

CROSSLINKED RESIN OF EPOXY COMPOUND AND ISOCYANATE AND  
PROCESS FOR PRODUCING SAME

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1           This invention relates to a crosslinked resin  
of an epoxy compound and an isocyanate compound excel-  
lent in heat resistance, toughness, moisture resistance,  
adhesiveness, etc. as well as to a process for producing  
5   said resin. Further, this invention relates to a pro-  
cess for producing resins which are most suitable for  
the production of laminates, molded articles and the  
like via the so-called B-stage reaction intermediates  
such as prepreg or molding material.

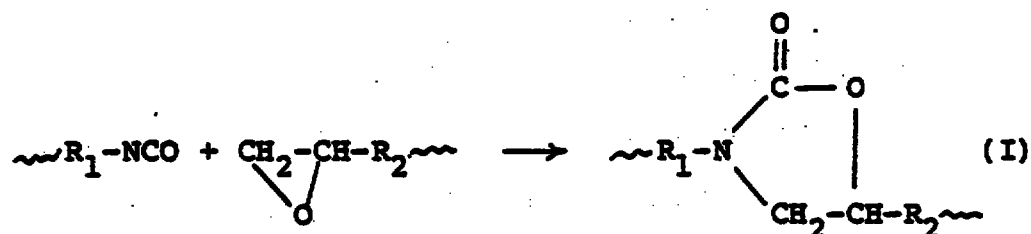
10           As curing agents for curing epoxy compounds,  
there have hitherto been known acid anhydrides, alipha-  
tic and aromatic amine compounds, phenol compounds and  
the like. Though the epoxy compounds cured with these  
curing agents were excellent in adhesiveness, toughness,  
15   moisture resistance, etc., they had the fault that the  
heat decomposition temperature and the heat softening  
temperature thereof were lower than those of cured  
polyimide resins and cured silicone resins. Therefore,  
they have not been able to respond sufficiently to the  
20   current tendency to require a high reliability in  
electronic appliances and the like, and have not been  
applied to uses requiring high reliability. On the  
other hand, polyimide resins and silicone resins are  
inferior in toughness, adhesiveness, moisture resist-

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1    ance, processability and workability which epoxy resins  
      have, though they are superior in heat resistance, and  
      moreover they are expensive, so that their use has  
      been extremely limited.

5            It is well known that an addition reaction  
      takes place between an epoxy compound and an isocyanate  
      compound in the presence of a catalyst to form a cyclic  
      oxazolidone compound as expressed by the following for-  
      mula (I):

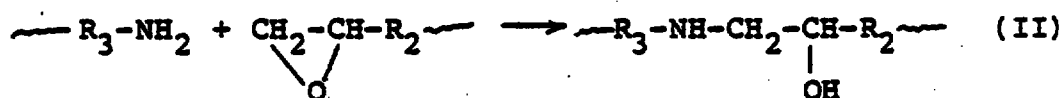
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     (for example, G. P. Speranza and W. J. Reppel, J. Org.  
      Chem., 23, 1922 (1958)). In such an addition reaction  
      of isocyanate compound to epoxy compound, the reaction  
      product has a cyclic structure, and therefore, it is  
      much superior in heat resistance to the reaction pro-  
      ducts of ring-opening addition reaction of the following  
      formula (II) in which an amine compound, an acid anhy-  
      dride, a phenolic compound or the like adds to an epoxy  
      compound to yield a chain-like structure:

25



1 That is, the cyclic structure is stiffer than the chain  
structure, and the change in motion of the main chain is  
smaller even though heat energy is applied from the  
exterior, so that the cyclic structure has a higher glass  
5 transition point. Furthermore, unlike the chain struc-  
ture, a bond scission at one position in the cyclic  
structure does not result in any reduction in molecular  
weight, so that the heat decomposition temperature beco-  
mes higher.

10 Though the ring-forming addition reaction of an  
isocyanate compound to an epoxy compound can give a cured  
product excellent in heat resistance as mentioned above,  
this process had a number of disadvantages. Thus the  
materials used have poor storage stability at room  
15 temperature in that the reaction progresses even at room  
temperature owing to the very high reactivity of iso-  
cyanate group, the isocyanate group is readily denatured  
by the reaction with the moisture in the air, and so on.  
The very high reactivity of isocyanate compounds is an  
20 important restriction on their use. In the field of  
urethane resin coating materials, however, the isocya-  
nate group is masked with phenol, cresol or the like to  
make it stable at room temperature in order to enhance  
the storage stability. At the time of curing, the  
25 masked compound is dissociated and the masking agent is  
evaporated off by the action of heat, thereby regenera-  
ting the isocyanate group, which is then used in the

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1 curing reaction. Such a method of masking the isocyanate group has been studied since a good many years ago (S. Peterson: Liebigs Ann. Chem., 562, 205 (1949)).

