

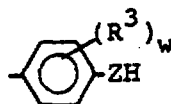
Description

Epoxy resins have long been produced by the reaction of a vicinal epoxide with a compound bearing phenolic hydroxyls in the presence of a catalyst in a so-called advancement reaction. A variety of catalysts have been reported in the art, including, for example, tertiary amines, quaternary ammonium halides, phosphonium halides, and phosphonium carboxylates. Processes for using these catalysts, as well as stoichiometric reagents have been detailed in US 2,216,099; 2,633,458; 2,658,855; 3,377,406; 3,477,990; 3,547,881; 3,547,885; 3,569,374; 3,694,407; 3,738,862; 3,948,855; 4,048,141; 4,177,216 and 4,302,574. CA-893,191, DE-PS 2,206,218 and 2,335,199, the texts *Handbook of Epoxy Resins* by H. Lee and K. Neville, McGraw-Hill (1967) and *Epoxy Resins Chemistry and Technology*, edited by C. A. May and Y. Tanaka, Marcel Decker, Inc. (1973) are also of interest.

The use of certain phosphonium trifluoroacetate salts as advancement catalysts for epoxy resins is disclosed in WO 83/00942. It is disclosed therein that these phosphonium salts may bear hydroxyphenyl or thiophenyl moieties. It should be noted that the hydroxyphenyl and thiophenyl were proposed by one of the inventors of the instant invention common to the above-identified application.

From GB-A-1 580 603 it is known to promote the reaction between epoxy resins and phenols and/or carboxylic acids or anhydrides thereof by trisubstituted (2,5-dihydroxyphenyl)phosphonium salts. Such phosphonium salt catalysts and in general the prior art catalysts or derivatives thereof can be extracted from the resulting epoxy resin product. In certain applications the presence of an extractable salt is undesirable. Accordingly it is the object of this invention to provide a process for the preparation of advanced epoxy resin compositions which contain reduced quantities of extractable residue from the catalyst.

This invention is directed to a process for reacting at an elevated temperature (a) an epoxy resin or thioepoxide bearing an average of more than one vicinal epoxide or thioepoxide group per molecule with (b) a polyhydric phenol, a polyhydric thiophenol, a carboxylic acid or a carboxylic acid anhydride, characterized by conducting the reaction in the presence of at least 0.01% by weight of the other reactants of (c) a trihydrocarbyl phosphine or quaternary phosphonium cation which bear on the average per molecule more than one moiety corresponding to the formula



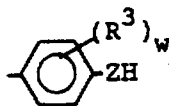
where Z is —O— or —S—, R^3 at each occurrence is independently a moiety essentially inert in this process, e.g. C_1 to C_4 alkyl or —Cl or —Br and w is an integer from 0 to 4, so as to promote the reaction of (a) with (b) and (c). These phosphorus compounds are not readily extracted from the resulting resins. Preferably, less than 25 weight percent of the phosphorus compounds initially present in the resulting resin are extracted in refluxing methanol in 12 hours.

The aforementioned phosphinophenols, phosphinothiophenols and quaternized derivatives thereof are incorporated into the resulting resins via reaction with the epoxides. Inasmuch as these phosphorous compounds undergo reaction with epoxides in the subject process, they are referred to herein as initiators rather than catalysts. The resins incorporating moieties derived from these phosphorus compounds are also believed novel.

Preferred phosphorus-containing initiators correspond to one of the following formulae I, II and III:

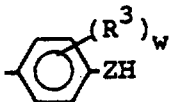


wherein R and R^2 are each independently

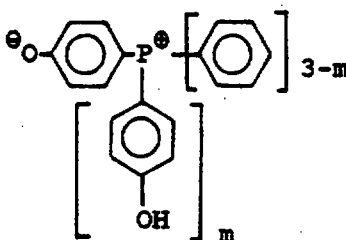


or monovalent hydrocarbon radicals, $X^\ominus$ is a compatible anion, R^1 is a monovalent hydrocarbon radical optionally including chlorine, bromine, phosphine, phosphonium, phenyl and thiophenyl moieties, Z is independently —O— or —S— at each occurrence, and A is a hydrocarbon radical bearing valences on one or more carbon atoms equal in total to $(n+1)$ where n is an integer 1, 2 or 3.

