

Description

Epoxy resins have heretofore been advanced in the presence of phosphonium catalysts disclosed by Dante in U.S. 3,477,990 and Perry in Canadian 893,191 and U.S. 3,948,855. However, the quantities of catalyst employed were that which would provide a resin having a percent epoxide value sufficiently close to the theoretical epoxide value that no improvement in properties were envisioned.

The process of the present invention provides for the production of advanced epoxy resins having an improvement in one or more properties such as, for example, reactivity or glass transition temperature of the cured resins. Resins having faster reactivity characteristics provide for increased productivity of articles produced therefrom over a unit time period. The increase in glass transition temperature of a cured resin permits articles prepared therefrom to be employed in higher temperature environments. Cured epoxy resins having increased glass transition temperatures provide products which can be employed in environments of higher temperatures i.e., the useful operating temperature is generally directly proportional to the glass transition temperature.

The present invention pertains to a process for producing an epoxy resin advanced in molecular weight by reacting at a temperature from 100 to 200°C (A) an epoxy resin which is a glycidyl ether of a dihydric phenol having an average of more than one glycidyl ether group per molecule with (B) a dihydric phenolic compound in the presence of (C) a phosphonium salt or complex thereof which has at least one aromatic ring attached to the phosphorous atom of the phosphonium group and at least one aliphatic hydrocarbon group attached to said phosphorous atom, employing components (A) and (B) in quantities such that the phenolic hydroxyl to epoxide equivalent ratio is that which will provide a theoretical percent epoxide of the resultant reaction product of from 7 to 12.5, wherein the catalyst component (C) is used in a quantity of 0.2 to 1.5 parts by weight per 100 parts by weight of the epoxy resin (A) to produce an advanced epoxy resin and wherein the difference obtained by subtracting the percent epoxide obtained by analysis from the theoretical percent epoxide is from 1 to 4, preferably from 1 to 2.

An epoxy resin produced by the process of this invention when cured provides the composition which has an improvement in glass transition temperature and/or increased reactivity.

The present invention also pertains to a process for preparing resin impregnated substrates for use in preparing electrical laminates by a process which comprises:

(i) saturating said substrate with a resin forming mixture comprising:

(A) an epoxy resin having an epoxide equivalent weight of from 300 to 600, preferably from 375 to 475 which has been prepared by reacting

(1) a glycidyl ether of a dihydric phenol having an average of more than one epoxide group per molecule and an epoxide equivalent weight (EEW) of from 156 to 400, preferably from 177 to 190, with

(2) a dihydric phenolic compound in the presence of

(3) a phosphonium catalyst for effecting the reaction between (1) and (2), wherein components (1) and (2) are employed in quantities which will provide a theoretical percent epoxide of the reaction product of from 8 to 15, preferably from 9.5 to 13;

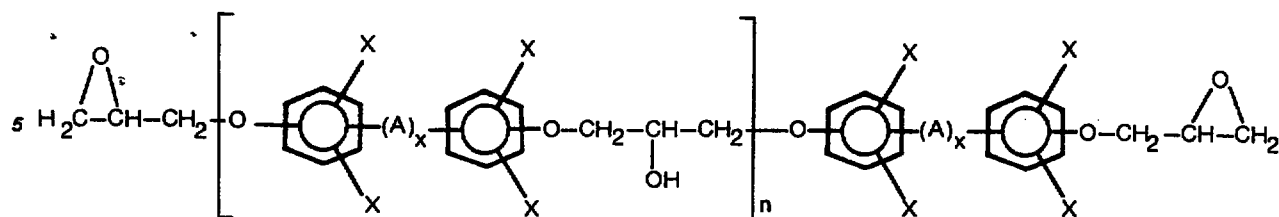
(B) a curing agent for said epoxy resin and

(C) a solvent system for Components A and B;

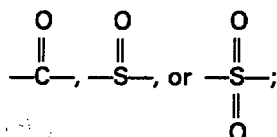
(ii) heating the resultant impregnated substrate to B-stage of the resin and removing the solvent system; characterized by employing as the catalyst, Component (A—3), a phosphonium salt or complex thereof which has at least one, preferably two, most preferably three aromatic ring(s) attached to the phosphorus atom of the phosphonium group and at least one aliphatic hydrocarbon group attached to said phosphorus atom, wherein said catalyst is employed in a quantity of 0.2 to 0.5 parts by weight of the epoxy resin to produce an advanced epoxy resin and wherein the difference obtained by subtracting the percent epoxide obtained by analysis from the theoretical percent epoxide is from 1 to 4, preferably from 1 to 2.

GB—A—1 494 971 describes inter alia the reaction of an epoxy resin with a polyhydric phenol in the presence of a phosphonium type catalyst. A broad range of from 0.001 to 10, preferably 0.05 to 5 percent by weight, based on the combined weight of the other components is suggested in the description of this patent, whereas the examples show only catalyst levels of from 0.041 to 0.20 per cent based on the combined other reactants. Example 11 uses mixtures of a diglycidyl ether of bisphenol A and of bisphenol B and a phosphonium catalyst in an amount of 0.20 percent by weight, based on the combined weights of reactants, corresponding to 0.265 parts of catalyst per 100 parts of starting epoxy resin. The difference between theoretical and actual percent epoxide is 0.59 for this example.

