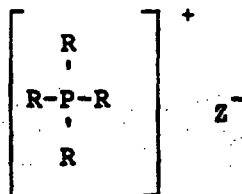


Description

Precatalyzed epoxy resin compositions containing a relatively low equivalent weight epoxy resin and a phosphonium compound have been employed to prepare relatively high molecular weight resins by reacting with a polyhydric phenol.

US-A-3 948 855 refers to a process of reacting a phenolic compound with a vinical epoxy resin to provide high molecular weight epoxy resins in the presence of a phosphonium salt as catalyst using a precatalyzed epoxy resin composition comprising an epoxy resin having an average of more than 1 epoxide group per molecule and the catalyst. The phosphonium salts are represented by the formula



wherein R is independently an aliphatic hydrocarbon group containing from 1 to 20 carbon atoms or a group R¹, wherein R¹ is an aliphatic hydrocarbon group containing from 1 to 20 carbon atoms and Y is Cl, Br, I, NO₂ or OH and Z is selected from a group of acids or esters comprising phosphoric acid. There is mentioned that a prestabilized mixture of a diglycidylether of bisphenol A, hydrolyzed diglycidylether of bisphenol A and the acetic acid complex of ethyltriphenyl phosphonium acetate is stable for 4 weeks at 50°C, that means without essential loss of epoxide content.

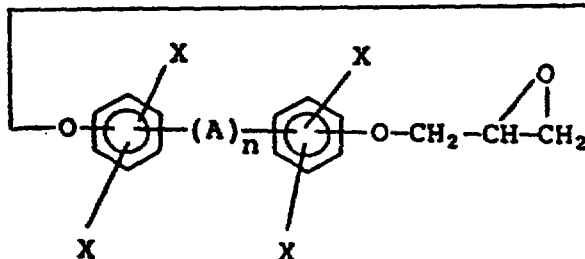
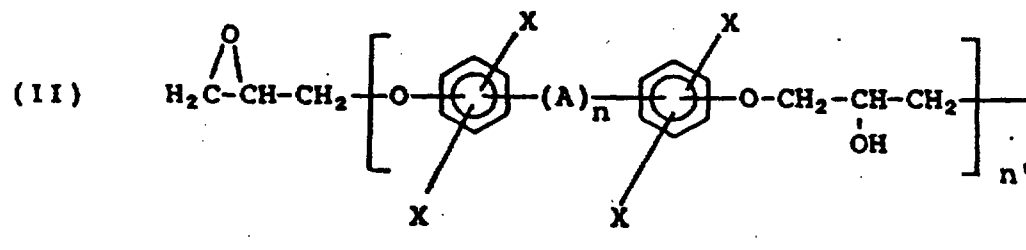
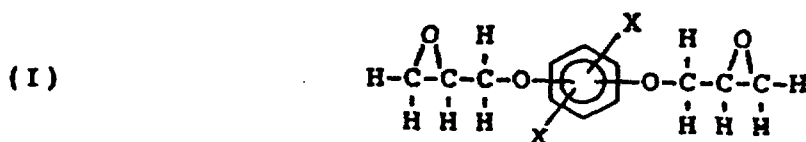
CA-A-893 141 describes a similar method and prestabilized compositions are mentioned without any data on the stability. Such compositions are subject to storage over prolonged periods of time and in many instances, the composition loses its catalytic activity after such storage at elevated temperatures, although in the US-A-3 948 855 it is mentioned that the compositions should be stable. Loss of catalytic activity results in an epoxy resin having a significantly different epoxide content than expected from a ratio of epoxy to phenolic hydroxy groups as well as detrimental increases in viscosity.

It is the object of the present invention to improve the long term stability of the known precatalyzed epoxy resin compositions at elevated temperatures up to 93.3°C (200°F) with regard to the catalytic activity, the epoxide value and the viscosity of the composition.

This object is solved by a specific method of preparing the composition.

Subject of the invention is a method for preparing a precatalyzed epoxy resin composition containing a mixture of

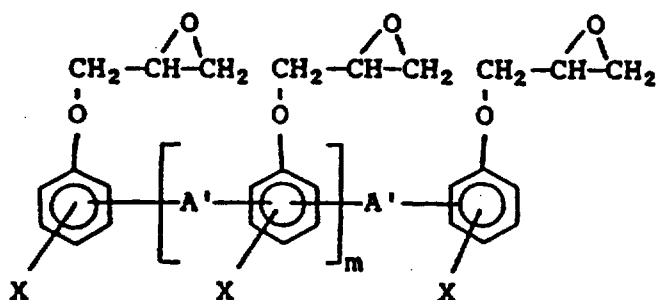
A) an epoxy resin represented by the formulas:



(III)

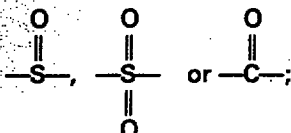
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wherein A is independently a divalent hydrocarbon group having from one to about 8 carbon atoms, —O—, —S—, —S—S—,

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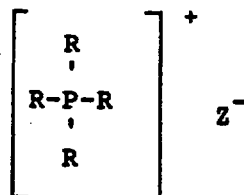
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each A' is independently a divalent hydrocarbon group having from one to about 8 carbon atoms; each X is independently hydrogen, bromine, chlorine or a hydrocarbon group having from one to about 8 carbon atoms; n has a value of zero or 1; n' has an average value less than about 0.9, preferably less than about 0.2, most preferably from about 0.01 to about 0.15 and m has an average value of from about 0.1 to about 4, preferably from about 0.8 to about 2.

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B) as a catalyst for the reaction between said epoxy resin and a phenolic-hydroxyl containing compound which is subsequently blended with said precatalyzed epoxy resin composition a phosphonium salt which is represented by the formula

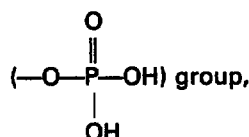
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wherein each R is independently a hydrocarbyl group having from 1 to 20 carbon atoms or the group R'Y wherein R' is an aliphatic hydrocarbon group having from 1 to 20 carbon atoms and Y is Cl, Br, I, NO₂, or OH and Z is a phosphate

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characterized by adding phosphoric acid to a mixture of (A) said epoxy resin and (B) a phosphonium compound wherein the anion portion of (B) is a bicarbonate, a halide or a carboxylate carboxylic acid complex, in a molar ratio phosphoric acid to phosphonium compound of one to one to stabilize the precatalyzed epoxy resin composition.

