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PATENT SPECIFICATION

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(54) RESIN COMPOSITION AND METHOD FOR ITS USE IN FORMING LAMINATES

(71) We, SUMITOMO BAKELITE COMPANY, LIMITED, a body corporate organised under the laws of Japan, of 2-2, Uchisaiwaicho-1-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a resin composition suitable for use in the production of high-density printed circuit boards for electronic equipment.

The board materials which have heretofore been used most frequently for printed wiring in electronic equipment are phenolic resin laminates and epoxy resin laminates. However, with the recent progress in space development and in the communications industry, the demands for improved functioning of equipment, higher reliability and higher wiring density have increased and the conventional materials have become unsatisfactory.

Phenolic resin laminates have been found to have unsatisfactory electrical properties and heat resistance and thus to be inadequate for carrying advanced functional elements such as ICs (integrated Circuits) and LSIs (Large Scale Integrated Circuits). Epoxy resin laminates, on the other hand, have a low glass transition temperature and therefore undergo appreciable dimensional change during circuit-forming treatment, and it has been found that printed circuit boards consisting epoxy resin laminates undergo, at elevated temperatures, deterioration in electrical and mechanical performance, resulting in a lack of reliability of the electronic equipment in which they are used.

It has been customary to assemble a multilayer printed board, which is a typical high-density printed circuit board, by the use of copper-clad epoxy resin-glass cloth laminates and preregs of the same materials. However, in the manufacture of large printed circuit backboards for computers or super-high-density multilayer (eight or more layers) printed circuit boards, for space development, it has been found that, if conventional copper-clad epoxy-glass laminates are used, the reproducibility of the wiring pattern is poor and the high-precision positioning of the circuits becomes impossible because of an intolerably large dimensional change in the face direction caused by the thermal history during circuit production and by the application of heat and pressure during the press-moulding of the assembled layers; drilling of the printed circuit board is often disturbed by the occurrence of warp and twist; and the through-hole is easily damaged by thermal shock while in use because of a relatively large linear expansion coefficient in the direction of thickness of the laminate. Consequently, the use of epoxy resin laminates in high-performance parts is limited.

Thermosetting polyaminobismaleimide resins have already been described and are obtained by the addition reaction of an N,N'-bismaleimide with a diamine;

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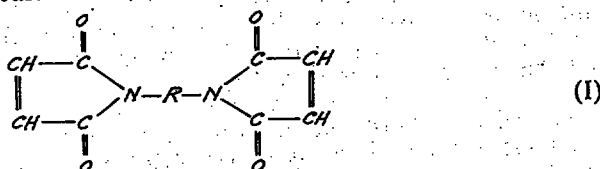
they have excellent mechanical characteristics at high temperature, excellent resistance to thermal deterioration, and a very small linear expansion coefficient. Polyaminobismaleimide resins alone, however, are poor in curability under the conditions usual for press-moulding a laminate, and hence require either pressing for a long period of time at a temperature as high as at least 200°C or, alternatively, after-baking at a temperature of 200°C or above, for a long period of time, after pressing at 170 to 200°C.

Polyaminobismaleimide resins moreover, are poor in flow property at the time of pressing, tends to occlude voids between layers of the base materials and are inferior with respect to bond strength between layers of the base materials. Therefore, cracks tend to be caused in the layers when drilling a laminate or forming an external shape. The resins moreover, provide extremely poor adhesion of the board to a copper foil, particularly adhesion of the prepreg to the copper foil of the inner layer circuit, which adhesion is the most important requirement for a multilayer printed circuit board. Such a defective board, therefore, cannot meet the requirements for processing and assembling, and would encounter great difficulties in actual service.

Since a polyaminobismaleimide resin, on the other hand, contains in its molecule reactive groups bearing active amino-hydrogen, it can be used jointly with, for example, an epoxy resin to improve, to a certain extent, the curability, mouldability, and adhesive strength when used in copper-clad laminates. Incorporation of a large amount of an epoxy resin, however, brings about a decrease in heat resistance, while adhesion of the inner layer of a multilayer printed circuit board is not sufficiently improved; an adhesive strength sufficient for practical use cannot be obtained even when the copper foil has been surface-treated mechanically or chemically.

The present inventors have conducted extensive research in an attempt to obtain a resin composition which has the excellent heat resistance and dimensional stability of polyaminobismaleimide resins, but is free from the above-mentioned disadvantages with respect to the production of laminates, and has a good adhesive strength. It has been found that incorporation of a particular type of copolymer into the polyaminobismaleimide/epoxy resin system is very effective in improving the properties of that system.

The present invention accordingly provides a resin composition comprising: 100 parts by weight of at least one polyaminobismaleimide prepolymer obtained by reacting at least one N, N'-bismaleimide of the formula I,



wherein R represents an aliphatic, cycloaliphatic or aromatic divalent radical, with at least one aliphatic, cycloaliphatic or aromatic diamine,

10 to 300 parts by weight of at least one epoxy compound containing at least two epoxy groups in the molecule, and

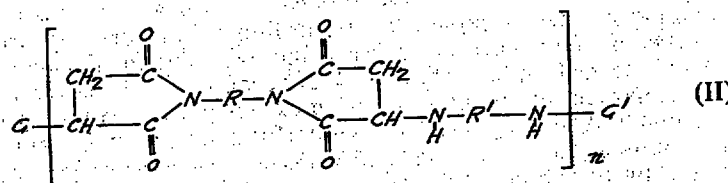
5 to 150 parts by weight of at least one copolymer having a number-average molecular weight within the range of from 1000 to 60 000 and selected from (A) copolymers of one or more aromatic vinyl compounds with maleic anhydride,

(B) partial alkyl esters of the said copolymers (A),

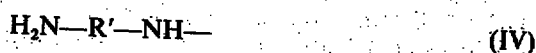
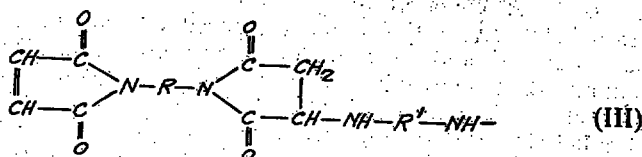
(C) copolymers of one or more aromatic vinyl compounds with one or more alkyl maleates, and

(D) copolymers of one or more aromatic vinyl compounds with maleic anhydride and with one or more alkyl maleates.

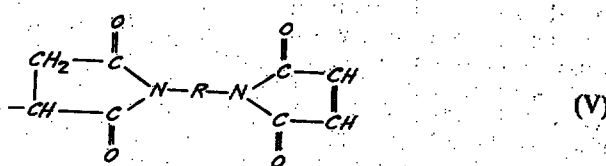
A typical polyaminobismaleimide prepolymer is one having the general formula II



wherein R and R', which may be the same or different, each represents an aliphatic, cycloaliphatic, or aromatic divalent radical; G represents a radical of the formula II or of the formula IV



in which R and R' are as defined above; G' is —H or a radical of the formula V



in which R is as defined above; and n is an integer of at least one, preferably 1 to 50.

