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EPOXY RESINS COMPRISING AN AROMATIC DIAMINE CURING AGENT

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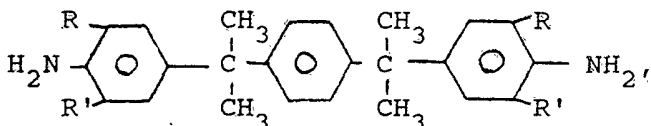
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(57) Claim

1. A composition comprising

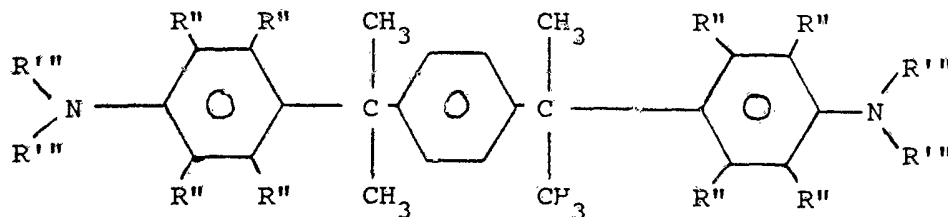
a) an epoxy resin and

b) a curing agent being an aromatic amine having the formula



in which each R is selected from C₂-C₇ alkyl and each R' is selected from C₁-C₇ alkyl.

4. The composition of any one of claims 1 to 3 in which the epoxy resin is a glycidated amine having the formula



in which each R'' is selected independently from H, C₁-C₁₀ alkyl and halides and each R''' is selected from

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H, CH₃, and CH₂CH₃, with the proviso that at

least one R'' at each N site is $\text{CH}_2\overset{\text{O}}{\text{CH}}_2\text{CH}_2$.

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COMPLETE SPECIFICATION

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Complete Specification for the invention entitled:

Epoxy Resins Comprising an Aromatic Diamine Curing Agent

The following statement is a full description of this invention, including the best method of performing it known to me/us

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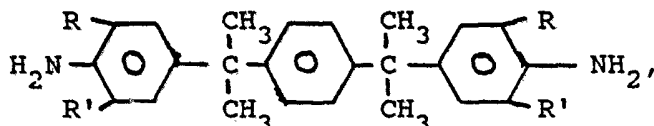
EPOXY RESINS COMPRISING
AN AROMATIC DIAMINE CURING AGENT

This invention relates to curing agents for epoxy resins. In one embodiment, the invention relates to epoxy resin systems having lengthened working time for applications in high-performance composites.

5 Epoxy resins are thermosettable materials which can be used, in combination with a selected curing agent, in high-performance applications such as electrical laminates and structural composites. For such applications, it is necessary to design epoxy/-curing agent systems which have a combination of high glass transition temperature, flexural strength and retention of modulus when wet. Such properties have been achieved in epoxy systems containing curing agents such as diaminodiphenylsulfone, alpha, alpha'-bis-
10 (4-aminophenyl)p-isopropenylbenzene and alpha, alpha'-bis(3,5-dimethyl-4-aminophenyl)-p-diisopropenylbenzene. The first of these suffers, however, from a deterioration of high-temperature properties under moist conditions. The latter two have good retention of
15 high-temperature properties under moist conditions, but for some applications have unacceptably short "out-time," or time during which the system applied to a prepreg remains tacky at room temperature, to permit convenient use in composites.
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25 It is therefore an object of the invention to provide an epoxy resin system which has good high-temperature properties, good property retention in a moist environment, and relatively long out-time.

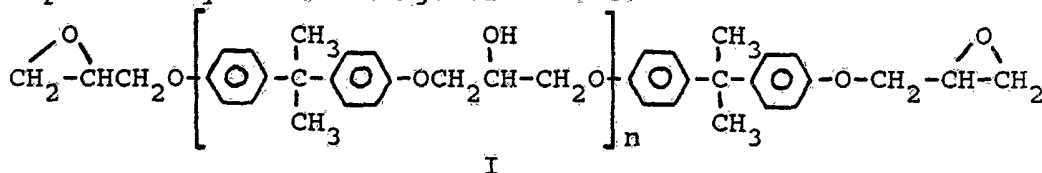
According to the invention, a composition is provided comprising an epoxy resin and a curing agent having the formula



in which each R is selected independently from C₂-C₇ alkyl and each R' is selected independently from C₁-C₇ alkyl.