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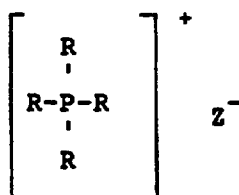
Another embodiment of the invention is the method for preparing a precatalyzed epoxy resin composition containing a mixture of

A) an epoxy resin represented by any one of the formulas (I) to (III) referred to above, and

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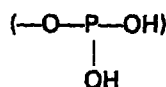
B) as a catalyst for the reaction between said epoxy resin and a phenolic-hydroxyl containing compound which is subsequently blended with said precatalyzed epoxy resin composition a phosphonium salt which is represented by the formula

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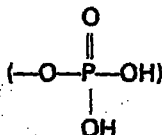


wherein each R is independently a hydrocarbyl group having from 1 to 20 carbon atoms or the group R'Y

wherein R¹ is an aliphatic hydrocarbon group having from 1 to 20 carbon atoms and Y is Cl, Br, I, NO₂ or OH characterized by using a phosphonium salt in which Z in the formula mentioned above is a phosphite



or a polyphosphate group or mixture thereof or mixture with a phosphonium compound wherein Z is a phosphate



group and adding phosphoric acid, phosphorous acid or polyphosphoric acid to a mixture of (A) said epoxy resin and (B) a phosphonium compound wherein said anion portion has been a bicarbonate, a halide or a carboxylate carboxylic acid complex, in a molar ratio acid to phosphonium compound of one to one to stabilize the precatalyzed epoxy resin composition.

The method of the present invention pertains to an improvement in a precatalyzed epoxy resin composition containing a mixture of (A) a relatively low equivalent weight epoxy resin having an average of more than one glycidyl ether group per molecule, which is subsequently blended with a phenolic-hydroxyl containing compound. The improvement is evidenced by

(1) after subjecting said precatalyzed epoxy resin composition to a temperature of about 200°F (93.3°C) for about 48 hours;

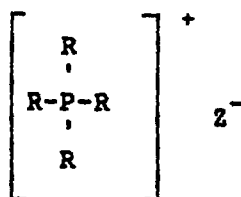
(a) not more than 50% of the phosphonium groups originally present in said mixture are deactivated; (b) the viscosity has not increased by more than 30% of the original value; and

(2) after subjecting said precatalyzed resin composition to a temperature of 200°F (93.3°C) for about 63 hours, the product resulting from its reaction with a phenolic hydroxyl-containing compound having an average of more than one phenolic hydroxyl group per molecule, has a % epoxide value not greater than the value obtained by dividing the theoretical % epoxide value by 0.9. The hydrocarbyl group in the phosphonium salt having preferably from 2 to 8, carbon atoms and the group R¹Y wherein R¹ is an aliphatic hydrocarbon group having preferably from 2 to about 8, carbon atoms.

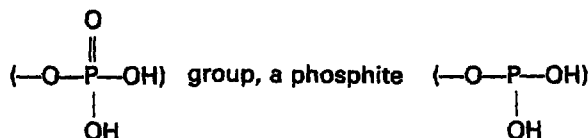
Detailed Description of the Invention

Suitable relatively low equivalent weight epoxy resins which can be employed in the compositions of the present invention include those represented by the formulas (I) to (III) referred to above.

Suitable phosphonium compounds which can be employed in the method of the present invention include those represented by the formula



wherein each R is independently a hydrocarbyl group having from 1 to 20, preferably from 2 to 8, carbon atoms or the group R¹Y wherein R¹ is an aliphatic hydrocarbon group having from 1 to 20 carbon atoms and Y is Cl, Br, I, NO₂ or OH and Z is a phosphate

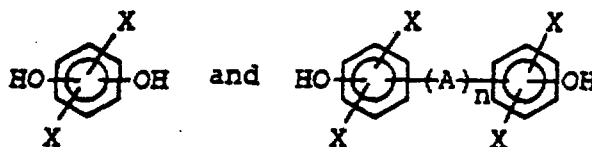


group or a polyphosphate group. Mixtures of such catalysts can also be employed.

Particularly suitable phosphonium catalysts which can be employed include, for example, ethyltriphenyl phosphonium phosphate, ethyltriphenyl phosphonium phosphite, tetrabutyl phosphonium phosphate, tetrabutyl phosphonium phosphite, mixtures thereof and the like.

Suitable aromatic hydroxyl containing compounds which can be reacted with the compositions prepared by the method of the present invention to prepare epoxy resins which are relatively high in

molecular weight include, for example, those represented by the formulas:



wherein each A, X and n are as defined above.

Particularly suitable aromatic hydroxyl-containing compounds are the bisphenols such as bisphenol A.

CATALYST A was the reaction product of a 70% solution of ethyltriphenyl phosphonium acetate-acetic acid complex in methanol and phosphoric acid in a molar ratio of one to one. The resultant product was diluted to 30% by weight with methanol.

CATALYST B was the reaction product of a 70% solution of ethyltriphenyl phosphonium acetate-acetic acid complex in methanol and phosphoric acid in a molar ratio of one to one. The by-product acetic acid was removed by recrystallization from methanol. The recrystallized ethyltriphenyl phosphonium phosphate was then diluted with methanol to provide a 30% by weight solution.

CATALYST C was the reaction product of a 70% solution of ethyltriphenyl phosphonium acetate-acetic acid complex and 118% phosphoric acid (polyphosphoric acid) in a molar ratio of one to one. The resultant product was diluted to 30% by weight with methanol.

CATALYST D was the reaction product of a 70% solution of ethyltriphenyl phosphonium acetate-acetic acid complex in methanol and phosphorous acid in a molar ratio of one to one. The resultant product was diluted to 30% by weight with methanol.

CATALYST E was the reaction product of a 70% solution of tetrabutyl phosphonium acetate-acetic acid complex in methanol and phosphoric acid in a molar ratio of one to one. The resultant product was diluted to 30% by weight with methanol.

COMPARATIVE CATALYST F was a 20% solution of ethyltriphenyl phosphonium iodide in the methyl ether of ethylene glycol.

COMPARATIVE CATALYST G was a 30% solution of ethyltriphenyl phosphonium acetate-acetic acid complex in methanol.

CATALYST H was the reaction product of Catalyst F with phosphoric acid in a molar ratio of one to one. The resultant product was diluted to 30% by weight with methanol.

CATALYST I was the reaction product of ethyl triphenyl phosphonium bicarbonate with diethyl phosphate in a molar ratio of one to one. The resultant product was diluted to 30% by weight with methanol.

COMPARATIVE CATALYST J was a 70% solution of tetrabutyl phosphonium acetate-acetic acid complex in methanol.

EPOXY RESIN A was a diglycidyl ether of bisphenol A having an average epoxide equivalent weight (EEW) of about 188.

EPOXY RESIN B was a diglycidyl ether of bisphenol A having an EEW of about 189.