These salts of formulae II and III can also be zwitterions, i.e. the anion is formed by deprotonation of one of the



groups, in one preferred embodiment of the invention the initiator corresponds to the formula

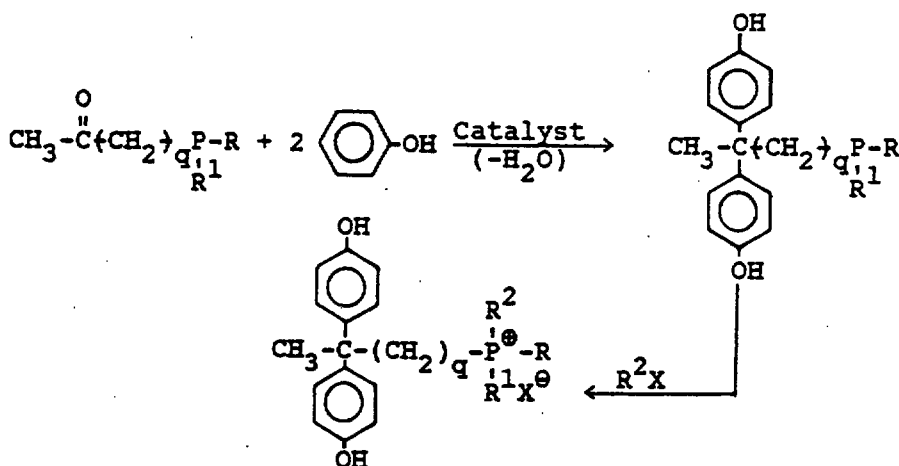


wherein m is an integer from 1 to 3, preferably 1 to 2.

Preferred initiators correspond to formulae I, II or III presented hereinbefore. Particularly preferred are compounds wherein R and R^2 are each independently phenyl, thiophenyl or hydroxyphenyl; R^1 is phenyl or C_1 to C_4 alkyl; A is an $(n+1)$ -valent alkyl radical having 1 to 12 carbon atoms; n is 2; w is 0, and $X^\ominus$ is fluoride, bromide, chloride, iodide, carboxylate (such as acetate), bicarbonate, bisphosphate, phenate or bisphenate anion. Preferably, each initiator bears a total of two hydroxyphenyl or thiophenyl moieties. Initiators bearing only one hydroxyphenyl or thiophenyl group produce resins of low molecular weight, whereas those bearing more than two such groups produce cross-linked resins when employed at high concentrations. Most preferably, Z at each occurrence in formulae I, II and III is —O—.

These initiators in general can be prepared by techniques known in the prior art. For example, Senear et al, *J. Org. Chem.*, 25, pp. 2001—2006 (1960), describe the preparation of certain compounds corresponding to Formula I and II.

Preferred compounds of Formula III can generally be prepared by the following reaction.



wherein q is an integer from 1 to 20 and the catalyst can be BF_3 .



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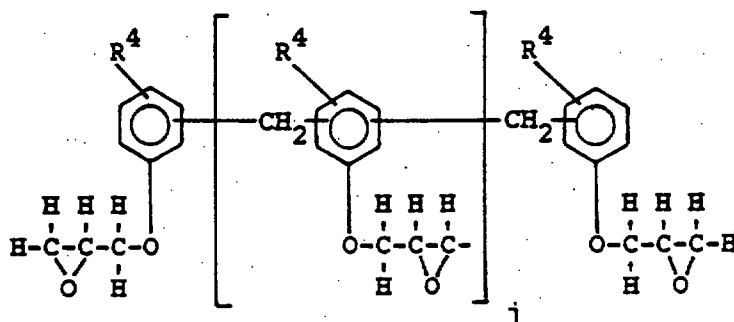
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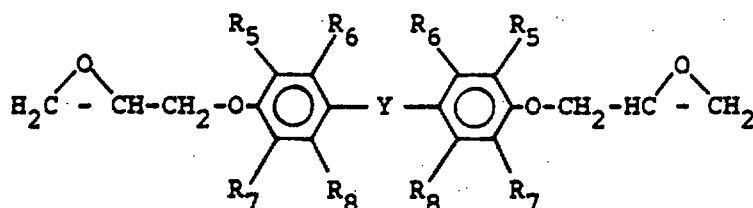
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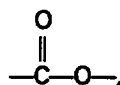
wherein each R^4 independently is hydrogen or an alkyl radical and j has an average value of from 0.1 to 10, preferably from 1 to 2. Preparation of these polyepoxides is illustrated in US 2,616,099 and 2,658,885. The preferred polyepoxides are those represented by the general formula V:

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wherein R_5 , R_6 , R_7 , and R_8 are each independently selected from hydrogen, bromine, chlorine and $-\text{CH}_2\text{CH}=\text{CH}_2$ and wherein Y is selected from oxygen, sulfur, $-\text{SO}-$, $-\text{SO}_2-$, bivalent hydrocarbon radicals containing up to 10 carbon atoms, oxygen-, sulfur-, and nitrogen-containing hydrocarbon radicals, such as $-\text{OR}'\text{O}-$, $-\text{OR}'-\text{O}-\text{R}'-\text{O}-$, $-\text{S}-\text{R}'-\text{S}-$, and

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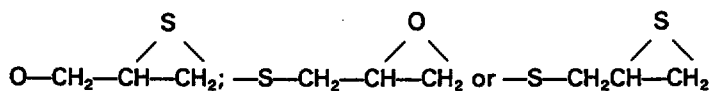
wherein R' is a bivalent hydrocarbon radical at each occurrence. "Y" preferably is an alkylene or alkylidene group having from 1 to 4 carbon atoms. In another preferred embodiment, "Y" is derived from the initiators corresponding to formulae I, II or III.

