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㉑ Applicant: THE DOW CHEMICAL COMPANY
2030 Abbott Road Midland,
Michigan 48640. (US)

㉒ Inventor: Clarke, James Albert
120 Blossom Lake Jackson
Brazoria Texas. (US)

㉔ Representative: Weickmann, Heinrich, Dipl.-Ing. et al
Postfach 860 820 Möhlstrasse 22
D-8000 München 86. (DE)

(54) Process for preparing high molecular weight polyether resins from bisphenols and epoxy resins.

(57) This invention is directed to a process for preparing high molecular weight polyhydroxyether resins by reacting an epoxy resin which is a glycidyl ether of a bisphenol with a bisphenol in the presence of a solvent and a catalyst. The process is characterized by adding after the reaction between the eopxy resin and the bisphenol is at least 97 percent complete based upon the phenolic hydroxyl content from 0.005 to 0.12 phenolic hydroxyl equivalents of a halogenated bisphenol per equivalent of the total phenolic hydroxyl content of the bisphenol and the halogenated bisphenol. The high molecular weight polyhydroxyether resins produced by this process are useful in coatings.

Croydon Printing Company Ltd.

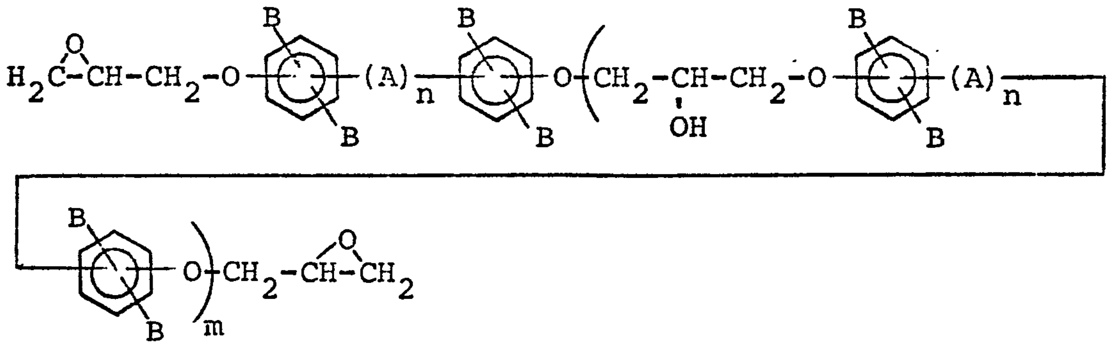
PROCESS FOR PREPARING HIGH MOLECULAR WEIGHT POLYETHER RESINS FROM BISPHENOLS AND EPOXY RESINS

High molecular weight resins have been prepared from bisphenols and epoxy resins as disclosed in U.S. Patent Nos. 3,306,872, 3,379,684 and 3,637,590. Such high molecular weight resins are prepared from essentially pure bisphenols containing very small quantities of ortho-para and ortho-ortho' isomers. Resins prepared from bisphenols containing significant quantities of these isomers have been found to have relatively lower molecular weights. The process of the present invention produces high molecular weight resins employing either type of bisphenols.

The present invention is directed to a process for preparing high molecular weight polyhydroxyether resins by reacting an epoxy resin (A) which is a glycidyl ether of a bisphenol with a bisphenol (B) in the presence of a solvent and a catalyst (C) characterized by adding after the reaction between Components (A) and (B) is at least 97 percent complete based upon the phenolic hydroxyl content from 0.005 to 0.12 phenolic hydroxyl equivalents of a halogenated bisphenol (D) per equivalent of the total phenolic hydroxyl content contained in (B) and (D). Preferably the percent completion is at least 98 percent.

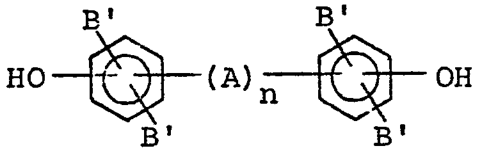
Preferably the amount of phenolic equivalents of halogenated bisphenol added per total phenolic hydroxyl equivalents is from 0.01 to 0.05.

Suitable epoxy resins employed as Component (A) in the process of the present invention are the glycidyl ethers of bisphenols such as, for example, those represented by the formula



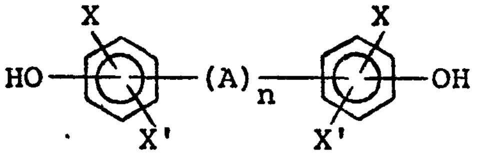
wherein each A is independently selected from a divalent hydrocarbon group containing from 1 to 8 carbon atoms, -O-, -S-, -S-S-, $-\overset{O}{\overset{\parallel}{\underset{\underset{O}{\parallel}}{S}}}-$ or $-\overset{O}{\overset{\parallel}{C}}-$; each B is independently selected from hydrogen, chlorine, bromine or an alkyl group containing from 1 to 4 carbon atoms, n has a value of 0 or 1 and m has an average value of from 0 to 2, preferably from 0 to 0.75.