EPOXY RESIN C was a mixture of 85% by weight of Epoxy Resin A and 15% by weight of an epoxy novolac resin having an EEW of about 181 and an average functionality of about 3, the resultant mixture having an EEW of about 192.

EPOXY RESIN D was a mixture of 98.5% by weight of Epoxy Resin A and 1.5% by weight of the hydrolysis product of the diglycidyl ether of bisphenol A and an EEW of about 188 prior to hydrolysis; the resultant mixture having an EEW of about 192.

②

HEAT AGING

The storage stability of precatalyzed epoxy resin compositions was provided by placing the following compositions in a 200°F (93.3°C) oven for various periods of time.

- 5 300 g epoxy resin
 12.5 g xylene
 0.313 g catalyst (solvent free basis)

The epoxy resin, catalysts employed and results, active catalyst remaining, are given in Table I.

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ACTIVE CATALYST DETERMINATION

- 1) 0.5 g of precatalyzed resin is dissolved in methylene chloride and brought to a 25 ml volume; 2) a 5 ml aliquot is taken, to which 15 ml of methylene chloride and 1 ml of 0.1% aqueous solution of methyl orange indicator are added all in a 2 oz. bottle; 3) this mixture is shaken for one minute, then allowed to stand for 5 minutes; 4) a 10 ml aliquot is then taken and filtered into a Klett tube, which is placed in the Klett colorimeter. The colorimeter measures the color intensity which is directly proportional to active catalyst (phosphonium cation) levels. Catalyst concentration is then taken based on the PPM active catalyst per Klett unit.

ADVANCEMENT AFTER AGING

- 1) After the aging period, a new EEW is calculated; 2) bisphenol A is added to theoretically provide a final product having a 3000 EEW (1.43% epoxy); 3) the n-butyl ether of ethylene glycol is added to bring the system to 85% solids, with this dilution, system should reach 1.27% epoxy if no solvent is lost. The epoxy resin, bisphenol A and n-butyl ether of ethylene glycol are added at room temperature and heated at 2—3°C/min. to 175°C, where the heating means is cut off and the system allowed to exotherm. The resin is cooked for four hours after exotherm to acquire the finished product.

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TABLE I

EXAMP. OR COMP. EXPT. NO.	CATALYST		EPOXY RESIN	HOURS AT 93.3°C	ACTIVE CATALYST PPM	% PHOS- PHONIUM GROUPS REMAINING	VISCOSITY		HOURS PAST EXO- THERM	RESIN ADVANCEMENT ³		VALUE OF THEORETICAL % EPOXIDE DIVIDED BY 0.9
							AT 25°C	% OF ORIGINAL		PERCENT EPOXIDE		
1	A	A	0	1000	100	2600	N.A. ⁶		1	1.60	1.41	
			24	755	75.5	N.D.		3	N.D. ⁴			
			48	650	65	3023	116	4	1.37			
			63	545	54.5	N.D.						
2	B	A	0	1000	100	2600	N.A.		1	1.48	1.41	
			24	840	84	N.D.		3	1.20			
			48	680	68	2966	114	4	1.14			
			63	670	67							
3 ¹	A	A	0	1000	100	8115	N.A.		1	1.42	1.41	
			24	655	65.5	N.D.		3	1.21			
			48	575	57.5	10286	127	4	1.16			
			63	510	51	N.D.						
4	A	B	0	1000	100	2114	N.A.		1	1.41	1.41	
			24	710	71	N.D.		3	1.14			
			48	645	64.5	2659	126	4	1.00			
			63	600	60							
5	C	A	0	1000	100	2600	N.A.		1	1.47	1.41	
			24	655	65.5	N.D.		3	1.16			
			48	555	55.5	2889	111	4	1.11			
			63	505	50.5	N.D.						

TABLE I (continued)

EXAMP. OR COMP. EXPT. NO.	CATALYST		EPOXY RESIN	HOURS AT 93.3°C	ACTIVE CATALYST PPM	% PHOS- PHONIUM GROUPS REMAINING	VISCOSITY		HOURS PAST EXO- THERM	RESIN ADVANCEMENT ³	
							AT 25°C	% OF ORIGINAL		PERCENT EPOXIDE	THEORETICAL % EPOXIDE DIVIDED BY 0.9
6	D	A	0	1000	100	2600	N.A.		1	1.22	1.41
			24	1000	100	N.D.		3	0.95		
			48	1000	100	3373	130	4	0.92		
			63	975	97.5	N.D.					
7	E	A	0	1000	100	2600	N.A.	1	1.25	1.41	
			24	1000	100	N.D.		3	0.98		
			48	1000	100	2966	114	4	0.92		
			63	985	98.5	N.D.					
A ²	F	A	0	1000	100	2600	N.A.	1	3.65	1.41	
			24	425	42.5	N.D.		3	N.D.		
			48	210	21.0	2996	115	4	1.89		
			63	185	18.5	N.D.					
B ²	G	A	0	1000	100	N.D.	N.D.	N.D.	N.D.		
			4	115	11.5	N.D.	N.D.				
B ⁵	A	A	0	1000	100	2939	N.A.	1	1.53	1.59	
			24	523	52.3	N.D.		3	1.40		
			48	538	53.8	3268	111	4	1.37		
			63	561	56.1	N.D.					

TABLE I (continued)

EXAMP. OR COMP. EXPT. NO.	CATALYST	EPOXY RESIN	HOURS AT 93.3°C	ACTIVE CATALYST PPM	% PHOS- PHONIUM GROUPS REMAINING	VISCOSITY AT 25°C		HOURS PAST EXO- THERM	RESIN ADVANCEMENT ³	
						mm ² /s	% OF ORIGINAL		PERCENT EPOXIDE	THEORETICAL % EPOXIDE DIVIDED BY 0.9
9	A	C	0	1000	100	3367	N.A.			1.41
			24	836	83.6	N.D.		1	1.46	
			48	627	62.7	3673	109	3	1.16	
			63	564	56.4			4	1.12	
10	H	A	0	1000	100	2600	N.A.			1.41
			24	871	87.1	N.D.		1	1.45	
			48	803	80.3	2941	113	3	1.16	
			63	750	75.0	N.D.		4	1.12	
C	I	A	0	1000	100	2600	N.A.			1.41
			24	351	35.1	N.D.		1	1.93	
			48	390	39.0	3371	130	3	1.67	
			63	357	35.7	N.D.		4	1.60	
D	I	D	0	1000	100	2940	N.A.			1.41
			24	350	35.0	N.D.		1	1.79	
			48	343	34.3	3435	117	3	1.39	
			63	364	36.4	N.D.		4	1.33	
E ²	J	A	0	1000	100	2600	N.A.			1.41
			24	1000	100			1	1.33	
			48	1000	100	8296	219	3	gelled after	
			63	1000	100			4	1.5 hrs.	

