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EXPLORATORY AROCLOR CHEMISTRY. PART III. GLYCIDYLATION OF HYDROLYZED AROCLORS

RD-58-Int. Report No. 1183 (l) October 9, 1958

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Job No.: 9411

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I. PURPOSE

This report is a continuation of Hydrolysis of Aroclors and Similar Compounds by J. Dazzi (R-1). The main market visualized for hydrolyzed Aroclors is as intermediates for preparations of the corresponding glycidyl ethers which, on curing, form epoxy resins. This is one of the fastest growing markets in the polymer field (R-1, -2).

The purpose of this project was to prepare glycidyl ethers from five hydrolyzed Aroclors, a model compound, and two additional Monsanto diphenolic development products, tetrachlorobisphenol A and dihydroxydiphenyl sulfone. The potential value of these glycidyl ethers as epoxy resin intermediates was shown by our local evaluation groups. Their data justified acceptance by the Organic Chemicals Division of hydrolyzed Aroclor 1268 as a new development chemical.

Reported experiments were carried out on a part time basis between March 1955 and July 1957.

II. SUMMARY

Hydrolyzed Aroclors 1262, 1268, 1270, 1271 and 5460, 4,4'-bi-(2,6-dichlorophenol), tetrachlorobisphenol-A, and dihydroxydiphenyl sulfone isomers react rapidly and quantitatively with excess epichlorohydrin (ECH). This forms the corresponding chlorohydrin glyceryl ether which on treatment with excess caustic forms the corresponding glycidyl ethers in high conversions and yields. Polymeric ether content is low, but careful control of reaction conditions for the dehydrochlorination step is required.

Glycidyl ethers of very high (90-97.5% of theory) di-epoxy content, (commercial Epon 828 is 97% epoxy) were prepared from di-hydrolyzed Aroclors 1262, 1270, 1271, tetrachlorobisphenol A, and the model molecule, 4,4'-bi-(2,6-dichlorophenol). Again, this model compound was of great help in this research program for interpretation of synthetic, curing, and analytical data.

Best glycidylation procedures with good reproducibility were worked out for di-hydrolyzed Aroclor 1262 and 1270 and for the model compound. Samples were prepared in larger quantities for the Evaluation Groups. Less time was spent on the glycidylation of compounds such as partly di-hydrolyzed Aroclor 1242, 1262, 1268, hydrolyzed Aroclor 5460, tetrachlorobisphenol A and p,p'- and p,o'-dihydroxydiphenyl sulfone. Glycidylation of di-hydrolyzed Aroclor 1262 was successfully achieved by adoption of the St. Louis Pilot Plant process recommended for the glycidylation of Monsanto's tetrachlorobisphenol A (R-4).

It was observed that epoxy content and melting point of glycidyl ethers derived from di-hydrolyzed Aroclors 1262 and 1270, and from the model diphenol are inversely related. For the first two compounds the highest epoxy content gave the lowest mp: 46°C for the 1262 and for the 1270 ethers. In the case of the model molecule it was reversed; high epoxy content product had a high mp 187°C. Low-melting glycidyl ethers are desirable for formulation ease. In all these cases the hydrolyzable Cl content was as low as 0.1%.

A new glycidyl ether is the product derived from hydrolyzed Aroclor 5460, a mixture of di- and tri-hydroxypolychlorobiphenyls. Glycidyl ethers derived from chlorinated biphenols are mentioned in a silicone patent (R-8), thus presenting basic patent coverage for our products from the biphenyl Aroclors.

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III. C O N C L U S I O N S

Glycidylation of hydrolyzed Aroclors, tetrachlorobisphenol A, 4,4'-bi-(2,6-dichlorophenol), and dihydroxydiphenyl sulfone went smoothly. This is a two step synthesis; first, the epoxy group of epichlorohydrin (ECH) reacts to form the 1-chloro-2-hydroxy-3-glyceryl ether; this, in the second step dehydrochlorination, re-forms an epoxy ring giving the glycidyl ether. The latter process step is critical and required development of special reaction conditions for each compound to get products with high epoxy and low hydrolyzable Cl content.

Glycidyl ethers derived from di-hydrolyzed Aroclor 1270 and 1268 show valuable properties as intermediates for epoxy resins. The St. Louis Pilot Plant process for the glycidylation of tetrachlorobisphenol A is the best method for dihydroxy Aroclor 1268; this diphenol is now an Organic Chemicals Division chemical.

Glycidyl ethers derived from partly dihydrolyzed Aroclors appear to be of little value for resins, per se, but may have application in surface coatings (Ref. 3).

Dihydrolyzed Aroclor 1268 can be used as a curing agent. It reacts faster with diglycidyl Aroclor 1268 than with Epon 828.

Our work with the model compound, 4,4'-bi-(2,6-dichlorophenol), gave valuable data which greatly facilitated solutions of problems encountered in the early work with the hydrolyzed Aroclors. Syntheses and evaluations of model compounds are most helpful and time saving for exploratory research in new fields as well as for analytical studies.

IV. RECOMMENDATIONS

We recommend investigation of the glycidylation using more efficient stirring and higher reaction temperatures, possibly by using chlorobenzene or dimethyl sulfoxide as solvents.

Further applied research on diglycidyl ethers derived from Aroclor 1268 and 1270 is justified.

Glycidyl ethers derived from Aroclor 5460, new compositions, are recommended for development first if Monsanto decides to enter the epoxy resin field with a product having patent protection. These epoxies may be of additional importance because each molecule has more than two glycidyl groups and the Trade has expressed interest in such systems.

Dihydrolyzed Aroclors should be promoted as flame-proofing, heat-stable, epoxy-curing agents comparable to HET anhydride. Dihydrolyzed Aroclors should be screened as curing agents for all new glycidyl ethers reaching the market.

For additional suggestions on the use on glycidyl ethers see References 1 and 2.

Glycidylation studies on dihydroxydiphenyl sulfones should be discontinued since these ethers are not new compositions.

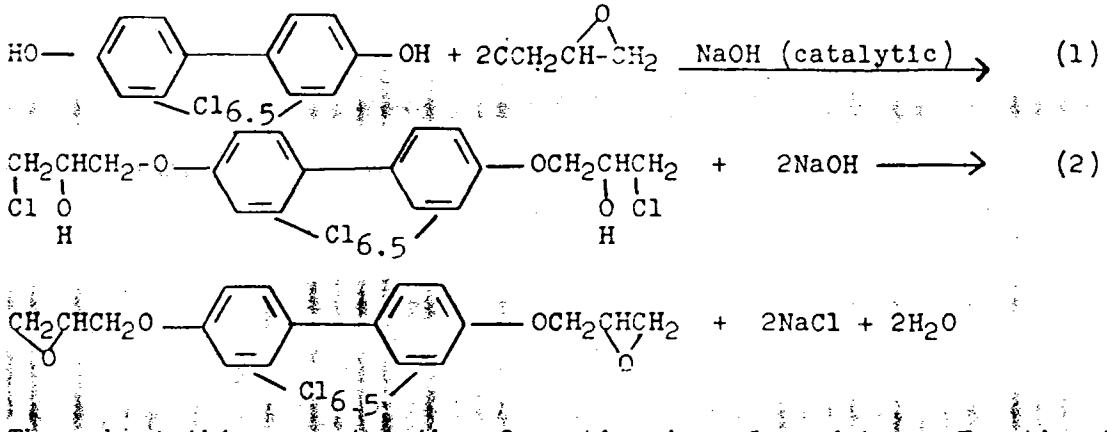
V. DATA AND DISCUSSION

1. General Discussion of Glycidylation

General features of glycidylation are given first, and more specific data are reported separately under the subdivisions.

Glycidylation of hydrolyzed Aroclors 1271, 1270, 1268, 1262, 1248, and 5460, 4,4'-bi-(2,6-dichlorophenol), tetrachlorobisphenol-A, p,p'- and o,p'-dihydroxydiphenyl sulfone takes place on contacting the phenolic compound with excess epichlorohydrin (ECH) in the presence of alkali. This is carried out stepwise. Initially, the phenolic group adds to the oxirane oxygen to form a 1-chloro-2-hydroxy-3-glyceryl ether, as shown in Equation 1. Alkali in less than stoichiometric amounts catalyzes this reaction. The excess ECH, which serves also as a good solvent, is distilled off and the chlorohydrin ether is stirred with excess alkali. This dehydrochlorinates the chlorohydrin completely, closing the ring and reforming the epoxy ring system, as shown in Equation 2.

The chemistry of glycidylation of dihydrolyzed Aroclor 1268 is as follows:



Throughout this report, ether formation is referred to as Equation 1 and dehydrochlorination is referred to as Equation 2. The ether formation is quantitative and rapid in the presence of excess ECH and alkali. The most convenient procedure found is to dissolve the phenolic material in ECH and add at once a part of the total caustic needed in a 30-50% aqueous solution. The mixture is refluxed until [illegible] the dehydrochlorination, which takes from 20-60 minutes depending [illegible] amount of NaOH present. It is important that enough solvent [illegible] ECH [illegible] material [illegible] solution

The excess ECH is distilled off at 100°C/20 mm with good stirring. The residue is liquid at this temperature. The epoxy ring closure can be effected directly, or NaCl formed in step 1 can be removed by dilution with a solvent such as benzene, toluene, chlorobenzene or dioxane, whereupon NaCl can be filtered off. Epoxy and hydrolyzable Cl values indicate that partial epoxy ring closure occurs at conditions used in Equation 1. The NaCl formed can be removed by water washing before or after removal of excess ECH.

The complete dehydrochlorination of the chloro ether to the glycidyl compounds shown in equation 2 is tricky. Specific reaction conditions had to be developed for each phenolic compound investigated; these were time-consuming studies. The recommended process consists of dissolving the chloro ether in a solvent such as benzene, toluene, chlorobenzene, diethylene glycol diethyl ether, or dioxane, than excess caustic is added as a 30-50% aqueous solution. This solution mixture is stirred at temperatures between 81-110°C for a period of time according to the rate of dehydrochlorination characteristic of the compound used. The model molecule was the slowest to dehydrochlorinate and required up to 50 hr reflux. Dihydrolyzed Aroclor 1268 and 1270 reacted much faster and this second step was completed in 8 hr or less. In some of the cases the water was removed during the dehydrochlorination step. This did not change the rate of reaction.