Examples of N,N'-bismaleimides represented by the general formula I include N,N'-ethylenebismaleimide, N,N'-hexamethylenebismaleimide, N,N'-decamethylenebismaleimide, N,N'-m-phenylenebismaleimide, N,N'-p-phenylenebismaleimide, N,N'-(4,4'-diphenyl methane)bismaleimide, N,N'-(4,4'-diphenyl ether)bismaleimide, N,N'-(4,4'-diphenyl sulphone)bismaleimide, N,N'-(4,4'-dicyclohexylmethane)bismaleimide, N,N'-m-xylenebismaleimide, and N,N'-(4,4'-diphenylcyclohexane)bismaleimide. Examples of diamines to be reacted with the bismaleimides include straight chain aliphatic diamines having 2 to 20 carbon atoms such as ethylenediamine, trimethylenediamine, tetramethylenediamine, and hexamethylenediamine; and aromatic and cycloaliphatic diamines such as m-phenylenediamine, p-phenylenediamine, p-xylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulphone, 4,4'-diaminodicyclohexane, 1,4-diaminocyclohexane, bis(4-aminophenyl)phenylmethane, 1,5-diaminonaphthalene, m-xylylenediamine, p-xylylenediamine, and 1,1-bis(4-aminophenyl)cyclohexane.

The prepolymer may, for example, be prepared according to Japanese Patent Publication No. 42,160/72 (Rhône-Poulenc Co., France), by reacting a bismaleimide and a diamine at 50 to 250°C, preferably 50 to 170°C, for several minutes to several hours. Although the ratio of the diamine to the bisimide is not critical, it is preferable to use the reactants in such proportions that 0.5 to 3 reactive amino hydrogen atoms may be available per one carbon-to-carbon double bond of the bisimide. The reaction between the bisimide and the diamine may be conducted either in the molten state or in a suitable solvent such as dimethylformamide, dimethyl sulphoxide, or N-methylpyrrolidone. In the case of reaction in the molten state, the reaction mixture obtained after the reaction for a predetermined period of time is cooled and the resulting solid prepolymer is pulverized. When the reaction is conducted in a solvent, the reaction mixture obtained after the reaction for a predetermined period of time is cooled and, if necessary, diluted to obtain a prepolymer solution.

In view of the reaction mechanism, the prepolymer thus prepared may contain, beside the addition product of the bisimide and the diamine, those polymers which are formed by radical polymerization of the bisimide or the prepolymer itself at the terminal double bonds. However, even if such polymers are present, the prepolymer can be used in the composition of this invention without causing any trouble. Any reaction mixture of the bisimide and the diamine may be used so long as it is a so-called B-stage product having a proper melting point range and a sufficient reactivity to cause curing on further heating. The melting point range of the prepolymer or the reaction mixture of the bisimide and the diamine can be properly regulated by controlling heating conditions and the aforesaid reactant ratio. A prepolymer having a melting point range within the range of from 50 to 150°C is preferred.

Having imide linkages in its molecule, the polyaminobismaleimide is very stable both thermally and chemically and imparts to the present resin composition a high resistance to thermal deterioration, excellent mechanical and electrical characteristics at elevated temperatures (above 150°C), and a distinguished dimensional stability, so that it is made possible to manufacture a laminate which can be processed and used under severe conditions. Since the polyaminobismaleimide contains residual reactive amino groups in its molecule, it is rich in self-polymerizability and reactivity with the polyepoxy compound incorporated in the present resin composition and imparts to the resin composition the B-stage properties which are necessary in coating or impregnating a laminating base material and also the property of further reacting, by heat and pressure applied in the moulding step, to form a three-dimensional structure, that is, the thermosetting property.

Although the epoxy compound for use in this invention may be any compound having in its molecule at least two epoxy groups, an ordinary epoxy resin having an epoxy equivalent of 100 to 4,000 is preferred. Examples of such polyepoxy compounds include diglycidyl ethers obtained by the reaction of bisphenol-A or halogenated bisphenol-A and epihalohydrin (Epikote (registered trademark) 828, 1001, 1004, 1007, 1045, etc. of Shell Chemical Corp.); polyether type polyglycidyl ethers obtained by reaction of epihalohydrin and a polyhydric alcohol obtained by reacting bisphenol-A with an alkylene oxide with an acid or alkali catalyst (for example EP-400, of Asahi Denka Kogyo Co.); polyglycidyl ethers or esters obtained by reaction of an aromatic polyhydric alcohol or aromatic polycarboxylic acid and an epihalohydrin; polyglycidyl ethers of an aliphatic polyether or polyhydric alcohol such as glycerol, trimethylolpropane, butanediol, or a polyalkylene glycol; cycloaliphatic polyepoxy compounds having a cyclohexene oxide or cyclopentadiene oxide structure; and polyglycidyl ethers of novolak-type phenolformaldehyde resins.

Such a polyepoxy compound enhances the curability of the polyaminobismaleimide in lamination and enables the resin composition to cure sufficiently at 170° to 200°C., so that after-baking is hardly necessary. The polyepoxy compound, moreover, brings about an improvement in flow property of the resin composition at the time of moulding, so that voids are prevented from being formed between the layers of the base materials, and the adhesion between the board and the copper foil are improved. Thus, the basic characteristics necessary for producing laminates and copper-clad laminates are imparted.

However, since the polyepoxy compound added in great excess relative to the polyaminobismaleimide tends to decrease the excellent heat resistance of the latter, there is a limit in respect of the amount of the polyepoxy compound to be added. In the present invention, 10 to 300 parts by weight of the polyepoxy compound can be used per 100 parts by weight of the polyaminobismaleimide. If the polyepoxy compound is used in an amount smaller than 10 parts by weight, the resin composition is not improved in curability and mouldability, while if the amount exceeds 300 parts by weight, the laminate becomes inferior with respect to the heat distortion temperature, the properties at temperatures above 150°C, and the resistance to thermal deterioration. The preferred mixing ratio is 20 to 200 parts by weight of the polyepoxy compound per 100 parts by weight of the polyaminobismaleimide.

As previously mentioned the resin composition of the invention contains a copolymer of an aromatic vinyl compound and a maleic acid derivative in addition to the above-noted polyaminobismaleimide and polyepoxy compound. The copolymer has a number-average molecular weight of from 1000 to 60,000 and is selected from the group consisting of

(A) copolymers of one or more aromatic vinyl compounds with maleic anhydride,

(B) partial alkyl esters of the said copolymers (A),

(C) copolymers of one or more aromatic vinyl compounds with one or more alkyl maleates, and

(D) copolymers of one or more aromatic vinyl compounds with maleic anhydride and with one or more alkyl maleates.

The aromatic vinyl compounds used in the copolymers (A), (B), (C), and (D) include, for example, styrene; styrene derivatives such as methylstyrene, dimethylstyrene, ethylstyrene, α -methylstyrene, α -methyl-p-isopropylstyrene, and divinylbenzene, and halogenated styrene derivatives. Copolymers containing two or more types of aromatic vinyl compounds may be used.

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The copolymer (A) may be obtained by copolymerization of an aromatic vinyl compound and maleic anhydride and preferably contains in the molecule at least 30 mole-% of the maleic anhydride structural unit.

The copolymer (B) may be obtained by partial esterification of a copolymer (A) with an aliphatic alcohol and may contain structural units of maleic anhydride, maleic acid, monoalkyl maleate, and dialkyl maleate. Preferably the copolymer has a degree of esterification of 50 mole-% or less based on the total amount of the maleic anhydride structural unit before esterification.