Suitable bisphenols employed as Component (B) in the process of the present invention are, for example, those represented by the formula



wherein A and n are as defined above and B' is selected from hydrogen or an alkyl group having from 1 to 4 carbon atoms.

Suitable halogenated bisphenols employed as Component (D) in the process of the present invention are, for example, those represented by the formula



wherein A and n are as defined above, each X is independently chlorine or bromine and each X' is independently hydrogen, chlorine, bromine or an alkyl group having from 1 to 4 carbon atoms.

Suitable catalysts which can be employed as Component (C) in the process of the present invention include any catalyst which will catalyze the reaction between a vicinal epoxy group and a phenolic hydroxyl group. Such catalysts include, for example, those disclosed in U.S. Patent Nos. 3,306,872, 3,379,684, 3,477,990, 3,547,881, 3,637,590 and 3,948,855.

Particularly preferred catalysts are those quaternary phosphonium compounds having as the anion portion, a halide or a carboxyl group such as, for example, ethyltriphenylphosphonium chloride, ethyltriphenylphosphonium bromide, ethyltriphenylphosphonium iodide, ethyltriphenylphosphonium acetate, ethyltriphenylphosphonium diacetate (ethyltriphenylphosphonium acetate acetic acid complex), tetrabutylphosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium iodide, tetrabutylphosphonium acetate, and tetrabutylphosphonium diacetate (tetrabutylphosphonium acetate acetic acid complex). Those having a carboxyl group as the anion, such as, for example, ethyltriphenylphosphonium diacetate, are most preferred.

The quantities of epoxy resin and bisphenol compounds employed are those required to obtain the desired molecular weight and are usually employed in such quantities as will provide an epoxide:total phenolic hydroxyl ratio of from 1.15:1 to 0.97:1, preferably from 1.06:1 to .99:1.

The quantity of catalyst employed depends upon the particular reactants and catalyst being utilized and is usually in the range of from .1 to 10 millimoles, preferably from .2 to 6 millimoles per equivalent of the epoxide reactant. The higher quantities of catalyst are desired when higher molecular weight products are to be prepared.

Suitable solvents which are employed in the present invention include ketones and ethers such as, for example, acetone, methyl ethyl ketone, cyclohexanone, mesityloxide, dioxane, tetrahydrofuran, dimethoxyethane, lower alkyl ethers of ethylene and propylene glycol and mixtures thereof. Any solvent is suitable so long as it maintains the reactants and reaction products in solution or intimate suspension at the reaction temperature employed and which will not react significantly with the reactants or reaction products or the catalyst and which can be readily removed, if desired from the reaction product. The solvent is conveniently employed in quantities of from 20 to 100, preferably from 30 to 50 parts by weight per 100 parts of epoxy resin (Component A) employed.

The temperature at which the reaction can be conducted depends upon the particular reactants and catalysts employed but usually ranges from 120°C to 220°C, preferably from 130°C to 160°C.

The higher the temperature and the higher the concentration of catalyst, the less time that is required for the reaction to reach a specific degree of completion.

EXAMPLES 1, 2, 3 and 4 and COMPARATIVE RUNS A, B and C

The following components were employed in the Examples and Comparative Runs.

The epoxy resin, Component (A), for all Examples and Comparative Runs was the glycidyl ether of bisphenol A having an epoxide equivalent weight of 182.5. In each Example and Comparative Run, 186.02 grams (1.02 equivalents) of the epoxide resin was employed.

In Examples 1, 2 and 3 and all Comparative Runs, the bisphenol, Component (B), employed was an impure bisphenol A (IPBPA) having an ortho-para isomer content of 2.2 percent and an ortho-ortho' isomer content of less than 0.02 percent. In Example 4, the bisphenol employed was a purified bisphenol A (PBPA) having an ortho-para isomer content of 0.2 percent and an ortho-ortho' isomer content of less than 0.01 percent.

The catalyst, Component (C), for all Examples and Comparative Runs was a 70 percent solution of ethyltriphenylphosphonium diacetate in methanol. It was employed at 3 millimoles per epoxy equivalent.

The solvent for all Examples and Comparative Runs was the ethyl ether of ethylene glycol. For all Examples and Comparative Runs B and C, 150 grams of the solvent was employed in each reaction mixture. In Comparative Run A, 30 grams of the solvent was employed.

The halogenated bisphenol, Component (D), for all Examples and for Comparative Run C was tetrabromo bisphenol A (TBBPA) having an hydroxyl equivalent weight of 272. No halogenated bisphenol was added in Comparative Run A. In Comparative Run B, an additional amount of IPBPA was added instead of TBBPA.

In all Examples and Comparative Runs, the combined phenolic hydroxyl equivalents of Components (B) and (D) was 1.00. Thus, the equivalents of halogenated bisphenol employed per equivalent of the total phenolic hydroxyl content is easily calculated.