The final product can be isolated from NaCl formed and excess NaOH used by washing with water or by filtration. Final product is always heated with stirring at reduced pressure to remove solvent. Finally, the material was always kept for 15-20 minutes at bath temperatures between 100-120°C. Partly hydrolyzed Aroclor glycidyl ethers, prepared during the early part of this investigation, were partly polymerized and melted above 100°C. These were first ground to a fine powder and then washed in a Waring Blendor.

Solutions in benzene, or chlorobenzene of the glycidyl ether of 4,4'-bi-(2,6-dichlorophenol), the model compound, were precipitated by hexane addition.

In some glycidylation experiments of hydrolyzed Aroclors, polyether formation took place. This undesirable reaction could not be controlled, especially in larger size batches. We do not know the conditions which cause this reaction. The model compound under similiar conditions always gave much less polyether. No explanation was found for this behavior.

a. Glycidylation of the model compound, 4,4'-bi-(2,6-dichlorophenol)

Glycidylation of the model compound, prepared by tetra- [illegible]

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benzene and filtered. Theory plus 10% excess of KOH was added and the system was refluxed for 36 hr to give partly epoxidized (63.5% of theory) glycidyl ether. This product was refluxed for 14 more hr in dioxane with excess caustic, and gave the ether in 81.2% conversion, based on diphenol charged. Di-epoxy content was 90.3% of theory.

Dioxane, being a solvent for the ether and water was added to the chlorobenzene solution after it had refluxed for 24 hrs. This mixture was heated for 6 more hr without increasing the epoxy content (Expt 2.). Again, the ether had to be refluxed for 16 more hr in dioxane to isolate a product analyzing 97.5% of theory diepoxy and 0.1% chloride.

Gradual addition of KOH and a reflux for only 10 hr gave a lower epoxy content (41.7% of theory). On heating this in dioxane with more NaOH, a high epoxy compound (96.8% of theory) in 90% conversion was obtained (Expt. 3).

Expts. 4-10 report variations investigated which led to the directions for a reproducible process (Expt 1-3) for the preparation of the model compound glycidyl ether, high in epoxy and low in chloride and polyether content.

In one variation an aqueous solution of the disodium salt of the diphenol was added to excess ECH. On refluxing for 2 hr only a 50% conversion to the glycidyl ether occurred (Expts. 5 and 8). Reheating of material under conditions given in Expt. 5 formed polyether.

Incomplete dehydrochlorination took place when the reaction was carried out in absence of a solvent using aqueous NaOH (30%) at 130°C (Expts 6-7). Epoxy content was 72% of theory with 1.58% Cl^-. Experiments 9-10 contain reaction conditions which led to the recommended process (Expt. 1-3).

With the model compound, data for Expts. 1-10 show that high epoxy content parallels high melting point of final product. Practically no polyether formation was noted in this series of experiments.

It was quite unexpected to note that the dehydrochlorination step was much slower for the model molecule than for other diphenols tried.

Reaction 2 always had to be carried out as a two step process. Indications are that it will be very difficult to force the dehydrochlorination of the model molecule to a one step reaction. Steric hindrance is a possible explanation for this unusual behavior.

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[illegible] Our [illegible] glycidylation [illegible] given in Experiments 1- [illegible] time specific analytical method were unavailable for [illegible] compounds. Conclusions were based on total Cl contents analyzed by a method which gave low values. Also, at the early stage of our investigations mis-interpretation of industry requirements led us to prepare high melting glycidyl ethers instead of products which were higher in epoxy content but had lower melting points. These two factors delayed solution of early difficulties.

The earliest glycidylation experiment was made by adding the disodium salt of hydrolyzed Aroclor 1271 to the calculated amount of ECH at 65°C, a product low (42.8%) in epoxy content (42.8%) was obtained. A polyether type product was prepared using less than the stoichiometric amount of ECH (Expt. 12). Isolated product is high melting (220-30°C) and low in epoxy (17%) and Cl^- contents. Using an excess of ECH increased the epoxy content immediately (Expt. 13).

The next successful step was to use excess ECH and only part of the alkali needed, and then to distill off unreacted ECH (Expt. 14). The liquid residue was diluted with a solvent such as chlorobenzene, KOH (40% excess) was added, and the mixture was refluxed 24 hr. Quantitative conversion to a low melting (60-64°C) glycidyl ether, very high in diepoxy content (96.2%) was obtained. This was the first Aroclor glycidyl ether sample which cured in a manner similar to the model compound. This behavior is attributed to complete di-functionality in the hydrolyzed Aroclor 1271 used.

Reaction conditions developed for the model molecule (see Expt. 1-3) were successfully applied to di-hydrolyzed Aroclor 1270 using dioxane as a solvent. With shorter reaction time, di-epoxy content was somewhat lower (87.57) and Cl^- was higher (0.90%). These reaction conditions were repeated in a six-fold scale up (Expt. 16). The latter gave completely dehydrochlorinated but partly polymerized product. The soluble lower melting fraction analyzed 66.47% epoxy while the insoluble material melts as high as 275-80°C and contains only 14.8% of theory epoxy.

Since the scaled-up Expt. 16 failed to duplicate Expt. 15, attempts were made to reduce the heating period and increase dehydrochlorination temperature. At 120° using diethylene glycol diethyl ether as solvent, the Cl^- content was reduced to 1.48% in 3 hr; reheating for 8 more hr at 120°C reduced the Cl^- to 0.1%, but the diepoxy content decreased to 75% of theory due to polyether formation (Expt. 17). The surface-coating evaluation group was especially interested in this material. A large size batch (502 g) was made as Expt. 18. It duplicated Expt. 17.

The early work on glycidylation of partly dihydrolyzed Aroclor 1268 is given in Expts. 19-21. Reaction was not complete and therefore the product was of little value. The next series (Expts. 22-28) was made after collecting experience and analytical data from our studies on the model compound. For process studies partly di-hydrolyzed Aroclor 1268 prepared in the St. Louis pilot plant was used, until di-hydrolyzed material was made available by the Dayton methanol process. The first large size (Expt. 22) gave quantitative conversion and 88.5% pure diglycidyl ether. The only variation in the next Expt. (23) was to add the NaOH gradually to the dioxane solution; this caused incomplete epoxidation (80%); retreatment with NaOH increased this to 90.2% of theory.

Attempts to force reaction 1 and 2 into one step by using theory or excess NaOH failed to increase the epoxy content (Expts. 24 and 27).

Starting with the sodium salt of hydrolyzed Aroclor 1268 and excess ECH and then heating, as suggested by a consultant (Dr. Leonard), was not successful; some polymer was formed (Expt. 25). Another variation was to start with sodium salt of hydrolyzed Aroclor 1268 plus excess NaOH and then add to excess ECH at 95°C., epoxy found was only 57.5% of theory (Expt. 28).

2. Di-hydrolyzed Aroclor 1268

This product, prepared by the methanolic-alkali, pressure hydrolysis was used as starting material for Expts. 29-35 and converted to the glycidyl ether using the best experimental details collected in previous runs. Solvents used were dioxane and benzene, the latter being preferred (Expt. 29 and 30). Data on these runs were also given in Reference 3.

The Organic Division recommended a pilot plant process which they developed for glycidylation of tetrachlorobisphenol-A. This was first duplicated in Expt. 31, giving, in 92.5% conversion, a diglycidyl Aroclor 1268 analyzing 89.5% of theory epoxy and very low Cl⁻ (0.1%). This run was duplicated on a four- and six-fold scale-up (Expts. 32 and 35). The final product is quantitatively obtained by filtration of the reaction mixture, thus removing NaCl and NaOH as solids. A clay treatment of the melted resin should eliminate traces of impurities; product in Expt. 35 contains 0.003 milliequivalent NaOH/g resin.

No studies were made of reduction in time for dehydrochlorination cycle since our main goal was to supply high epoxy materials to the Evaluation Groups. A feasible modification would be to rei[illegible] chlorobenzene [illegible] allow up to 50°C higher [illegible]

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[illegible] hydrochlor-

Glycidylation of partly di-hydrolyzed Aroclors 1262 and 1248

During the early stage of glycidylation studies, these two partly hydrolyzed Aroclors were investigated on a very preliminary basis (Expts. 36-39). Glycidylation of hydrolyzed Aroclor 1262 prepared in the St. Louis pilot plant was then assigned to Springfield, where Dr. S. Gebura developed a good process using dioxane as solvent (R-5). Valuable information from Dr. Gebura's process work were then used in our work (R-6).

e. Glycidylation of hydrolyzed Aroclor 5460

New glycidyl ethers were prepared from hydrolyzed Aroclor 5460, a mixture of di- and tri-hydroxypolychloroterphenyl. The material from Expt. 43 contains some polyether but it is low in Cl^- and cures in a manner similar to the diglycidyl ethers. Minor variation of the glycidylation procedure, i.e., replacing dioxane by benzene or chlorobenzene, should reduce the dehydrochlorination cycle and consequently reduce polyether content and mp of final product.

In addition to patentability, this product may be partly trifunctional. The trade is most anxious to get a tri-glycidyl ether to be used in epoxy resins. Hydrolysis of a completely chlorinated terphenyl ($C_{18}Cl_{14}$) might yield trihydroxy polychloroterphenyl for use in such an application.

f. Glycidylation of tetrachlorobisphenol A

The first glycidylation of tetrachlorobisphenol A inside Monsanto was carried out in Expts. 39-41 at the request of the Organic Division. Products were then cured by J. Herbig (R-3). Glycidylation went smoothly to obtain in the second attempt (Expt. 40) a product high in epoxy (88% of theory) and very low in Cl^- content (0.12%). Conversion was quantitative. Expt. 41 is a duplication of recommended pilot plant procedure given in (R-4).

g. Glycidylation of dihydroxydiphenyl sulfone

Since Monsanto has a good process but no market for p,p' and o,p'-dihydroxydiphenyl sulfone it was logical to investigate the glycidylation of these two compounds; the corresponding glycidyl ethers are not indexed in Chemical Abstracts but were found later in patents. Incomplete glycidylation occurred in Expts. 45-46. Since this composition is not patentable, no further work is justified on glycidylation of these known compounds.

