittle solid	3.93	0.31	407
TCBPA - BPA (8.4% - TCBPA)	2:1	semi solid			
BPA	100% Excess	Amber liquid	7.24	1.13	221
BPA	1.57:1	Brittle solid	3.11	0.24 max.	515

TABLE XII

REACTIONS OF TCBPA WITH EXCESS ECH

RUN No.	TCBPA (EQ)	ECH (EQ)	NaOH (EQ)*1	Temp. *2	% ECH Recovered *3	% E.O. (% DGE)	% Hyd. Cl (% DGMH)	Total Anal. % DGE + % DGMH	Yield	Conditions for Second Stage of Reaction
1	0.9	2	0.2	115	85.5	-	10.6 (82.4)	-	-	-
2	1	2	0.2	120	86.7	1.12 (16.7)	10.59 (82.3)	99.0	-	-
						6.47 (96.8)	0.30 (2.3)	99.1	97.5%	Dioxane solvent; 10% excess NaOH; Reflux 9.5 hours
3	1	2	0.2	97	93.4	4.64 (69.5)	3.75 (29.2)	98.7	99%	10% excess NaOH; 100-105° for 1/2 hour
4	1	2	0.2	995	93.4	6.58 (98.4)	0.27 (2.1)	100.5	99%	10% excess NaOH; 110-11° for 8 hours
5	7	13.8	1.4	85	95.5	6.39 (95.5)	0.47 (3.65)	99.2	99.7%	10% excess NaOH; 110-13° for 8.75 hours
6	14.98	30	3.0	83	97.8	6.44 (96.4)	0.27 (2.17)	98.6	-	10% excess NaOH; 111-112° for 11 hours
7	8	16	1.6	85	96	6.52 (97.4)	0.16 (1.2)	98.6	>95%	10% excess NaOH; 110-115° for 10 hours
8	1	2	0.10	85	93.4	5.44 (96.4)	0.20 (1.55)	97.9	233g	10% excess NaOH, 113° for 9.75 hours
9	1	2	0.05	85	96.8	6.46 (96.7)	0.185 (1.44)	98.1	198g	10% excess NaOH 112-113° for 9.5 hours. Product isolated from benzene
10	1	2	0.35	85	98.4	6.16 (92.2)	0.48 (3.74)	95.9	234g	10% excess NaOH 114-115° for 8.75 hours. Product isolated from benzene *5.
11	1	2	0.80	85	72	4.51 (67.4)	2.60 (20.5)	87.9	232g	40% excess NaOH, 77-78° for 1.25 hours. Benzene solvent
12	1	2	0.2	55	96.5	6.38 (95.5)	-	>95.5	211g	10% excess NaOH; 112-16° for 9 hours. Product isolated from benzene *4
13	1	2	0.2	75	89	-	-	-	230g	10% excess NaOH; 111-113° for 9 hours

*1 NaOH solution, 0.30g/cc
*2 Temperature at which NaOH was added
*3 Assuming 98% minimum ECH
*4 After filtration through a Celite bed
*5 Without filtration through Celite

Appendix C: Composition of Hydrolyzed Aroclor 1262 and its Derivatives.

The hydrolysis of Aroclor 1262 at Dayton and St. Louis has apparently produced a mixture of mono and dihydroxy derivatives. Analysis for chlorine and equivalent weight has given results which indicate strongly that the product is a mixture of hydroxy materials. To our knowledge, this has not been considered previously.

Considering hydrolyzed Aroclor 1262 as a mixture of mono and dihydroxy products, the percentage composition can be calculated in terms of (a) its chlorine analysis and (b) its equivalent weight. From these data, the theoretical aromatic chlorine content of the derivatives of hydrolyzed Aroclor 1262 can be calculated.

It is also possible to visualize a reaction of hydrolyzed Aroclor 1262 to its glycidyl ether and chlorohydrin derivatives, in which structures are ignored and only the equivalent weight is considered. By reference to the chlorine analysis of hydrolyzed Aroclor 1262, the aromatic chlorine content of the glycidyl ether and chlorohydrin derivatives can be calculated.

From the calculations the following conclusions have been reached:

a. The chlorine analysis and equivalent weight determination are in agreement with each other.