In all Examples and Comparative Run C, the reaction mixture was heated to 132°C for a period of time. Then the halogenated bisphenol, Component (D), was added and the reaction continued for a total reaction time of 7 hours. For Comparative Run A, the reaction mixture was heated to 135°C for a total of 7 hours without any halogenated bisphenol being added. For Comparative Run B, IPPBA was added instead of a halogenated bisphenol, and the reaction was run at 132°C for a total of 7 hours.

In all Examples and Comparative Runs, the equivalents of epoxide remaining in the reaction mixture was determined by titration employing the method described by R. R. Jay in <u>Analytical Chemistry</u>, volume 36, number 3, pages 667-8, March 1964.

In all Examples and Comparative Runs, the equivalents of phenolic hydroxyl remaining in the reaction mixture were determined by a potentiometric titration procedure. A sample containing about 0.1 milliequivalent of phenolic hydroxyl was weighed into a beaker and then dissolved in 20 grams of dimethylformamide. 75 ml of dimethylformamide is added to a second beaker and two drops of o-nitroaniline indicator is added. The solution is stirred and sparged with nitrogen gas to remove dissolved carbon dioxide. The dimethylformamide in the second beaker is then titrated potentiometrically with a 0.1 molar solution of tetrabutylammonium hydroxide in 90 weight percent toluene-10 weight percent methanol solvent. The endpoint is the center of the break in the titration curve corresponding to the color change of the indicator from yellow to orange. The sample dissolved in dimethylformamide is then added to the second beaker and titrated to the same endpoint as the solvent blank. The amount of carbon dioxide in the first 20 grams of dimethylformamide employed to dissolve the sample was assumed to be negligible.

The percent completion of the reaction between Components (A) and (B) after the first reaction period is calculated from the initial equivalents of phenolic hydroxyl and the equivalents of phenolic hydroxyl remaining after the first reaction period.

The weight average molecular weight, $\bar{M}w$, is determined by gel permeation chromatography.

Table I contains a summary of Examples 1 to 4 and Comparative Runs A, B and C.

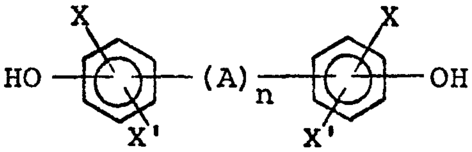
TABLE I

Reactants	Examples 1	2	3	4	Comparative Runs A	B	C
Equivalent Epoxy Resin	1.02	1.02	1.02	1.02	1.02	1.02	1.02
Equivalent IPBPA	0.98	0.95	0.92	--	1.0	0.98	0.98
Equivalent PBPA	--	--	--	0.98	--	--	--
At Time of Addition of Halogenated Bisphenol							
Elapsed Reaction Time, Hours	3	3	3	3	3	3	1-2/3
Epoxy Equivalent	0.037	0.058	0.085	0.031	0.033	0.0395	0.053
Phenolic Equivalent	0.019	0.0185	0.0125	0.022	0.027	0.026	0.033
Percent Completion	98.1	98.1	93.6	97.8	97.3	97.3	96.6
Equivalent TBBPA Added	0.02	0.05	0.08	0.02	--	--	0.02
Equivalent IPBPA Added	--	--	--	--	--	0.02	--
Analysis of Final Product							
$\bar{M}_w$	45500	38950	47750	38900	24100	26700	22450

Claims:

1. A process for preparing high molecular weight polyhydroxyether resins by reacting an epoxy resin (A) which is a glycidyl ether of a bisphenol with a bisphenol (B) in the presence of a solvent and a catalyst (C) characterized by adding after the reaction between Components (A) and (B) is at least 97 percent complete based upon the phenolic hydroxyl content from 0.005 to 0.12 phenolic hydroxyl equivalents of a halogenated bisphenol (D) per equivalent of the total phenolic hydroxyl content contained in (B) and (D).

2. The process as in Claim 1 characterized in that the halogenated bisphenol (D) is represented by the formula



wherein A is a divalent hydrocarbon group containing from 1 to 8 carbon atoms, -O-, -S-, -S-S-, $-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-$ or $-\overset{O}{\overset{\|}{C}}-$, n has a value of 0 or 1, each X is independently chlorine or bromine, and each X' is independently hydrogen, chlorine, bromine or an alkyl group having from 1 to 4 carbon atoms.

3. The process as in Claim 2 characterized in that A is $-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-$, n is 1, X and X' are both bromine.

4. The process as in Claim 1 characterized by adding from 0.01 to 0.05 phenolic hydroxyl equivalents of the halogenated bisphenol (D) per equivalent of the total phenolic hydroxyl content contained in (B) and (D).

5. The process as in Claim 1 characterized by adding the halogenated bisphenol (D) after the reaction between Components (A) and (B) is at least 98 percent complete.

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EUROPEAN SEARCH REPORT

Application number
EP 78 10 0495

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.²)
A	FR - A - 1 407 306 (U.C.C.) * Abstract * ----	1-2	C 08 G 59/62

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

C 08 G 59/62
C 08 G 59/24

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☒ The present search raport has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague		DECOCKER