The invention composition includes an epoxy resin which can be any curable epoxy resin having, on the average, more than one vicinal epoxide group per molecule. The epoxy resin can be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic, and may bear substituents which do not materially interfere with the curing reaction. They may be monomeric or polymeric.

Suitable epoxy resins include glycidyl ethers prepared by the reaction of epichlorohydrin with a compound containing at least one hydroxyl group carried out under alkaline reaction conditions. The epoxy resin products obtained when the hydroxyl group-containing compound is bisphenol-A are represented below by structure I wherein n is zero or a number greater than 0, commonly in the range of 0 to 10, preferably in the range of 0 to 2.

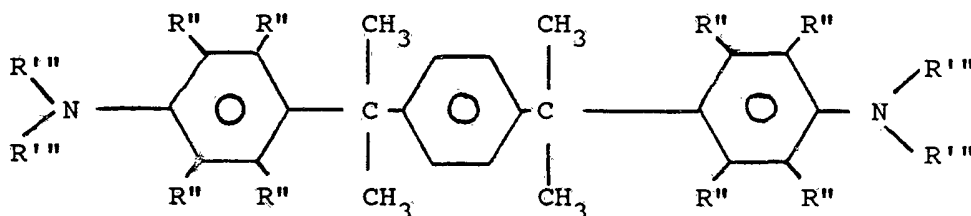


Other suitable epoxy resins can be prepared by the reaction of epichlorohydrin with mononuclear di- and trihydroxy phenolic compounds such as resorcinol and phloroglucinol, selected polynuclear polyhydroxy phenolic compounds such as bis(p-hydroxyphenyl)methane

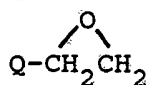
and 4,4'-dihydroxybiphenyl, or aliphatic polyols such as 1,4-butanediol and glycerol.

Epoxy resins particularly suitable for blending in the invention compositions have molecular weights generally within the range of 50 to 10,000, preferably 200 to 1500. The commercially available epoxy resin EPON Resin 825 (EPON is a registered trade mark), a reaction product of epichlorohydrin and 2,2-bis(4-hydroxyphenyl) propane (bisphenol-A) having a molecular weight of 400, an epoxide equivalent (ASTM D-1652) of 172-178, and an n value in formula I above of about 0, is a preferred epoxy resin blending component because of its commercial availability and the processing characteristics imparted to the resulting composition.

The preferred epoxy resin component of the invention composition is a glycidated aromatic amine having the formula

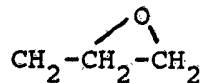


wherein each R''' is selected independently from H, CH₃, CH₂CH₃ and at least one R''' at each N site is

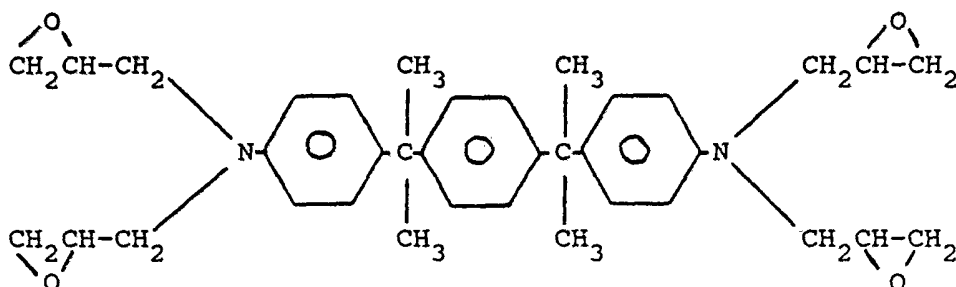


wherein each Q is selected independently from CH₂ and CH₂CH₂, and each R'' is selected independently from H, C₁-C₁₀ alkyl and halide.

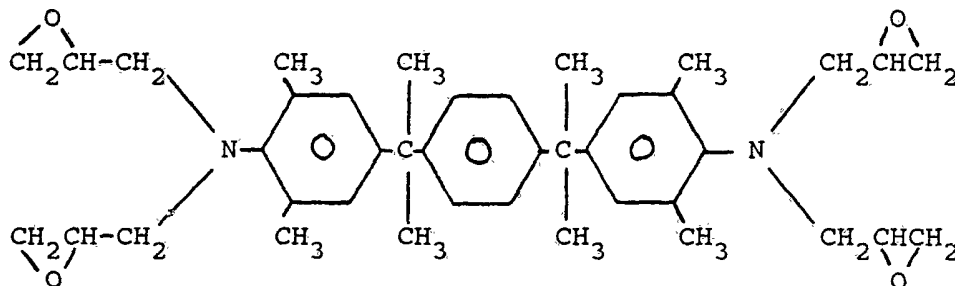
Preferred polyglycidyl amines can be described by the above formula wherein each R'' is selected independently from H, CH₃ and F, and each R''' is