In Japanese Patent Publication No. 14,095/78,  
5 this process is used as it is when curing an epoxy compound with an isocyanate compound. That is, the isocyanate group is previously reacted with a masking agent such as phenol, cresol or the like to convert it to a urethane compound stable at room temperature, and this  
10 urethane compound is heated at the time of curing to dissociate and evaporate off the masking agent thereby regenerating the isocyanate group, and this generated isocyanate group is reacted with the epoxy group.  
According to this process, however, the working environ-  
15 ment is markedly polluted by the dissociated masking agent. Furthermore, when a laminate or a molded article is to be cured and formed, the dissociated masking agent remains in the laminate or molded product which produces voids and deteriorate the appearance, and, in addition,  
20 greatly decreases the mechanical strength, heat resistance, moisture resistance, etc. of the final product. Therefore, this process is by no means applicable to practical uses.

As a result of extensive research, the present  
25 inventors have solved the above-mentioned problems in the prior art arising at the time of cure. That is, they have succeeded in obtaining a prepolymer in the B-

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- 1 stage stable at room temperature and also obtaining therefrom a cured product with excellent properties. No volatile matter is emitted and the product therefore is free from voids, unlike the prior art materials.
- 5 The present invention provides a crosslinked resin obtained by reacting one equivalent of an isocyanate compound having isocyanate groups in the molecule with an epoxy compound having at least one alcoholic hydroxyl group and at least two epoxy groups in the molecule in an
- 10 amount corresponding to 0.5 to 5, preferably 0.5 to 2.6, epoxy equivalents per isocyanate equivalent and at least one alcoholic hydroxyl equivalent per isocyanate equivalent to first react isocyanate groups of the isocyanate compound with alcoholic hydroxyl groups of the epoxy
- 15 compound, thereby forming an epoxy prepolymer having urethane linkages stable at room temperature; subsequently heating the resulting prepolymer at a temperature at least 70°C, preferably at least 100°C, higher than the reaction temperature for the formation of the prepolymer to
- 20 dissociate the urethane linkages and regenerate the isocyanate groups; and then reacting the said isocyanate groups with the epoxy groups of the epoxy compound.

The crosslinked resin of the invention is thus a resin which is obtained by contacting an epoxy compound

25 having at least one alcoholic hydroxyl group and at least two epoxy groups in its molecule with an isocyanate compound having isocyanate groups in its molecule under mild conditions, and in the proportions specified

1 above, to react alcoholic hydroxyl groups with isocyanate  
groups to produce a prepolymer having urethane linkages  
stable at room temperature, along with the free epoxy  
groups, then subjecting said prepolymer to conditions  
5 such that said urethane linkages are dissociated to  
regenerate the isocyanate groups and reacting the rege-  
nerated isocyanate groups with the epoxy groups of said  
epoxy compound.

Further, according to this invention, there is al-  
10 so provided a process for producing said crosslinked  
resin.

The crosslinked resin of this invention is quite  
excellent in apperance, heat resistance, toughness,  
adhesive properties, moisture resistance, etc.

15 The first characteristic feature of this invention  
consists in subjecting an epoxy compound having at least one  
alcoholic hydroxyl group and at least two epoxy groups  
in its molecule with an isocyanate compound having  
isocyanate groups in its molecule to reaction conditions  
20 to react

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1 the alcoholic hydroxyl groups with the isocyanate  
groups, thereby forming a prepolymer having urethane  
linkages stable at room temperature. Though this reac-  
tion can take place even at low temperatures, it is com-  
5 pleted rapidly upon heating. However, since the disso-  
ciation of the formed urethane linkages or side reac-  
tions can take place at too high a temperature, the  
reaction is advantageously carried out at a temperature  
of 200°C or below, and preferably 100°C or below.

10 As mentioned above, in this invention, the isocya-  
nate groups are masked with alcoholic hydroxyl groups  
in the first place. Therefore, the prepolymer of this  
invention has a very good storage stability and has a  
pot life of at least two months in the form of a prepreg  
15 or a molding material in the B-stage.

At the time of final cure, this prepolymer is  
heated to dissociate the urethane linkages and regenerate  
the isocyanate groups, and the regenerated isocyanate  
groups are reacted with epoxy groups to form oxazoli-  
20 done rings. Since the epoxy compound which is the mask-  
ing agent for the isocyanate group reacts at the final  
curing stage, too, no volatile matter is generated.  
Accordingly, shaped articles formed from resins of the  
invention are free from voids and have excellent pro-  
25 perties. This is greatly different from where the iso-  
cyanate groups are masked with phenol or cresol, in  
which the phenol or cresol is volatilised in the final  
curing

1 reaction.