Other examples of polyepoxides include the epoxidized esters of the polyethylenically unsaturated monocarboxylic acids, such as epoxidized linseed, soybean, perilla, oiticica, tung, walnut and dehydrated castor oil, methyl lineate, butyl lineate, ethyl 9,12-octadecanedioate, butyl 9,12,15-octadecanetriate, butyl oleostearate, mono- or diglycerides of tung oil, monoglycerides of soybean oil, sunflower oil, rapeseed oil, hempseed oil, sardine oil, and cottonseed oil.

Other epoxy-containing reactants useful in the disclosed process are obvious to one of ordinary skill in the art. Such reactants are described in U.S. Patent 4,302,574.

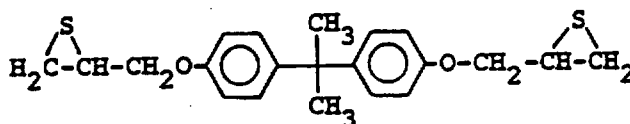
Sulfur analogs of glycidyl ether groups. i.e. compounds bearing

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are also operable. For example,

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can be used in place of an epoxide reactant.

Phenolic and Thiophenolic Reactants:

The phenolic and thiophenolic reactants are organic compounds having one or more hydroxyl or thiol groups attached to an aromatic carbocyclic nucleus. This class of compounds therefore includes thiophenol, phenol, alpha and beta naphthol, o-, m-, or p-chlorophenol, alkylated derivatives of phenol (e.g., o-methyl-,

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3,5-dimethyl-, p-t-butyl- and p-nonylphenol) and other monohydric phenols as well as polyhydric phenols, such as resorcinol, hydroquinone, dithiophenol, p,p'-dimercaptophenyl ether, p,p'-dimercaptobiphenyl, and p-hydroxythiophenol.

Mixtures of phenolic and thiophenolic reactants can be employed. However, phenolic reactants are generally preferred.

The polyhydric phenols bearing from 2 to 6 hydroxyl groups and having from 6 to 30 carbon atoms are particularly useful as reactants in the reaction with epoxy resins to form high molecular weight resins. Representative of these preferred phenols are 2,4', 4'-tri(hydroxyphenyl)methane and phenolphthalein. Particularly preferred as phenol reactants are those compounds corresponding to formula V. The most preferred phenols are bisphenol A (4,4'-isopropylidenediphenol), bisphenol F (4,4'-methylenediphenol), 2,2', 6,6'-tetrachlorobisphenol A, 2,2',6,6'-tetrabromobisphenol A, bisphenol S (4,4'-sulfonyldiphenol), 4,4'-dihydroxybiphenyl and 2,2'-diallyl bisphenol A. Bisphenol A is the polyhydric phenol of choice.

The subject phosphorus-containing initiators are themselves phenolic or thiophenolic reactants. These initiators comprise up to 100 mole percent of the total phenolic and thiophenolic reactants present, preferably comprise no more than 10 mole percent of these reactants.

The Carboxylic Acid Reactants:

The organic carboxylic acids and anhydrides are likewise well known. The acids bear one or more carboxyl groups on the organic nucleus. The anhydrides are prepared from such carboxylic acids by the removal of water therefrom in an intra- or intermolecular condensation. This class of compounds therefore includes acetic, propionic, octanoic, stearic, acrylic, methacrylic, oleic, benzoic, phthalic, isophthalic, maleic, succinic, adipic, itaconic, polyacrylic and polymethacrylic acids, and anhydrides thereof, such as acetic anhydride, phthalic anhydride, and hexahydrophthalic anhydride.

A preferred subclass of acids is comprised of members which are useful in cross-linking epoxy resins. The members of this subclass are normally di- or tribasic acids, or anhydrides thereof, and are preferably liquid or low melting solids such as succinic, maleic, or hexahydrophthalic acids or anhydrides. Other such acids and anhydrides are shown, for example, in US 2,970,983 and 3,547,885.

Typically, resins prepared from the reaction of epoxides with phenols or thiophenols have more diverse utilities than those prepared from carboxylic acids or anhydrides.

Process for Reacting Epoxide and Phenol:

The reaction conditions employed in the process may be varied. Generally, however, convenient rates of reaction are obtained at reaction temperatures in the range of from 50°C to 300°C and reaction pressures ranging from about subatmospheric (0.1 millimeter Hg or 13 Pa) to about 150 psig (1034 kPa).

The ratio of the epoxide to the phenol, thiophenol or carboxylic acid or anhydride reactants to be employed in the process may vary over a wide range depending upon the type of reactants and the type of product desired. For example, if a product terminated with a phenolic hydroxyl group is desired, one would employ an excess of the polyhydric phenol in the process.

The amount of the phosphorus-containing initiator employed in the process of this invention can likewise vary over a wide range, so long as an effective amount is present. The initiator is added in amounts of at least 0.01 percent, preferably from 0.1 percent to 10 percent, by weight of the other reactants.