Such preferred polyglycidyl amines include compounds having the structure



5 N,N'-tetraglycidyl-alpha,alpha'-bis(4-aminophenyl)-p-diisopropylbenzene, a solid tetraglycidyl amine having a glass transition temperature (uncured) of 23°C, and

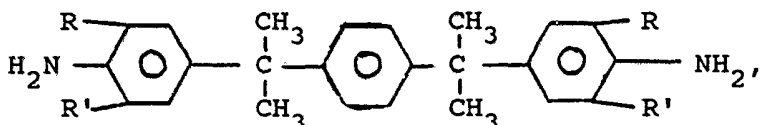


10 N,N'-tetraglycidyl-alpha,alpha'-bis(3,5-dimethyl-4-aminophenyl)-p-diisopropylbenzene, a solid tetraglycidyl amine having a glass transition temperature (uncured) of 41°C. One or more R'' can be halide, as might be desirable when flame retardancy is needed. Halide R'' is preferably chlorine, fluorine or bromine.

15 Such polyglycidyl aromatic amines can be prepared by reacting the corresponding polyaromatic amine with epichlorohydrin. The polyaromatic amine can be prepared by reacting the corresponding aniline with diisopropenylbenzene or its precursor bis(hydroxy-

isopropylbenzene) in the presence of hydrochloric acid or acid clay catalyst, as shown in Example 1 below.

The invention composition includes a polyaromatic polyamine curing agent which can be represented by the formula



in which each R is selected independently from C₂-C₇ alkyl and each R' is selected from C₁-C₇ alkyl.

Examples of such polyaromatic amines include alpha, alpha'-bis(3,5-diethyl-4-aminophenyl)-p-diisopropylbenzene, in which each R and each R' is -CH₂CH₃, and alpha, alpha'-bis(3-ethyl-5-methyl-4-aminophenyl)-p-diisopropylbenzene, in which each R is -CH₂CH₃ and each R' is CH₃.

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The curing agent will be present in the composition in an amount effective to cure the epoxy resin component of the composition. Generally, the curing agent will be present in an amount of from 0.5 to 1.5 equivalents per equivalent of the epoxy resin, usually from 0.8 to 1.3 equivalents. In terms of weight percent, the curing agent will generally be present in an amount of 20 to 50, preferably 30 to 40 weight percent, based on the weight of the epoxy/curing agent composition.

25
The curing conditions will vary widely depending upon the epoxy resin, the curing agent and the cured properties desired. Curing conditions for curing a polyaromatic polyglycidyl amine with the preferred curing agents will generally include heating the resin to a temperature within the range of 125°C to 225°C, preferably 170°C to 200°C for 1 to 3 hours.

30
The invention composition can contain a co-curing agent. Effective curing agents for epoxy resins, include, for example, amines, acids, anhydrides and

imidazoles. The preferred curing agents for imparting good strength, water resistance and high temperature resistance to the composition are substituted or unsubstituted aromatic amines. The aromatic amines are preferably aromatic diamines and triamines such as, for example, methylene dianiline, m-phenylene diamine, alpha, alpha'-bis(3,5-dimethyl-4-aminophenyl)-p-diisopropenylbenzene and blends of aromatic diamines available commercially as EPON Curing Agents Y and Z.

The composition can include one or more additional thermosetting or thermoplastic components, such as functionalized elastomers and bismaleimides.

The invention composition can, for applications such as prepregging, include an organic solvent or diluent present in an amount effective to decrease the viscosity of the system for easier processing. Polar organic solvents such as ketones, alcohols and glycol ethers, for example, are suitable. The proportion of solid components in the composition will vary widely depending upon the amount of other constituents present and the intended application of the composition, but for prepregging applications the solvent will generally constitute at least about 15 weight percent of the total weight of the epoxy/curing agent solution. The epoxy-containing solution with a curing agent makes up the "varnish" or laminating composition.