Further, if at least one member selected from the group consisting of amine compounds, carboxylic acid anhydrides, phenol novolac compounds, polyvinyl-phenol compounds and bisimide compounds exists in the stage of final cure, various linkages can be introduced and an excellent crosslinked product (i.e. cured product) having characteristic features corresponding to them can be obtained. For example, in the presence of at least one member selected from the group consisting of amine compounds, carboxylic acid anhydrides, phenol novolac compounds and polyvinyl phenol compounds, a reaction between these compounds and the epoxy group can take place in addition to the oxazolidone ring formation due to the reaction between the epoxy group and the isocyanate group dissociated and regenerated from the urethane linkage, so that the cured product has excellent heat resistance in addition to the excellent toughness, adhesiveness, moisture resistance, etc. which the conventional cured epoxy resins have. Further, if a bisimide compound exists in the stage of final cure, an imide linkage is introduced into the cured product owing to the thermal polymerization of the bisimide, so that the heat resistance of the cured product becomes higher.

25 When a bisimide compound and at least one compound selected from amine compounds, carboxylic acid anhydrides, phenol novolac compounds and

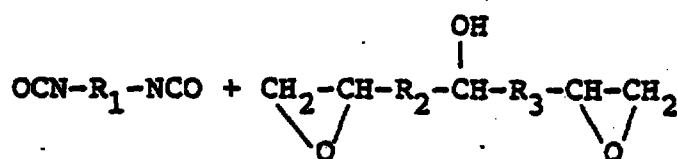
1 polyvinyl-phenol compounds are present at the final curing stage, not only is an oxazolidone ring formed due to reaction between the isocyanate group and the epoxy group, but also various other reactions may take place. Examples  
5 of such reactions are the thermal polymerization of the bisimide compound, a reaction between the epoxy compound and the amine compound, and the polycarboxylic acid anhydride, the phenol-novolac compound or the polyvinyl-phenol compound, and a reaction between the amine compound and  
10 the bisimide compound. The cured product therefore has excellent heat resistance, toughness, adhesiveness, moisture resistance, etc. Heating is necessary at the time of final cure, and the heating temperature is preferably 50-300°C, more preferably 100-200°C. Moreover, the heating  
15 temperature is at least 70°C higher than the aforementioned reaction temperature for forming a prepolymer having urethane linkages. If the heating temperature is less than 50°C, the curing reaction cannot take place sufficiently. If it is more than 300°C, decomposition  
20 reactions and the like can take place in addition to the curing reaction so that the properties of cured product are deteriorated.

The urethane linkage formed by masking the isocyanate group with the alcoholic hydroxyl group in this  
25 invention has a higher dissociation temperature than the hitherto known urethane linkage formed by masking the isocyanate groups with phenolic hydroxyl groups. Therefore, the dissociation of the urethane linkage and the formation of free isocyanate groups can-

- 1 not take place in, for example, the drying step for pre-
- paring a prepreg for laminate or the high temperature
- kneading step for preparing a B-stage molding material,
- and hence, a very stable prepreg, molding material and
- 5 the like can be obtained.

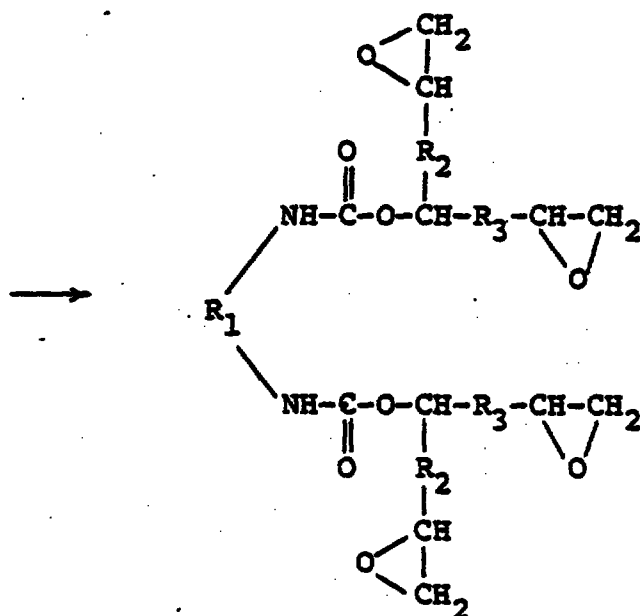
An example of the process of this invention will be explained below with reference to reaction formulae:

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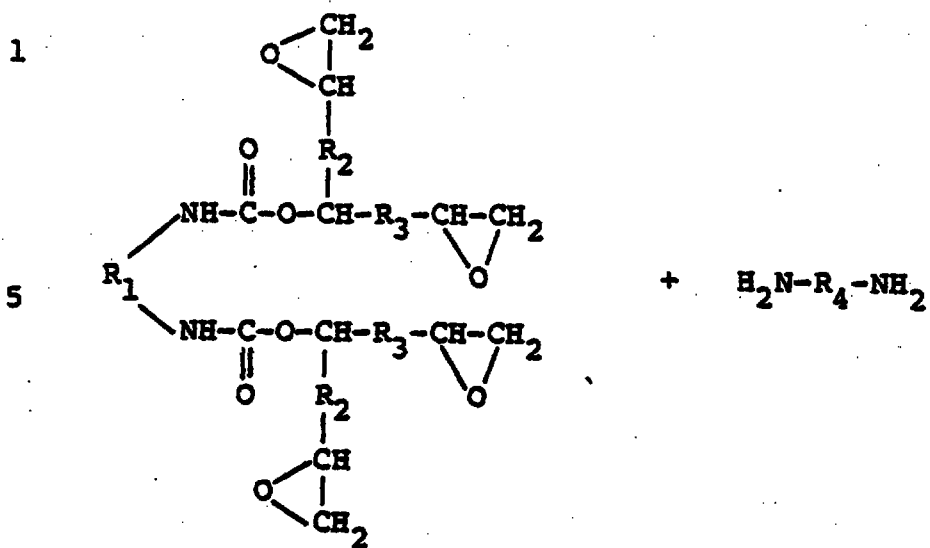
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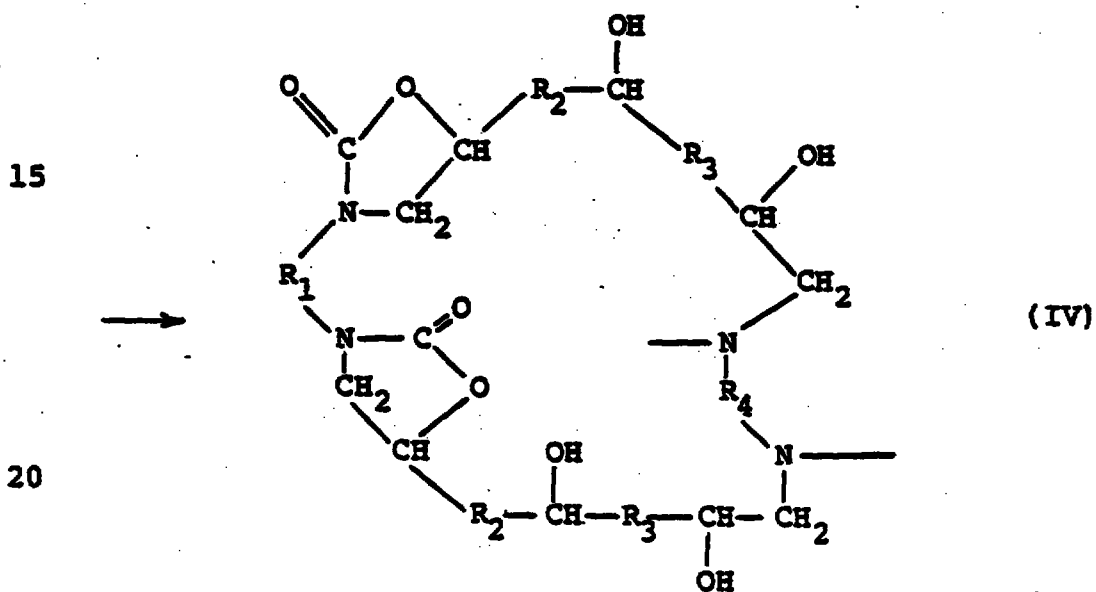


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1           In the above formulas,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$   
represent independently organic groups having at least  
one carbon atom.

5           First, as shown in formula (III), the iso-  
cyanate group of the isocyanate compound is reacted with  
the alcoholic hydroxyl group of the epoxy compound to  
produce an epoxy prepolymer stable at room temperature.