2. Evaluation Data

a. Evaluation of glycidyl ethers other than in epoxy resins

A sample of glycidyl ether of partly hydrolyzed Arpolor 1262, a viscous liquid, was also submitted for evaluation as a plasticizer and stabilizer for polyvinyl chloride formulation. This product, evaluated as Lot No. P-1087, was compatible with polyvinyl chloride at 40% plasticizer concentration. It had a poor flex of + 20°C, but volatility was low (0.4%) as was kerosene extraction (0.1%) (R-7). Costwise, P-1087 is out of the plasticizer price range. Nevertheless, this compound might be considered in combination with another plasticizer (to reduce the flex) for specific applications requiring a very low kerosene extraction combined with fire retarding properties. Contrasting to P-1087, the glycidyl ethers of bisphenol A and tetrachlorobisphenol A are both incompatible with polyvinyl chloride.

As a stabilizer for polyvinyl chloride, P-1087 is comparable, as expected, to Paraplex G-62 (epoxidized soybean oil); the latter is the commercial stabilizer most used for PVC (R-7). Diglycidyl Aroclor 1268 was submitted for biological toxicant screening as CP 16137-3. Of incomplete evaluation data received, no biological activity has been uncovered.

b. Curing studies using dihydroxy Aroclor 1268

The value of a diglycidyl ether is its ability to cure to a polymeric material. This was shown at an early stage of our investigation when diglycidyl Aroclor 1268 (NBP 316083-4) was heated with maleic anhydride in a test tube to yield a polymer melting above 330°C. Systematic curing studies on the glycidyl ethers described in this report were made by J. Herbig and later by J. K. Craver and J. Schwendeman; results are reported in R&E Dayton final report 1115 (R-3).

Di-hydrolyzed Aroclor 1268 acts also as a curing agent for its glycidyl ether. This behavior contrasts to that of bisphenol A and tetrachlorobisphenol-A, which do not react with their corresponding glycidyl ethers. Data on di-hydrolyzed Aroclor 1268 as a curing agent for its glycidyl ether and Epon 828, respectively, are given on Table I. The former glycidyl ether reacts faster than the latter as shown by the N.E. values found. A possible explanation for this reactivity of the hydrolyzed Aroclor is its high acidity (pH 3.5). It is possible that the curing properties found for di-hydrolyzed Aroclor 1268 and homologs open up a substantial market for this compound, which might compete with hexachlorocyclopentadiene-maleic anhydride 1:1 adduct (HET). The latter gives off HCl gas on heating which is its main draw-back. This is not the case for hydrolyzed Aroclor [illegible] by the authors that hydrolyzed Aroclor stands a good chance to compete with HET as a curing agent for epoxy resins.

bisphenol A, a Monsanto development chemical, is equa[illegible] as a curing agent for Epoxide 201. The cured material melts at 430°F. For details see NBP 399463-5 as reported by Richard A. Grant.

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1. Apparatus

All experiments were conducted in standard taper, Pyrex glass equipment. The ether formation was carried out in 3-necked round-bottom flasks equipped with dropping funnel, condenser and thermometer. Excess ECH was distilled off at reduced pressure with good stirring using a 10" Vigreux column. The flask was heated by a hot water bath while the receiver was kept in ice water.

Dehydrohalogenation was carried out in 4-necked, round-bottom flasks equipped with dropping funnel, stirrer, thermometer and Dean and Stark trap carrying a reflux condenser. The flask was heated by means of a heating mantle. Low boilers of the final resins were always removed at 1-2 mm under good stirring. Where necessary, heating by means of an oil bath eliminates local overheating.

2. Materials Used

Some of the hydrolyzed Aroclors used were prepared by the Author; their preparation is reported under Final Report No. 1182. on Hydrolysis of Aroclors and similar chloro compounds. St. Louis Pilot Plant partly di-hydrolyzed Aroclor, and Dayton Methanolic-process di-hydrolyzed Aroclor were also employed. The partly di-hydrolyzed Aroclor was from the St. Louis pilot plant batch run in ethylene glycol.

Dihydroxydiphenylsulfone, the p,p'- and the o,p'-isomers were obtained from the Organic Chemicals Division

Tetrachlorobisphenol A, St. Louis pilot plant material.

Epon 828, Shell's trade name for bisglycidyl ether of bisphenol A; epoxy content 8.23%.

Epichlorohydrin, Shell, technical grade 95%.

All other chemicals used were stockroom items.

3. Experimental Details

a. Glycidation of 4,4'-bi-(2,6-dichlorophenol)

This section contains the diglycidylation of 4,4'-bi-(2,6-dichlorophenol), the model molecule used for synthetic, analytical and curing studies. The recommended procedure is given [illegible]

[illegible]

[illegible] 292 g) [illegible] temperature. To this solution was added KOH, (0.36 mole, [illegible] ml of 40% aqueous solution) in 6 minutes; no exothermic reaction was noted. After 20 minutes, the solution was neutral to phenolphthalein, after 40 minutes it was neutral to acid-alkaline paper. The excess epichlorohydrin was distilled off while stirring at reduced pressure at 100°C bath temperature; 1029 g epichlorohydrin was collected in an ice cooled receiver. The residue was filtered from solid KCl, washed with chlorobenzene, and diluted with more chlorobenzene (total 1150g). It was refluxed while KOH (1.67 moles, 235 ml 40% aqueous solution, 10% excess) was added. After four hours, reflux water was drawn off the Dean and Stark trap (total 60 ml). Refluxing was continued for 36 more hr giving 60 more ml of H_2O. The reaction mixture, consisting of two layers, was diluted with 600 ml of hot water and washed with 3 x 400 ml of hot water using a preheated separatory funnel. The organic layer was dried by azeotroping benzene-water mixture. The glycidyl ether was precipitated by adding the solution to 2.8 l. of hexane. The cooled mixture was filtered, giving 360 g.

Anal. Found (%): Epoxy, 4.65, 4.67; Cl^-, 4.63; Total Cl, 35.67, 35.77; C, 47.51; H, 3.13.

Based on this epoxy value only 63.5% diglycidyl ether formed. Analysis of the combined wash waters indicate a low NaOH content, equal to 8.65 ml N.

The partly reacted material (350 g) was dissolved in 1200 ml of dioxane, 0.75 mole NaOH was added as 30% aqueous solution, and the system was refluxed for 14 hr. The two layers were separated and filtered. The organic solution was divided into equal volumes and added to 2 l. of hexane each, giving 281 g ether, mp 182 and 185°C. Concentration of the solvent gave 31 g additional ether II mp 182-186°C.

Anal. Found (%): I epoxy, 6.57, 6.60 equal to 89.3% of theory; Cl^- 0.17; II epoxy, 6.69, 6.75 equal to 91.3% of theory; Cl^- 0.34.

Conversion 81.8% based on biphenol charged.

Expt. 2 347318, 347324

This experiment is close to a duplication of Expt. 1 using 1 mole biphenol (324 g) dissolved in 18 moles of epichlorohydrin. To this was added KOH (0.4 mole) as a 40% solution. After

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[illegible] unreacted epichlorohydrin [illegible] in 1200 g of chlorobenzene, refluxed [illegible] dioxane was added, and reflux continued for 6 more hr. After washing, there was obtained 410 g. of product, mp 126-31°C, analyzing 4.73 and 4.76% epoxy, and 4.45% of Cl^-. Total alkali found in wash water equal to 21.4 ml N.

The partly reacted ether (408 g) was diluted with 1400 ml of dioxane. To this was added 0.9 mole of NaOH as a 30% aqueous solution and the system was refluxed for 16 hr. 200 ml more dioxane was added, the slurry was filtered and washed. The filtrate solution (2410 ml) was divided into equal parts and each added to 2 l. of hexane, cooled and filtered to isolate 328 g, mp 183°C (sharp), containing 7.08 and 7.26% epoxy equal to 97.5% of theory; Cl^- was 0.10%. Concentration of hexane solution gave 32 g, mp 184°C; Cl^- was 0.21, 0.32%. Conversion was 82.5%.

Expt. 3: 347323, 353871

Charge and reaction conditions were the same as in Expt. 2. The aqueous KOH (1.[illegible] mole) was added gradually, instead of at the beginning, and reflux was run for a total of 10 hr while the solution was kept at a pH of [illegible]. The material was washed, and the wash water contained 0.96 ml N unreacted KOH. Precipitation of 1930 g of solution in hexane gave 441 g, mp 116-17°C, analyzing 3.00 and 3.14% epoxy, and 7.61 and 7.65% hydrolyzable Cl^-. Part of this product (400 g) was dissolved in dioxane (1500 ml), 100 ml NaOH was added as 30% aqueous solution, and the system was refluxed for 8 hr. Then 70 ml NaOH was added (total 1.275 moles), followed by reflux for 10 more hr.

Isolation by standard procedure gave 357 g, mp 185-187°C analyzing 7.10, 7.12% epoxy (96.8% of theory), Cl^-, 0.25, 0.26%. Concentration of hexane solution gave 22 g, mp 186°C, Cl^- 0.19%. Total conversion 90.%.

From the data given in the next six experiments the recommended procedure was developed for the glycidylation of 4,4'-bi-(2,6-dichlorophenol) (Expts. 1-3).

Expt. 1: 341253-4

The biphenol (0.5 mole, 171 g) failed to dissolve at reflux temperature in six moles (555 g) of epichlorohydrin, therefore it was necessary to add 100 g of dioxane to achieve solution. At 75°C was added 0.2 mole (26.6 ml) of 30% aqueous NaOH and the system was refluxed for 3 hr. After distilling off excess epichlorohydrin and dioxane at reduced pressure, 266 g of [illegible], mp 115-118°C, was isolated. This NaCl-free sample [illegible] 7.0, 7.1% of Cl^-.

[illegible] of the biphenol (0.12 [illegible] added [illegible] 27% aq. NaOH (10% excess) in a 2.[illegible] [illegible] 25 min (pot [illegible] 1 mole) 2.[illegible] NaOH and refluxed for 2 hr. After removing excess ECH and sodium chloride, 65 g product, mp 80°C (not sharp), was isolated, containing 6.90, 7.00% Cl^-. This indicates only 50% conversion to the glycidyl ether. To complete the dehydrohalogenation, 54 g (0.115 mole) was dissolved in 330 g of dioxane, 0.126 mole (10% excess) of NaOH was added (2.5 N aqueous) and reflux continued for 4.5 hr; the mixture became neutral. Total isolated material was 47 g, mp 150-158°C, analysis 0.6% Cl^-, epoxy 3.92%. The latter value is meaningless since the product failed to dissolve completely in the analytical reagent.