FOOTNOTES TO TABLE

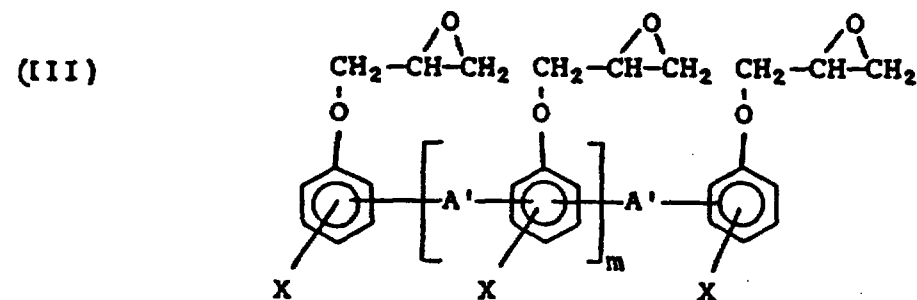
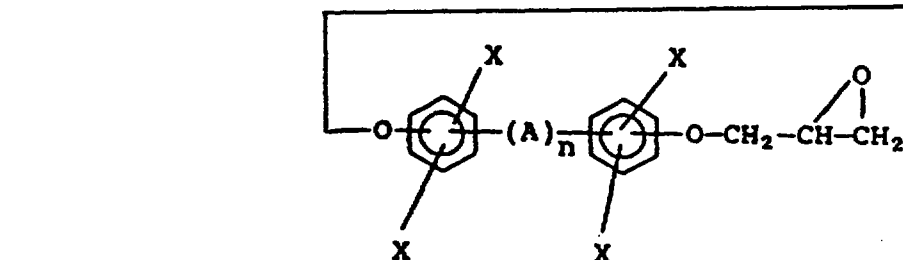
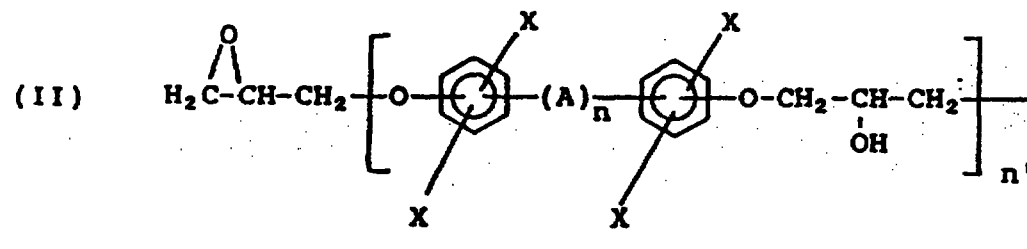
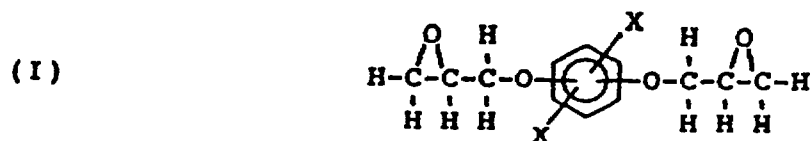
¹ Xylene was omitted from the heat aging composition.² Comparative Experiment³ The resin-catalyst mixture was advanced with bisphenol A after aging at 200°F for 63 hours. The % epoxide was measured after 1, 3 and 4 hours after exotherm was recorded and the % epoxide is based on total composition including solvent. The theoretical % epoxide was 1.27%.⁴ N.D. = Not Determined.⁵ The epoxidation was conducted without solvent therefore the theoretical % epoxide was 1.43% instead of 1.27%.⁶ N.A. = Not Applicable.



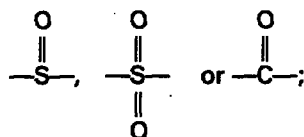
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Claims

1. A method for preparing a precatalyzed epoxy resin composition containing a mixture of
A) an epoxy resin represented by the formulas:

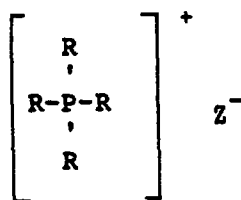


wherein A is independently a divalent hydrocarbon group having from one to about 8 carbon atoms, —O—, —S—, —S—S—,



each A' is independently a divalent hydrocarbon group having from one to about 8 carbon atoms; each X is independently hydrogen, bromine, chlorine or a hydrocarbon group having from one to about 8 carbon atoms; n has a value of zero or 1; n' has an average value less than about 0.9, and m has an average value of from about 0.1 to about 4, and

B) as a catalyst for the reaction between said epoxy resin and a phenolic-hydroxyl containing compound which is subsequently blended with said precatalyzed epoxy resin composition a phosphonium salt which is represented by the formula



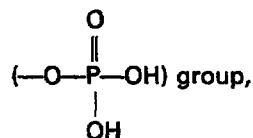


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wherein each R is independently a hydrocarbonyl group having from 1 to 20 carbon atoms or the group R'Y wherein R' is an aliphatic hydrocarbon group having from 1 to 20 carbon atoms and Y is Cl, Br, I, NO₂ or OH and Z is a phosphate

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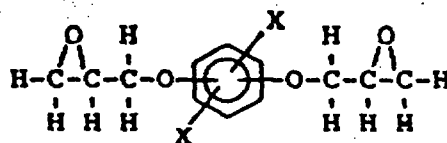


10 characterized by adding phosphoric acid to a mixture of (A) said epoxy resin and (B) a phosphonium compound wherein the anion portion of (B) is a bicarbonate, a halide or a carboxylate carboxylic acid complex, in a molar ratio phosphoric acid to phosphonium compound of one to one, to stabilize the precatalyzed epoxy resin composition.