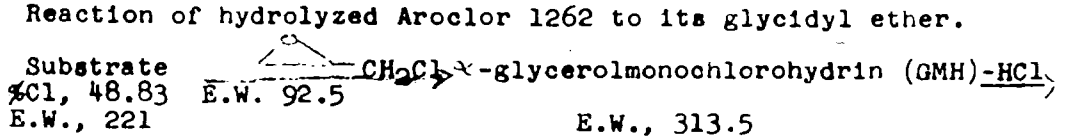
b. Hydrolyzed Aroclor 1262 may contain as much as 24% of the monohydroxy derivative, according to calculations based on the equivalent weight.

c. Calculations based on the chlorine analysis of hydrolyzed Aroclor 1262 gave a percentage composition from which the correct aromatic chlorine % for the derivatives could not be calculated. It was found, however, that only a small difference in the chlorine analysis of hydrolyzed Aroclor 1262 (about 1%) reflects a large difference in the percentage composition calculations.

Analytical data supplied with hydrolyzed Aroclor 1262:

% Cl: 48.83
Equivalent weight: 221

I. Reaction of hydrolyzed Aroclor 1262 to its glycidyl ether.



(1)

Glycidyl ether (GE)
E.W., 277

DSW 621097

Calculation of per cent epoxy oxygen (E.O.) for G E and percent aliphatic chlorine in GMH, based on the HY 1262 equivalent weight 221 which is a determined value.

$$\% \text{ E.O.} = \frac{16}{277} \times 100 = 5.77$$

$$\% \text{ Aliph. Cl} = \frac{35.46}{313.5} \times 100 = 11.31$$

The percent aromatic chlorine for GMH and GE was calculated by multiplying the percent chlorine found for hydrolyzed Aroclor 1262 by a factor indicating the increase in the E.W. of GMH and GE.

$$\text{For GMH, \% Aromatic Cl} = \frac{221}{313.5} \times 48.83 = 34.42$$

$$\text{For GE, \% Aromatic Cl} = \frac{221}{277} \times 48.83 = 38.85$$

The percent of GE in any mixture of GMH and GE is found by dividing the % E.O. found by the maximum value of E.O. possible.

$$\% \text{ GE} = \frac{\% \text{ E.O. Found}}{5.77}$$

The percent GMH is similarly found by dividing % aliphatic chlorine found by the maximum value aliphatic chlorine possible.

$$\% \text{ GMH} = \frac{\% \text{ Aliph Cl Found}}{11.3}$$

The theoretical aromatic chlorine for any mixture of GMH and GE is the sum of the percent GE and GMH found in the mixture multiplied by the theoretical % Aromatic Cl for each component respectively.

For any mixture containing only GMH and GE:

$$\% \text{ Aromatic Cl} = \left(\frac{\% \text{ Aliphatic Chlorine Found}}{11.3}\right) 34.42 + \left(\frac{\% \text{ EO Found}}{5.77}\right) 38.8$$

$$\% \text{ Aromatic Cl} = \% \text{ Aliphatic Cl} \times 3.04 + \% \text{ E.O.} \times 6.73$$

Results:

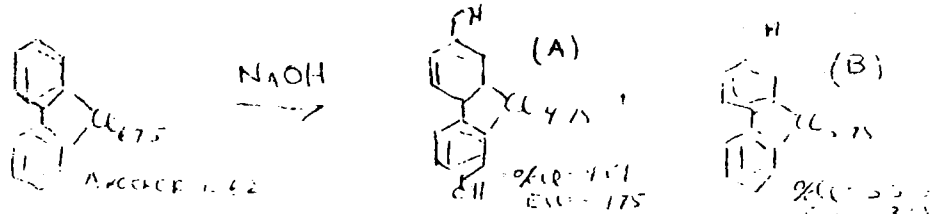
Sample	% E.O.	% Aliph Cl	% Aromatic Cl Calcd.	% Aromatic Cl Found*	
EP 1262 (FD-3)	3.38	4.98	37.89	37.18	-0.71
EP 1262 (FD-3A)	5.38	0.55	37.88	39.00	+1.12
EP 1262 (FD-4)	3.52	4.53	37.46	36.38	-1.08
EP 1262 (FD-6B)	5.37	0.53	37.69	39.09	+1.40
EP 1262 (FD-7A)	5.48	0.49	38.37	39.10	+0.73
EP 1262 (FD-8)	1.14	9.08	35.27	35.49	+0.22

*After subtracting % Aliph Cl found.