The reaction may be conducted in the presence or absence of solvents or diluents, but is conveniently conducted in a liquid phase. In most cases, the reactants will be liquid or low melting solids and the reaction may be at least initially easily effected without the addition of solvents or diluents. As the advancement reaction proceeds and the average molecular weight of the product increases, the reaction mixture becomes progressively more viscous and may solidify. To maintain efficient blending of the reaction mixture, it may be necessary to add diluents, increase the temperature of the reaction mixture to the fusion point of the reactants or to utilize very efficient blending means. Suitable diluents are those organic compounds which are inert to the reactants and in the liquid phase at the reaction temperature, for example, ethylene glycol ethyl ether, xylene, toluene, and cyclohexane. The diluent is desirably substantially free of impurities which will decrease the activity of the catalyst, such as hydrogen peroxide or uncomplexed transition metal ions and moieties which react with phosphonium ylids, e.g., water, aldehydes and ketones.

If solvents are employed in the reaction and the resulting product is to be used for coating purposes, the solvent may be retained in the reaction mixture. Otherwise, the solvent can be removed by any suitable method such as distillation.

Desirably, substantially equivalent quantities of polyhydric phenol (or thiophenol) and polyepoxide reactants should be employed in the overall reaction (i.e., no more than about 2 percent excess of either reactant). As the reaction between the polyepoxide and the polyhydric phenol approaches completion, it is desirable, but not essential, to introduce sufficient tetrabromobisphenol A to react the vicinal epoxy groups completely and to increase molecular weight of the product in the manner taught in US 4,104,257.

Advancement Reaction Products:

The products obtained by reacting a polyepoxide with a phenol in the presence of the described initiators are phenolic hydroxy ether compounds. Their physical characteristics will depend upon the

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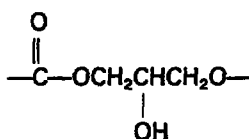
reactants and proportions employed. In general, the products will vary from liquids to solids, and in the case of the high molecular weight resins will vary from viscous liquids to hard solids. The products will possess an aliphatic OH group formed by each reaction of an epoxide and a phenolic OH group, and can be further reacted through this group if desired. The polyfunctional reactants will also give products terminated in phenolic OH groups and/or epoxy groups, and these will be available for further reaction. For example, if the initiator bears more than two aromatic hydroxy groups, the product will have branched or cross-linked structure.

The control of the equivalent ratio of the polyepoxides and polyhydric phenols during the advancement reaction permits the preparation of a variety of products. Those products which use an excess of the polyepoxide in their preparation will be terminated in epoxy groups and can be used as polyepoxides in known reactions of polyepoxides with curing agents. The high molecular weight polyepoxides are particularly useful in preparing surface coatings, adhesives, laminates, filament windings, coatings for highways and airfields, structural applications, and formations of foams. Those prepared from the halogenated polyhydric phenols or containing a large weight percentage of phosphorus moieties are particularly useful as flame-proofing resins for forming laminates coatings.

If the advanced resins are prepared under essentially anhydrous conditions (eliminating essentially all water from the reactants) and at temperatures less than 170°C, the phosphorus moieties though polymer-bound retain catalytic activity. The reaction conditions are further described in US 4,438,254. These resins exhibit accelerated curing with amines and anhydrides.

Resins prepared at higher temperatures or in the presence of water will generally contain phosphorus moieties present as polymer-bound tertiary phosphine oxides or phosphonium cations. These moieties exhibit little catalytic activity but improve ignition retardance of the resin.

The reaction products terminated in epoxy groups can also be used to prepare vinyl ester resins. Vinyl ester resins are described in U.S. 3,367,992 wherein dicarboxylic acid half esters of hydroxyalkyl acrylates or methacrylates are reacted with polyepoxide resins. US 3,066,112 and 3,179,623 describes the preparation of vinyl ester resins from unsaturated monocarboxylic acids such as acrylic and methacrylic acid. Vinyl ester resins based on epoxy novolac resins are described in US 3,301,743. US 3,256,226 describe also vinyl ester resins wherein the molecular weight of the polyepoxide is increased by reacting a dicarboxylic acid with the polyepoxide resin as well as acrylic acid. Other difunctional compounds containing a group which is reactive with an epoxide groups, such as an amine, mercaptan, may be utilized in place of the dicarboxylic acid. All of the above-described resins, which contain the characteristic linkages



and terminal, polymerizable vinylidene groups, are classified as vinyl ester resins.

The unsaturated monocarboxylic acids which can be reacted with a polyepoxide in the presence of the described catalysts to prepare a vinyl ester resin include, for example, acrylic acid, methacrylic acid, halogenated acrylic acid or methacrylic acid, cinnamic acid and mixtures thereof, and hydroxyalkyl acrylate or methacrylate half esters of dicarboxylic acids as described in US 3,367,992, wherein the hydroxyalkyl group preferably has from 2 to 6 carbon atoms.

The products prepared by the reaction of epoxides with thiophenols are generally similar in properties and utilities to those prepared from phenols.