2. A method for preparing a precatalyzed epoxy resin composition containing a mixture of
15 A) an epoxy resin represented by the formulas:

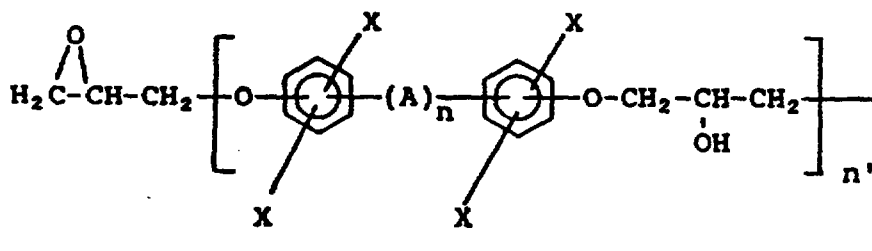
(I)

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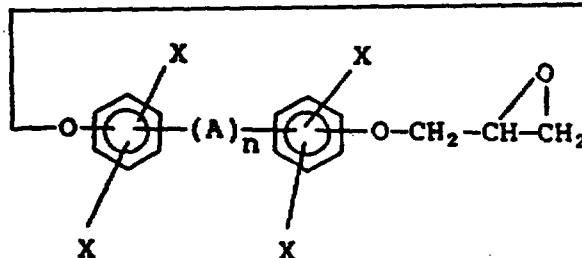
(II)

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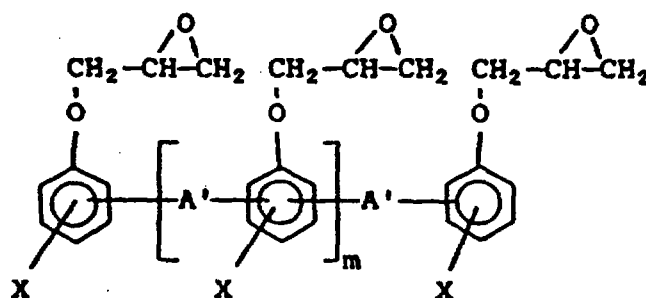
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(III)

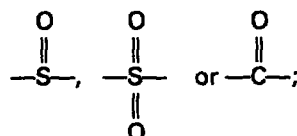
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55 wherein A is independently a divalent hydrocarbon group having from one to about 8 carbon atoms, —O—, —S—, —S—S—,

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65 each A' is independently a divalent hydrocarbon group having from one to about 8 carbon atoms; each X is independently hydrogen, bromine, chlorine or a hydrocarbon group having from one to about 8 carbon

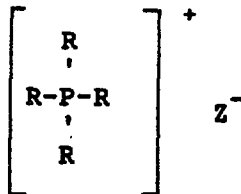


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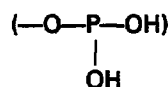
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atoms; n has a value of zero or 1; n' has an average value less than about 0.9, and m has an average value of from about 0.1 to about 4, and

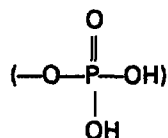
B) as a catalyst for the reaction between said epoxy resin and a phenolic-hydroxyl containing compound which is subsequently blended with said precatalyzed epoxy resin composition a phosphonium salt which is represented by the formula



wherein each R is independently a hydrocarbyl group having from 1 to 20 carbon atoms or the group R¹Y wherein R¹ is an aliphatic hydrocarbon group having from 1 to 20 carbon atoms and Y is Cl, Br, I, NO₂, or OH characterized by using a phosphonium salt in which Z is the formula mentioned above is a phosphite



or a polyphosphate group or mixture thereof or mixture with a phosphonium compound wherein Z is a phosphate



group and adding phosphoric acid, phosphorous acid or polyphosphoric acid to a mixture of (A) said epoxy resin and (B) a phosphonium compound wherein said anion portion has been a bicarbonate, a halide or a carboxylate carboxylic acid complex, in a molar ratio acid to phosphonium compound of one to one, to stabilize the precatalyzed epoxy resin composition.

3. The method of claims 1 or 2 characterized by using as the epoxy resin a diglycidyl ether of bisphenol A having an average epoxide equivalent weight of from about 175 to about 195 and as the catalyst ethyltriphenyl phosphonium phosphate, ethyltriphenyl phosphonium phosphite, ethyltriphenyl phosphonium polyphosphate, tetrabutylphosphonium phosphate or mixture thereof.

4. The method of claims 1 or 2 characterized by using as the epoxy resin a mixture of a diglycidyl ether of bisphenol A and a phenol formaldehyde epoxy novolac resin and as the catalyst ethyltriphenyl phosphonium phosphate, ethyltriphenyl phosphonium phosphite, ethyltriphenyl phosphonium polyphosphate, tetrabutylphosphonium phosphate or mixture thereof.

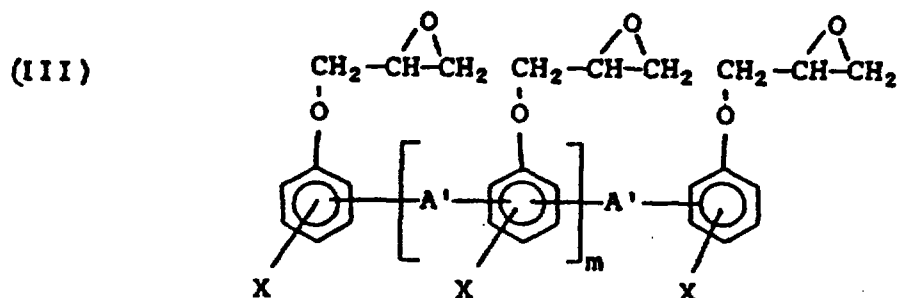
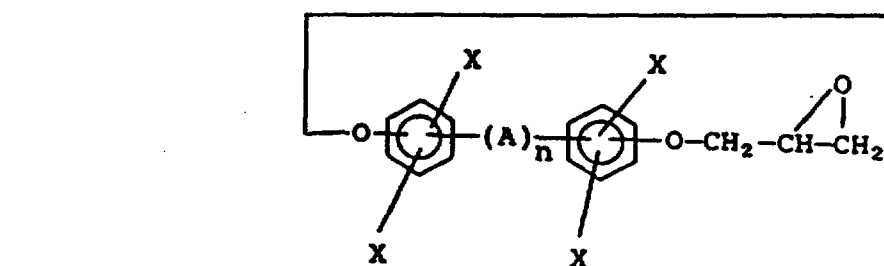
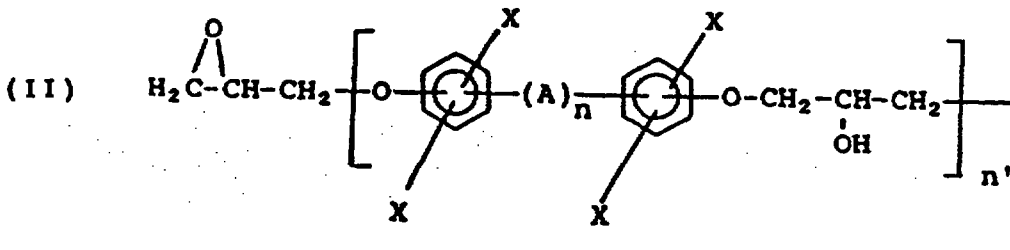
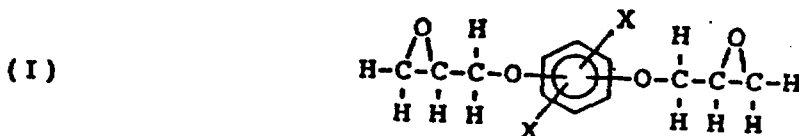
5. The method of claims 1 or 4 characterized by using a phosphonium compound wherein said anion is an iodide or an acetate acetic acid complex.