DSW 621098

The fair agreement between the calculated and found values for aromatic Cl indicates that the analyzed perdent Cl and E.W. of hydrolyzed Aroclor 1262 are in agreement.

II. Calculation of the percentage composition of hydrolyzed Aroclor 1262 from the equivalent weight 221 (analytical value):



Assuming that only the species (A) and (B) are present.

Let x = % A in the mixture

y = % B in the mixture

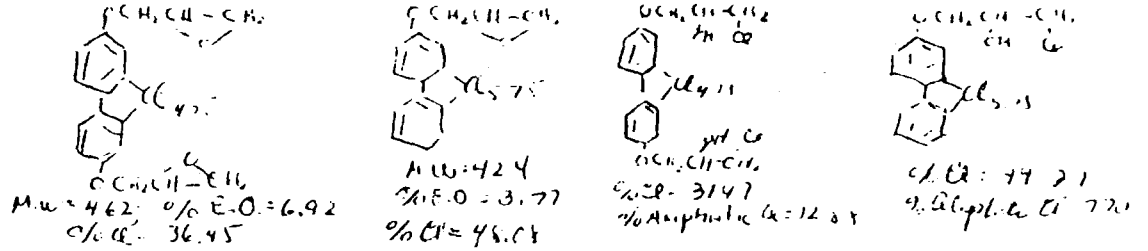
175 (.01x) = Contribution of (A) to the equivalent weight.

368 (.01y) = Contribution of (B) to the equivalent weight.

Then $x + y = 100$
$1.75x + 3.68y = 221$

And $x = 76.2$
$y = 23.8$

If it is assumed that only 4 components can be present in the reaction mixture resulting from HY 1262 and epichlorohydrin,



then the % aromatic chlorine, % E.O., and % aliphatic chlorine is found by adding the contributions of each component to that per cent. The contributions are in turn found by multiplying the theoretical constants listed under each component by the percent of that component present in the mixture, calculated in the equations (2).

For GMH: % Aromatic Cl = 31.47 (.762) + 44.27 (.238) = 34.51
% Aliphatic Cl = 12.88 (.762) + 7.70 (.238) = 11.64

For GE: % Aromatic Cl = 36.45 (.762) + 48.08 (.238) = 39.21
% E.O. = 6.92 (.762) + 3.77 (.238) = 6.06

DSW 621099

Using the same argument discussed previously, for any mixture containing GMH and GE,

$$\% \text{ Aromatic Cl} = \left(\frac{\% \text{ Aliph Cl Found}}{11.64}\right) 34.51 + \left(\frac{\text{E.O. Found}}{6.06}\right) 39.21$$

$$= \% \text{ Aliph Cl } (2.96) + \% \text{ E.O. } (6.47)$$

Results:

Sample	% E.O.	% Aliph Cl	% Aromatic Cl Calcd.	% Aromatic Cl Found*	
EP 1262 (FD-3)	3.38	4.98	36.65	37.18	+0.53
EP 1262 (FD-3A)	5.38	0.55	36.40	39.00	+2.60
EP 1262 (FD-4)	3.52	4.53	36.18	36.38	+0.20
EP 1262 (FD-6B)	5.37	0.53	36.21	39.09	+2.88
EP 1262 (FD-7A)	5.48	0.49	36.91	39.10	+2.19
EP 1262 (FD-8)	1.14	9.08	34.26	35.49	+1.23

*After subtracting % Aliphatic Chlorine found.

Although the spread in calculated and found values for aromatic chlorine is much greater than in the preceeding case, the data nevertheless indicates that hydrolyzed Aroclor 1262 contains a substantial percent of the monohydroxy derivative.

Calculation of theoretical chlorine for hydrolyzed Aroclor 1262 bas on the percentage composition found from the analytical equivalent weight 221:

$$48.1\ (.762) + 55.3\ (.238) = 49.81\%$$

This is 0.98% off from the found value of 48.83%.

This same method was used to calculate the percentage composition of hydrolyzed Aroclor 1262 Lot No. Z-2201 for which the analyses were 50.0% Cl and E.W. = 219.