The copolymer (C) may be obtained by copolymerization of an aromatic vinyl compound with a monoalkyl maleate and a dialkyl maleate and preferably contains in the molecule at least 30 mole-% of the monoalkyl maleate structural unit.

The copolymer (D) may be obtained by copolymerization of an aromatic vinyl compound, maleic anhydride, and a monoalkyl maleate and/or a dialkyl maleate, and preferably contains in the molecule at least 30 mole-% of the maleic anhydride structural unit or at least 30 mole-% in total of the maleic anhydride structural unit and the monoalkyl maleate structural unit.

The alkyl groups of the alkyl maleates in the copolymers (B), (C), and (D) are preferably those having from 1 to 20, more preferably from 1 to 10, carbon atoms, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, tert-amyl, n-heptyl, n-octyl, 2-ethyl-1-hexyl, n-nonyl, and n-decyl. The copolymers (C) and (D) may, if desired, contain two or more alkyl groups.

These copolymers have a number-average molecular weight of 1,000 to 60,000, preferably 2,000 to 30,000. They are thermally stable, high molecular weight substances and, owing to the high carboxylic anhydride group content or high carboxyl group content, can react not only with the polyepoxy compound but also with the residual amino groups in the polyaminobismaleimide to increase the density of cross-linking between the resin components.

Consequently, by the concomitant use of the copolymer component, it is possible to counteract the decrease in heat resistance caused by the addition of the polyepoxy compound, and hence the polyepoxy compound can be added in an amount as great as 100 parts by weight or more per 100 parts by weight of the polyaminobismaleimide to improve markedly the mouldability and other properties of the resin composition without causing a deterioration in the heat resistance.

Further, the addition of the copolymer component brings about a marked improvement in adhesive properties between the polyaminobismaleimide/epoxy resin composition and metal foil, particularly copper foil. As a result, the adhesive strength of the inner copper foil has, for the first time, reached a level sufficient to allow the production of a multilayer printed circuit boards which have to endure severe treatment conditions. Moreover, the reactivity of the copolymer with the polyaminobismaleimide and the epoxy resin is very high and results in an increase in the cure rate of the resin composition, so that the resin composition can be cured adequately at 150–170°C, which is the normal pressing temperature range for laminates.

The copolymer selected from the types (A), (B), (C), and (D) is incorporated into the resin composition in an amount of 5 to 150, preferably 10 to 100, parts by weight per 100 parts by weight of the polyaminobismaleimide. If the amount incorporated is below 5 parts by weight, the effect on heat resistance and adhesion is insufficient, while if it exceeds 150 parts by weight, the mechanical properties and chemical resistance of the laminate are detrimentally affected.

The weight ratio of the polyepoxy compound to the copolymer component in the present resin composition, though not critical, is preferably in the range of from 0.5 to 10.0.

The present resin composition may, if necessary, be admixed with small amounts of conventional hardeners for epoxy resins, low-molecular-weight epoxy compounds, flame retardants, fillers, and colourants. The addition of such ingredients enables the resulting laminate to be used for special purposes.

In manufacturing a laminate by use of the present resin composition, a varnish of a concentration of 20 to 50% by weight is prepared by dissolving the resin composition in an inert solvent such as an amide, for example, N,N-dimethylformamide or N,N-dimethylacetamide; a lactone, for example, N-methyl-2-pyrrolidone or γ -butyrolactone; or a lactam, for example, caprolactam; or in a mixture of the inert solvent and an aromatic hydrocarbon or a ketone. A fibrous base material selected from glass cloth, glass paper, asbestos paper and carbon

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fibre cloth, which has been treated with an appropriate coupling agent, is impregnated with the above varnish, for example by means of a coater-drier, and dried at $130^{\circ} \pm 40^{\circ}\text{C}$. for 1 to 30 minutes to prepare a B-stage prepreg having a resin content of from 30 to 60% by weight. To produce a laminate, sheets of the prepreg are placed one on another to a desired total thickness of 0.1 mm to several millimetres and, if necessary, a foil of a metal such as copper, aluminium or nichrome is placed on one or both sides of the resulting assembly. The assembly thus obtained is subjected to heating under pressure by means of a hot-platen press to obtain a laminate or a metal-clad laminate. The heating under pressure is preferably conducted at a temperature of from 120 to 250°C , and at a pressure of from 5 to 200 kg/cm^2 , for 15 to 240 minutes. On account of the markedly improved curability of the present resin composition, the moulding of the laminate can be effected at a temperature much lower than the moulding temperature in the case where a conventional polyimide resin or polyaminobismaleimide resin is used alone, for example, at 150 to 180°C for 30 to 180 min.

A moulded laminate produced according to the invention has satisfactory properties without being after-baked. However, in order to relieve the strain developed during the moulding cycle and to develop effectively the excellent dimensional stability of the resin composition, it is preferable to subject the moulded laminate to heat treatment to a certain extent, and, if necessary, the moulded laminate may be after-baked at 180 to 250°C for up to twenty hours.

A multilayer printed circuit board may be manufactured in the following way using the present resin composition. For example, an inner printed circuit board is formed by use of the above-mentioned both side-copper-clad laminate of glass-cloth base material, and, if necessary, surface-treated chemically or mechanically. A prepreg produced according to the invention is interposed as the interlayer adhesive sheet between several sheets of the inner circuit board and between the inner circuit and the board side of the one-side copper-clad laminate for surface circuit, and the positions of the prepreg, the inner circuit boards and the surface circuit laminate are adjusted to the respective correct positions by means of a metal plate with a guide pin, and the resulting assembly is press-moulded between hot platens under application of heat and pressure to form a multilayer board. Surface circuits and through-holes are formed to obtain a finished multilayer printed circuit board.

The laminate and copper-clad laminate manufactured by use of the present resin composition show little deterioration in flexural strength, modulus of elasticity in flexure, and adhesive strength when exposed to an elevated temperature above 150°C and in mechanical properties and adhesive strength when used at an elevated temperature within the range of from 150 to 200°C for a long period of time, and hence, have a sufficiently high reliability to be used as a material for electronic parts. Since the said laminates have, in a temperature region above 150°C , a linear expansion coefficient as small as one-half to one-third of that of a conventional epoxy resin-glass cloth laminate, the dimensional change in the face direction resulting from the thermal history in the processing of the printed circuit board and in the pressing of a multilayered assembly is very small. Such a high dimensional stability facilitates the fabrication of a printed circuit board having a reference grid size of 1.27 mm and the fabrication of a super high density circuit board such as a printed circuit board of eight or more layers, such fabrication having been difficult with conventional epoxy-glass-type laminates. Since the linear expansion coefficient in the direction of thickness of the multilayer printed circuit board is small, the formation of defects based on the difference in thermal expansion and contraction between the copper-plated layer in the through-hole portion and the board when subjected to temperature shock is little and, as a result, the reliability of electronic equipment such as computers is enhanced.

A multilayer printed circuit board produced according to the invention is excellent with respect to properties, such as machinability in drilling, moisture resistance, soldering heat-resistance and electric properties, which are required for a multilayer printed circuit board. Flame resistance can also be imparted.