Typically, the thiophenol-derived resins exhibit higher molecular weights than their phenolic counterparts.

The following examples are illustrative of the subject invention and are not to be construed as limiting the scope thereof. All parts and percentages are by weight unless otherwise indicated. For the purposes of these examples, the theoretical epoxide content has been calculated neglecting the reaction of the initiator as a phenolic reactant. The inclusion of the initiator as a phenolic reactant in these calculations would increase the theoretical epoxide content slightly, typically about 0.1 percent (e.g., 8.1% instead of 8.0%).

Examples 1 to 4

Preparation of tri(p-hydroxyphenyl)phosphine, the hydrobromide thereof, and tri(p-hydroxyphenyl)-methylphosphonium iodide.

Magnesium turnings (9.72 gram (g), 0.4 mole) were placed on a 1-liter, 3-neck, round-bottom flask equipped with a condenser and drying tube (CaCl₂), addition funnel, magnetic stirrer, and N₂ bubbler. The assembly was flame-dried using a Bunsen burner with a constant stream of dry N₂ passing through the vessel. Upon cooling to room temperature, 200 ml absolute ether was added, followed by dropwise addition of p-bromoanisole (74.8 g, 0.4 mole) over 30 minutes. When the reaction began to effervesce, it was partially cooled in a salt/ice bath. After 2 hours only traces of magnesium remained and the solution was cooled to -10°C. Phosphorus trichloride (18.3 g, 0.13 mole) in 70 ml ether was then added over 2 hours. The solution was allowed to warm to room temperature overnight, diluted with 300 ml dry toluene.

and the ether distilled off. This solution was cooled to 0°C and NH₄Cl (25 g in 100 ml H₂O) was added. After 2 hours the toluene layer was separated, dried over MgSO₅, filtered, and solvent removed on a rotary evaporator leaving an oil that quickly solidified. Recrystallization from absolute ethanol gave 19 g (47%) white rosettes which were confirmed by conventional analytical techniques to be tri(p-methoxyphenyl)phosphine (m.p. 126-128°C). NMR (CD₃OD); δ (ppm, TMS) 3.60 (s, 3H, CH₃), 6.9-7.6 (m, 4H, aromatic).

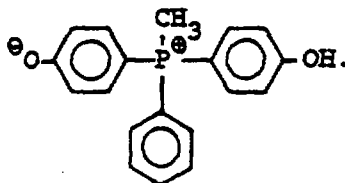
To 30 ml 48% HBr in a 50 ml round bottom flask was added 1 gram (0.0033 mole) of tri(p-methoxyphenyl)-phosphine. The homogenous solution was heated to reflux (124°C) under a stream of N₂ (to remove CH₃Br) and within 40 minutes a white precipitate formed. After 2 hours reflux, the mixture was filtered, washed with water, and vacuum dried to give 1.11 g (98%) tri(p-hydroxyphenyl)phosphine hydrobromide.

This hydrobromide salt was stirred in 10 ml 3% NaOH for 1 hour at room temperature. Dry ice (CO₂) was added to neutralize excess NaOH and a precipitate quickly formed. This mixture was extracted with 3 × 50 ml absolute ether, dried over MgSO₅, filtered and ether was removed on a rotary evaporator leaving 0.88 g of tri(p-hydroxyphenyl)phosphine (86%), (m.p. 128-133°C). NMR (CD₃OD); δ (ppm, TMS) 6.9-7.6 (m, aromatic).

Tri(p-hydroxyphenyl)phosphine (4 g, 1.29 millimole (mmole)) was stirred in 150 ml absolute ether at room temperature in a 250 ml round-bottom flask. Methyl iodide (2.75 g, 19.4 mmol, 1.21 ml) was added, and the solution stirred overnight. A test for unreacted phosphine in the ether solution (maleic anhydride in acetone) was negative, and the product was filtered off as a white precipitate and vacuum dried at room temperature overnight giving 5.76 g of tri(p-hydroxyphenyl)methylphosphonium iodide (98.8% yield). NMR (CD₃OD); δ (ppm, TMS) 2.80 (d, 3H, CH₃), 6.82-7.52 (m, 12H, arom.).

In a similar manner methyl di(p-hydroxyphenyl)phenyl phosphonium iodide was prepared using phenyldichlorophosphine in place of phosphorus trichloride.

The solid methyl di(p-hydroxyphenyl)phenyl phosphonium iodide was added to excess 1.0 Normal aqueous NaOH and stirred for 15 minutes at 25°C. Solid dry ice was added slowly to precipitate a white solid. This solid was determined by proton magnetic resonance and other conventional techniques to correspond to the formula



In a similar manner methyl(p-hydroxyphenyl)diphenyl phosphonium iodide was prepared using diphenylchlorophosphine in place of phosphorus trichloride.