Suitable glycidyl ethers of a dihydric phenol which can be employed in the present invention include those represented by the formula



10 wherein A is a divalent hydrocarbon group having from 1 to 8 carbon atoms, ---S--- , ---S---S--- , ---O--- ,

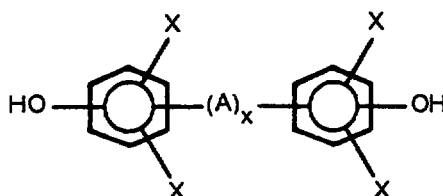


each X is independently hydrogen, chlorine or bromine;

x has a value of zero or one and n has a value such that the EEW is from 156 to 400, preferably from 177 to 190, calculated on the basis of X being hydrogen.

Particularly suitable are the diglycidyl ethers of bisphenol A and tetrabromobisphenol A.

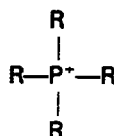
Suitable dihydric phenolic compounds include, for example, catechol, hydroquinone, resorcinol and bisphenols such as those represented by the formula



wherein X, A and x are defined above.

Particularly suitable dihydric phenolic compounds are bisphenol A and tetrabromobisphenol A.

Suitable phosphonium catalysts which can be employed herein include, for example, those compounds having at least one phosphonium cation group represented by the formula



wherein each R is independently a hydrocarbyl or substituted hydrocarbyl group having from 1 to 20, preferably from 1 to 6, carbon atoms or substituted hydrocarbyl groups. At least one, preferably two and most preferably three of the R groups are an aromatic group i.e., an aryl group or an alkaryl group such that the phosphorus atom is attached directly to the aromatic ring of such aryl or alkaryl group.

By the term hydrocarbyl, it is meant that the groups can be alkyl, aryl, alkaryl and the alkyl can be either cyclic or acyclic. By substituted hydrocarbyl it is meant that the hydrocarbyl groups can contain one or more inert substituent groups such as, for example, Cl, Br, I, NO_2 , or mixtures thereof.

The R groups can contain any substituent group which is inert to the system, i.e. will not deactivate the catalyst under the conditions in which they are employed.

Suitable anions include the halides, such as for example, Cl, Br, I, carboxylates, dicarboxylates, phosphates, nitrates, sulfates, nitrites, sulfites, borates, chromates, or mixtures thereof.

The preferred anions are the strong acids, i.e. those having a pK_a value less than 4.5, preferably less than 3.7, because the catalysts containing such are generally more efficient, in that it takes less catalyst to effect the lowering of the epoxide value to the desired value below the theoretical value.

The dihydric phenol and the glycidyl ether of a dihydric phenol are employed in quantities such that the theoretical percent epoxide of the resultant product is from 7 to 12.5.

The quantity of catalyst varies depending upon the particular catalyst employed from 0.1 to 1.5, preferably from 0.2 to 0.8, parts catalyst by weight per 100 parts by weight of glycidyl ether of dihydric phenol.

The reaction conditions employed to prepare the advanced epoxy resins can vary, but temperatures of from 100°C to 200°C , preferably from 120°C to 160°C , are used. Lower temperatures usually require longer reaction times whereas higher temperatures usually require shorter reaction times.

The pressure employed is not particularly important and can be from 1 mm Hg vacuum (0.13 kPa) to

100 psig (791 kPa). However, it is usually preferred to employ pressures of from 5 psig (136 kPa) to 20 psig (239 kPa).

Within the stated limits the particular reaction conditions are not important so long as for the particular phosphonium catalyst and quantity thereof employed, the reaction conditions produce the desired result i.e., the resultant advanced epoxy resin has the required difference between the theoretical percent epoxide and the actual percent epoxide value obtained by analysis.

Any of the well known curing agents can be employed to cure the advanced epoxy resins obtained by the process of the invention.

Such curing agents include amines, amides, guanidines, phenolic hydroxyl-containing materials, carboxylic acids, carboxylic acid anhydrides, imidazoles, biguanides, or mixtures thereof.

Particularly suitable curing agents include, for example, guanidines such as for example, dicyandiamide and tetramethyl guanidine and biguanides such as 1,6-xylylene biguanide, polyhydric phenols, or mixtures thereof.

The quantity of curing agent employed depends upon the particular curing agent employed and the properties desired in the resultant cured resin, all of which is well known by those persons reasonably skilled in the art and discussed in *HANDBOOK OF EPOXY RESINS*, by Lee and Neville, McGraw Hill, 1967.

The theoretical percent epoxide is calculated by the following formula:

$$\text{THEORETICAL \% EPOXIDE} = \frac{4300 (\text{EqER} - \text{EqDHP})}{\text{WtER} + \text{WtDHP}}$$

EqER = epoxide equivalents from the epoxy resin.

EqDHP = phenolic hydroxyl equivalents from the dihydric phenol.

WtER = weight of epoxy resin employed.

WtDHP = weight of dihydric phenol employed.

The actual percent epoxide was determined experimentally by titration with perchloric acid in glacial acetic acid by the liberation of hydrogen bromide generated by the addition of tetraethylammonium bromide in glacial acetic acid using crystal violet as an indicator. The epoxy groups react stoichiometrically with hydrogen bromide generated from the reaction of perchloric acid with tetraethyl ammonium bromide. When the epoxy groups have been reacted, the free hydrogen bromide causes the crystal violet to change color.