The resin composition of the present invention is markedly improved with respect to its laminating property, curability, and adhesive property, in comparison with prior art polyaminobismaleimide-based resin compositions. With regard to the manufacture of a super-high-density printed circuit board, the advantages offered by the present resin composition are great improvements in accuracy, yield, cost, and adhesive strength to copper foil (initial adhesion,

adhesion when heated, change in adhesive strength with the lapse of time, and that of inner layers).

Although the resin composition of the invention is very effective for use in the production of multilayer printed circuit boards which require the highest technique and the highest quality, it can also be widely used to produce laminates for use in heat-resistance structural parts for the space development industry, aircrafts, heavy electrical machinery and automobiles; and laminates and printed circuit boards for use in the functional parts of electronic communication equipment, household electrical appliances, and industrial equipment. Incorporation of a filler into the resin composition allows the composition to be used as a heat-resistant moulding material.

The following Examples illustrate the invention.

Example 1.

A varnish containing 45% by weight of a resin composition was prepared by dissolving in N-methyl-2-pyrrolidone 100 parts by weight of a polyaminobis-maleimide obtained by reacting 1 mole of N,N'-4,4'-diphenylmethanebis-maleimide with 1 mole of 4,4'-diaminodiphenylethane in the molten state of 150°C for 30 minutes; 100 parts by weight of a bisphenol-A-type diglycidyl ether having an epoxy equivalent from 450 to 500 (Epikote (registered trademark) 1001 of Shell Chemical Corp.); 10 parts by weight of a styrene-maleic anhydride copolymer containing 50 mole-% of maleic anhydride.

A sheet of glass cloth, 0.1 mm in thickness which had been treated with γ -glycidoxypolytriethoxysilane, was impregnated with the said varnish and dried at 130°C for 7 minutes by means of a coater-drier to obtain a sheet of B-stage prepreg with a resin content of 40% by weight.

Sixteen sheets of the prepreg were placed one on another, and electrolytic copper foil of 35 μ m thickness was placed on both outer sides of the resulting assembly and the thus obtained assembly was inserted between two sheets of stainless steel, and heated at 170°C under a pressure of 50 kg/cm² for 2 hrs. by means of a hot-platen press to obtain a two-side copper-clad laminate, 1.6 mm in overall thickness.

The results of the test for the performance characteristics of the copper-clad laminate thus obtained were as shown in Table 1, wherein the curability was expressed in terms of gel time (seconds) when the varnish, prepared as mentioned above, was heated on a hot plate at 150°C.

As is seen from Table 1, as compared with a conventional polyaminobis-maleimide-based resin composition, the present composition was greatly superior in low-temperature curing ability, and a copper-clad laminate obtained therefrom had excellent mechanical properties and adhesive strength at elevated temperatures and showed little deterioration in these properties even after a long-period heat treatment. The present copper-clad laminate, moreover, had a thermal expansion coefficient as small as one-half to one-third of that of a conventional epoxy resin laminate, a markedly improved soldering heat-resistance, and other excellent characteristic properties requisite to a heat-resistant laminate even without heat treatment after moulding.

As shown in Table 1, when the copper-clad laminate was subjected to after-baking at 200°C for 24 hours, the thermal characteristics were somewhat enhanced, but there was only a small difference between before and after the after-baking.

Comparative Example 1.

The same polyaminobismaleimide as in Example 1 was dissolved in N-methyl-2-pyrrolidone to prepare a varnish containing 50% by weight of the resin. In the same manner as in Example 1, a sheet of glass cloth, 0.1 mm in thickness, which had been treated with γ -glycidoxypolytriethoxysilane, was impregnated with the said varnish and dried at 150°C for 10 minutes to obtain a sheet of B-stage prepreg of a resin content of 40% by weight.

The prepreg sheets thus prepared were assembled in the same manner as in Example 1 and the assembly was heated at 180°C under a pressure of 100 kg/cm² for 2.5 hours to obtain a two-side copper-clad laminate, 1.6 mm in overall thickness.

The copper-clad laminate, which had been obtained as mentioned above and then subjected to after-baking at 200°C for 24 hours, was, as shown in Table 1, excellent in mechanical properties at elevated temperatures and thermal

expansion coefficient, but very low in adhesive strength between the copper foil and the board, and hence, was unsatisfactory for use in a multilayer printed circuit board.

The polyaminobismaleimide resin varnish obtained as mentioned above had a markedly prolonged gel time, and the curing reaction thereof was slow. Accordingly, sufficient characteristics could not be imparted by the mere press-moulding mentioned above, and particularly the adhesive strength to copper foil before after-baking was 0.3 kg/cm. Therefore, the laminate could not be used in practice.

Comparative Example 2.

A varnish containing 30% by weight of a resin composition was prepared by dissolving 100 parts by weight of a bisphenol-A-type diglycidyl ether having an epoxy equivalent from 450 to 500 [Epikote (registered trademark) 1001] and 12 parts by weight of methanedianiline in methyl ethyl ketone.

In the same manner as in Example 1, a sheet of glass cloth, 0.1 mm in thickness, which had been treated with γ -glycidoxypropyltriethoxysilane, was impregnated with the varnish obtained above, and then dried at 130°C for 7 minutes to obtain a sheet of B-stage prepreg with a resin content of 40% by weight.

In the same manner as in Example 1, an assembly of the prepreg sheets obtained above was subjected to heat and pressure by means of a hot-platen press, at 170°C and 70 kg/cm² for 2.5 hours to obtain a two-side copper-clad laminate, 1.6 mm in overall thickness.

The said copper-clad laminate was, as shown in Table 1, inferior in mechanical strength and adhesive strength to copper foil at elevated temperatures, deteriorated markedly as a result of the heat-treatment at elevated temperatures, and was unsatisfactory with respect to soldering heat-resistance. Therefore, the above copper-clad laminate could not be used as a heat-resistant laminate in practice. Furthermore, said copper-clad laminate had too large a linear expansion coefficient to be used in a high density multilayer printed circuit board.

Comparative Example 3.

A varnish containing 45% by weight of a resin composition was prepared by dissolving 100 parts by weight of the same polyaminobismaleimide as used in Example 1 and 100 parts by weight of a bisphenol-A-type diglycidyl ether having an epoxy equivalent from 450 to 500 [Epikote (registered trademark) 1001] in N-methyl-2-pyrrolidone.

In the same manner as in Example 1, a sheet of glass cloth, 0.1 mm in thickness, which had been treated with γ -glycidoxypropyltriethoxysilane, was impregnated with the varnish obtained above, and then dried at 150°C for 5 minutes to obtain a sheet of B-stage prepreg with a resin content of 40% by weight.

In the same manner as in Example 1, an assembly of the prepreg sheets obtained as mentioned above was subjected to heat and pressure by means of a hot-platen press, at 170°C and 50 kg/cm² for 2.5 hours to obtain a both side copper-clad laminate, 1.6 mm in overall thickness.

The performance characteristics of this copper-clad laminate were as shown in Table 1. Although the laminate showed relatively good heat resistance without having been subjected to after-baking, yet the excellent heat resistance of the polyaminobismaleimide was not fully developed. After having been subjected to after-baking at 200°C for 24 hours, the laminate showed some improvement in mechanical properties at elevated temperatures and in linear expansion coefficient, but these properties were still inadequate for a heat-resisting laminate.

As compared with a laminate in which a polyaminobismaleimide was used alone, the adhesive strength between the copper foil and the board in this copper-clad laminate was improved to some extent in initial value but still inadequate for a multi-layer printed circuit board which must withstand severe conditions under which the laminate is to be processed and used.