Tri(p-hydroxyphenyl)phosphine hydrobromide, methyl di(p-hydroxyphenyl)phenyl phosphonium iodide and methyl(p-hydroxyphenyl)diphenyl phosphonium iodide were used to promote the reaction of bisphenol A and a commercial epoxy resin prepared from bisphenol A and epichlorohydrin and having an epoxy equivalent weight between 177 and 188. This epoxy resin is sold by the Dow Chemical Company under the trademark of D.E.R. 330®. To a flask equipped with a stirrer, thermometer, heating mantle and nitrogen purge line was charged 224.2 grams of D.E.R. 330® epoxy resin and 75.8 grams of bisphenol A. The mixture was heated with stirring to 50°C and then 0.3 or 3.0 grams of each initiator in 20 milliliters (ml) of methanol were added in separate runs.

The resulting reaction mixtures were heated rapidly to 150°C at which point heating was discontinued and the reaction allowed to exotherm. After the exotherm had subsided to 160°C, this temperature was maintained for an additional three hours. The products were poured into trays and allowed to cool. The product from the tri(p-hydroxyphenyl)phosphine hydrobromide was very viscous at 160°C, while the other products were free-flowing liquids.

The solid resins were analyzed via conventional methods to determine the final epoxide content. The theoretical epoxide content in each case was 8 percent. A 150-gram sample of each resin was refluxed in methanol overnight in a Soxhlet extractor. The extract was concentrated, dissolved in ethylene glycol ethyl ether to prepare a 50 percent solution and analyzed by phosphorus-31 nuclear magnetic resonance to determine what percentage of the phosphorus present in the resin had been extracted. The results of these experiments are tabulated in Table I:

TABLE I

Example	Initiator (%)	Peak Exotherm (°C)	Observed % Epoxide	Phosphorus Compounds in Extract (% Initial P)
1	$(\text{HO}-\text{C}_6\text{H}_4)_3\text{P HBr (1.0\%)}$	191	5.90	None Observed
2	$(\text{HO}-\text{C}_6\text{H}_4)_2\text{P}^{\ominus}(\text{Phenyl})\text{I}^{\ominus} \text{ (1.0\%)}$ CH_3	182	6.30	" "
3	" (0.1%)	230	8.13	" "
4	$\text{HO}-\text{C}_6\text{H}_4-\text{P}^{\oplus}(\text{Phenyl})_2\text{I}^{\ominus} \text{ (1.0\%)}$ CH_3	205	6.93	" "

The data presented in Table I indicates that all of these initiators effectively promote reaction of epoxides and phenolic hydroxyls. The phosphorus-containing residue from the initiators was not extractable.

Comparative Experiments A, B and C

In a series of comparative experiments, conventional epoxy advancement catalysts were used in place of the initiators in reactions and tests otherwise similar to Examples 1 through 4. The catalysts were all employed at a loading of 1 weight percent based on the reactants. The catalysts included triphenylphosphine hydrobromide, ethyltriphenylphosphonium iodide and ethyltriphenylphosphonium acetate. The results of these experiments are compiled in Table II:

TABLE II

Comp. Exp.	Catalyst	Peak Exotherm (°C)	Observed % Epoxide	Phosphorus Compounds in Extract (% Initial P)
A	$(\text{Phenyl})_3\text{P HBr}$	195	7.60	$(\text{Phenyl})_3\text{P=O (100\%)}$
B	$(\text{C}_2\text{H}_5)_3\text{P}^{\oplus}-(\text{Phenyl})_3$ $\text{HC}_3\text{CO}_2^{\ominus} \text{H}_3\text{CCO}_2\text{H}$	185	7.76	$\text{C}_2\text{H}_5-\text{P}^{\oplus}(\text{Phenyl})_2 \text{ (100\%)}$ O
C	$(\text{CH}_2\text{H}_5)_3\text{P}^{\oplus}-(\text{Phenyl})_3 \text{I}^{\ominus}$	179	7.17	$\text{C}_2\text{H}_5-\text{P}^{\oplus}(\text{Phenyl})_2 \text{ (9.2\%);}$ O $(\text{Phenyl})_3\text{P=O (84.8\%)}$

It is apparent that phosphorus-containing compositions derived from conventional catalysts can be extracted from epoxy resins made using these catalysts.

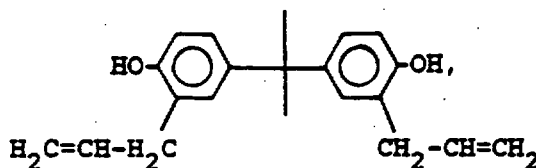
Example 5

To a reaction vessel were charged D.E.R. 330[®] epoxy resin and di-mercaptophenyl ether in a ratio which in theory should produce an advanced resin having 3.0 percent epoxide. To this mixture was added a phenyl di(p-hydroxyphenyl)phosphine initiator in a ratio of 0.5 parts per hundred resin (phr). The advancement reaction was then conducted in the general manner of Example 4.

The resulting resin was determined to contain 2.90 percent epoxide. No phosphorus compounds were extracted from the resin in refluxing methanol.