The glass transition temperature, T_g, was determined by the method of ASTM D3418-75 on cured specimens prepared in the following manner. A mixture of 10 grams of the resultant epoxy resin, 0.3 gram of dicyandiamide and 0.01 gram of 2-methyl imidazole was melt mixed on a 100°C hot plate for 3 minutes. The mixture was finely ground in a mortar and pestle. The powder was transferred to an aluminium weighing dish and cured at 715°C for 2 hours.

The stroke cure reactivity was determined by the following procedure.

An acetone solution of epoxy resin is prepared by blending 10 grams of acetone with 30 grams of molten epoxy resin warmed to between 80°C and 100°C. The solution is allowed to cool at room temperature and then 9 grams of a 10 percent solution of dicyandiamide in the monomethylether of ethylene glycol and 0.75 gram of a 10 percent solution of benzyldiamethylamine (BDMA) in acetone is added (3 phr dicyandiamide, 0.25 phr BDMA). The solution is mixed well and allowed to stand at room temperature for a period of 2 hours. The catalyzed resin is then drawn in an eye dropper and placed on a hotplate at 175°C ± 1°C. The stop watch is immediately started. The sample is allowed to rest on the hot plate undisturbed for 60 ± 1 seconds. At this point, begin stroking with a wooden spatula. Stroking should be done by pushing the resin puddle back and forth over an area about 1 square inch using the same side of the spatula in contact with the resin. The resin will thicken as it is continuously stroked. Eventually the resin will become stringy and immediately after, becomes a rubber gel that releases from the hotplate. This is the end point. Stop the stopwatch and record the reading. The fewer the number of seconds, the higher the reactivity.

The following examples are illustrative of the present invention, but are not to be construed as to limiting the scope thereof in any manner.

Various catalysts employed in the examples and comparative experiments were prepared by the following procedures.

Catalyst Procedure A

To a single necked 100 ml round bottom flask (RBF) was charged the particular phosphonium catalyst precursor as a 70 percent solution in methanol. The particular acid employed was dissolved in methanol and charged to the RBF. The solvents and excess acid were removed under vacuum while heating to a final temperature of 75°C at 1 mm Hg (0.13 kPa). The resultant liquor was acetone washed thereby yielding a white solid phosphonium salt of the acid employed.

Catalyst Procedure B

To a 500 ml single neck RBF was charged the particular precursor as a 70 percent solution in methanol. The particular acid employed was slowly added to the solution while swirling the flask. The solvent and excess acid were removed under vacuum while heating to a final temperature of 120°C at 1 mm Hg (0.13 kPa). The resultant product was acetone washed thereby yielding the phosphonium salt of the acid employed.

Catalyst Procedure C

To a single neck 500 ml RBF was charged the phosphonium bicarbonate precursor in methanol. The particular acid employed was dissolved in methanol in a beaker and then slowly added to the RBF while swirling the RBF. Swirling was maintained until CO₂ evolution subsided. The solution was then rotoevaporated until a vacuum could be maintained at 1 mm Hg (0.13 kPa) at 75°C. The resultant liquor was washed twice with acetone to remove excess acid impurities to yield a white solid phosphonium salt of the acid.

Catalyst Procedure D

To a 2.54 cm diameter glass column equipped with a stopcock was charged a methanol slurry of 65 g (70 percent by weight H₂O) of an anion exchange resin in the acetate form (200—400 mesh; 0.8 meq. per ml resin bed; 3.5 meq. per dry gram; 70 to 78 wt. percent moisture; styrene type quaternary ammonium; wet mesh range 80—200) available from BIO-RAD Laboratories as AG1—X2. A 5 percent solution in methanol of potassium hydroxide was slowly eluted through the column at a rate of 2 drops per second. The column was then washed with methanol until neutral to litmus paper. The phosphonium catalyst precursor, as a 70 percent solution in methanol, was then added to the column and slowly eluted through the ion exchange resin until the dark band was washed through the column. The eluted material was caught in a RBF containing an excess molar ratio of the acid. This solution was then rotoevaporated and acetone washed to yield a white solid phosphonium salt of the acid.

Catalyst Procedure E

To a 4 oz (0.12 liter) bottle was charged 100 g (0.17 mol) of a 70 percent methanol solution of ethyltriphenylphosphonium acetate-acetic acid complex followed by the addition of 20.44 g (0.1622 mol) of oxalic acid dihydrate. The mixture was mixed until all of the oxalic acid had dissolved. The resultant solution contained about 51.14 wt. percent ethyltriphenylphosphonium oxalate.

Catalyst Procedure F

To a 2 gallon (7.6 liter) bottle was charged 1000 g (1.707 mol) of a 70 percent methanol solution of ethyltriphenylphosphonium acetate-acetic acid complex followed by the addition of 204.4 g (1.622 mol) of oxalic acid dihydrate. The mixture was mixed until all the oxalic acid had dissolved and then 31.5 g of methanol was added to give a resultant solution of 50 wt. percent ethyltriphenylphosphonium oxalate.

The precursors and acids employed, reaction conditions and results are provided in the following Table I for which the abbreviations employed therein have the following meaning.