Based on the E. W. 219, the percentage composition was calculated to be:

$$\% \text{ A} = 77.2 \text{ (di-hydroxy)}$$
$$\% \text{ B} = 22.8 \text{ (mono-hydroxy)}$$

From this percentage composition the theoretical chlorine was calculated:

$$48.1\ (.772) + 55.3\ (.228) = 49.74\%$$

This is only 0.26% off from the found value of 50.0%.

III. Calculation of percentage composition of hydrolyzed.

Aroclor 1262 using the chlorine analysis 48.8% which was obtained on a sample with an analytical E.W. of 221.

The same species used under II are considered.

Let x = % A; $48.1x$ = Contribution of (A) to Cl anal.

y = % B; $55.3y$ = Contribution of (B) to Cl anal.

Then $x + y = 1$

$$48.1\,x + 55.3\,y = 48.8 \qquad (3)$$

And $x = 0.903$

$y = 0.097$

By reference to the components listed on page (5)

For GMH, % Aromatic Cl = 31.47 (.903) + 44.27 (.097) = 32.72

% Aliphatic Cl = 12.88 (.903) + 7.70 (.097) = 12.38

For GE, % Aromatic Cl = 36.45 (.903) + 48.08 (.097) = 37.57

% E.O. = 6.92 (.903) + 3.77 (.097) = 6.60

Using the argument previously discussed, for any mixture containing GMH and GE,

$$\% \text{ Aromatic Cl} = \left(\frac{\% \text{ Aliph Cl Found}}{12.38}\right) 32.72 + \left(\frac{\% \text{ E.O. Found}}{6.60}\right) 37.57$$

$$= \% \text{ Aliph Cl } (2.64) + \% \text{ E.O. } (5.69)$$

Results:

Sample	% E.O.	% Aliph Cl.	% Aromatic Cl Calcd.	% Aromatic Cl Found*	
EP 1262 (FD-3)	3.38	4.98	32.38	37.18	+4.80
EP 1262 (FD-3A)	5.38	0.55	32.05	39.00	+6.95
EP 1262 (FD-4)	3.52	4.53	31.99	36.38	+4.39
EP 1262 (FD-6B)	5.37	0.53	31.96	39.09	+7.13
EP 1262 (FD-7A)	5.48	0.49	32.47	39.10	+6.63
EP 1262 (FD-8)	1.14	9.08	30.46	35.49	+5.03

*After subtracting % Aliph Cl found.

The wide spread in the calculated and found values for aromatic chlorine indicated that the percentage composition calculated from % Cl, found for hydrolyzed Aroclor 1262, is not a suitable criterion for calculating theoretical aromatic Cl for GMH and GE. It should be noted here, however, that a difference of only about 1% in the chlorine analysis of hydrolyzed Aroclor 1262 reflects a large difference in the percentage composition calculations. Thus, if it is assumed that the theoretical % Cl for hydrolyzed Aroclor 1262, as calculated from the E. W. = 221 (pg.55), is correct, then

$$x + y = 1$$
$$48.1\,x + 55.3g = 49.81$$
$$x = 76.4 \ (\% \text{ A})$$
$$y = 23.6 \ (\% \text{ B})$$

A difference of 0.98% Cl has reflected a difference of 90.3 - 76.4 = 13.9% in percentage (A) in the mixture.

Similarly for Lot No. Z-2201, a difference of 0.26% Cl was found to reflect a difference of 4.6% in the percentage (A) in the mixture.

IV. Calculations of the equivalent weight of GE using the percentage composition determined by (a) E.W. = 221 and (b) % Cl = 48.8:

(cf components listed on page 54)

(a) 231 (.762) + 424 (.238) = 277

(b) 231 (.903) + 424 (.097) = 250

The experimentally determined equivalent weight of GE was 281.

Therefore, the reaction (1) and the percentage composition determined from the E.W. = 221 equations (2) gave values for the equivalent weight of GE which were in close agreement with the found value, while the percentage composition determined by % Cl = 48.8 equations (3) gave a value for the equivalent weight of GE which differed widely from the found value.