Expt. 6 NBP 341283-5

In order to keep the biphenol in solution it was necessary to dissolve it (0.2 mole, 64.8 g) in 600 g (6.5 moles) of ECH. Then 10.8 ml of 30% NaOH was added and the system was refluxed for 1.25 hr. The isolated material melts over a wide range ca 100°C. It was treated with 50 ml of 30% aqueous NaOH for 6.5 hr at 125°C bath temperature. The mixture turned solid after 5 hr stirring. The reaction product was ground to a fine powder, suspended in water and washed free of NaCl, to give 81.5 g, mp 145-7°C.

Anal. Found (%): Epoxy, 4.90, 4.91; Cl^-, 2.87; C, 48.07; H. 327; residue 1.07.

These values reveal that only partial dehydrohalogenation occurred.

Expt. 7 341287, 341289

A solution containing biphenol (0.6 mole, 194.4 g) and ECH (16.2 moles, 1600 g) was refluxed while NaOH (0.25 mole, 32.4 ml aqueous solution) was added at once; no exothermic reaction occurred. After refluxing for 2.5 hr, excess ECH (1320 g) was distilled off giving 409 g of crude material. It was heated in the same container up to 140°C pot temperature and then 150 ml of 30% NaOH was added; the system was stirred for 10 hr at 130°C bath temperature (pot temperature 110°C).

The reaction mixture was worked up to give 267 g of ether, mp 154°C, analyzing 5.25 and 5.23% epoxy, equal to 72% of theory. Hydrolyzable Cl was 1.58%. A total of 0.114 mole of NaOH charged remained unreacted as shown by analysis of the wash waters. Conversion was 100% calculated as diglycidyl ether.

biphenol (64.7 g) was dissolved in 160 ml of 10% NaOH. This solution was added over 2.2 hr to 2 moles (185 g) of ECH at reflux temperature. Reaction took place immediately. This mixture was refluxed for 3 more hr. The water layer contained 0.196 mole NaCl. The organic layer was heated to remove excess ECH. To this residue was added 30 ml of 30% NaOH over a 4.5 hr period while the solution was kept slightly alkaline. Product was isolated by standard procedure to collect 90 g, mp 120°C.

Anal. Found (%): C, 46.20; H, 3.59; residue 0.12; epoxy, 2.99, 3.00; Cl^- 6.49.

These data indicate only 41% dehydrochlorination to diglycidyl ether.

Expt. 9 341297, 347301

A mixture consisting of biphenol (0.25 mole, 81 g) and excess ECH, (4.4 moles, 502 g) was refluxed, and KOH (0.1 mole, 18.7 ml of 30% solution) was added at once. Heating was continued for 1.5 more hr. After filtration, excess ECH was distilled off. The residue was dissolved in 220 ml of chlorobenzene, and 93.5 ml of 30% KOH (0.5 mole) was added over 0.5 hr. The turbid mixture was refluxed for 14 hr at 98-105°C, and then diluted with hot water, with good layer separation. This chlorobenzene solution of the ether was precipitated hot from 500 ml of hexane to collect 100 g of a nice white material analyzing 4.39 and 4.40% epoxy (60% of theory) and 5.25% Cl^-. This material is more soluble than samples prepared in previous experiments; this could be attributed to less cross linkage. The material (90 g) was dissolved in 540 g of dioxane; to this was added at once 0.152 mole NaOH as 30% aqueous solution. The system was refluxed for 12 hr, while the solution turned neutral. Total isolated material was 84 g, mp 180°C, analyzing 0.41% Cl^- and 6.71 and 6.71% epoxy, equal to 91.5% of theory. Conversion was 80.3% based on combined steps.

Expt. 10 341299, -300

A larger size batch was used in this expt. using method established in the previous run. Biphenol (0.8 mole, 260 g) was dissolved in 1200 ml of ECH, refluxed, and 0.32 mole of KOH 30% solution was added at once (temp. 85°C). After 20 more minutes the solution was neutral to phenolphthalein; reflux was continued for 30 more minutes, then 112 g of ECH (some of it evaporated) was distilled off at reduced pressure. The 387 g of white crude distillation residue was diluted with 700 ml of chlorobenzene, refluxed, and KOH (0.44 mole, [illegible] % excess as 30% solution) was added [illegible]

was 75.6% and total alkali found in wash water was equal to 40.5 ml N. This experiment was started using 1000 ml of ECH, but on cooling to 85°C the bisphenol started to precipitate; this required more ECH.

b. Glycidylation of hydrolyzed Aroclor 1270

Expt. 11 310446-7

A solution of hydrolyzed Aroclor 1271 (0.25 mole, 115.5 g; Anal.(%): C, 31.58; H, 1.12; Cl, 61.86) was dissolved in 200 g of 10% NaOH and heated at 65°C while 0.5 mole (46.3 g) of ECH was added dropwise over a 1-hr period at 65°C. The mixture turned solid and was worked up by washing the powder by means of a Waring Blendor to isolate 130 g mp 120-125°C.

Anal. Found (%): C, 36.58; H, 2.0; Cl, 49.60; epoxy, 2.31, 2.44.

These values were obtained much later, after an accurate analytical method was developed.

Conversion in this run was 91.8%.

Expt. 12 316058-60

This experiment was made according to the directions given in U. S. Patent 2,615,008, example 8, recommended for the preparation of a high melting partly polymerized bisphenol A glycidyl ether. Hydrolyzed Aroclor 1270 (0.97 mole, 442 g (NEP 310445) was stirred in 1.61 moles of 10% NaOH and then ECH (1.25 moles, 114.8 g) was added over 85 minutes while the temperature was gradually increased from 42° to 100°C. After 15 ml ECH were added all phenol was in solution. The formed ether precipitated after 30 minutes when a total of 59 ml of ECH was added. The material gradually solidified. It was heated for 1 more hr. The hard material was ground to a powder and washed by means of a Waring Blendor to isolate 491 g, mp 220-280°C, equal to 96.5% conversion.

Anal. Found (%): C, 34.46; H, 1.71; res, 3.24 (NaCl); total Cl, 52.40; Cl⁻, 0.25, 0.25; epoxy 0.87, 1.02 (equal to 17.1% of theory).

The last two determinations were run much later using modified methods.

DSW 621612

[illegible] dissolved in NaOH (0.2 mole, 2.5 N) and added to excess (0.6 mole) ECH at 40-45°C over a 70 minute period; it was kept for 0.5 hr at 45-50°C. Product isolated weighed 52 g, mp 65-82°C; epoxy content 3.32 3.24%. A rerun after 36 days gave 3.03 and 3.06% epoxy. This experiment shows that excess epichlorohydrin increases the epoxy content of final product.

Expt. 13 NPB 328979-80

The purpose of this experiment was to increase the epoxy content by using an excess of ECH. Hydrolyzed Aroclor 1270 (0.15 mole, 67 g, (NBP 310445) was dissolved in ECH (0.90 mole, 83.5 g, mole ratio 1:6) and stirred at 44°C while NaOH (0.3 mole, 30% aqueous solution) was added over 2.15 hr; no exothermic reaction occurred and all caustic added was used up. Excess ECH was distilled off and final product purified by dissolving in ethyl methyl ketone to collect 58 g, mp 42-46°C.

Anal. Found (%): C, 35.67; H, 2.09; total Cl, 50.41, 50.51; epoxy, 2.00, 1.99 (equal to 36% of theory).

Correctness of the latter value is questionable assuming the material is free of solvent, since such a low mp always indicates high epoxy content.

Expt. 14 347350

A mixture containing hydrolyzed Aroclor 1271 (0.25 mole, 115.5 g, (NBP 334601-2, analyzing 7.48 and 7.72% OH) was dissolved in 2.5 moles of ECH and refluxed while 0.1 mole of KOH (as 30% solution) was added at once; no exothermic reaction occurred. The mixture turned neutral after 20 minutes heating, the excess ECH was distilled off, and the residue (liquid at 100°C) was diluted with 300 g of chlorobenzene and refluxed while 0.44 mole of KOH (40% solution) was added over a 3 hr period. After 24 hr reflux, filtration and distillation at 100°C/1 mm gave as residue 144 g, mp 60-64°C, of a yellow resin analyzing 0.32, 0.33% Cl⁻ and 5.31, 5.37% epoxy (equal to 98.5% of theory). Conversion was 100%. This product cures in a manner similar to the model molecule.

Expt. 15 353855

The purpose of this experiment was to adapt the model molecule process to the hydrolyzed Aroclor 1270. (NBP 347447, analysis [illegible]) A mixture of this hydrolyzed [illegible] was heated [illegible] 2 moles KOH was added as 40% solution [illegible]

up [illegible] to collect 123 g, mp 58°C (not sharp), of a light yellow resin; conversion was 86%.

Anal. Found (%): Cl^-, 0.87; epoxy, 5.03, 5.06% (equal to 90.5% of theory).

Expt. 16 353862-64

This experiment represents a six-fold scale-up of the previous run. Hydrolyzed Aroclor 1270 (1.5 mole, 661 g from combined samples 328989 and 353853) and six moles of ECH (555 g) were heated to 85°C, then 0.6 mole NaOH as 30% solution was added and system was refluxed for 3 hr. Then 163 g of ECH and 71 g of water was distilled off, giving 1100 g of residue. It was diluted with dioxane, filtered, (36 g of NaCl) and the filtrate was diluted with more dioxane to a total wt. of 2400 g. To this refluxing solution was added theory + 20% excess of NaOH (2.88 moles, as 30% solution) over six hr. The mixture was refluxed for 12 hr, and filtered. The filtrate was again refluxed for 8 hr while 0.6 moles of NaOH was added gradually, keeping the pH at 8. Layer separation of the reaction mixture was poor, therefore 1 liter of chlorobenzene was added. The solution was refluxed overnight in the presence of 0.3 mole of NaOH as 30% solution. Next day the liquid and solid organic layer were worked up separately. The liquid fraction (I) gave 627 g of a light yellow brittle resin, mp 65°C.

Anal. Found (%): Cl^-, 0.089, 0.096; epoxy, 3.79, 3.86% (equal to 66.4% of theory); C, 37.98; H, 1.83%; no residue; Cl, 49.05, 49.19; OH, 7.57, 8.41.

