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EXPLORATORY AROCLOR CHEMISTRY. PART III. GLYCIDYLATION OF HYDROLYZED AROCLORS

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[illegible] contact between ether and NaOH by improved stirrer design should definitely reduce the time cycle of the dehydrochlorination step.

d. 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 (38% 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.

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f. Glycidylation of hydrolyzed Aroclor 5460

Expt. 42 NBP 328981

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 since by mistake not enough KOH was used. To this solution was added 2 moles of ECH over an 87 minute period at 65-67°C; temperature was gradually

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