6. The method of claim 5 characterized by using a phosphonium compound wherein the cation portion of said phosphonium compound is ethyl triphenyl or tetrabutyl.

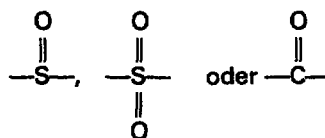


Patentansprüche

1. Verfahren zum Herstellen einer vorkatalysierten Epoxyharzzusammensetzung, enthaltend eine Mischung von A) eines Epoxyharzes der Formeln:

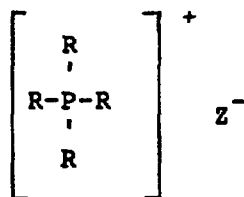


in denen A unabhängig voneinander eine zweiwertige Kohlenwasserstoffgruppe mit 1 bis etwa 8 Kohlenstoffatomen, $-\text{O}-$, $-\text{S}-$, $-\text{S}-\text{S}-$,



ist, jedes A' ist unabhängig voneinander eine zweiwertige Kohlenwasserstoffgruppe mit 1 bis etwa 8 Kohlenstoffatomen, jedes X ist unabhängig voneinander Wasserstoff, Brom, Chlor oder eine Kohlenwasserstoffgruppe mit 1 bis etwa 8 Kohlenstoffatomen, n hat einen Wert von 0 oder 1, n' hat einen Mittelwert von kleiner als etwa 0,9 und m hat einen Mittelwert von etwa 0,1 bis etwa 4, und

B) als einen Katalysator für die Umsetzung zwischen dem Epoxyharz und einer phenolisches Hydroxyl enthaltenden Verbindung, die anschliessend mit der vorkatalysierten Epoxyharzzusammensetzung gemischt wird, ein Phosphoniumsalz der Formel



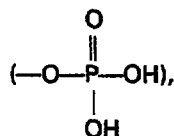


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in der jedes R unabhängig voneinander eine Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen oder die R'-Y-Gruppe ist, in der R' eine aliphatische Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen ist und Y Cl, Br, I, NO₂ oder OH ist und Z eine Phosphatgruppe der Formel

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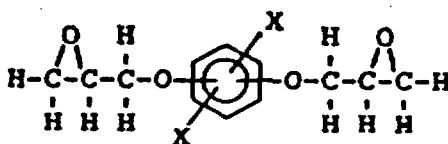
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ist, gekennzeichnet durch Zugabe von Phosphorsäure zu einer Mischung von (A), dem Epoxyharz und (B), einer Phosphoniumverbindung, in der der anionische Teil von (B) ein Bicarbonat, ein Halogenid oder ein Carboxylat-Carbonsäurekomplex ist, in einem Molverhältnis Phosphorsäure:Phosphoniumverbindung von 1:1, um die vorkatalysierte Epoxyharzzusammensetzung zu stabilisieren.

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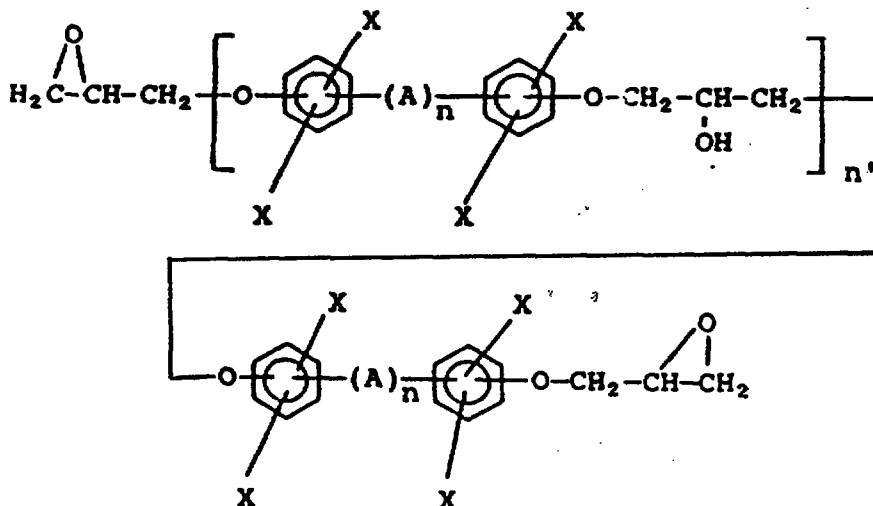
2. Verfahren zum Herstellen einer vorkatalysierten Epoxyharzzusammensetzung, enthaltend eine Mischung von A) eines Epoxyharzes der Formeln:

20 (I)



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(II)

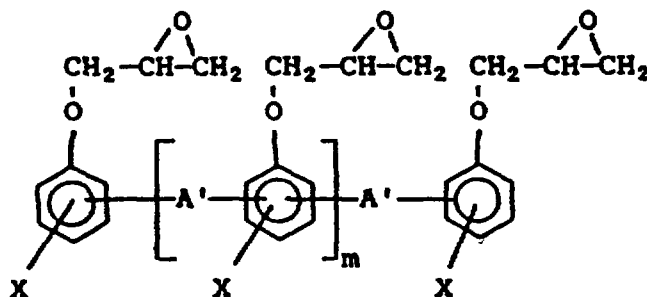


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(III)

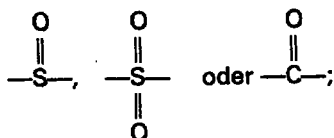


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in denen A unabhängig voneinander eine zweiwertige Kohlenwasserstoffgruppe mit 1 bis etwa 8 Kohlenstoffatomen, -O-, -S-, -S-S-,

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ist, jedes A' ist unabhängig voneinander eine zweiwertige Kohlenwasserstoffgruppe mit 1 bis etwa 8 Kohlenstoffatomen, jedes X ist unabhängig voneinander Wasserstoff, Brom, Chlor oder eine Kohlenwasserstoffgruppe mit 1 bis etwa 8 Kohlenstoffatomen. n hat einen Wert von 0 oder 1, n' hat einen Mittelwert von kleiner als etwa 0,9 und m hat einen Mittelwert von 0,1 bis etwa 4 und