The above-mentioned varnish had a gel time considerably shortened by the addition of the polyepoxy compound, as compared with a varnish containing the polyaminobismaleimide alone, but not enough to be comparable to that of a varnish containing the present resin composition.

Example 2.

A varnish containing 40% by weight of a resin composition was prepared by dissolving in dimethylformamide 100 parts by weight of a polyaminobismaleimide

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obtained by reacting 1.5 moles of N,N'-4,4'-diphenylmethanebismaleimide and 1 mole of N,N'-diaminodiphenylmethane in the molten state at 160°C for 30 minutes; 200 parts by weight of a brominated bisphenol-A-type diglycidyl ether having an epoxy equivalent from 450 to 500 [Epikote (registered trademark) 1045 of Shell Chemical Co.]; and 50 parts by weight of an isobutyl half-ester of a styrene-maleic anhydride copolymer containing 50 mole-% of maleic anhydride.

In the same manner as in Example 1, a sheet of glass cloth, 0.1 mm in thickness, which had been treated with γ -aminopropyltriethoxysilane, was impregnated with the said varnish and dried at 140°C for 5 minutes to obtain a sheet of B-stage prepreg containing 45% by weight of a resin composition.

In the same manner as in Example 1, an assembly of the prepreg sheets obtained as mentioned above was subjected to heat and pressure by means of a hot-platen press, at 170°C and 40 kg/cm² for 2 hours, to obtain a two-side copper-clad laminate, 1.6 mm in overall thickness.

As shown in Table 1, this copper-clad laminate was excellent in mechanical properties at elevated temperatures, linear expansion coefficient and soldering heat-resistance, and the adhesive strength between the copper foil and the board was high in the initial stage, at elevated temperatures, and after heat treatment for a long period of time. Therefore, the laminate would be excellent as a heat-resistant laminate. This laminate had an excellent flame resistance, UL class V-O, as tested by UL vertical burning procedure.

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TABLE 1

Item of test (unit)	Testing method	Treatment and condition	Sample No.	Example 1	Example 1 (after-cured)	Comparative Example 1 (after-cured)
Flexural strength (kg/mm ²)	JIS C 6481	Room temp.		50	51	54
		150°C.		46	48	49
		After heat treatment *1		43	42	45
Volume resistivity (Ω.cm)	JIS C 6481	A		3×10 ¹⁵	1×10 ¹⁵	5×10 ¹⁴
		C-96/40/90		4×10 ¹⁴	2×10 ¹⁴	4×10 ¹⁴
		Below Tg		3.2×10 ⁻³	3.0×10 ⁻³	2.9×10 ⁻³
Thermal expansion coefficient perpendicular to laminate (°C ⁻¹)		Above Tg		1.4×10 ⁻⁴	1.3×10 ⁻⁴	1.0×10 ⁻³
		Room temp.		2.0	2.1	1.1
		150°C.		1.7	1.8	1.0
Peel strength (separation angle: 90° (kg/cm)	JIS C 6481	After heat treatment *1		1.6	1.6	0.8
		Solder bath, 30 sec floating	260°C.	No change	No change	No change
			280°C.	No change	No change	No change
Soldering heat-resistance	JIS C 6481		300°C.	No change	No change	No change
Curability (min.sec)		Gel time on hot platen at 150°C		5.20		30.00

Note: *1 After heating in the air at 200°C. for 1,000 hours.

*2 After heating in the air at 200°C. for 200 hours.

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TABLE 1 (Continued)

Comparative Example 2	Comparative Example 3	Comparative Example 3 (after-cured)	— Example 2
36	44	46	45
7	25	28	42
12 *2	31	32	40
5×10^{15}	2×10^{15}	2×10^{15}	6×10^{15}
6×10^{14}	1×10^{14}	2×10^{14}	1×10^{15}
7.1×10^{-5}	4.2×10^{-5}	3.7×10^{-5}	3.5×10^{-5}
3.8×10^{-4}	2.0×10^{-4}	1.8×10^{-4}	1.5×10^{-4}
1.8	1.4	1.5	2.2
0.4	0.9	1.2	1.8
0.7 *2	1.0	1.0	1.6
No change	No change	No change	No change
Peeling	No change	No change	No change
Peeling	Peeling	Peeling	No change
7.30	8.50		4.20

Examples 3 to 9.

In a manner similar to that described in Example 1, a number of varnishes of various resin compositions were prepared by dissolving different combinations of polyaminobismaleimides, polyepoxy compounds, and acid type copolymers in a mixed solvent of N-methyl-2-pyrrolidone and methyl ethyl ketone. A sheet of glass cloth (product of Asahi Schwebel Co.; treated for polyimide laminate), 0.1 mm in thickness, was impregnated with the varnish and dried at 130—150°C for 5—10 min. to obtain a prepreg having a resin content of 35—50% by weight. The resulting prepreg was heated under pressure together with electrolytic copper foils having a thickness of 35 μ m by means of a hot platen press at 160—180°C at 40—80 kg/cm² for 1.5—2.5 hrs. to obtain a two-side copper-clad laminate having an overall thickness of 1.6 mm.

Formulation of the resin composition is shown in Table 2, and gel time of the varnish as well as performance characteristics of the copper-clad laminate are shown in Table 3. As is apparent from Table 3, the present resin compositions showed, over a wide range of formulation, excellent properties at elevated temperatures and an excellent heat resistance; in particular, the low-temperature curing ability and adhesive strength to copper foil were greatly superior to those of a conventional polyamide-based resin composition.

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TABLE 2

Component of resin composition		Sample No.	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
1. Polyaminobismaleimide		Bisimide/diamine mole ratio	Parts by weight	Parts by weight	Parts by weight	Parts by weight	Parts by weight	Parts by weight	Parts by weight
N,N'-Bismaleimide	Diamine								
N,N'-4,4'-Diphenylmethanebismaleimide	4,4'-Diaminodiphenylmethane	2.0/1.0	100				80		
N,N'-4,4'-Diphenylmethanebismaleimide	4,4'-Diaminodiphenylmethane	1.0/1.0		60		100			100
N,N'-m-Phenylenebismaleimide	4,4'-Diaminodiphenylether	1.0/1.0			100			50	
N,N'-Hexamethylenebismaleimide	4,4'-Diaminodicyclohexane	1.0/1.0		40			20	50	
2. Polyepoxy compound		Epoxy equivalent							
Bisphenol-based, Epikote(R) 828		184/194	80				50		
Bisphenol-based, Epikote(R) 1001		450-500		20		30		10	100
Polyether-type, Adeka Resin(R) EP-4000		330-360	20				100		200
Novolak-type, Epikote(R) 154		176-181			200	20			
3. Copolymer		Monomer ratio (mole-%)							
Maleic anhydride/styrene/dimethylstyrene copolymer		50/33/17	50		50				100
40 mole-% Isobutyl ester of maleic anhydride/dimethylstyrene copolymer		60/40		5				10	
Monoisopropyl maleate/styrene/ α -methylstyrene copolymer		50/33/17				30			

TABLE 2 (Continued)

Component of resin composition		Sample No.	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
1. Polyaminobismaleimide		Bisimide/ diamine mole ratio	Parts by weight	Parts by weight	Parts by weight	Parts by weight	Parts by weight	Parts by weight	Parts by weight
N,N'-Bismaleimide	Diamine								
Maleic anhydride/mono-n-pentyl maleate/ styrene copolymer									
Monoethyl maleate/dimethylstyrene copolymer		20/20/60					70		
		30/70			100				

Note: Adeka Resin (registered trademark) EP4000: a polyepoxy compound manufactured by Asahi Denka Kogyo Co.