10           Then, an amine compound, for example, is added  
to the prepolymer and final cure is carried out. Thus,  
as shown in formula (IV), the formation of an oxazoli-  
done ring by the isocyanate group-epoxy group reaction,  
the reaction between the amino group and the isocyanate  
group and so on take place, and the cured product be-  
comes quite excellent in heat resistance, toughness,  
15   moisture resistance, etc. When a carboxylic acid an-  
hydride, a phenol novolac compound or a polyvinyl-phenol  
compound is added to this prepolymer, a reaction takes  
place between the epoxy group and the acid anhydride  
group or between the epoxy group and the hydroxyl group  
20   of the phenol novolac or polyvinyl-phenol compound, in  
addition to the formation of an oxazolidone ring by the  
isocyanate group-epoxy group reaction, and the cured  
product also has the same structure as in the conven-  
tional cured epoxy resin as in the case of adding an  
25   amine compound. Thus, there can be obtained a cured  
product simultaneously having so excellent heat resist-  
ance as not to be seen in the conventional cured epoxy

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1 resin and the excellent adhesiveness, toughness, moisture resistance, etc. which the conventional cured epoxy resins have.

5 Further, if a bisimide compound is present in the final curing stage a thermal polymerization of the double bond of the bisimide compound takes place, and there also occurs an addition of the amino group to the double bond in the presence of an amine compound, so that the imide group is introduced into the cured product. Thus,  
10 a cured product having an excellent heat resistance, toughness, adhesiveness, moisture resistance, etc. and very well balanced properties can be obtained.

In this invention, the epoxy compound having at least one alcoholic hydroxyl group and at least two epoxy  
15 groups in its molecule may be used either alone or in admixture with an epoxy compound free from alcoholic hydroxyl groups. Examples of compounds having at least one alcoholic hydroxyl group and at least two epoxy groups in their molecules include diglycidyl ethers having  
20 alcoholic hydroxyl groups obtained by the reaction of epichlorohydrin and Bisphenol A, Bisphenol F or hydrogenated Bisphenol A; diglycidyl ethers having alcoholic hydroxyl groups obtained by the reaction of  $\beta$ -methyl-substituted epichlorohydrin and Bisphenol A;  
25 diglycidyl ethers having alcoholic hydroxyl groups obtained by the reaction of epichlorohydrin and oxybenzoic acid; compounds obtained by partially converting the hydroxyl groups of polyol compounds, such as propy-

lene triol, butylene triol and the like, to glycidyl ethers, brominated products of the above-mentioned epoxy compounds; and so on. On the other hand, examples of epoxy compounds free from alcoholic hydroxyl groups include polyglycidyl ethers of phenol novolac or cresol novolac; diglycidyl ethers of polyhydric phenols such as resorcinol, hydroquinone, catechol and the like; diglycidyl esters of aromatic dicarboxylic acids; vinylcyclohexene diepoxide; dicyclopentadiene diepoxide; diglycidyl methylhydantoin; triglycidyl isocyanurate; diglycidyl ethers free from alcoholic hydroxyl group obtained by the reaction between epichlorohydrin and Bisphenol A, Bisphenol F, hydrogenated Bisphenol A or oxybenzoic acid; diglycidyl ethers free from alcoholic hydroxyl group obtained by the reactions between  $\beta$ -methyl-substituted epichlorohydrin and Bisphenol A; brominated products of the above-mentioned epoxy compounds; and so on. Among these epoxy compounds having alcoholic hydroxyl group, excellent are the diglycidyl ethers having an average molecular weight of 400-1,000 derived from Bisphenol A and epichlorohydrin, which produce cured products excellent in electrical properties, toughness and adhesiveness, and which are most largely produced industrially. If the average molecular weight is less than 400, the content of alcoholic hydroxyl group is so small that the action as a masking agent for isocyanate group decreases and a B-stage com-

1 pound stable at room temperature is difficult to obtain. If the molecular weight is more than 1,000, the cross-linking density of the final cured product is too low and the heat resistance is reduced.

5 In this invention, examples of the isocyanate compound having isocyanate groups in its molecule include methane diisocyanate, ethane-1,2-diisocyanate, butane-1,1-diisocyanate, butane-1,2-diisocyanate, butane-1,4-diisocyanate, propane-1,3-diisocyanate,  
10 trans-vinylene diisocyanate, 2-butene-1,4-diisocyanate, 2-methylbutane-1,4-diisocyanate, pentane-1,5-diisocyanate, 2,2-dimethylpentane-1,5-diisocyanate, hexane-1,6-diisocyanate, heptane-1,7-diisocyanate, octane-1,8-diisocyanate, nonane-1,9-diisocyanate, decane-1,10-  
15 diisocyanate, dimethylsilane diisocyanate, diphenylsilane diisocyanate,  $\omega, \omega'$ -1,3-dimethylbenzene diisocyanate,  $\omega, \omega'$ -1,4-dimethylbenzene diisocyanate,  $\omega, \omega'$ -1,3-dimethylcyclohexane diisocyanate,  $\omega, \omega'$ -1,4-dimethylcyclohexane diisocyanate,  $\omega, \omega'$ -1,3-dimethylnaphthalene  
20 diisocyanate,  $\omega, \omega'$ -1,4-dimethylnaphthalene diisocyanate,  $\omega, \omega'$ -1,5-dimethylnaphthalene diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-tolylene diisocyanate, 2,5-tolylene diisocyanate, 2,6-tolylene diisocyanate, 3,5-tolylene diisocyanate, diphenyl ether-4,4'-  
25 diisocyanate, diphenyl ether-2,4-diisocyanate, naphtha-