For preparation of reinforced laminates from the varnish, a fibrous substrate of glass, carbon, quartz, Kevlar, polyester, polytetrafluoroethylene, polybenzothiazole, boron, paper or like material, in chopped, mat or woven form, is first impregnated with the varnish. A prepreg is formed by heating the impregnated substrate in an oven at a temperature sufficient to remove the solvent and to partially cure without gelation, or "B-stage," the blended resin system, generally 40°C to

200°C, preferably 150°C to 190°C, for a time of up to 100 minutes, preferably 30 seconds to 2 minutes. A laminate is fabricated by subjecting a set of layered prepregs to conditions effective to cure the resins and to integrate the prepregs into a laminated structure. The laminate can optionally include one or more layers of a conductive material such as copper. Laminating conditions generally include a time of 30 minutes to 4 hours, preferably 1 hour to 2 hours, and a temperature of 160°C to 300°C, preferably 170°C to 200°C. The composition can include optional constituents such as inorganic fillers and flame retardants, for example. The laminate can be optionally "post-cured" by heating at a temperature of 200°C to 230°C for 1 to 6 hours to improve thermal properties.

The polyglycidyl amine can be applied to the fibrous reinforcing material from the melt or solution by methods known in the art. The polyglycidyl amine/-curing agent-impregnated substrate, or "prepreg," or a laminate prepared from a plurality of prepregs, is then cured, generally at a temperature of 160°C to 300°C for 30 minutes to 4 hours to form the structural composite article.

The invention composition can optionally include additives for control or modification of various properties of the composition in its cured or uncured state, including cure rate accelerators or retardants, tackifiers and the like.

The invention compositions are useful as the curable components of coatings, adhesives and structural composites.

Example 1

This example illustrates the preparation of alpha, alpha'-bis(3,5-diethyl-4-aminophenyl)-p-diisopropylbenzene.

Into a 4 liter, 4-necked round flask equipped with a stirrer, Dean-stark trap, condenser, thermocouple, and nitrogen sweep, was charged 3660.0g of 2,6-diethyl-aniline, 391.7g 1,4-bis(hydroxyisopropylbenzene (p-diol) and 161g Filtrol Grade #1 (Harshaw Chemical Company). The reaction mixture was heated with stirring to 170°C while water of dehydration was removed with the Dean-stark trap. The reaction mixture was held at temperature until no more water collected in the Dean-stark trap. The mixture was filtered hot to remove the Filtrol and the aniline was removed under vacuum. Yield was 816g or 89%.

Examples 2-7

Five epoxy resin curing agent compositions were prepared as follows:

100 parts of tetraglycidyl- α,α' -bis(4-aminophenyl)-p-diisopropylbenzene available under the tradename EPON HPT Resin 1071 was weighed into a beaker and melted in an oven at 150°C. 33.5 parts of 4,4'-diaminodiphenyl sulfone (DDS) available under the tradename Suncure S was heated to 170°C and added to the resin with hand mixing. The mixture was returned to an oven at 170°C until the DDS dissolved. The mixture was then quickly cooled to ambient temperature and aliquots were taken over a period of time for gel time studies. For the gel time studies, an aliquot of the resin/curing agent system was placed on a gel plate preheated to 175°C. The gel point was that point at which "strings" of the molten material could no longer be drawn with a spatula.

100 parts of EPON HPT 1071 tetraglycidyl amine was weighed into a beaker and melted in an oven at 150°C. 51.8 parts of α,α' -bis(4-aminophenyl)-p-diisopropylbenzene was melted at 150°C and added to the resin with hand mixing. The mixture was then quickly cooled

to ambient temperature and aliquots were taken over a period to time for gel time studies.

100 parts of EPON HPT 1071 tetraglycidyl amine was weighed into a beaker and melted in an oven at 150°C.

5 60.4 parts of an alpha, alpha'-bis(3,5-dimethyl-4-amino-phenyl)-p-diisopropyl-benzene was melted at 150°C and added to the resin with hand mixing. The mixture was then quickly cooled to ambient temperature and aliquots were taken over a period of time for gel time studies.

10 100 parts of EPON HPT 1071 tetraglycidyl amine was weighed into a beaker and melted in an oven at 150°C.

69.0 parts of the amine of Example 1 was melted at 150°C and added to the resin with hand mixing. The mixture was then quickly cooled to ambient temperature and aliquots were taken over a period of time for gel time studies.

100 parts of EPON HPT 1071 tetraglycidyl amine was weighed into a beaker and melted in an oven at 150°C.