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TABLE 3

Item of test (unit)	Treat- ment and condition	Sample No.	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Flexural strength (kg/mm ²)	Room temperature		48	45	40	54	47	43	40
	150°C.		44	42	36	51	43	40	36
	After heat treatment		42	40	32	46	42	38	32
Volume resistivity (Ω.cm)	A		4×10 ¹⁵	2×10 ¹⁵	7×10 ¹⁴	1×10 ¹⁵	5×10 ¹⁴	9×10 ¹⁴	6×10 ¹⁴
	C-96/40/90		2×10 ¹⁴	3×10 ¹⁴	5×10 ¹⁴	8×10 ¹⁴	2×10 ¹⁴	6×10 ¹⁴	3×10 ¹⁴
	Below Tg		3.2×10 ⁻⁵	3.0×10 ⁻⁵	3.8×10 ⁻⁵	2.8×10 ⁻⁵	3.1×10 ⁻⁵	3.3×10 ⁻⁵	3.6×10 ⁻⁵
Thermal expansion coefficient perpendicular to laminate (°C ⁻¹)	Above Tg		1.2×10 ⁻⁴	1.3×10 ⁻⁴	2.1×10 ⁻⁴	1.0×10 ⁻⁴	1.3×10 ⁻⁴	1.5×10 ⁻⁴	2.0×10 ⁻⁴
	Room temperature		2.1	1.8	2.2	2.0	2.3	1.7	1.9
	150°C.		1.8	1.6	1.6	1.7	1.6	1.5	1.7
Peel strength (separation angle: 90°) (kg/cm)	After heat treatment		1.9	1.7	1.9	1.8	1.8	1.6	1.7
	Solder bath 260°C. 30 sec. floating		No change	No change	No change	No change	No change	No change	No change
	280°C. 300°C.		No change	No change	No change	No change	No change	No change	No change
Soldering heat- resistance			No change	No change	No change	No change	No change	No change	No change
Curability (min.sec)	Gel time on hot platen at 150°C.		3.30	10.00	2.10	8.40	5.20	7.50	3.20

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Example 10.

A sheet of glass cloth, 0.1 mm in thickness was impregnated with the same resin composition as used in Example 1, and dried. In the same manner as in Example 1, an assembly of the prepreg and copper foil was subjected to heat and pressure by means of a hot-platen press to form a two-side copper-clad laminate (75 μ m in thickness of copper foil) having an overall thickness of 0.2 mm. An inner circuit board for test bearing a high-density pattern was formed from the laminate. A multilayer board, 2.0 mm in thickness, was formed from three sheets of the inner circuit board, two sheets of copper-clad laminate with 35 μ m copper foil on one side, and several sheets of the prepreg, 0.1 mm in thickness, obtained by use of the resin composition of Example 1. The resulting multilayer board was further fabricated to carry surface circuits and through-holes, thereby obtained a finished eight-layer printed circuit board. Main performance characteristics of this board were as shown in Table 4.

For comparison, multilayer printed circuit boards were prepared by use of the polyaminobismaleimide resin alone, the epoxy resin, and the polyaminobismaleimide-epoxy resin composition, respectively, used in Comparative Examples 1 to 3, and compared in properties.

As shown in Table 4, the present resin composition exhibited distinguished properties under severe conditions of processing and treatment of the eight-layer printed circuit board; in particular, excellent in the adhesive strength of the inner copper foil and in the dimensional stability of the board which are required for high-precision printed circuit boards.

On the contrary, when a conventional resin composition was used, adhesive strength to the inner copper foil was insufficient, deterioration was marked when the board was subjected to temperature-humidity treatment, and the dimensional stability of the board was inferior, and did not meet the requirements for a high-precision multilayer printed circuit board.

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TABLE 4

Item of test (unit)	Treatment and condition	Sample	Example 9	Comparative Example 4 *1	Comparative Example 5 *2	Comparative Example 6 *3
Soldering heat-resistance	A	260°C, 60 sec	No change	No change	No change	No change
	D-2/100	Same as above	Same as above	Same as above	Measling	Measling
	After temperature cycle *4	Same as above	Same as above	Peeling	Same as above	Peeling
Inner layer peel strength (kg/cm)	A Separation angle: 90°		1.3	0.3	0.7	0.5
Halo test	Immersion in HCl=1/1 at room temp. for 7 min.		No change	No change	Clouding	No change
Dimensional change of board (%)	Parallel to laminate	After formation of circuit	-0.01	-0.01	-0.03	-0.02
		After heat treatment E -0.5/170	-0.02	-0.03	-0.08	-0.04
		After temperature cycle *5	-0.03	-0.05	-0.10	-0.06
Linear expansion coeff. of board (°C ⁻¹)	Perpendicular to laminate	Below Tg	3.1×10 ⁻⁵	3.5×10 ⁻⁵	6.6×10 ⁻⁵	4.0×10 ⁻⁵
		Above Tg	1.4×10 ⁻⁴	1.5×10 ⁻⁴	3.1×10 ⁻⁴	1.8×10 ⁻⁴

Note: *1 Polyaminobismaleimide in Comparative Example 1 was used.

*2 Epoxy resin in Comparative Example 2 was used.

*3 Polyaminobismaleimide/epoxy resin in Comparative Example 3 was used.

*4 -60°C 10 min. → 100°C 10 min.; 20 cycles.

*5 -65°C 0.5 hr → 25°C 15 min. → 125°C 0.5 hr → 25°C 15 min.; 5 cycles.

Example 11.

A varnish containing 50% by weight of resin composition was prepared by dissolving in a dimethylformamide-toluene mixture 100 parts by weight of the same polyaminobismaleimide as used in Example 1, 50 parts by weight of a polyether-type diglycidyl compound obtained by reaction of epichlorohydrin and a dihydric alcohol obtained by reacting bisphenol-A with propylene oxide (Adeka Resin EP-400 of Asahi Denka Kogyo Co.), and 10 parts by weight of maleic anhydride- α -methylstyrene (45:55 mole-%) copolymer.

A sheet of carbon fibre cloth, 0.3 mm in thickness, which had been treated with γ -aminopropyltriethoxysilane, was impregnated with the varnish and dried at 150°C for 5 minutes to obtain a prepreg of a resin content of 40% by weight.

A stack of seven sheets of the prepreg was subjected to heat and pressure by means of a hot-platen press at 170°C and 80 kg/cm² for 2 hours to obtain a carbon fibre-cloth-based laminate, 2.0 mm in thickness. The laminate had a flexural strength of 57 kg/cm² at room temperature and 43 kg/cm² at 200°C. It was suitable for use in heat-resistant functional parts.

Example 12.