1 lene-1,4-diisocyanate, naphthalene-1,5-diisocyanate,  
biphenyl-4,4'-diisocyanate, 3,3'-dimethylbiphenyl-4,4'-  
diisocyanate, 2,3-dimethoxybiphenyl-4,4'-diisocyanate,  
5 diphenylmethane-4,4'-diisocyanate, 3,3'-dimethoxydi-  
phenylmethane-4,4'-diisocyanate, 4,4'-dimethoxydiphenyl-  
methane-3,3'-diisocyanate, diphenyl sulfide-4,4'-diiso-  
cyanate, diphenylsulfone-4,4'-diisocyanate, polymethy-  
lenepolyphenyl isocyanate, triphenylmethane triiso-  
cyanate, benzene triisocyanate, tris (4-phenyl isocya-  
10 nate thiophosphate), 3,3',4,4'-diphenylmethane tetraiso-  
cyanate and the like, as well as their polymers such as  
dimers, trimers, tetramers, pentamers and the like.

Some of these compounds have an isocyanurate ring in the  
molecule, examples of which are preferably trimers of  
15 2,4-tolylene diisocyanate, 2,5-tolylene diisocyanate,  
2,6-tolylene diisocyanate and 3,5-tolylene diisocyanate,  
a trimer of hexane-1,6-diisocyanate, a copolymer of  
2,4-tolylene, 2,5-tolylene, 2,6-tolylene or 3,5-toly-  
lene diisocyanate and hexane-1,6-diisocyanate, and when  
20 they are used a product excellent in heat resistance  
can be obtained owing to the high heat stability of the  
isocyanurate ring.

In this invention, the proportions of the epoxy  
compound having at least one alcoholic hydroxyl group  
25 and the isocyanate compound may be selected appropri-  
ately provided that they are used in a proportion of  
0.5 to 5, preferably 0.5 to 2.6, equivalents of epoxy  
group per equivalent of isocyanate group and at least one

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1 equivalent of alcoholic hydroxyl group per equivalent of  
isocyanate group. If the amount of the epoxy group is  
less than 0.5 equivalent per equivalent of isocyanate  
group, there is a tendency that many urethane linkages  
5 or free isocyanate groups remain in the final cured pro-  
duct so that the heat resistance and moisture resistance  
of the cured product decrease. If the amount of the  
epoxy group exceeds 5 equivalents, the proportion of  
oxazolidone ring in the final cured product becomes  
10 small, and heat resistance decreases. On the other  
hand, if the amount of the alcoholic hydroxyl group is  
less than one equivalent per equivalent of isocyanate  
group, a large amount of free isocyanate remains in the  
epoxy prepolymer, so that the storage stability de-  
15 creases.

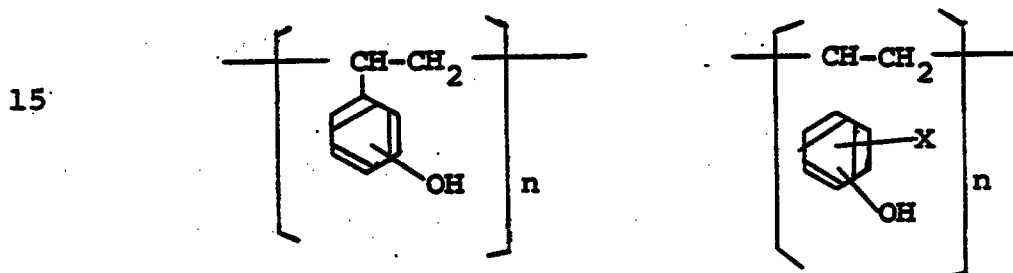
Examples of the amine compound usable in this  
invention include aliphatic amines such as ethylenedi-  
amine, propylenediamine, diethylenetriamine, imino-  
bispropylamine, triethylenetetramine, tetraethylene-  
20 pentamine, diethylaminopropylamine, aminoethylethanol-  
amine, m-xylylenediamine, tetrachloro-p-xylylenediamine,  
cyanoethylated diethylenetriamine and the like; ali-  
cyclic amines such as methanediamine, N-aminoethyl-  
piperazine, 1,3-diaminocyclohexane, isophoronediamine  
25 and the like; aromatic amines such as o-phenylenedi-  
amine, m-phenylenediamine, p-phenylenediamine, diamino-  
diphenyl ether, diaminodiphenyl sulfone, diaminodi-