BTPP = butyltriphenylphosphonium

ClAc = chloroacetate

ETPP = ethyltriphenylphosphonium

ETPPAc·HAc = ethyltriphenylphosphonium acetate acetic acid complex

HCO₃ = bicarbonate

TABLE I

No.	CATALYST	PROCEDURE	ACID EMPLOYED		PRECURSOR EMPLOYED	
			TYPE	g/moles	TYPE	g/moles
						pKa
1	BTPP FORMATE	C	Formic	2.73/0.06	BTPPHCO ₃	13.2/0.035
2	ETPP FORMATE	C	Formic	2.73/0.06	ETPPHCO ₃	13.2/0.035
3	ETPP FORMATE	D	Formic	4.1/0.09	ETPPAC·HAC	3.5/0.009
4	BTPP OXALATE	C	Oxalic	2.47/0.027	BTPPHCO ₃	9.9/0.026
5	ETPP PHOSPHATE	B	Phosphoric	6.38/0.065	ETPPAC·HAC	26.7/0.0651
6	ETPP SUCCINATE	B	Succinic	14/0.119	ETPPAC·HAC	48.8 /0.119
7	ETPP MALONATE	B	Malonic	1:56/0.016	ETPPAC·HAC	5.88/0.014
8	ETPP OXALATE	A	Oxalic	1.94/0.015	ETPPAC·HAC	6.3/0.015
9	BTPPClAC	C	Chloro-acetic	2.84/0.03	BTPPHCO ₃	9.9/0.026
10	ETPP OXALATE	E	Oxalic	20.44/0.1622	ETPPAC·HAC	70/0.171
11	ETPPAC·HAC	Purchased from Cincinatti Milacron, Inc.			N.A.	N.A.
12	ETPP OXALATE	F	Oxalic	204.4/1.622	ETPPAC·HAC	700/1.71
						4.6

TABLE I (Continued)

No.	METHANOL SOLVENT (total Quant.) grams	REACTION TEMP. °C	MELTING POINT AND YIELD °C/%	COMMENTS
1	37	100	190/N.D. ¹	white solid
2	37	100	N.A. ² /N.D.	brown liquid
3	200	100	N.A./95	brown liquid
4	35	75	155/78	white solid
5	11	25	175-189/100	white solid
6	21	120	N.A./N.D.	brown liquid
7	40	120	N.A./N.D.	brown liquid
8	23	70	151/91	white solid
9	13	75	212-215/76	white solid
10	30	25	N.A./N.D.	mixture contains free acetic acid
11	N.A.	N.A.	N.A.	70% solution in methanol
12	81.6	25	N.A./N.D.	mixture contains free acetic acid

¹ N.D. = not determined² N.A. = not applicable

General Procedure for Resin Preparation

To a reaction vessel equipped with a means for stirring, temperature control and indication and nitrogen purge was charged the desired weight of the specified liquid diglycidyl ether of bisphenol A and the desired weight of the specified dihydric phenol. The mixture was heated at a rate of 5°C/minute. When the temperature of the mixture reached 70°C, the desired amount of the specified phosphonium catalyst dissolved in methanol was added. The mixture was heated at the desired reaction conditions to give the resultant product.

Epoxy Resin A

Epoxy Resin A was a liquid diglycidyl ether of bisphenol A having an average epoxide equivalent weight of 189, percent epoxide of 22.75 percent and aliphatic chloride content of 3410 ppm.

Epoxy Resin B

Epoxy Resin B was a liquid diglycidyl ether of bisphenol A having an average epoxide equivalent weight of 188, percent epoxide of 22.82 percent and an aliphatic chloride content of 3700 ppm.

Epoxy Resin C

Epoxy Resin C was a liquid diglycidyl ether of bisphenol-A having an average epoxide equivalent weight of 186.5, percent epoxide of 23.06 and an aliphatic chloride content of 2200 parts per million.

Dihydric phenol A

Dihydric phenol A was tetrabromobisphenol A having a phenolic hydroxyl equivalent weight of 272 and percent bromine content of 58.8 percent.

Dihydric phenol B

Dihydric phenol B was a bisphenol A having a phenol hydroxyl equivalent weight of 114.

Examples 1—21 and Comparative Experiments A—G

The components, reaction conditions and results are given in the following Table II.

TABLE II

EX. OR COMP. EXPT. NO.	EPOXY RESIN Type/Equiv.	DIHYDRIC PHENOL Type/Equiv.	CATALYST Type/moles	GRAMS PER 100 GRAMS EPOXY RESIN	REACTION CONDITIONS			
					1st Hour °C	2nd Hour °C	3rd Hour °C	4th Hour °C
A	A/1.244	A/0.422	No. 10/0.0002	0.032	120	130	150	150
B	A/1.164	A/0.333	No. 10/0.00022	0.038	120	130	150	150
C	A/11.64	A/3.33	No. 10/0.0087	0.150	120	130	150	150
D	A/11.64	A/3.33	No. 10/0.013	0.225	120	130	150	150
1	A/11.64	A/3.33	No. 10/0.0174	0.301	120	130	150	150
2	A/11.64	A/3.33	No. 10/0.0256	0.443	120	130	150	150
3	A/11.64	A/3.33	No. 10/0.0337	0.583	120	130	150	150
E	A/1.06	A/0.303	No. 11/0.00024	0.049	120	130	150	150
F	A/1.06	A/0.232	No. 11/0.00024	0.049	120	130	150	150
4	A/1.335	A/0.359	No. 11/0.00730	1.187	120	130	150	150
5	A/1.06	A/0.28	No. 8/0.0026	0.494	120	130	150	150
6	A/1.06	A/0.28	No. 11/0.0026	N.C.	120	130	150	150
			X ¹ /0.0026					

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TABLE II (Continued)

EX. OR COMP. EXPT. NO.	THEORY % EPOXIDE	ACTUAL % EPOXIDE	DIFF. IN % EPOXIDE	175°C STROKE CURE Sec.	Tg °C
A	10.1	10	0.1	289	103
B	11.5	11.48	0.02	320	109
C	11.5	10.97	0.53	310	117
D	11.5	10.76	0.74	305	121
1	11.5	10.1	1.4	280	128
2	11.5	10.05	1.45	268	131
3	11.5	9.09	2.41	255	127
E	11.5	11.5	0	340	110
F	12.00	12	0	325	114
4	12.00	10.21	1.79	269	127
5	12.00	10.3	1.7	N.D. ³	N.D.
6 ¹	12.00	10.2	1.8	N.D.	N.D.