No conclusions can be drawn from these OH values since the resin failed to dissolve completely in the reagent. The solid fraction II represents, after refining, 193 g of a yellow powder, mp 275-280°C, which is very heat stable and does not change color on heating up to 270°C.

Anal. Found (%): Cl^-, 0.31, 0.35; epoxy, 0.70, 0.96.

Expt. 17 353894-6

Since the scaled-up experiment was not successful, additional modifications were needed. In this run 0.96 mole (443 g, NBP 353865) of hydrolyzed Aroclor 1270 was dissolved in 4 moles of ECH and refluxed at 95°C while 0.4 mole of NaOH (53.3 ml)

two layers were formed, the organic was washed with hot water, and then heated up to 95°C 20 mm to collect 632 g of residue. Total unreacted NaOH found was equal to 0.077 g. Hoping to get a faster and more complete dehydrochlorination at higher temperature, 1200 ml of diethylene glycol diethyl ether was used as solvent for the 632 g residue. This mixture was stirred at 120°C while 1.5 moles NaOH (50% solution was added over 3 hr, and the mixture was kept for 2 more hr at 120°C. The mixture was separated from the NaCl formed, and then distilled to remove solvent at 100°C/1 mm; total recovery of solvent was 1198 g, n_D^{25} 1.4093, of diethylene glycol diethyl ether. The residue (691 g) was washed with hot water until free of sodium chloride, and then heated to 120°C/1-2 mm to collect 574 g of yellow brown resin, mp 58°C, still containing 1.47, 1.49% of Cl^-. The resin was retreated by dissolving it in 1200 ml of recovered diethylene glycol diethyl ether, then 0.5 mole of NaOH was added as 50% solution, and the system was stirred at 120°C for 8 hr. The material was isolated as described above to collect 532 g of resin analyzing 0.11, 0.10% Cl^- and 4.14, 4.17 epoxy (equal to 75% of theory). The latter value indicates partial formation of polyether.

Expt 18 353898-900

The evaluation groups requested additional quantities of material similar in epoxy content to the product prepared in Expt. 17. Hydrolyzed Aroclor 1270 (1.06 moles, 487 g (NBP 353889 and 353891) was dissolved in 4.4 moles of ECH. To this was added 0.53 mole of NaOH (50% solution) and the system was refluxed for 4 hr. The excess ECH and NaCl were removed and the residue (602 g) diluted with 1200 ml of diethylene glycol diethyl ether. Caustic (1.25 moles, as 50% solution) was added and the system was stirred for 6 hr at 120°C, then filtered. Total unreacted NaOH was equal to 20 ml N. The salt free resin solution was retreated with 0.62 mole of NaOH solution and heated for 5 more hr at 120-125°C. A small sample was worked up separately and found to be free of Cl^-. The whole batch was worked up as described in Expt. 17, to give 511 g, mp 56-8°C, analyzing Cl^-, 0.09, 0.11%; epoxy 4.37, 4.49%. This is a good duplication and corresponds to the values requested by the evaluation group. From the wash water was isolated an additional 96 g of resin, mp 135-39°C. Total unreacted alkali found in wash water was equal to 24.8 ml N. Combined conversion was 99.5%.

Expt. 19 310944, 310448-9

Crude hydrolyzed Aroclor 1268 was prepared by refluxing 1.03 moles of Aroclor with 4.47 moles of KOH in 1500 g ethylene glycol for 8 hr. The crude hydrolyzed mixture (620 g) was dissolved in 2 moles of NaOH (12%), heated to 65°C and 2 moles of ECH was added over 1.25 hr. The mixture turned solid. A total of 554 g, mp 92°C, was isolated.

Anal. Found (%): C, 37.94; H, 2.70; residue, 2.25 (NaCl); total Cl, 42.27, 42.42; epoxy, 2.06, 2.06 (analyzed later).

Conversion was quantitative.

Expt. 20 323108, 323110-1, 323336

In order to get a better precipitation of the resin, glycidylation was carried out in a special flask equipped with a high speed stirrer but the resin failed to precipitate in the desired fine form. A mixture consisting of 0.5 mole (208 g) of crude hydrolyzed Aroclor 1268 (321025, made by J. Katon) was dissolved in one mole of 12% NaOH and heated at 65°C while 1.05 moles of ECH was added dropwise. No exothermic reaction occurred. A Waring Blendor was used for the tedious isolation of the resin to collect 256 g as a fine, yellow-white powder, mp 100-102°C.

Anal. Found (%): C, 33.79; H, 2.83; residue, 1.59; Cl, 38.63.

This experiment was repeated twice under similar conditions giving identical partially dehydrochlorinated ethers which are of no value as epoxy resins (see NBP 323110-323111).

Expt. 21 323112, 323132-3

In this experiment the hydrolyzed Aroclor 1268 (0.5 mole (321022) was dissolved in 1 mole of 10% NaOH and added over 115 minutes to 4 moles (300% excess) of ECH stirred at high speed at 65-70°C. This mixture was heated for one more hr at 70°C. The separated material was viscous. It was washed in a Waring Blendor. The product remained liquid. It was not analyzed since at that time the epoxy values were inaccurate.

Partly hydrolyzed Aroclor 1268 (0.5 mole) was dissolved in NaOH (1 mole, 40 g in 285 g H_2O) and added to 2 mole epichlorohydrin at 65°C. Isolated material (297 g) melts at 90-95°C.

Anal. Found: [illegible]

DSW 621616

[illegible] 558-

[illegible] compound 4,4'-bi(2,6-dichlorophenol) (Expts. 1-10). Partly dihydrolyzed Aroclor 1268 (analyses given in Table II) prepared in the St. Louis pilot plant was used for this process study.

A mixture containing 440 g (equal to 2 equivalents) of partly hydrolyzed Aroclor 1268 and 4 moles ECH (100% excess) was stirred at 75°C while 0.4 mole NaOH (30%) was added over 20 minutes. The mixture turned neutral after 1 hr. Excess ECH and water were distilled off. The residue (669 g) was diluted with dioxane and then filtered. To the filtrate (1421 g) was added 1.92 moles (20% excess) of 30% NaOH and reflux was continued for 4 hr. The mixture was washed with hot water to collect 557 g, mp 40-55°C, of a light brown resin.

Anal. Found (%): C, 31.13; H, 2.51; no residue; Cl^-, 0.58; 0.56%; epoxy, 5.12, 5.13% (equal to 88.5% of theory).

Conversion was quantitative. Unreacted NaOH found was equal to 0.123 mole.

Expt. 22 353560, -61, 353997

In this experiment, the charge was scaled up by 50% over Expt. 22 using exactly the same reaction conditions and reagents. The only variation used was that the NaOH (2.98 moles, 20% excess) was added gradually to the refluxing dioxane solution (1849 g) at the rate reaction took place. The reaction medium was kept at a pH of 8. Total duration was 5.5 hr, then the mixture turned neutral. At this point was added 0.375 mole NaOH solution, and reflux continued for an additional 6 hr. Isolated material (848 g) still contains 2.07, 2.09% Cl^-; epoxy was 4.47, 4.49%.

For complete dehydrohalogenation 820 g of this material was dissolved in 1700 ml of dioxane, and 0.7 mole of NaOH as 50% solution was added at once. After a 6-hr reflux, 765 g of resin was isolated, mp 55°C; analysis Cl^-, 0.34, 0.36; epoxy 5.23, 5.25% (equal to 90.2% of theory). Conversion was 95.5% for this two step dehydrochlorination.

Expt. 24 360248-9

To reduce the dehydrochlorination time more caustic was used for the ether formation step. A solution of hydrolyzed Aroclor 1268 (0.5 mole equivalent, 220 g) in four moles of ECH was heated at 90°C while 1 mole NaOH (50% solution) was added over 3 minutes. [illegible] exothermic. This mixture was refluxed [illegible] water and

Submitted to distillation to isolate excess ECH and water. The distillation residue was diluted with 130 g of toluene and 0.5 mole of 50% aqueous NaOH was added, and reflux was maintained for 5 hr (pot temperature 110°C); 23 ml of water was distilled off. A small sample was collected after 3 hr reflux and analyzed 3.82% epoxy. The final material analyzed 3.83% epoxy. Some resin on the walls of the flask (insoluble in boiling toluene) contained 2.33% epoxy and 0.68% Cl^-. This is a polymer, mp 270°C. The isolation of the ether was complicated due to emulsion formation. Some of the ether polymerized during the heating.

Expt. 25 360240-1

Consultant Dr. N. J. Leonard suggested reaction of hydrolyzed Aroclor 1268 (0.6 mole 264 g) excess ECH (2.4 moles) and 1.2 moles NaOH (30%) at 60°C followed by a reflux period. After 1 hr the mixture was neutral. ECH and water were distilled off. The residue was in this case partly rubbery and failed to dissolve completely in 450 ml of benzene. The mixture was refluxed for 4 hr. Analysis shows 3.80% epoxy content. Sample analyzed after 3 more hr reflux gave an epoxy content of 3.72% while additional 12 hr reflux failed to change the epoxy content (3.76% found). All epoxy values are based on benzene soluble material; as stated above not all material (polymer) is benzene soluble. This suggested variation does not look promising.

Expt. 26 367452

A mixture consisting of 0.75 mole hydrolyzed Aroclor (330 g) and four moles ECH was heated to 80°C, then 1.45 moles NaOH 50% (by mistake, wanted to add 0.66 mole) was added at 80°C over 5 minute time. The mixture was refluxed for 2 hr while it turned neutral. Then it was washed, distilled to remove excess ECH and water, and the residue was diluted with benzene, dried and filtered. Removal of the solvent gave 393 residue, mp 56-8°C, analyzing 3.99% epoxy and 1.70, 1.75% Cl^-. Total Cl^- found in wash water equal to 1.28 moles of NaCl. A portion (370 g) of the residue was dissolved in 400 ml of benzene, theory + 50% excess NaOH (21.6 ml 50% solution) was added and system was refluxed at 81°C; 22 ml of water was collected. The solution was filtered (17 g of partly water soluble solids) to give 666 g of filtrate. Isolation methods varied as follows: In one case 42 g of solution was heated to 100°C at 1-2 mm pressure to collect 23.1 g of resin analyzing 4.38, 3.69% epoxy; Cl^-, 0.11, 0.15%.

DSW 621618

3.87, 3.88% epoxy and 0.21% of Cl^-. Under the reaction conditions used reheating only reduced the CL- content without further epoxy formation.