- 5 B) als einen Katalysator für die Umsetzung zwischen dem Epoxyharz und einer phenolisches Hydroxyl enthaltende Verbindung, die anschliessend mit der vorkatalysierten Epoxyharzzusammensetzung gemischt wird, ein Phosphoniumsalz der Formel



in der jedes R unabhängig voneinander eine Hydrocarbylgruppe mit 1 bis 20 Kohlenstoffatomen oder die Gruppe R¹Y ist, in der R¹ eine aliphatische Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen ist, und Y Cl, Br, I, NO₂ oder OH ist, gekennzeichnet durch Verwendung eines Phosphoniumsalzes, in dessen zuvor genannter Formel Z eine Phosphitgruppe



oder eine Polyphosphatgruppe oder eine Mischung derselben, oder eine Mischung mit einer Phosphoniumverbindung, in der Z eine Phosphatgruppe



35 ist, und Zugabe von Phosphorsäure, phosphoriger Säure oder Polyphosphorsäure zu einer Mischung aus (A), dem Epoxyharz und (B) einer Phosphoniumverbindung, in der der anionische Teil von (B) ein Bicarbonat, ein Halogenid oder ein Carboxylat-Carbonsäurekomplex ist, in einem Molverhältnis Säure:Phosphoniumverbindung von 1:1, um die vorkatalysierte Epoxyharzzusammensetzung zu stabilisieren.

40 3. Verfahren nach Ansprüchen 1 oder 2, gekennzeichnet durch Verwendung eines Diglycidylethers von Bisphenol A als Epoxyharz, mit einem mittleren Epoxyäquivalentgewicht von etwa 175 bis etwa 195 und Ethyltriphenylphosphoniumphosphat, Ethyltriphenylphosphoniumphosphit, Ethyltriphenylphosphoniumpolyphosphat, Tetrabutylphosphoniumphosphat oder einer Mischung derselben als dem Katalysator.

45 4. Verfahren nach Ansprüchen 1 oder 2, gekennzeichnet durch Verwenden einer Mischung eines Diglycidylethers von Bisphenol A und einem Phenolformaldehydepoxynovolakharz als Epoxyharz, und Ethyltriphenylphosphoniumphosphat, Ethyltriphenylphosphoniumphosphit, Ethyltriphenylphosphoniumpolyphosphat, Tetrabutylphosphoniumphosphat oder einer Mischung derselben als dem Katalysator.

50 5. Verfahren nach Ansprüche 1 bis 4, gekennzeichnet durch Verwendung einer Phosphoniumverbindung, in der das Anion Jodid oder ein Acetat-Essigsäurekomplex ist.

6. Verfahren nach Anspruch 5, gekennzeichnet durch Verwendung einer Phosphoniumverbindung, in der der kationische Teil der Phosphoniumverbindung Ethyltriphenyl oder Tetrabutyl ist.

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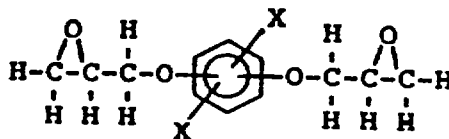
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Revendications

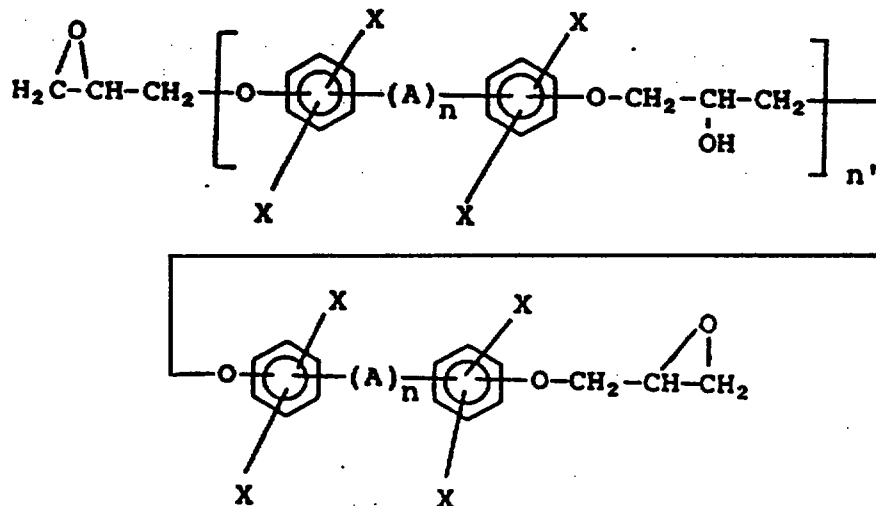
1. Procédé pour la préparation d'une composition de résine époxyde précatalysée contenant un mélange de:

5 A) une résine époxyde représentée par les formules:

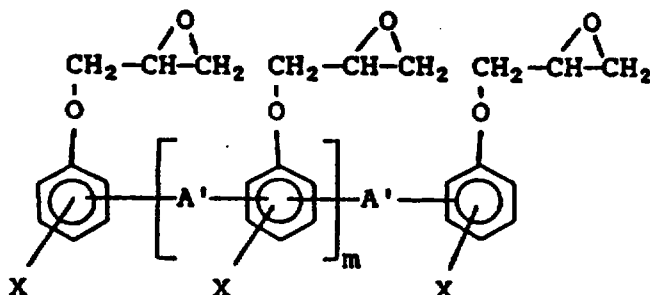
10 (I)



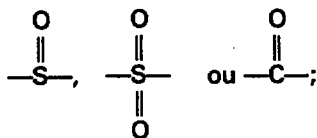
15 (II)



35 (III)



50 dans lesquelles A représente de manière indépendante un groupe hydrocarbure divalent ayant de 1 à environ 8 atomes de carbone, —O—, —S—, —S—S—,



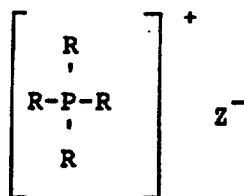
chaque A' représente de manière indépendante un groupe hydrocarbure divalent ayant de 1 à environ 8 atomes de carbone; chaque X représente de manière indépendante un atome d'hydrogène, de brome, de chlore ou un groupe hydrocarbure ayant de 1 à environ 8 atomes de carbone; n prend la valeur 0 ou 1; n' possède une valeur moyenne inférieure à environ 0,9, et m possède une valeur moyenne allant d'environ 0,1 à environ 4, et

65 B) à titre de catalyseur pour la réaction entre ladite résine époxyde et un composé contenant un groupe hydroxyle phénolique qui est ultérieurement mélangé avec ladite composition de résine époxyde précatalysée, un sel de phosphonium qui est représenté par la formule



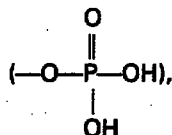
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10 dans laquelle chaque R représente de manière indépendante un groupe hydrocarboné ayant de 1 à 20 atomes de carbone ou le groupe R¹Y dans lequel R¹ est un groupe hydrocarbure aliphatique ayant de 1 à 20 atomes de carbone et Y est Cl, Br, I, NO₂ ou OH et Z est un groupe phosphate

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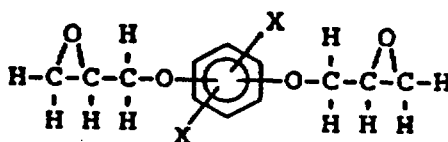
20 caractérisé par l'addition d'acide phosphorique à un mélange de (A) ladite résine époxyde et de (B) un composé phosphonium dans lequel la portion anion de (B) est un bicarbonate, un halogénure ou un complexe carboxylate-acide carboxylique, dans un rapport molaire de l'acide phosphorique au composé phosphonium de un à un, afin de stabiliser la composition de résine époxyde précatalysée.