TABLE II (Continued)

EX. OR COMP. EXPT. NO.	EPOXY RESIN Type/Equiv.	DIHYDRIC PHENOL Type/Equiv.	CATALYST Type/moles	GRAMS PER 100 GRAMS EPOXY RESIN	REACTION CONDITIONS			
					1st Hour °C	2nd Hour °C	3rd Hour °C	4th Hour °C
7	A/23.12	A/6.21	No. 6/0.12	N.C.	120	130	150	150
8	A/11.45	A/3.07	No. 5/0.0653	1.172	120	130	150	150
9	A/1.114	A/0.3	No. 9/0.00277	0.557	120	130	150	150
10	A/1.09	A/0.293	No. 7/0.0038	0.728	120	130	150	150
11	B/1.06	A/0.288	No. 1/0.0041	N.C.	150	150	150	150
12	B/1.06	A/0.285	No. 3/0.003	N.C.	120	130	150	150
13	B/1.06	A/0.285	No. 4/0.0026	N.C.	120	130	150	150
14	B/1.06	A/0.288	No. 2/0.0032	N.C.	150	150	150	150
15	A/22.14	B/7.94	No. 10/0.0664	0.604	120	130	150	150
G	A/1.04	B/0.29	No. 10/0.000097	0.018	150	150	N.A.*	N.A.
16	A/1.01	B/0.28	No. 10/0.00184	0.367	140	140	140	140
H	A/1.02	B/0.72	No. 10/0.000184	0.036	150	150	150	N.A.
17	A/1.58	B/1.12	No. 10/0.00288	0.357	155	155	155	155
J	A/1.01	B/0.83	No. 10/0.00028	0.056	150	150	150	150
18	A/1.01	B/0.83	No. 10/0.00185	0.368	195	195	195	195
19	C/88.36	A/25.64	No. 12/0.15	0.346	120	130	160	N.A.

TABLE II (Continued)

EX. OR COMP. EXPT. NO.	THEORY % EPOXIDE	ACTUAL % EPOXIDE	DIFF. IN % EPOXIDE	175°C STROKE CURE Sec.	Tg °C
7	12.00	9.8	2.2	N.D.	N.D.
8	12.00	10.65	1.35	N.D.	130
9	12.00	10.66	1.34	290	127
10	12.00	11.00	1	293	N.D.
11	11.89	8.6	3.29	N.D.	N.D.
12	12.00	10.00	2	N.D.	N.D.
13	12.00	9.8	2.2	N.D.	N.D.
14	11.89	10.2	1.69	N.D.	N.D.
15	12.00	9.8	2.2	205	130
G	14.00	13.99	0.01	274	N.D.
16	14.00	12.13	1.87	255	N.D.
H	4.65	4.39	0.26	300	N.D.
17	4.65	3.51	1.14	280	N.D.
J	2.70	2.46	0.24	255	N.D.
18	2.70	1.70	1	164	N.D.
19	11.50	10.00	1.50	N.D.	130

¹ Insitu preparation of catalyst (ETPP Oxalate) by adding the catalyst precursor (ETPPAc·HAc) plus acid (oxalic acid dihydrate designated X) to the mixture of epoxy resin and dihydric phenol.

² N.C. = not calculated

³ N.D. = not determined

⁴ N.A. = not applicable

Example 23 (Preparation of Electrical Laminate)

A. Preparation of Prepreg Varnish Formulation

A prepreg varnish formulation was prepared by blending 5411 g of a 75 per cent solution by weight in acetone of the resin of example #22 with 1225 g of a 10 percent solution of dicyandiamide in the monomethylether of ethylene glycol (~3 phr dicyandiamide), 6.13 g of benzyldiamethylamine (~0.15 phr BDMA) and 200 g acetone. The viscosity of the solution at 25°C was 25 seconds using a #2 Zahn cup. The 175°C stroke cure reactivity of the prepreg varnish was about 245 seconds.

B. Preparation of Laminate

Fiberglass cloth (type 7628 and 1399 finish) was impregnated by passing it through the prepreg varnish described in A above, followed by a pair of doctor bars set at 15 mils (0.38 mm) clearance to control resin pickup, and finally through an oven at 300°F (149°C) for a dwell time of approximately 4 minutes. The resulting B-staged impregnated cloth of prepreg had a gel time of 93 seconds at 175°C.

A laminate was then prepared from the above prepared preimpregnated fiberglass employing 6 plies of 12 in. × 12 in. × 0.13 in. (3 cm × 3 cm × .33 mm) sheets of 7628 style glass all of which were 1399 finish. The laminate was prepared by pressing at 500 psig (3549 kPa) for 60 minutes at 175°C. The laminate was then tested.