A varnish containing 55% by weight of resin composition was prepared by dissolving in N-methyl-2-pyrrolidone 100 parts by weight of the same polyaminobismaleimide as used in Example 3, 30 parts by weight of a brominated bisphenol-A-type diglycidyl ether having an epoxy equivalent from 450 to 500 [Epikote (registered trademark) 1045], and 30 parts by weight of a maleic anhydride- α -methyl-p-isopropylstyrene copolymer containing 30 mole-% of maleic anhydride.

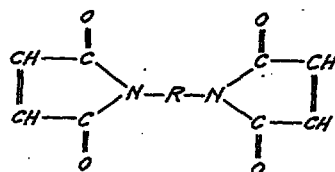
A sheet of mixed glass-asbestos paper, 0.3 mm in thickness, was impregnated with the varnish and dried at 150°C for 10 minutes to obtain a sheet of prepreg containing 60% by weight of the resin composition.

A stack of 6 sheets of the prepreg with a nichrome foil, 0.1 mm in thickness, placed on one side of the stack was subjected to heat and pressure at 180°C and 100 kg/cm² for 2.5 hours to obtain a one-side nichrome-clad laminate, 1.6 mm in thickness. This laminate had a heat distortion temperature of 182°C., a volume resistivity A of $2 \times 10^{15} \Omega \cdot \text{cm}$ and $5 \times 10^{14} \Omega \cdot \text{cm}$ (C-96/40/90) and a flame resistance corresponding to UL class V-O, as tested according to the UL method for vertical burning test. This laminate would be suitable for use, for example in a heat-resistant resistor circuit board or a heater board.

WHAT WE CLAIM IS:—

1. A resin composition comprising:

100 parts by weight of at least one polyaminobismaleimide prepolymer obtained by reacting at least one N, N'-bismaleimide of the formula I,



(I)

wherein R represents an aliphatic, cycloaliphatic or aromatic divalent radical, with at least one aliphatic, cycloaliphatic or aromatic diamine,

10 to 300 parts by weight of at least one epoxy compound containing at least two epoxy groups in the molecule, and

5 to 150 parts by weight of at least one copolymer having a number-average molecular weight within the range of from 1000 to 60 000 and selected from (A) copolymers of one or more aromatic vinyl compounds with maleic anhydride,

(B) partial alkyl esters of the said copolymers (A),

(C) copolymers of one or more aromatic vinyl compounds with one or more alkyl maleates, and

(D) copolymers of one or more aromatic vinyl compounds with maleic anhydride and with one or more alkyl maleates.

2. A composition as claimed in claim 1, when the polyaminobismaleimide prepolymer is of the general formula II,



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Example 11.

A varnish containing 50% by weight of resin composition was prepared by dissolving in a dimethylformamide-toluene mixture 100 parts by weight of the same polyaminobismaleimide as used in Example 1, 50 parts by weight of a polyether-type diglycidyl compound obtained by reaction of epichlorohydrin and a dihydric alcohol obtained by reacting bisphenol-A with propylene oxide (Adeka Resin EP-400 of Asahi Denka Kogyo Co.), and 10 parts by weight of maleic anhydride- α -methylstyrene (45:55 mole-%) copolymer.

A sheet of carbon fibre cloth, 0.3 mm in thickness, which had been treated with γ -aminopropyltriethoxysilane, was impregnated with the varnish and dried at 150°C for 5 minutes to obtain a prepreg of a resin content of 40% by weight.

A stack of seven sheets of the prepreg was subjected to heat and pressure by means of a hot-platen press at 170°C and 80 kg/cm² for 2 hours to obtain a carbon fibre-cloth-based laminate, 2.0 mm in thickness. The laminate had a flexural strength of 57 kg/cm² at room temperature and 43 kg/cm² at 200°C. It was suitable for use in heat-resistant functional parts.

Example 12.

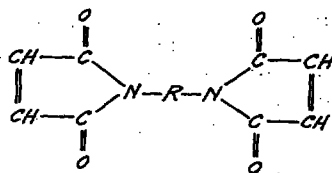
A varnish containing 55% by weight of resin composition was prepared by dissolving in N-methyl-2-pyrrolidone 100 parts by weight of the same polyaminobismaleimide as used in Example 3, 30 parts by weight of a brominated bisphenol-A-type diglycidyl ether having an epoxy equivalent from 450 to 500 (Epikote (registered trademark) 1045), and 30 parts by weight of a maleic anhydride- α -methyl-p-isopropylstyrene copolymer containing 30 mole-% of maleic anhydride.

A sheet of mixed glass-asbestos paper, 0.3 mm in thickness, was impregnated with the varnish and dried at 150°C for 10 minutes to obtain a sheet of prepreg containing 60% by weight of the resin composition.

A stack of 6 sheets of the prepreg with a nichrome foil, 0.1 mm in thickness, placed on one side of the stack was subjected to heat and pressure at 180°C and 100 kg/cm² for 2.5 hours to obtain a one-side nichrome-clad laminate, 1.6 mm in thickness. This laminate had a heat distortion temperature of 182°C., a volume resistivity A of $2 \times 10^{15} \Omega \cdot \text{cm}$ and $5 \times 10^{14} \Omega \cdot \text{cm}$ (C-96/40/90) and a flame resistance corresponding to UL class V-O, as tested according to the UL method for vertical burning test. This laminate would be suitable for use, for example in a heat-resistant resistor circuit board or a heater board.

WHAT WE CLAIM IS:—

1. A resin composition comprising:
100 parts by weight of at least one polyaminobismaleimide prepolymer obtained by reacting at least one N, N'-bismaleimide of the formula I,



wherein R represents an aliphatic, cycloaliphatic or aromatic divalent radical, with at least one aliphatic, cycloaliphatic or aromatic diamine,

10 to 300 parts by weight of at least one epoxy compound containing at least two epoxy groups in the molecule, and

5 to 150 parts by weight of at least one copolymer having a number-average molecular weight within the range of from 1000 to 60 000 and selected from

(A) copolymers of one or more aromatic vinyl compounds with maleic anhydride,

(B) partial alkyl esters of the said copolymers (A),

(C) copolymers of one or more aromatic vinyl compounds with one or more alkyl maleates, and

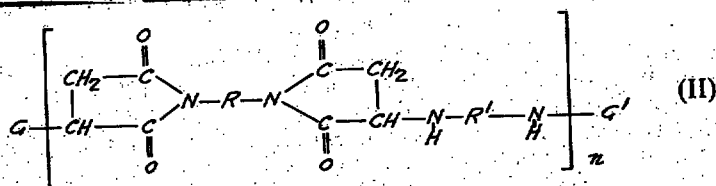
(D) copolymers of one or more aromatic vinyl compounds with maleic anhydride and with one or more alkyl maleates.

2. A composition as claimed in claim 1, when the polyaminobismaleimide prepolymer is of the general formula II,

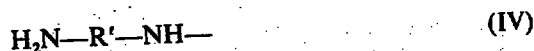
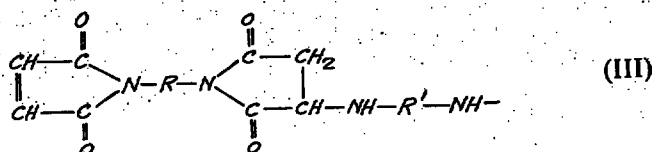


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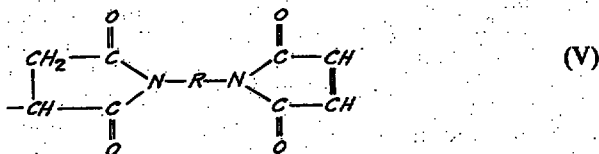
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wherein R and R', which may be the same or different, each represents an aliphatic, cycloaliphatic or aromatic divalent radical, G represents a radical of the formula III or of the formula IV,



in which R and R' are as defined above, and G' represents a hydrogen atom or a radical of the formula V,



in which R is as defined above, and n is an integer of at least 1.