Expt. 27 367455-6

The use of more caustic was investigated in this experiment. Hydrolyzed Aroclor 1268 (0.7 mole, 308 g) was dissolved in 4.2 moles of ECH and NaOH (1.68 moles, 20% excess as 50% solution) was added over 5 minutes at 80°C. Some heat was given off. This mixture was then refluxed for 1.5 hr, 100 ml of water was added and reflux continued for 1.5 mor hr. A 100 ml portion of benzene was added and solution was washed (good layer separation). Total unreacted NaOH found in 2137 g wash water was equal to 0.33 g NaOH. The ECH and water were distilled off. The residue was solvent purified to remove all NaCl and then heated at 140°C/1-2 mm for 15 minutes to collect 372 g resin containing 1.52, 1.72% Cl^- and 4.18, 4.18% epoxy. This material was dissolved in 400 ml of benzene and 0.27 mole NaOH as 50% solution was added. This mixture was heated for 2.5 hr while removing water. Isolation, exactly as given in the first part of this experiment, gave 349 g of resin, mp 96-8°C, analyzing epoxy, 3.86, 3.88%; Cl^-, 0.26%. Longer heating gave again dehydrohalogenation and polymerization but epoxy content was not increased.

Expt. 28 367457-8

Another variation tried was to dissolve the hydrolyzed Aroclor 1268 (0.5 mole, 220 g) in 20% NaOH (240 ml using a 20% excess) and add this solution over a 40 minute period to 3 moles of boiling ECH. The mixture turned neutral after 1-hr heating. More NaOH (0.09 mole) was added in two portions while reflux was continued for 2 more hr. The resin was isolated and heated at 100°C/1-2 mm for 0.5 hr to isolate 284 g, analyzing 4.41% Cl^- and 3.26, 3.30% epoxy (equal to 57.7% of theory). Analysis of the wash water shows that some of the caustic charged was also used up to hydrolyze ECH as shown by the 1.33 moles of NaCl found in the wash waters.

(1) Glycidyl ethers derived from di-hydrolyzed Aroclor 1268. MW. 416.7

Expt. 29 367460-61

All the experiments described in this section were made from di-hydrolyzed Aroclor 1268 prepared by John LeBlanc using the methanolic-alkali pressure process. Di-hydrolyzed Aroclor 1268 (0.25 mole, 106 g, NE 366.96) was dissolved in 1.5 moles

chlorination (Cl^-, 2.95, 2.96%; epoxy, 4.08, 4.11%). The resin was diluted with 238 g of benzene and 0.125 mole of NaOH (50%) was added. Reflux was continued for 2 hr and resin was purified by standard procedure. Final resin was kept at 140°C/1 mm for 15 minutes to give 128 g, mp 58°C, analyzing 4.97, 5.02% epoxy (equal to 81.9% of theory), Cl^- content was 1.09%; conversion was 97.8%.

Expt. 30 367463-65

The best procedure found for glycidylation of partly hydrolyzed Aroclor 1268 (Expt. 23) was used in this experiment. Di-hydrolyzed Aroclor 1268 (0.25 moles 105.5 NBP. 355855) was dissolved in 2 moles of ECH, heated to 90°C and 0.1 mole NaOH was added at once. After 20 minutes 0.1 mole additional NaOH as 40% solution was added and system was refluxed for 1.5 hr. Excess ECH was removed by distillation. The residue was diluted with 220 g of dioxane and refluxed while 0.4 mole NaOH (40%) was added over 3 hr, and reflux was continued for 8 more hr. Filtration gave 17 g of NaCl. The filtrate was distilled and the residue was dissolved in benzene, filtered, and solvent was removed. The residue was kept at 140°/1-2 mm for 15 minutes to give 121 g, mp 52°C, analyzing Cl^-, 0.90, 0.93%; epoxy, 5.31, 5.32% (equal to 87.3% of theory). Conversion was 92.8%. Reheating of 110 g of this resin with 0.125 mole of NaOH (50%) in 250 g of benzene for 1 hr at reflux gave, after purification, 102 g, mp 50°C, analyzing Cl^-, 0.17, 0.20%, and 5.35, 5.40% epoxy. These data reveal that further heating reduced the Cl^- content <u>without</u> increasing epoxy content.

Expt. 31, NBP 367466-8

This experiment is an attempt to adapt the St. Louis process for the glycidylation of tetrachlorobisphenol A to our di-hydrolyzed Aroclors. Di-hydrolyzed Aroclor 1268 (0.25 mole, 103 g. J. R. LeBlanc's Expts. No. 12, 14, 15) was dissolved in 1.5 mole of ECH. At 90°C, 0.25 mole NaOH (50%) was added over 12 minutes, then reflux was continued for 30 more minutes. The ECH was distilled off at 100°C/1-2 mm, then 0.5 mole NaOH was added as 50% solution over 20 minutes. The system was stirred for 5.5 hr at 100°C. Next day, 150 ml of benzene was added, the mixture was heated to 80°C and filtered (42 g analyzing 8 g NaOH; calculated NaCl is 29.25 g plus 10 g excess NaOH). The solvent was distilled off at 100°C, the solution was then kept at 140°/-1 for 20 minutes to give 121 g resin, mp 49-50°C, analyzing Cl^-, 0.10, 0.10% and epoxy, 5.39, 5.49% (equal to 89.5% of theory). Conversion was 92.8%.

[redacted]

phase transfer glycidylation process on a four-gallon scale. Di-hydrolyzed Aroclor 1268 (1 mole, 411 g; N.E. 204, NBP 365971) was dissolved in 6 moles of ECH and 1 mole of NaOH was added as 50% solution. Exothermic reaction started after 7 minutes, when 45 ml caustic had been added; the remaining NaOH was added over the next 10 minutes. The mixture was refluxed for 40 more minutes then distilled giving 183 g ECH and 40 ml H_2O. The residue was stirred at 100°C/1-2 mm for 20 minutes. The residue was diluted with 340 g of benzene, refluxed and 2 moles of NaOH (50%) was added over a 10 minute period. Reflux was continued while collecting 150 ml of water during the next 90 minutes. Total reflux time was 5.5 hr. Since this reaction mixture filtered slowly it was diluted with 400 ml of benzene and filtered (181 g $NaCl^-$ resin mixture). The filtrate was concentrated, the residue was kept 10 min. at 100°C/1 mm, then 20 min at 140°C at 1-2 mm, to give 442 g, mp 49-50°C, analyzing, 0.07, 0.09% Cl^- and 5.33, 5.47% epoxy (equal to 89.5% of theory). This system seems to eliminate completely the base since 1 g of sample is neutralized by only 0.013 milliequivalent of acid. Resin found in 181 g of salt mixture was 27 g. Overall conversion was 89.7%.

Expt. 33 NBP 367471-2

The purpose of this experiment was to modify the general directions given in the two previous runs by eliminating a part of the NaCl before distilling off the ECH. The di-hydrolyzed Aroclor 1268 (0.5 mole, NBP 365971) was dissolved in 3 moles of ECH, and 1 mole 50% NaOH solution was added over 2 minutes. The mixture was refluxed for 40 minutes then 350 ml of water was added. The organic layer was separated from the neutral aqueous layer. Excess ECH was distilled off; benzene (2.2 moles 170 g) was added then NaOH (0.5 mole) as 50% solution was added and the system was refluxed for 4 hr (5.5 in previous expt.), azeotroping off the water. The reaction mixture was then diluted with 200 ml of benzene and filtered (very fast) to give 255 g of resin, mp 47-8°C isolated by the procedure given in the previous 2 runs. Conversion 97.6% Analysis gave Cl^-, 0.18, 0.21% and epoxy, 5.14, 5.20% (equal to 85.1% of theory). There is no advantage in this modification.

Expt. 34 NBP 367489

In this experiment more ECH was used in an effort to increase the epoxy content. The final resin solution was contacted with water to make sure all alkali and salt are removed. A mixture consisting of 0.5 mole di-hydrolyzed Aroclor 1268 (NBP 365971) and 6 moles ECH were treated with 0.5 mole of NaOH added over 10 minutes and reflux continued for 35 minutes. Excess ECH and water were distilled off, then 350 g of benzene was added

time was 7.5 hr, removing water as formed. The reaction mixture was diluted with more benzene, filtered (125 g salt), and washed with more solvent. The filtrate (1200 ml) was thoroughly washed with 1,800 ml of water and the resin isolated by standard procedure to collect 221 g, mp 47°C.

Anal. Found (%): total Cl, 42.94, 43.16; Cl^-, 0.11, 0.12; epoxy, 5.47, 5.65 (equal to 91.2% of theory. Total water-insoluble material found in the salt residue was 16.3 g. Combined conversion was 91.5%.

Expt. 35, NBP 367491-95

The purpose of this run was to demonstrate glycidylation on a larger size batch. Di-hydrolyzed Aroclor 1268 (1.5 moles, 618 g) was stirred in 6 moles of ECH at 90°C then 1.5 moles of 50% NaOH was added over 35 minutes. After 40 minutes the solution was neutral. It was diluted at 58°C with 700 ml of water, good layer separation. After removing excess ECH, benzene (500 g) was added and reflux was continued at 87°C while NaOH (1.5 mole as 50% solution) was added at once. It was refluxed for 7 hr while the water was collected at the rate of distillation. It was refluxed for 8 more hr. The hot solution was decanted from salt, and three benzene wash-decantations of the salt were carried out (1.0, 0.8 and 0.8 l. benzene). The benzene solution was filtered and washed (emulsion) then dried to give 617.5 g of resin mp 46-47°C of excellent purity, analyzing Cl^-, 0.08, 0.09% and epoxy, 5.49, 5.54%. The yield is 90.5% of theory, and conversion is 79.5%, not counting resin in the salt mixture. The epoxy and Cl^- content check very well with the values of the previous experiment.

d. Glycidylation of hydrolyzed Aroclor 1262 and 1248

Expt. 36 316063-4

Partly hydrolyzed crude Aroclor 1262 (1.33 moles, 382 g, NE 308.6) was dissolved in 810 g of H_2O containing 2.24 moles of NaOH. It was heated at 40°C, then ECH (1.75 moles, 161 g) was added over 105 minutes. The temperature was increased gradually to 101°C, and kept for 1.25 hr at 102-104°C. In the same time solid polyether precipitated. It was worked up using a Waring Blendor to collect 532 g, mp 150-160°C, equal to 92% conversion. The product is mostly polyether and contains only 0.14, 0.14% epoxy and Cl^-, 0.41, 0.40% (determined later); earlier analytical data were C, 40.80%; H, 2.46%; no residue; total Cl, 43.14%.