(28)

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The pressure cooker-solder test was conducted by

(i) cutting 2 in. × 4 in. (5 cm × 10 cm) coupons from prepared laminate,

(ii) placing 3 coupons edgewise on a rack in a pressure cooker and maintaining 15 psig (205 kPa) steam pressure for ~1.5 hour, and

5 (iii) then immersing the coupons in 500°F (260°C) solder for 20 seconds.

Six sides of the 3 coupons were evaluated and rated by the number of sides passing. In order to pass, the side must be free of blisters after immersion in hot solder. A 1/2 side pass consisted of the side having only 1 edge blister.

10 The laminate had a glass transition temperature (T_g) of 130°C. After subjecting to 15 psig (205 kPa) steam pressure for 1—1/2 hours and immersion in 500°F (260°C) solder for 20 seconds, 5—1/2 sides of the laminate out of six sides passed the test.

Claims

15 1. A process for producing an epoxy resin advanced in molecular weight by reacting at a temperature from 100 to 200°C (A) an epoxy resin which is a glycidyl ether of a dihydric phenol having an average of more than one glycidyl ether group per molecule with (B) a dihydric phenolic compound in the presence of (C) a phosphonium salt or complex thereof which has at least one aromatic ring attached to the phosphorus atom of the phosphonium group and at least one aliphatic hydrocarbon group attached to said phosphorus atom, employing components (A) and (B) in quantities such that the phenolic hydroxyl to epoxide equivalent ratio is that which will provide a theoretical percent epoxide of the resultant reaction product of from 7 to 12.5, wherein the catalyst, component (C) is used in a quantity of 0.2 to 1.5 parts by weight per 100 parts by weight of the epoxy resin (A) to produce an advanced epoxy resin, and wherein the difference obtained by subtracting the percent epoxide obtained by analysis from the theoretical percent epoxide is from 1 to 4.

2. The process of Claim 1 characterized in that component (C) is employed in a quantity which will provide a difference obtained by subtracting the percent epoxide obtained by analysis from the theoretical percent epoxide of from 1 to 2.

3. A process for preparing resin impregnated substrates for use in preparing electrical laminates by a process which comprises:

(I) saturating said substrate with a resin forming mixture comprising;

(A) an epoxy resin having an epoxide equivalent weight of from 300 to 600 which has been prepared by reacting

35 (1) a glycidyl ether of a dihydric phenol having an average of more than one epoxide group per molecule and an epoxide equivalent weight (EEW) of from 156 to 400; with

(2) a dihydric phenolic compound; in the presence of

(3) a phosphonium catalyst for effecting the reaction between (1) and (2), wherein components (1) and (2) are employed in quantities which provide a theoretical percent epoxide of the reaction product of from 8 to 15;

40 (B) a curing agent for said epoxy resin and

(C) a solvent system for components (A) and (B);

45 (II) heating the resultant impregnated substrate to B-stage of the resin and remove the solvent system; characterized by employing as the catalyst, component (A—3), a phosphonium salt or complex thereof which has at least one aromatic ring attached to the phosphorus atom of the phosphonium group and at least one aliphatic hydrocarbon group attached to said phosphorus atom, wherein said catalyst is employed in a quantity of 0.2 to 1.5 parts by weight per 100 parts by weight of the epoxy resin to produce an advanced epoxy resin and wherein the difference obtained by subtracting the percent epoxide obtained by analysis from the theoretical percent epoxide is from 1 to 4.

50 4. A process of claim 3 characterized in that component (A—3) has two aromatic rings attached to the phosphorus atom and is employed in a quantity which provides a difference obtained by subtracting the percent epoxide obtained by analysis from the theoretical percent epoxide of from 1 to 2.

5. The process of claim 4 characterized in that component (A—3) has three aromatic rings attached to the phosphorus atom.

55 Patentansprüche

1. Verfahren zum Herstellen eines Epoxyharzes mit weiterentwickeltem Molekulargewicht durch Umsetzen bei einer Temperatur von 100 bis 200°C (A) eines Epoxyharzes, das ein Glycidylether eines zweiwertigen Phenols mit im Mittel mehr als einer Glycidylethergruppe pro Molekül mit (B) einer zweiwertigen Phenolverbindung in Gegenwart von (C) einem Phosphoniumsalz oder Komplex desselben, das mindestens einen aromatischen Ring am Phosphoratom der Phosphoniumgruppe und mindestens eine aliphatische Kohlenwasserstoffgruppe an diesem Phosphoratom aufweist, wobei die Bestandteile (A) und (B) in solchen Mengen verwendet werden, daß das Verhältnis von phenolischem Hydroxyl zu Epoxid-äquivalent einen theoretischen Epoxidgehalt in Prozent im erhaltenen Reaktionsprodukt von 7 bis 12,5 ergibt, wobei der Katalysator, Bestandteil (C), in einer Menge von 0,2 bis 1,5 Gewichtsteilen pro 100



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The pressure cooker-solder test was conducted by

(i) cutting 2 in. x 4 in. (5 cm x 10 cm) coupons from prepared laminate,

(ii) placing 3 coupons edgewise on a rack in a pressure cooker and maintaining 15 psig (205 kPa) steam pressure for ~1.5 hour, and

5 (iii) then immersing the coupons in 500°F (260°C) solder for 20 seconds.

Six sides of the 3 coupons were evaluated and rated by the number of sides passing. In order to pass, the side must be free of blisters after immersion in hot solder. A 1/2 side pass consisted of the side having only 1 edge blister.