2. Procédé pour la préparation d'une composition de résine époxyde précatalysée contenant un mélange de:

25 A) un résine époxyde représentée par les formules:

(I)

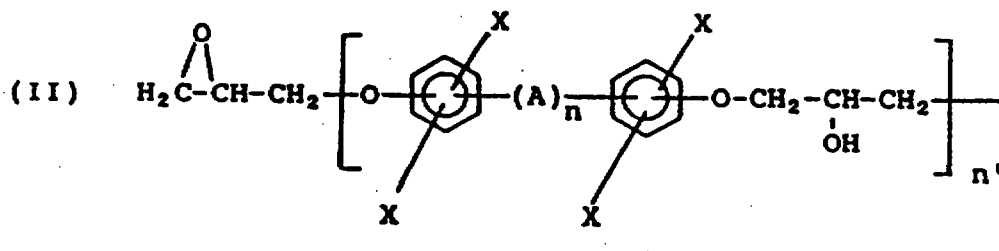
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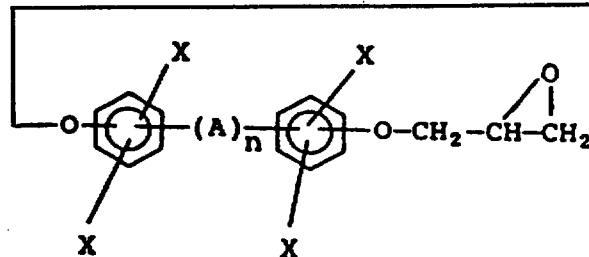
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(II)

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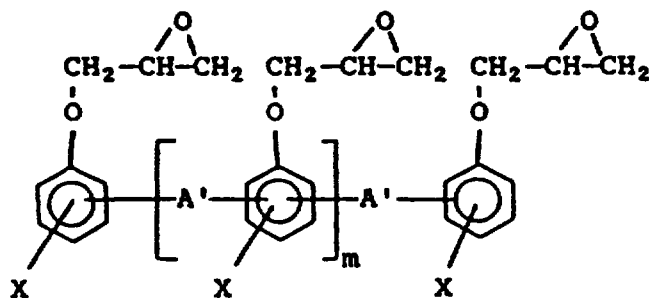


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(III)

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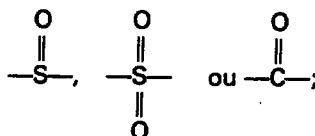
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dans lesquelles A représente de manière indépendante un groupe hydrocarbure divalent ayant de 1 à environ 8 atomes de carbone, —O—, —S—, —S—S—,

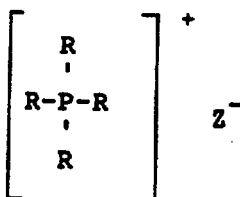
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10 chaque A' représente de manière indépendante un groupe hydrocarbure divalent ayant de 1 à environ 8 atomes de carbone; chaque X représente de manière indépendante un atome d'hydrogène, de brome, de chlore ou un groupe hydrocarbure ayant de 1 à environ 8 atomes de carbone; n prend la valeur 0 ou 1; n' possède une valeur moyenne inférieure à environ 0,9, et m possède une valeur moyenne comprise entre environ 0,1 et environ 4, et

15 B) à titre de catalyseur pour la réaction entre ladite résine époxyde et un composé contenant le groupe hydroxyle phénolique qui est ultérieurement mélangé avec ladite composition de résine époxyde précatalysée, un sel de phosphonium qui est représenté par la formule

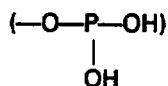
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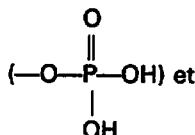
30 dans laquelle chaque R représente indépendamment un groupe hydrocarboné ayant de 1 à 20 atomes de carbone ou le groupe R¹Y dans lequel R¹ est un groupe hydrocarbure aliphatique ayant de 1 à 20 atomes de carbone et Y est Cl, Br, I, NO₂ ou OH, caractérisé par l'utilisation d'un sel de phosphonium dans lequel Z dans la formule mentionnée ci-dessus est un groupe phosphite

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ou un groupe polyphosphate ou un de leurs mélanges ou un mélange avec un composé phosphonium dans lequel Z est un groupe phosphate

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l'addition d'acide phosphorique, d'acide phosphoreux ou d'acide polyphosphorique à un mélange de (A) ladite résine époxyde et de (B) un composé phosphonium dans lequel ladite portion anion est un bicarbonate, un halogénure ou un complexe carboxylate-acide carboxylique, dans un rapport molaire de l'acide au composé phosphonium de un à un, afin de stabiliser la composition de résine époxyde précatalysée.

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3. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'on utilise à titre de résine époxyde un éther diglycidyle du bisphénol A ayant un poids moyen d'équivalent époxyde allant d'environ 175 à environ 195, et à titre de catalyseur, le phosphate d'éthyltriphenylphosphonium, le phosphite d'éthyltriphenylphosphonium, le polyphosphate d'éthyltriphenylphosphonium, le phosphate de tétrabutylphosphonium ou un de leurs mélanges.

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4. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'on utilise à titre de résine époxyde, un mélange d'un éther diglycidyle de bisphénol A et d'une résine époxyde Novolac, phénol-formaldéhyde et à titre de catalyseur, le phosphate d'éthyltriphenylphosphonium, le phosphite d'éthyltriphenylphosphonium, le polyphosphate d'éthyltriphenylphosphonium, le phosphate de tétrabutylphosphonium ou un de leurs mélanges.

60

5. Procédé selon les revendications 1 à 4, caractérisé en ce que l'on utilise un composé phosphonium dans lequel ledit anion est un iodure ou un complexe acétate-acide acétique.

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6. Procédé selon la revendication 5, caractérisé en ce que l'on utilise un composé phosphonium dans lequel la portion cation dudit composé phosphonium est éthyltriphenyle ou tétrabutyle.