In this run attempts were made to reduce the extent of polymer or resin by using more ECH thence reducing polyether formation. Hydrolyzed Aroclor 1262 (0.3 mole, 106 g (NBP 327016) was dissolved in 0.6 mole NaOH (2.5 N). To this solution was added at 70°C, 0.6 mole of ECH over 1 hr; heating was continued for 1 hr at 70°C. The solid reaction product was purified in the Waring Blendor to collect 120 g, mp 95-100°C.

Anal. Found (%): C, 42.19; H, 2.65; Cl, 43.58, 43.76 (by old unmodified Cl⁻ method).

Glycidylation of hydrolyzed Aroclor 1248

Expt. 38 323114

One mole of partly hydrolyzed Aroclor 1248 (251 g, J. Katon, 321037-1) was dissolved in 2 moles of 10% NaOH while 2 moles of ECH were added at 70°C over 102 minutes. Reaction was slightly exothermic and gave, after longer heating (1.25 hr) a light viscous resin. It was not worked up since starting phenol was mostly monofunctional, therefore product is of no value as an epoxy resin.

e. Diglycidyl ether of tetrachlorobisphenol A

The purpose of this series of experiments was to supply material for evaluating glycidyl ethers made from Monsanto tetrachlorobisphenol A.

Expt. 39 334642-4

A solution containing tetrachlorobisphenol A (0.3 mole, 109.5 g, mp 134.1-134.9°C) and ECH (1.2 moles, 111 g) was stirred at 80°C and 0.11 mole NaOH was added as 30% solution. After a 1-hr reflux unreacted ECH was distilled off. The residue was diluted with dioxane, filtered, and the filtrate was diluted with dioxane to a total of 500 g. This solution was treated with 0.46 mole NaOH (30% solution, theory + 10% excess) and refluxed for 45 minutes. Total isolated ether was 151 g, analyzing 3.54, 3.57% Cl⁻, and 4.37, 4.49% epoxy (equal to 66% diglycidyl ether content).

Expt. 40 334645-6

A solution containing tetrachlorobisphenol A (1 mole, 365.5 g) and ECH (4 moles, 370 g, 100% excess) was stirred at 75°C and 0.4 mole NaOH was added as 30% solution over 10 minutes. A mild exothermic reaction started which brought the pot temperature gradually to 96°C in the next 10 minutes. Over the

[illegible] mixture [illegible] for [illegible] hr, then [illegible] to remove [illegible] (178 g) [illegible] dioxane [illegible] (precipitate washed with dioxane) to give [illegible] of filtrate. It was heated to reflux and 1.76 moles (10% excess) of 30% NaOH solution was added, reflux was continued for 4 hr. The two layers were separated and the dioxane was distilled off at reduced pressure (100°C pot temperature) to give 478 g residue (quantitative conversion), n_D^{25} 1.5882. Solvent purification (by J. Herbig) increased the mp to 95°C.

Anal. $C_{21}H_{20}O_4$ (crude material)

	Calcd.	Found
C	52.6	52.95
H	4.18	4.34
epoxy oxygen	6.66	5.87, 5.97 (88% of theory)
hydrolyzable Cl	0.0	0.12, 0.12

Expt. 41 360245

This experiment was performed much later to become familiar with the St. Louis pilot plant process recommended by R. C. Cass (R 4) for the glycidylation of tetrachlorobisphenol A. It was desired to adapt the process to the glycidylation of our hydrolyzed Aroclors. Tetrachlorobisphenol A (0.55 mole, 202 g) was dissolved in 3.3 moles of ECH (mole ratio 1:6) then 1.1 moles of NaOH was added as a 50% solution at 80°C over 55 minutes, some heat was given off. Mixture started to reflux in 12 minutes, after 33 ml of NaOH solution were added. The mixture was heated for 10 more minutes, then distilled at 20 mm to give 139 g distillate containing 105 g ECH, (bath temperature to 150°C). The crude residue was diluted with 190 g of benzene, heated to 80°C, and 0.55 mole NaOH as 50% solution was added; reflux was continued for 6 hr. A small sample was isolated and analyzed 5.87% of epoxy. Original reaction material was diluted with water and washed 3 times to neutrality. Solution was dried using azeotropic distillation, 2.5 g charcoal and 2.5 g of filteraid was added and filtered. The filtrate was distilled and finally kept at 150°C (bath temperature) and 20 mm to collect 238 g, analyzing 0.61, 0.66% Cl^- and 6.09, 6.15% epoxy (equal to 91.25% theory). Conversion was 91.5%. This confirms data reported by St. Louis (R 4).

[illegible] of Hydrolyzed Aroclor 5460

Expt. [illegible] 353865-5

Hydrolyzed Aroclor 5460 (0.2 mole, 96.7 g containing 46.22% Cl and 8.31% OH NBP 328967 II) was dissolved in ECH (1.8 moles, 167 g) then 0.6 mole of NaOH (40%) was added over 3.5 hr. Pot temperature was increased gradually from 42° to 95°C, and the system was stirred for 6 hr. Material was worked up to isolate a resinous product (121 g).

Anal. Found (%): C, 44.12; H, 3.02; no residue; total Cl, 42.82; Cl^-, 7.28, 7.31.

This high Cl^- content indicates incomplete dehydrohalogenation. This synthesis was repeated later when we had collected more experience on glycidylation.

Expt. 43 353865-6

A mixture of hydrolyzed Aroclor 5460 (0.2 mole, 196 g, same batch as previous run) was dissolved in 1.6 moles ECH at 85°C, then 0.2 mole NaOH (30%) was added, followed by reflux for 1.5 hr. The excess ECH was distilled off, the residue was diluted with dioxane, filtered, and the filtrate (350 g) was refluxed. To this was added NaOH (0.8 mole, 30%) over six hr and reflux was continued overnight. The solution remained alkaline. After removing the NaCl and solvent the resin was dried at 115°C/1-2 mm pressure, to give 228 g of a yellow-amber resin, mp 85°C, analyzing 0.04, 0.17% Cl^- and 3.60, 3.61 epoxy. The latter value shows that some material has polymerized. Most likely this was caused by the relatively long heating period. This product possesses good properties in coating application (R-3).

g. Attempted reaction between Aroclor 1268 and glycerol

Expt. 44 NBP 288842-3

Since Aroclors react smoothly with mono hydroxy alcohols an unsuccessful attempt was made to react Aroclor 1268 with glycerol in the presence of NaOH. No ether was formed. It was planned to dehydrate the glyceryl ether to the corresponding glycidyl ether.

h. Glycidylation of dihydroxy diphenyl sulfone

Expt. 45 316056-7

Monsanto's 4,4'-dihydroxydiphenyl sulfone (1.5 moles, 372.5 g) was heated with 2 moles of KOH in 1000 ml of water. Ethanol (200 ml) was added to dissolve the material [illegible] enough ECH to the solution was added 2 moles of ECH over [illegible] at 75-85° temperature was gradually

[illegible] to dissolve completely in the reagent, therefore this value is low. Other analytical data found were C, 55.13%; H, 4.95%; S, 8.91%. Only the S content checks with the calculated value of 8.85%. The product is partly polymerized.

Expt. 46 323103-5

The next step was to start with o,p'-dihydroxydiphenyl sulfone, the lower cost isomer. The sulfone (1 mole, 250 g) was dissolved in 2 moles of NaOH (10%) and to this solution was added 2 moles of ECH at 75°C over a 77 minute period. Some exothermic reaction took place. Material precipitated in one piece. It is not homogenous and was not further worked up.

The next experiment was made using a high speed stirrer and a beaker container. The sulfone (0.25 mole) was again dissolved in 10% NaOH (200 ml) stirred at 70°C while ECH (0.55 mole, 10% excess, 51 g) was added over 35 minutes. Isolation of material gave 70.1 g resin, mp 115-120°C.

Anal. Found (%): C, 57.64; H, 5.03; S, 9.42

No epoxy analysis was available at that time.

1. Di-hydrolyzed aroclors as curing agents for bis-glycidyl ethers

This work was carried out by J. Schwendeman and J. K. Craver. The purpose of these few experiments was to investigate dihydrolyzed Aroclor 1268 as a curing agent for its glycidyl ether as well as for Epon 828. It was stated by Dave Cummings that Epon 828 and glycidyl ether of tetrachlorobisphenol A do not cure with their corresponding bisphenols. Samples of Epon 828 and diglycidyl ethers of Aroclor 1268 were stirred with dihydrolyzed Aroclor 1268 in a 500 ml flask at 180°C under N_2. Samples were withdrawn after 1 and 2 hr period, respectively. Data on these experiments are summarized in Table I.

Preliminary curing studies of glycidyl Aroclor 1268 using diethylenetriamine, succinic anhydride or maleic anhydride were made by the author using test tube size experiments. In one instance when glycidyl ether prepared from partly hydrolyzed Aroclor 1268 and maleic anhydride were heated in test tube and then kept at 110°C overnight, a clear resin melting above 328°C was formed (see NBP 316083-4).

Glycidylation of biphenolic material has been quoted in many patents. As stated in the remarks given under reference a preliminary study of the patent problems associated with making and selling epoxy resins formed from hydrolyzed Aroclors and epichlorohydrin was prepared by Mr. F. C. Wellington of Dayton and given in the Appendix Section.

Four patent disclosures were submitted on glycidyl ethers, their curing and uses on work given in this report.

D-1869 Dazzi New halogenated epoxy compounds and their uses, dated 4-1-55.

D-2320 Dazzi Glycidyl ether derived from Aroclors as stabilizers for polyvinyl chloride, dated 12-11-56.

D-2321 Dazzi Glycidyl ethers derived from Aroclors as plasticizers for polyvinyl chloride.

D-2477 Dazzi-Herbig Hydrolyzed Aroclors as curing agents for glycidyl ethers.

Disclosure D-1870 (Dazzi) New Glycidyl ethers derived from dihydroxydiphenyl sulfone will be abandoned since it was found in the patent literature.