20 64.6 parts of alpha, alpha'-bis(3-ethyl-5-methyl-4-amino-phenyl)-p-diisopropylbenzene was melted at 150°C and added to the resin with hand mixing. The mixture was then quickly cooled to ambient temperature and aliquots were taken over a period of time for gel time studies.

100 parts of EPON HPT 1071 tetraglycidyl amine was weighed into a beaker and placed in an oven at 150°C to melt.

25 55.2 parts of alpha, alpha'-bis(3-ethyl-5-methyl-4-aminophenyl)-p-diisopropylbenzene and 13.0 parts of alpha, alpha'-bis-(3,5-diethyl-4-aminophenyl)-p-diisopropylbenzene were melted at 150°C and added to the resin with hand mixing. The mixture was then quickly cooled to ambient temperature and aliquots were taken over a period of time for gel time studies.

30 Table 1 show that gel times (at 175°C) of the invention compositions (Examples 4-7) are generally comparable to or greater than that of the conventional
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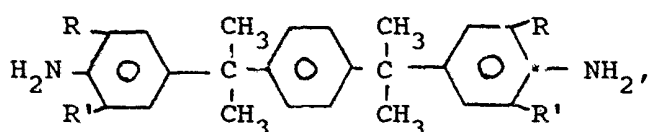
TGMDA (N,N'-tetraglycidyl-4,4'-diaminodiphenyl methane)/4,4' diaminodiphenyl sulfone (DDS) system.

Table 1

| <u>Composition</u> | <u>Gel Time in Minutes</u> | | | |
|--------------------|----------------------------|----------------|----------------|----------------|
| | <u>Initial</u> | <u>14 Days</u> | <u>28 Days</u> | <u>63 Days</u> |
| TGMDA/DDS | 27.0 | 30.5 | 27.0 | 24.6 |
| Example 2 | 34.0 | 31.0 | 27.0 | 25.9 |
| Example 3 | 5.8 | 3.2 | 2.4 | 2.1 |
| Example 4 | 30.3 | 29.3 | 20.3 | 20.4 |
| Example 5 | 50.9 | 54.4 | 48.0 | 35.0 |
| Example 6 | 40.2 | 36.3 | 35.0 | 19.4 |
| Example 7 | 51.8 | 49.9 | 47.0 | 29.4 |

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A composition comprising
 - a) an epoxy resin and
 - b) a curing agent being an aromatic amine having the formula

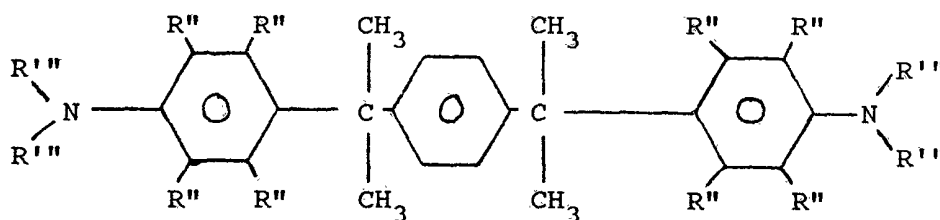


5 in which each R is selected from C₂-C₇ alkyl and each R' is selected from C₁-C₇ alkyl.

2. The composition of claim 1 in which the aromatic amine is alpha, alpha'-bis(3,5-diethyl-4-aminophenyl)-p-diisopropylbenzene or alpha, alpha'-bis(3-ethyl-5-methyl-4-aminophenyl)-p-diisopropylbenzene.

10 3. The composition of claim 1 or 2 in which the aromatic amine is present in the composition in an amount of from 20 to 50 %w, based on the weight of the composition.

4. The composition of any one of claims 1 to 3 in which the epoxy resin is a glycidated amine having the formula



20 in which each R'' is selected independently from H, C₁-C₁₀ alkyl and halides and each R''' is selected from H, CH₃, and CH₂CH₃, with the proviso that at

least one R''' at each N site is $\text{CH}_2\overset{\text{O}}{\text{CH}_2}\text{CH}_2$.

5. The composition of any one of claims 1 to 4 which further comprises at least one further component being a bismaleimide or a functionalized elastomer.

6. Epoxy resins comprising an aromatic diamine curing agent substantially as hereinbefore described with reference to any one of the Examples.

DATED this SEVENTH day of DECEMBER 1988
Shell Internationale Research Maatschappij B.V.

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