1 phenylmethane, benzidine, 4,4'-bis(o-toluidine), 4,4'-  
thiodianiline, dianisidine, methylenebis(o-chloroani-  
line), 2,4-toluenediamine, bis(3,4-diaminophenyl)-  
sulfone, diaminoditolylsulfone, 2,6-diaminopyridine, 4-  
5 chloro-o-phenylenediamine, 4-methoxy-6-methyl-m-pheny-  
lenediamine, m-aminobenzylamine and the like; secondary  
and tertiary amines such as piperidine, pyrrolidine,  
morpholine, N-methylmorpholine, pyridine, benzyldi-  
methylamine, tris(dimethylaminomethyl)phenol and the  
10 like; polyamides having terminal amino groups produced  
from linolenic acid dimer and ethylenediamine or di-  
ethylenetriamine; dicyandiamides boron trifluoride-amine  
complexes; imidazole compounds and so on. Among them,  
aromatic amine compounds and dicyandiamide are particu-  
15 larly useful on the point that the storage stability in  
the B stage is good.

Examples of the carboxylic acid anhydrides  
usable in this invention include phthalic anhydride,  
itaconic anhydride, succinic anhydride,  
20 dodecenylsuccinic anhydride, tricarballic  
anhydride, linoleic acid adduct of maleic anhydride,  
chlorendic anhydride, maleic anhydride-vinyl ether copo-  
lymer, maleic anhydride-styrene copolymer, nadic an-  
hydride, methylnadic anhydride, hexahydrophthalic an-  
25 hydride, methylhexahydrophthalic anhydride, tetrahydro-  
phthalic anhydride, methyltetrahydrophthalic anhydride,  
trimellitic anhydride, pyromellitic anhydride, cyclo-

1 pentane-tetracarboxylic anhydride, benzophenone-tetra-  
carboxylic anhydride, benzotetracarboxylic anhydride,  
ethylene glycol-bis(trimellitate), glycerin-tris(tri-  
mellitate) and the like.

5 The phenol novolac compounds usable in this invention  
are advantageously those produced by reacting a phenol such  
as phenol, cresol, xylenol, trimethylphenol, allylphenol,  
alkenylphenol, resorcinol, hydroquinone, pyrocatechol,  
pyrogallol or the like with formaldehyde, paraformaldehyde  
10 or the like in the presence of an acid catalyst. The  
polyvinyl-phenol compounds usable in this invention are  
polymers comprising as the monomeric unit o-vinylphenol,  
m-vinylphenol, p-vinylphenol or a mixture  
thereof as represented by the following formulae:



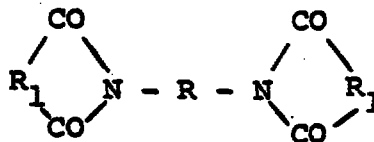
wherein X represents one or more halogen atoms.

Said polyvinylphenol compounds can be produced  
easily by polymerizing the vinylphenols of the above-  
mentioned formulae by, for example, thermal polymeriza-  
20 tion, ionic polymerization or the like.

The bisimide compounds unsable in this inven-

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1 tion are advantageously compounds represented by the following formula:



5 wherein  $\text{R}_1$  represents a divalent organic residue having carbon-carbon double bond and  $\text{R}_2$  represents a divalent organic residue having at least two carbon atoms. Examples of said bisimide compound include N,N'-ethylene-  
10 bismaleimide, N,N'-hexamethylene-bismaleimide, N,N'-m-phenylene-bismaleimide, N,N'-p-phenylene-bismaleimide, N,N'-4,4'-diphenylmethane-bismaleimide, N,N'-4,4'-diphenylether-bismaleimide, N,N'-4,4'-diphenylsulfone-bismaleimide, N,N'-4,4'-dicyclohexylmethane-bismale-  
15 imide, N,N'- $\alpha,\alpha'$ -4,4'-dimethylenecyclohexane-bismaleimide, N,N'-m-xylene-bismaleimide, N,N'-diphenylcyclohexane-bismaleimide and the like.