Glycidylation of phenolic compounds, especially bisphenol-A and further reaction of the oxirane ring (curing) is reported in several hundred U.S. patents, and very few summaries. Most pertinent data are found in a good summary "Chemistry of Poly Epoxides", by R. Wegler, Angew. Chem. Vol 67, page 582-592, 1955. (209 references). Trade literature from Shell teaches how to cure their glycidyl ethers derived from bisphenol A. Few details were published on epoxy resins back in 1955 when this work was started. Now more is being published in form of symposia papers presented in U.S. and England.

1. Dazzi-New Epoxy compounds derived from Aroclor, Memo to the Idea Review Committee, dated 11-16-54.

2. Dazzi, "The Aroclors and other Halogenated Aromatics as Chemical Intermediates". Memo to Dr. C. A. Hochwalt by J. Dazzi dated 1-16-56. Part I (part II and III as continuation).

3. J. H. Schwendeman. J. K. Craver, J. Dazzi, J. R. LeBlanc and J. A. Herbig. RD-58 Final Report No. 1115 "Synthesis and Application studies on hydrolyzed Aroclors and Derivatives".

4. Cass, R.C., St. Louis, Research Report No. P-762, "Suggested Procedure for the Preparation of Diglycidyl Ethers of Tetrachlorobisphenol A".

5. Dazzi, J., to S. E. Gebura. Preparation of glycidyl ethers derived from hydrolyzed Aroclors 1262, 1268, 1270, memo dated 9-6-55.

6. Gebura, S.E., Preparation of high epoxy oxygen resins from hydrolyzed Aroclor 1262, memo to M. F. Drumm, Springfield, CC to J. Dazzi.

7. Touchette, N.W., St. Louis, Evaluation of glycidyl ether of hydrolyzed Aroclor 1262 as polyvinyl chloride plasticizer and stabilizer, memo to J. Dazzi dated 8-14-56.

8. Wellington, F. C., Epoxy Resins Utilizing hydrolyzed Aroclor, See Appendix.

IX. COST ESTIMATES

None were prepared on compounds described in this report.

C. RECOMMENDED PROCESS

No complete process studies were made. The best laboratory glycidylation procedure for di-hydrolyzed Aroclor 1270 is shown in Expts. No. 14 and 15; for di-hydrolyzed Aroclor 1268 in Expt. 31 and 32, and for the model compound 4,4'-bi-(2,6-dichlorophenol) in Expt. 1.

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MATERIAL SPECIFICATIONS

No material specifications were set on any of the products described. Specification for hydrolyzable chlorine in glycidyl ethers derived from bisphenol A (Epons) is 0.25%. Low hydrolyzable Cl content is very important in curing epoxy resins.

XII. ANALYTICAL PROCEDURES

Epoxy content was determined by the E-2-55 procedure. For hydrolyzable chlorine, the C-38-56 method was used.

Combustion analyses for carbon and hydrogen were run at 800°C. Total chlorine was determined by the C-35-55 and H-8-57 methods. The latter was developed specifically for Aroclors and is superior to previous methods. For details see Final Report on hydrolysis of Aroclors by J. Dazzi, No. 1182.

XIII. TOXICITY AND HAZARDS

No toxicity data have been obtained on products reported here. Special care should be exercized in handling epichlorohydrin, a toxic material. Longer exposure to Aroclors, octachloronaphthalene and their derivatives can cause skin irritation, which was experienced by the author.

ACKNOWLEDGMENT

Mr. J. A. Herbig's curing studies on the early glycidyl ether samples and his very valuable suggestions are gratefully acknowledged. We thank the Plastic Division, especially Dr. S. Gebura, Springfield, for the process study on glycidylation of hydrolyzed Aroclor 1262.

Most helpful in this project were the evaluations, suggestions and team work given by Messrs. J. K. Craver and J. L. Schwendeman from the surface coating group. We thank Mr. J. R. LeBlanc for developing a process for making completely di-hydrolyzed Aroclor 1268.

Messrs. F. R. Short and H. W. Schwartz of the Analytical Group developed a procedure for epoxy determination for Aroclor derivatives. Their contributions are gratefully acknowledged. We thank Mr. J. R. Darby's group, St. Louis for screening samples.

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D. B. Sharp - Dayton
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To Mr. H. J. Krase

At Dayton, Ohio

March 20, 1956

EPOXY RESINS UTILIZING HYDROLYZED AROCLORS

This is a summary of a preliminary study of the patent problems associated with making and selling epoxy resins formed from hydrolyzed Aroclors and epichlorohydrin.

Infringement

Castan - U. S. 2,324,483 would be infringed if the subject epoxy resins were condensed with a polybasic carboxylic acid anhydride (such as maleic anhydride). However, this patent expires in July of 1960.

Greenlee (Devoe & Raynolds) - U. S. 2,698,315 might be infringed-depending upon whether the term "diphenol" includes the substituted (i.e., chlorinated) diphenols obtained by hydrolyzing Aroclors. The file history of this patent has been ordered in an attempt to clarify the interpretation of this patent.

No study has been made of the validity of either the Castan or the Greenlee patents.

There are a large number of other patents directed to epoxy resins modified or mixed with other resins or cured according to specific techniques. Many of these could be infringed if the particular modification or curing technique of the patent were to be utilized with the hydrolyzed Aroclor epoxy resin.

Patentability

The method of hydrolyzing Aroclors in ethylene glycol with sodium hydroxide is unpatentable over Smith (Monsanto) - U. S. 2,449,088

The hydrolyzed Aroclor product obtained from the fully chlorinated diphenyl (i.e., p,p'-dihydroxyoctachlorodiphenyl) is also unpatentable over the Smith patent. The chlorinated dihydroxydiphenyl compounds containing fewer than eight chloride atoms per molecule might conceivably be patentable if found to have unexpectedly superior properties when compared with the octachloro or lesser chlorinated dihydroxydiphenyl compounds. At the present time we know of no such superior properties.

The use of hydrolyzed Aroclors, as a general class, in epoxy resins is unpatentable over Moss (Celanese) - U. S. 2,319,876, Carpenter et al (Courtalds) - U. S. 2,602,075, or Hatcher (Allied Chemical & Dye) - U. S. 2,695,276, all of which disclose the use of 4,4'-dihydroxydiphenyl in epoxy resins and state that the dihydroxydiphenyl compounds can be substituted with halo radicals (expressly including chloro radicals). It is possible that some specific halogenated dihydroxydiphenyl compound will be found to have unexpectedly superior properties which will make that compound patentable over the broad class of chlorinated dihydroxydiphenyl. At the present time we know of no such properties.

There is also a possibility for patent protection relative to particular types of Aroclor hydrolysis products - e.g., chlorinated trihydroxydiphenyl or trihydroxyterphenyl. However, these products have not yet been evaluated.

The prior art does leave a fair degree of latitude for making patentable inventions with respect to modified (e.g., esterified) resins, blends (e.g., with urea, melamine or phenolic resins) or for special curing techniques utilizing epoxy resins based upon hydrolyzed Aroclors. Thus, it is not at all unlikely that Monsanto could still obtain a significant patent position to back up a manufacturing and sales effort with respect to hydrolyzed Aroclor epoxy resins. It should be emphasized, however, that the inventions necessary for such a patent position have not yet been made. Efforts to obtain these patents would probably have to be preceded (or at least accompanied) by a fairly sizable applications or formulation research program. If such a patent position is to be achieved, the hydrolyzed Aroclors should not be released or disclosed to the trade until our position has been established.

F. C. Wellington

APPENDIX C TABLES

I. Curing of Diglycidyl Ethers with Dihydrolyzed Aroclor 1268.

II. Analysis of Partly Hydrolyzed Aroclor 1268, St. Louis Pilot Plant.

III. Calculated Analysis of Diglycidyl Ethers Derived From Hydrolyzed Aroclors.

TABLE I

CURING OF DIGLYCIDYL ETHERS WITH DIHYDROLYZED ARALDITE [illegible] AT 175°C UNDER N_2

Expt. No.[4]	1	2	3	4	5	6	7	8
Charge (g)								
Diglycidyl Ar-1268[1]	50.3	50.3	50.3	50.3				
Epon 828[2]					190	190	190	190
Dihydrolyzed Ar-1268[3]	4.1	4.1	8.2	8.2	20.5	20.5	41	41
Mole radio: Phenol/ether	1:10	1:10	1:5	1:5	1:10	1:10	1:5	1:5
Duration (Hr)	1	2	1	2	1	2	1	2
Anal.Found: epoxy	4.82	5.01	3.27	3.09	6.73	6.59	4.80	4.80
Calc'd epoxy	5.05	5.05	4.79	4.74	7.6	7.6	6.95	6.95
N. Eq.	0.06	0.08	0.05	0.06	1.83	0.95	3.31	1.49
Calc'd MW (based on epoxy content found)	758	821	975	1028	571	585	662	667

1 Anal. Found: epoxy, 5.37, 5.49; OH, 0.07, 0.09; Mol. Wt. 590

2 " " " 8.19, 8.26; Mol. Wt. 389

3 " " N. Eq. 204; OH, 8.05

4 See Notebook Pages 367475-6, 367484, 367486, 367488

TABLE II

ANALYSIS OF PARTLY HYDROLYZED AROCLOR 1268 PREPARED IN ST. LOUIS PILOT PLANT[1]

Analysis	Calculated mono-	Calculated dihydroxy	Found	
C	34.6	33.15	35.56	35.60
H	0.8	0.53	1.34	1.42
Residue			0.00	0.00
Chlorine 1) peroxide	63.0	57.2	52.85	54.78
2) Hawkins			55.42	55.69
OH	3.9	8.20	7.62	7.74
Neut. Eq.	435	208	223.2	220

[1] Preparation is given St. Louis Research Report No. 1706 by D. K. Lynch.

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TABLE III

CALCULATED[1] ANALYSIS OF DIGLYCIDYL ETHERS DERIVED FROM HYDROLYZED AROCLORS[2]

Aroclor	M.W.	%Epoxy	%Cl
$C_{12}Cl_{10}$	573.93	5.57	49.42
1271	571.78	5.59	49.24
1270	566.71	5.64	46.95
1268	528.89	6.05	44.94
1262	462.53	6.92	36.57
5460	639.66	5.00	41.85
5460[3]	677.27	7.08	34.29

1 Based on Cl content of Aroclor used. Aroclor 1270 used contained 71% Cl.

2 Calculations assume samples are free of polyether.

3 Calculated as triglycidyl ether.