Example 6

To a reaction vessel were charged D.E.R. 330® epoxy resin and di (—3,3'-allyl-4,4'-hydroxyphenyl)isopropylidene, i.e.,



in a ratio which in theory should produce an advanced resin having 8.0 percent epoxide. To this mixture was added the same initiator as in Example 9 in a ratio of 0.2 part phr. The advancement reaction was conducted in the general manner of Examples 1 to 4.

The resulting resin was determined to contain 7.88 percent epoxide. No phosphorus compounds were extracted from the resin in refluxing methanol.

Example 7

To a reaction vessel were charged the same epoxy resin and dihydric phenol as in Example 9 in a ratio which in theory should produce an advanced resin containing 1.0 percent epoxide. To this mixture was added methyl di(p-hydroxyphenyl)phenyl phosphonium acetate in a ratio of 0.4 part phr. The advancement reaction was conducted in the general manner of Example 4.

The resulting resin was determined to contain 1.22 percent epoxide. No phosphorus compounds were extracted from the resin in refluxing methanol.

Examples 8-17

A series of reactions were conducted in which various polyepoxides and dihydric phenols or thiophenols were reacted in the presence of various initiators in accordance with the general procedure of Example 4. The epoxide content of the resulting resin was determined as well as the percentage of phosphorus which could not be extracted by refluxing methanol. The reactants, initiators, percent epoxide and other parameters or results are tabulated in Table III.

TABLE III

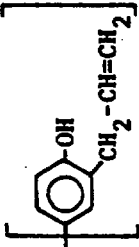
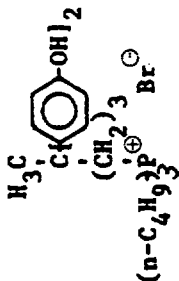
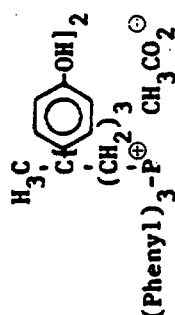
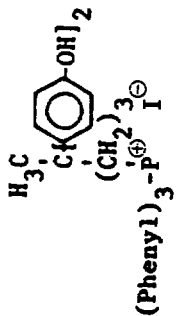
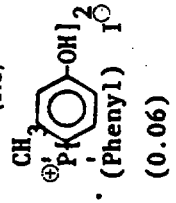
Example	Epoxide	Phenol	Initiator (phr)	% Epoxide Theoretical	Observed	% Phosphorus Not Extracted
8	D.E.R. 330®		 (0.6)	8.0	7.94	90%
9	"	"	 (0.35)	4.0	3.97	65%
10	D.E.R. 330®	Bisphenol A	 (0.35)	8.0	7.95	70%
11	"		"	1.0	1.31	70%
12	"	Bisphenol A	 (0.06)	1.0	1.4	100%

TABLE III (Continued)

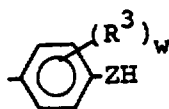
Example	Epoxide	Phenol	Initiator (phr)	% Epoxide Theoretical	Observed	% Phosphorus Not Extracted
13				6.0	5.82	70%
14	"	"		6.0	5.97	60%
15		Bisphenol A	Same as in Ex. 14	N.D.	N.D.	N.D.
16	"		"	"	"	"
17	D.E.R. 330®	Bisphenol A		8.0	7.7	100

® — Trademark of The Dow Chemical Company
N.D. — Not Determined.



Claims

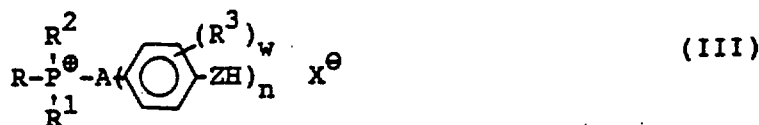
1. A process for reacting at an elevated temperature (a) an epoxy resin or thioepoxide bearing an average of more than one vicinal epoxide or thioepoxide group per molecule with (b) a polyhydric phenol, a polyhydric thiophenol, a carboxylic acid or a carboxylic acid anhydride, characterized by conducting the reaction in the presence of at least 0.01% by weight of the other reactants of (c) a trihydrocarbyl phosphine or quaternary phosphonium cation which bear on the average per molecule more than one moiety corresponding to the formula



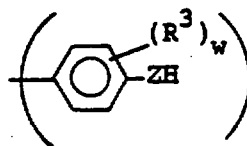
wherein Z is —O— or —S—, R^3 at each occurrence is independently a moiety essentially inert in this process and w is an integer from 0 to 4, so as to promote the reaction of (a) with (b) and (c).

2. The process of Claim 1 characterized in that less than 25 weight percent of (c) or derivatives thereof based on the quantity (c) present initially can be extracted in refluxing methanol in 12 hours or water from the resulting resin.