Appendix D: Infra red Spectra

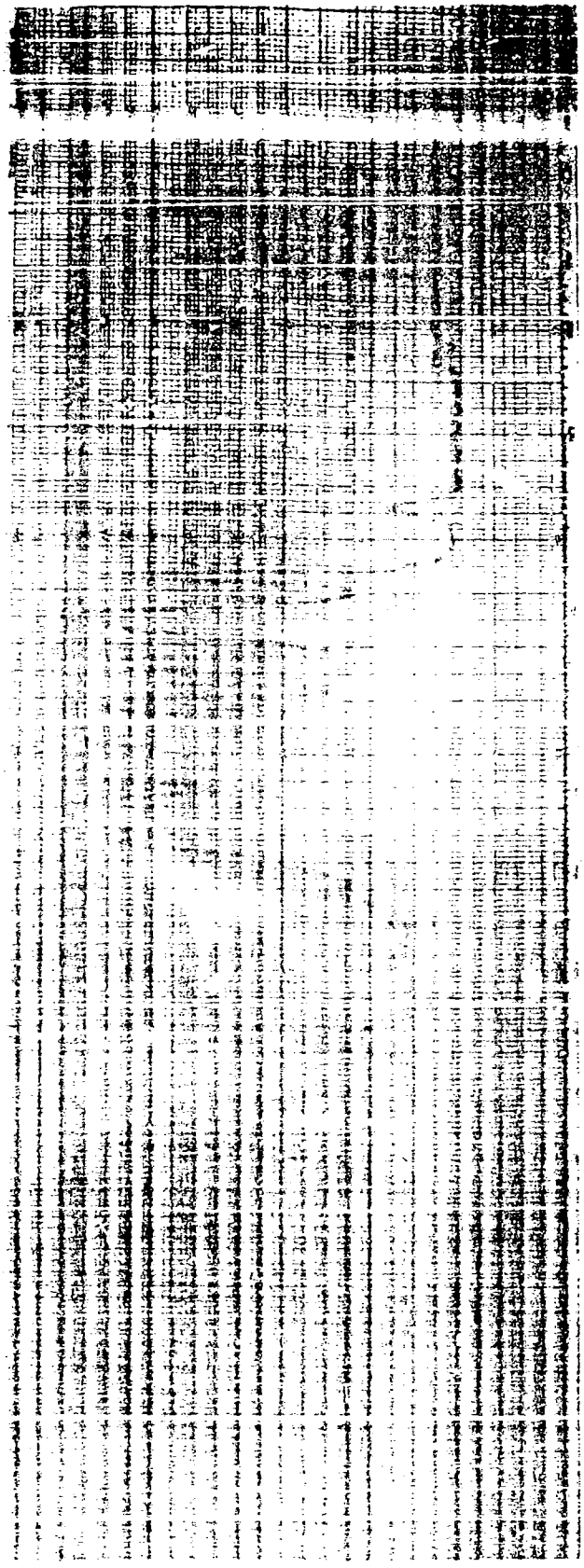
The infra red spectra were obtained on the solid phases of the compounds using a NaCl resin and a Perkin Elmer Model 21 spectrometer.

A. Tetrachlorobisphenol-A
B. Tetrachlorobisphenol-A diglycidyl ether.
   The band at about 11 μ was taken to be the oxirane band.
   The spectrum shows only a negligible amount of hydroxyl absorption.
C. Tetrachlorobisphenol-A di- α-glycerolmonochlorohydrin.
   In this spectrum the oxirane band is absent and the OH band appeared as expected.

The spectra of the epoxides of bisphenol and glycerol have been published previously. In these spectra the band at 10.95 μ was assigned to the oxirane group (Ref 31).