3. A composition as claimed in claim 2, wherein n is an integer of from 1 to 50.

4. A composition as claimed in any one of claims 1 to 3, wherein the or each diamine is a straight-chain aliphatic diamine having from 2 to 20 carbon atoms, an aromatic diamine or a cycloaliphatic diamine.

5. A composition as claimed in any one of claims 1 to 4 wherein the prepolymer is obtainable by reacting the N,N'-bismaleimide and the diamine at a temperature within the range of from 50 to 250°C.

6. A composition as claimed in any one of claims 1 to 5, wherein the prepolymer is obtainable by reacting the N,N'-bismaleimide and the diamine at a temperature within the range of from 50 to 170°C.

7. A composition as claimed in any one of claims 1 to 5, wherein the ratio of the N,N'-bismaleimide to the diamine is one mole of the double bond present in the said bisimide to 0.5 to 3 moles of the active hydrogen present in said diamine.

8. A composition as claimed in any one of claims 1 to 7, wherein the polyaminobismaleimide has a melting point range within the range of from 50° to 150°C.

9. A composition as claimed in any one of claims 1 to 8, wherein the epoxy compound is an epoxy resin having an epoxy equivalent within the range of from 100 to 4000.

10. A composition as claimed in any one of claims 1 to 8, which comprises 20 to 200 parts by weight of the epoxy compound.

11. A composition as claimed in any one of claims 1 to 10, which includes a copolymer (A) containing at least 30 mole-% of maleic anhydride structural units in the molecule.

12. A composition as claimed in any one of claims 1 to 11, which includes a copolymer (B) having an esterification degree of at most 50 mole-%, based on the total maleic anhydride structural units before esterification.

13. A composition as claimed in any one of claims 1 to 12, which includes a copolymer (C) containing at least 30 mole-% of monoalkyl maleate structural units in the molecule.

14. A composition as claimed in any one of claims 1 to 13, which includes a copolymer (D) containing at least 30 mole-% of maleic anhydride structural units in the molecule.



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15. A composition as claimed in any one of claims 1 to 13, which includes a copolymer (D) containing at least 30 mole-%, in total, of maleic anhydride structural units and monoalkyl maleate structural units in the molecule.

5 16. A composition as claimed in any one of claims 1 to 15, wherein the copolymer (A), (B), (C) or (D) has a number-average molecular weight of from 2000 to 30 000. 5

17. A composition as claimed in any one of claims 1 to 16, which contains 10 to 100 parts by weight of the constituent consisting of at least one copolymer selected from copolymers (A), (B), (C) and (D).

10 18. A composition as claimed in any one of claims 1 to 17, wherein the weight ratio of the polyepoxy compound to the constituent consisting of at least one copolymer selected from the group consisting of the copolymers (A), (B), (C) and (D) is within the range of from 0.5 to 10.0. 10

15 19. A composition as claimed in claim 1, substantially as described in any one of the Examples herein. 15

20. A process for preparing a prepreg for use in the production of a heat-resistant resin laminate, which comprises impregnating a fibrous base material selected from glass fabric, asbestos fabric and carbon fibre fabric, which material has been treated with a coupling agent, with a solution, in an inert solvent or solvent mixture, of a resin composition as claimed in any one of claims 1 to 19, a resin concentration within the range of from 20 to 50% by weight, and so heating the resulting impregnated base material at a temperature within the range of from 90 to 170°C for 1 to 30 minutes while the solvent or solvent mixture is evaporated to dryness that the resin composition reacts as far as the B-stage. 20

25 21. A process as claimed in claim 20, carried out substantially as described in anyone of the Examples herein. 25

22. A prepreg prepared by a process as claimed in claim 20 or claim 21.

30 23. A process for the production of a heat-resistant resin laminate, which comprises so subjecting a stack of superposed prepreps as claimed in claim 22 to heat under pressure that a laminate having a thickness of at least 0.1 mm is formed. 30

24. A process as claimed in claim 23, wherein the prepreg or stack of prepreps is heated at a temperature within the range of from 120 to 250°C.

35 25. A process as claimed in claim 24, wherein the prepreg or stack of prepreps is heated at a temperature within the range of from 150 to 180°C. 35

26. A process as claimed in any one of claims 23 to 25, wherein the prepreg or stack or prepreps is subjected to a pressure within the range of from 5 to 200 kg/cm² while being heated.

40 27. A process as claimed in any one of claims 23 to 26, wherein the prepreg or stack of prepreps is heated under pressure for 15 to 240 minutes. 40

28. A process as claimed in claim 27, wherein the prepreg or stack of prepreps is heated under pressure for 30 to 180 minutes.

45 29. A process as claimed in any one of claims 23 to 28, wherein the laminate obtained is subsequently after-baked at a temperature within the range of from 180 to 250°C for up to 20 hours. 45

30. A process as claimed in claim 23, carried out substantially as described in any one of the Examples herein.

31. A heat-resistant resin laminate produced by a process as claimed in any one of claims 23 to 30.

50 32. A process for the production of a metal-clad heat-resistant resin laminate, which comprises so subjecting to heat under pressure a stack of two or more prepreps as claimed in claim 22, having metal foil on one or both sides, that a metal-clad laminate having a thickness of at least 0.1 mm is formed. 50

33. A process as claimed in claim 32, wherein the heating under pressure is carried out as specified in any one of claims 24 to 29.

55 34. A process as claimed in claim 32 or claim 33, wherein the metal foil comprises copper, aluminium or nichrome. 55

35. A process as claimed in claim 32, carried out substantially as described in any one of the Examples herein.

60 36. A metal-clad heat resistant resin laminate produced by a process as claimed in any one of claims 32 to 35. 60

37. A process for the manufacture of a multilayer printed circuit board comprising a surface circuit board and one or more inner circuit boards, wherein at least one prepreg as claimed in claim 22 is used to form the inner circuit board(s) and the surface board and is used as in interlayer adhesive sheet between two circuit boards. 65

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38. A process as claimed in claim 37, which comprises forming a stack comprising one or more inner circuit boards, each comprising a prepreg as claimed in claim 22 or a laminate as claimed in claim 31 or claim 36, a surface circuit board comprising a metal-clad laminate as claimed in claim 36 having metal foil on one side only, the side without foil being adjacent the inner circuit board(s), and, optionally, one or more prepreps as claimed in claim 22 as interlayer adhesives positioned between adjacent circuit boards, and subjecting the said stack to heat under pressure.

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39. A multilayer printed circuit board manufactured by a process as claimed in claim 38.

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40. A multilayer printed circuit board which includes one or prepreps as claimed in claim 22 and/or one or more heat-resistant resin laminates as claimed in claim 31 and/or one or more metal-clad heat-resistant resin laminates as claimed in claim 36.

41. Electrical or electronic equipment containing a multilayer printed circuit board as claimed in claim 39 or claim 40.

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