3. The process of Claim 1 characterised in that (c) corresponds to one of the formulae I, II, III:



wherein R and R^2 are each independently

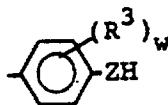


or monovalent hydrocarbon radicals, X^- is a compatible anion, R^1 is a monovalent hydrocarbon radical optionally including chlorine, bromine, phosphine, phosphonium, phenyl and thiophenyl moieties, Z at each occurrence is independently —O— or —S— at each occurrence and A is a hydrocarbon radical bearing valences on one or more carbon atoms equal in total to (n+1), where n is an integer 1, 2, or 3.

Patentansprüche

1. Verfahren des Umsetzens bei erhöhter Temperatur von (a) eines Epoxiharzes oder Thioepoxids, das im Mittel mehr als eine benachbarte Epoxi- oder Thioepoxigruppe pro Molekül aufweist, mit (b) einem mehrwertigen Phenol, einem mehrwertigen Thiophenol, einer Carbonsäure oder einem Carbonsäureanhydrid, dadurch gekennzeichnet, daß die Reaktion in Gegenwart von mindestens 0,01 Gew.% weiterer Reaktanten

(c) eines Trihydrocarbylphosphins oder quaternären Phosphonium kations, das im Mittel mehr als eine Gruppe der Formel



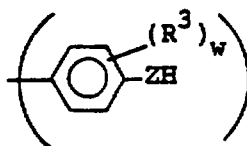
in der Z—O— oder —S—, R³ bei jedem Auftreten unabhängig voneinander eine in diesem Verfahren inerte Gruppe ist und w eine ganze Zahl von 0 bis 4 ist, pro Molekül aufweist, ausgeführt wird, um die Reaktion von (a) mit (b) und (c) zu fördern.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man aus dem entstehenden Harz durch zwölfstündiges Kochen am Rückfluß mit Methanol oder mit Wasser weniger als 25 Gew. % von (c) oder darauf basierenden Derivaten bezogen auf die Anfangsmenge von (c) extrahieren kann.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß (c) die Formeln I, II, III aufweist:



in denen R und R² jeweils unabhängig voneinander

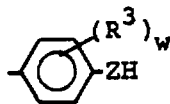


oder ein einwertiger Kohlenwasserstoffrest ist, X[⊖] ist ein verträgliches Anion, R¹ ist ein einwertiger Kohlenwasserstoffrest, der gegebenenfalls Chlor, Brom, Phosphin, Phosphonium, Phenyl und Thiophenylgruppen aufweisen kann, Z ist bei jedem Auftreten unabhängig voneinander —O— oder —S— und A ist ein Kohlenwasserstoffrest, der an einem oder mehreren Kohlenstoffatomen Wertigkeiten aufweist, die insgesamt gleich (n+1) sind, wobei n eine ganze Zahl von 1, 2 oder 3 ist.

Revendications

1. Procédé pour faire réagir à chaud (a) une résine époxy ou un thioépoxyde portant une moyenne de plus d'un groupe époxyde ou thioépoxyde vicinal par molécule avec (b) un polyphénol, un thiophénol polyhydrique, un acide carboxylique ou un anhydride d'acide carboxylique, caractérisé par le fait qu'on effectue la réaction en présence d'au moins 0,01% en poids d'autres réactifs, à savoir

(c) une trihydrocarbylphosphine ou un cation phosphonium quaternaire qui porte en moyenne, par molécule, plus d'un motif répondant à la formule



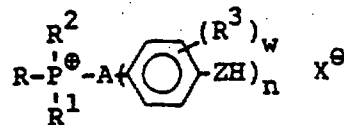
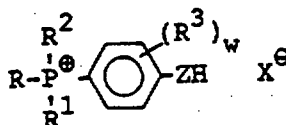
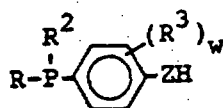
dans laquelle Z est —O— ou —S—, R³ est dans chaque cas, indépendamment, un motif pratiquement inerte dans ce procédé et w est un entier de 0 à 4, de manière à favoriser la réaction de (a) avec (b) et (c).

2. Procédé de la revendication 1, caractérisé par le fait que moins de 25% en poids de (c) ou de dérivés de celui-ci par rapport à la quantité de (c) initialement présente peuvent être extraits dans du méthanol au reflux en 12 heures, ou dans de l'eau, hors de la résine obtenue.

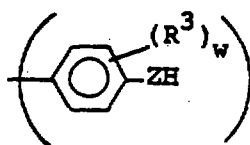
3. Procédé de la revendication 1, caractérisé par le fait que (c) répondant à l'une des formules I, II, III:



(21)



dans lesquelles R et R² sont chacun indépendamment:



ou des radicaux hydrocarbonés monovalents, X[⊖] est un anion compatible, R¹ est un radical hydrocarboné monovalent comprenant éventuellement du chlore, du brome, des motifs phosphine, phosphonium, phényle et thiophényle, Z est dans chaque cas indépendamment —O— ou —S— et A est un radical hydrocarboné portant des valences sur un ou plusieurs atomes de carbone dont le nombre total est égal à (n+1), où n est un entier égal à 1, 2 ou 3.