A. TETRACHLOROBISPHENOL-A

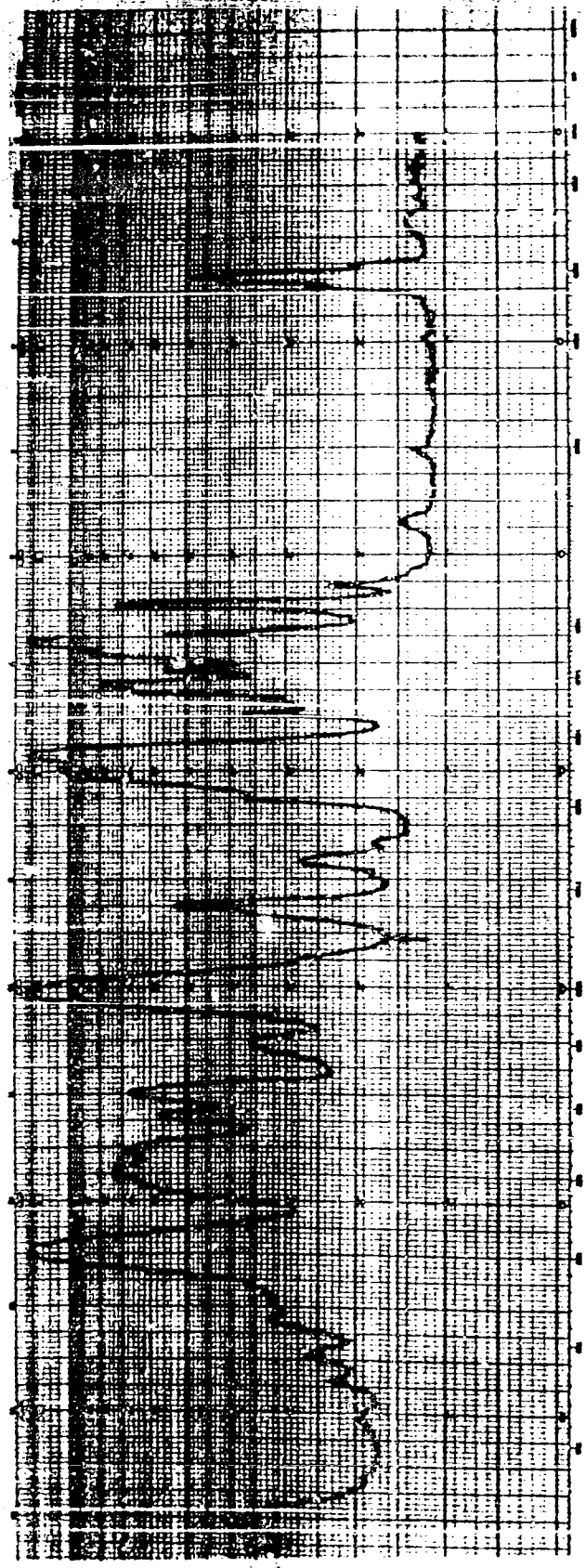
DSW 621103



DSW 621104

B. TETRACHLOROBISPHENOL-A DIGLYCIDYL ETHER

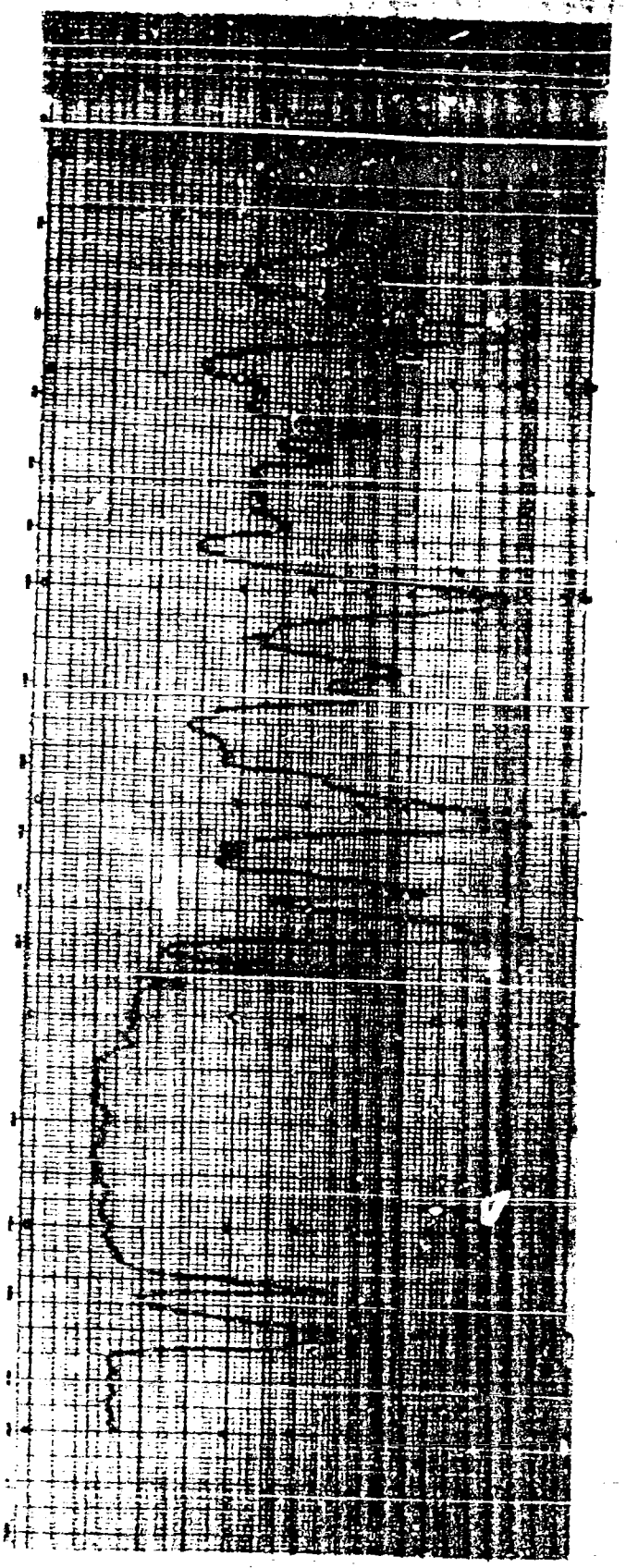
DSW 621105



DSW 621106

C. TETRACHLOROBISPHENOL-A
DI- -GLYCEROLMONOCHLOROHYDRIN

DSW 621107

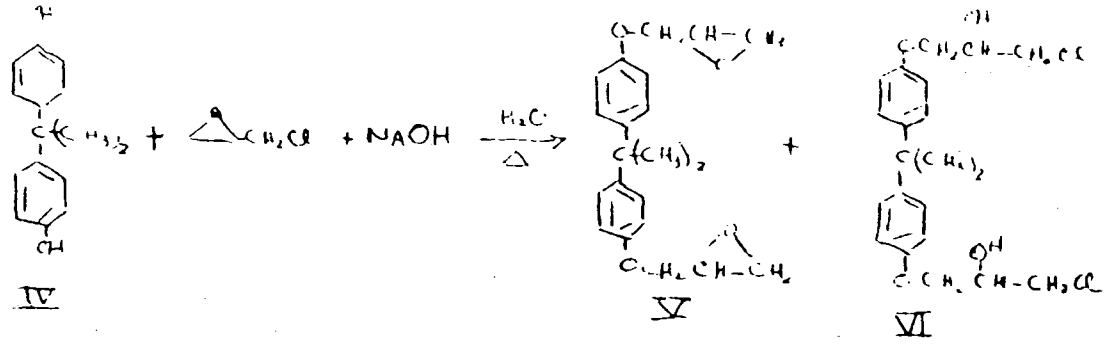


DSW 621108

drolyzed Aroclor 1262. This phase of the epoxy program was carried out cooperatively with Dr. J. Dazzi and Mr. J. Herbig at Dayton. Because the composition of hydrolyzed Aroclor 1262 was a mixture whose composition varied, it was desirable to track the course of its addition reaction with ECH by considering the equivalent weight of the mixture only. (Aromatic chlorine analysis was also considered but was rejected because the oxygen analysis of the initial mixtures received for epoxidation were inconsistent with a dihydroxy product). The nature of the products was reasoned from the ECH stoichiometry of the reaction, epoxy oxygen analysis, hydrolyzable chloride analysis and total chlorine analysis. From these data it was possible to obtain some approximate calculations from which it could be shown that hydrolyzed Aroclor 1262 was a mixture of hydroxy materials which contained as much as 24% of monohydroxy derivatives. These calculations and their results are shown in Appendix C.

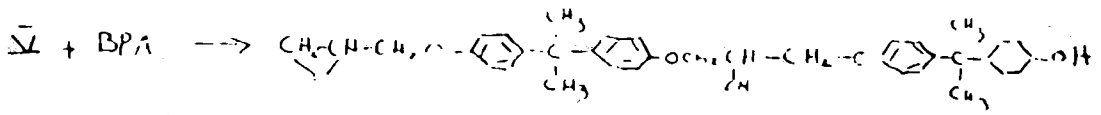
(C) Reaction of Bisphenol-A with Excess ECH

When a limited amount of aqueous NaOH is added to a solution of BPA in excess ECH above 45°, the predominant exothermic reaction which takes place is:



IV V VI

The reaction is however, incomplete. Part of the unconverted BPA reacts with V which has formed to give the higher polymer:



VII