10 The laminate had a glass transition temperature (T_g) of 130°C. After subjecting to 15 psig (205 kPa) steam pressure for 1—1/2 hours and immersion in 500°F (260°C) solder for 20 seconds, 5—1/2 sides of the laminate out of six sides passed the test.

Claims

15 1. A process for producing an epoxy resin advanced in molecular weight by reacting at a temperature from 100 to 200°C (A) an epoxy resin which is a glycidyl ether of a dihydric phenol having an average of more than one glycidyl ether group per molecule with (B) a dihydric phenolic compound in the presence of (C) a phosphonium salt or complex thereof which has at least one aromatic ring attached to the phosphorus atom of the phosphonium group and at least one aliphatic hydrocarbon group attached to said phosphorus atom, employing components (A) and (B) in quantities such that the phenolic hydroxyl to epoxide equivalent ratio is that which will provide a theoretical percent epoxide of the resultant reaction product of from 7 to 12.5, wherein the catalyst, component (C) is used in a quantity of 0.2 to 1.5 parts by weight per 100 parts by weight of the epoxy resin (A) to produce an advanced epoxy resin, and wherein the difference obtained by subtracting the percent epoxide obtained by analysis from the theoretical percent epoxide is from 1 to 4.

25 2. The process of Claim 1 characterized in that component (C) is employed in a quantity which will provide a difference obtained by subtracting the percent epoxide obtained by analysis from the theoretical percent epoxide of from 1 to 2.

30 3. A process for preparing resin impregnated substrates for use in preparing electrical laminates by a process which comprises:

(I) saturating said substrate with a resin forming mixture comprising;

(A) an epoxy resin having an epoxide equivalent weight of from 300 to 600 which has been prepared by reacting

35 (1) a glycidyl ether of a dihydric phenol having an average of more than one epoxide group per molecule and an epoxide equivalent weight (EEW) of from 156 to 400; with

(2) a dihydric phenolic compound; in the presence of

(3) a phosphonium catalyst for effecting the reaction between (1) and (2), wherein components (1) and (2) are employed in quantities which provide a theoretical percent epoxide of the reaction product of from 8 to 15;

40 (B) a curing agent for said epoxy resin and

(C) a solvent system for components (A) and (B);

(II) heating the resultant impregnated substrate to B-stage of the resin and remove the solvent system; characterized by employing as the catalyst, component (A—3), a phosphonium salt or complex thereof which has at least one aromatic ring attached to the phosphorus atom of the phosphonium group and at least one aliphatic hydrocarbon group attached to said phosphorus atom,

45 wherein said catalyst is employed in a quantity of 0.2 to 1.5 parts by weight per 100 parts by weight of the epoxy resin to produce an advanced epoxy resin and wherein the difference obtained by subtracting the percent epoxide obtained by analysis from the theoretical percent epoxide is from 1 to 4.

50 4. A process of claim 3 characterized in that component (A—3) has two aromatic rings attached to the phosphorus atom and is employed in a quantity which provides a difference obtained by subtracting the percent epoxide obtained by analysis from the theoretical percent epoxide of from 1 to 2.

5. The process of claim 4 characterized in that component (A—3) has three aromatic rings attached to the phosphorus atom.

55 Patentansprüche

1. Verfahren zum Herstellen eines Epoxyharzes mit weiterentwickeltem Molekulargewicht durch Umsetzen bei einer Temperatur von 100 bis 200°C (A) eines Epoxyharzes, das ein Glycidylether eines zweiwertigen Phenols mit im Mittel mehr als einer Glycidylethergruppe pro Molekül mit (B) einer zweiwertigen Phenolverbindung in Gegenwart von (C) einem Phosphoniumsalz oder Komplex desselben, das mindestens einen aromatischen Ring am Phosphoratom der Phosphoniumgruppe und mindestens eine aliphatische Kohlenwasserstoffgruppe an diesem Phosphoratom aufweist, wobei die Bestandteile (A) und (B) in solchen Mengen verwendet werden, daß das Verhältnis von phenolischem Hydroxyl zu Epoxid-äquivalent einen theoretischen Epoxidgehalt in Prozent im erhaltenen Reaktionsprodukt von 7 bis 12,5 ergibt, wobei der Katalysator, Bestandteil (C), in einer Menge von 0,2 bis 1,5 Gewichtsteilen pro 100



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Gewichtsteile Epoxyharz (A) verwendet wird, um ein weiterentwickeltes Epoxyharz herzustellen, und wobei die durch Subtrahieren der Prozente ermittelte Differenz zwischen dem theoretischen Epoxidgehalt und dem erhaltenen Epoxidgehalt von 1 bis 4 beträgt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Bestandteil (C) in einer solchen Menge verwendet wird, daß die durch Subtrahieren der Prozente ermittelte Differenz zwischen dem theoretischen Epoxidgehalt und dem erhaltenen Epoxidgehalt von 1 bis 2 beträgt.

3. Verfahren zum Herstellen von mit Harz imprägnierten Substraten für die Herstellung von elektrischen Laminaten durch ein Verfahren enthaltend:

(I) Sättigen des Substrates mit einem Harz unter Bilden einer Mischung enthaltend:

(A) ein Epoxyharz mit einem Epoxidäquivalentgewicht von 300 bis 600, das hergestellt wurde durch Umsetzen

(1) eines Glycidylethers eines zweiwertigen Phenols mit im Mittel mehr als einer Epoxidgruppe pro Molekül und einem Epoxidäquivalentgewicht (EEW) von 156 bis 400 mit

(2) einer zweiwertigen Phenolverbindung in Gegenwart von

(3) einem Phosphoniumkatalysator zum Beeinflussen der Reaktion zwischen (1) und (2), wobei die Bestandteile (1) und (2) in Mengen verwendet werden, die einen theoretischen Gehalt an Epoxid in Prozent im Reaktionsprodukt von 8 bis 15 ergeben,

(B) einem Härtungsmittel für das Epoxyharz und

(C) einem Lösungsmittelsystem für die Bestandteile (A) und (B),

(II) Erwärmen des erhaltenen imprägnierten Substrates zur B-Stufe des Harzes und Entfernen des Lösungsmittelsystems, gekennzeichnet durch Verwenden als den Katalysator, Bestandteil (A-3), ein Phosphoniumsalz oder Komplex desselben, das mindestens einen aromatischen Ring am Phosphoratom der Phosphoniumgruppe und mindestens eine aliphatische Kohlenwasserstoffgruppe an diesem Phosphoratom aufweist, wobei der Katalysator in einer Menge von 0,2 bis 1,5 Gewichtsteilen pro 100 Gewichtsteile Epoxyharz verwendet wird, um ein weiterentwickeltes Epoxyharz herzustellen, und wobei die durch Subtrahieren der Prozente ermittelte Differenz zwischen dem theoretischen Epoxidgehalt und dem erhaltenen Epoxidgehalt von 1 bis 4 beträgt.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß der Bestandteil (A-3) am Phosphoratom zwei aromatische Ringe aufweist und er in einer Menge verwendet wird, die eine durch Subtrahieren der Prozente ermittelte Differenz zwischen dem theoretischen Epoxidgehalt und dem erhaltenen Epoxidgehalt von 1 bis 2 ergibt.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß der Bestandteil (A-3) am Phosphoratom drei aromatische Ringe aufweist.

Revendications

1. Procédé de production d'une résine époxy de masse molaire améliorée, en faisant réagir à une température comprise entre 100 et 200°C (A) une résine époxy qui est un éther glycidyle d'un diphenol, comportant en moyenne plus d'un groupe éther glycidyle par molécule, avec (B) un composé diphenolique, en présence de (C) un sel de phosphonium ou un complexe de celui-ci comportant au moins un noyau aromatique lié à l'atome de phosphore du groupe phosphonium et au moins un groupe hydrocarbure aliphatique lié audit atome de phosphore, en utilisant les composants (A) et (B) en des quantités telles que le rapport d'équivalents des hydroxyles phénoliques aux époxydes soit de nature à fournir un pourcentage théorique d'époxyde dans le produit de réaction résultant compris entre 7 et 12,5, dans lequel le catalyseur, composant (C), est utilisé et une quantité de 0,2 à 1,5 partie en poids pour 100 parties en poids de la résine époxy (A) pour produire une résine époxy améliorée, et dans lequel la différence qu'on obtient en soustrayant le pourcentage d'époxyde obtenu par analyse de pourcentage théorique d'époxyde est de 1 à 4.

2. Procédé selon la revendication 1, caractérisé en ce qu'on utilise le composant (C) en une quantité qui donne une différence de 1 à 2 quand on soustrait le pourcentage d'époxyde obtenu par analyse du pourcentage théorique d'époxyde.

3. Procédé de préparation de substrats imprégnés de résine servant à préparer des stratifiés électriques, par un procédé qui consiste:

(I) à saturer ledit substrat avec un mélange formant une résine comprenant:

(A) une résine époxy ayant un poids d'équivalent époxyde compris entre 300 et 600 et qu'on prépare en faisant réagir:

(1) un éther glycidyle d'un diphenol ayant en moyenne plus d'un groupe époxyde par molécule et un poids d'équivalent époxyde (PEE) de 156 à 400; avec

(2) un composé diphenolique; en présence de

(3) un catalyseur phosphonium, afin d'effectuer la réaction entre (1) et (2), les composants (1) et (2) étant utilisés en des quantités qui fournissent un pourcentage théorique d'époxyde de 8 à 15 dans le produit de réaction;

(B) un durcisseur pour ladite résine époxy; et

(C) un système solvant pour les composants (A) et (B);

(II) à chauffer le substrat imprégné résultant au stade-B de la résine et à éliminer le système solvant;



caractérisé en ce qu'on utilise, en qualité de catalyseur, composant (A—3), un sel de phosphonium ou son complexe, comportant au moins un noyau aromatique lié à l'atome de phosphore du groupe phosphonium et au moins un groupe hydrocarbure aliphatique lié audit atome de phosphore, dans lequel on utilise ledit catalyseur en une quantité de 0,2 à 1,5 partie en poids pour 100 parties en poids de résine époxy, pour obtenir une résine époxy améliorée et dans lequel la différence qu'on obtient en soustrayant le pourcentage d'époxyde obtenu par analyse du pourcentage théorique d'époxyde est comprise entre 1 et 4.

4. Procédé selon la revendication 3, caractérisé en ce que le composant (A—3) comporte deux noyaux aromatiques liés à l'atome et on l'utilise en une quantité qui fournit une différence de 1 à 2 quand on soustrait le pourcentage d'époxyde obtenu par analyse du pourcentage théorique d'époxyde.

5. Procédé selon la revendication 4, caractérisé en ce que le composant (A—3) comporte trois noyaux aromatiques liés à l'atome de phosphore.

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