In this invention, when at least one member selected from the group consisting of amine compounds,  
20 carboxylic acid anhydrides, phenol novolac compounds and polyvinyl-phenol compounds is mixed with the prepolymer obtained by reacting the/or an alcoholic hydroxyl group of the epoxy compound having alcoholic hydroxyl group with an isocyanate group of the polyisocyanate compound,  
25 the proportions of the compounds may be selected appropriately depending on the purposes. Preferably, however, 0.1-2 equivalents of amine, 0.1-2 equivalents of acid

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1 anhydride or 0.1-2 equivalents of hydroxyl group is used  
per equivalent of the epoxy group of said prepolymer.  
If the amount exceeds 2 equivalents, the amine compound,  
the polycarboxylic acid anhydride, the phenol novolac  
5 compound or the polyvinyl-phenol compound is apt to  
remain unreacted, so that heat resistance, moisture  
resistance and chemical resistance decrease. On the  
other hand, in mixing a bisimide compound, the amount of  
the bisimide compound may also be selected appropriately  
10 depending upon the purposes. Preferably, however, it is  
100 parts by weight or less per 10 parts by weight of  
the prepolymer. If the amount of the bisimide compound  
is larger than the above, the cured product is apt to  
become so brittle that the toughness decreases. When a  
15 bisimide compound is used, a simultaneous use of an  
organic peroxide is useful because it remarkably enhances  
the curing velocity.

In this invention, the addition of a catalyst  
is useful because it enables the reaction to progress  
20 more rapidly. As the catalyst of this invention, those  
conventionally used as urethane group-forming catalyst or  
as oxazolidone ring-forming catalyst may be employed.  
Examples of said catalyst include quaternary ammonium  
salts such as cetyltrimethylammonium bromide, cetyltri-  
25 methylammonium chloride, dodecyltrimethylammonium  
iodide, trimethyldodecylammonium iodide, trimethyl-  
dodecylammonium chloride and the like; metal halides

1 such as lithium chloride, tin chloride, iron chloride,  
zinc chloride, aluminum chloride and the like; metal  
alkoxides and phenoxides such as lithium butoxide,  
potassium butoxide, aluminum isopropoxide, aluminum phe-  
5 noxide, calcium ethoxide, magnesium ethoxide and the  
like; cobalt naphthenate; organometallic compounds such  
as tetrabutyltin, trimethyltin hydroxide, dimethyltin  
dichloride, dibutyltin dilaurate and the like; and  
imidazole compounds such as 2-methylimidazole, 2-ethyl-  
10 imidazole, 2-phenylimidazole, 2-ethyl-4-methylimidazole,  
2-phenyl-4-methylimidazole, 1-benzyl-2-methylimidazole,  
2-isopropylimidazole, 1-cyanoethyl-2-methylimidazole,  
1-cyanoethyl-2-ethyl-4-methylimidazole, 1-cyanoethyl-  
2-isopropylimidazole, 1-cyanoethyl-2-phenylimidazole,  
15 2-undecylimidazole, 2-heptadecylimidazole, 1-cyanoethyl-  
2-undecylimidazole, 1-azine-2-methylimidazole, 1-azine-  
2-ethyl-4-methylimidazole, 1-azine-2-undecylimidazole  
and the like. Further, various amines such as tri-  
methylamine, triethylamine, benzyldimethylamine, tris-  
20 (dimethylaminomethyl)phenol, tetramethylbutanediamine,  
N-methylmorpholine, N-ethylmorpholine, triethylene-  
diamine and the like also have a catalytic action.

The above-mentioned catalysts are useful  
because, if at least one of them is added, the reaction  
25 progresses rapidly. The catalyst may be added at the  
time of reacting the isocyanate group with the alcoholic  
hydroxyl group to form a prepolymer, or it may also be

1 added at the stage of final cure.

If necessary, various additives such as flame retardant, pigment, dye, reinforcing agent and the like; fillers, and the like, may be added in this invention.

5 The process for producing a crosslinked resin of this invention can advantageously be applied to the production of a laminate. In this case, the laminate can be produced by reacting one equivalent of an isocyanate compound having isocyanate groups in the molecule  
10 with an epoxy compound having at least one alcoholic hydroxyl group and at least two epoxy groups in the molecule in an amount corresponding to 0.5 to 5, preferably 0.5 to 2.6, equivalents per isocyanate equivalent and at least one alcoholic hydroxyl equivalent per isocyanate  
15 equivalent to first react isocyanate groups of the isocyanate compound with alcoholic hydroxyl groups of the epoxy compound, thereby forming an epoxy prepolymer having urethane linkages stable at room temperature, optionally adding to the prepolymer a bisimide compound and/or at  
20 least one member selected from the group consisting of amine compounds, polycarboxylic acid anhydrides, phenol novolac compounds, and polyvinyl-phenol compounds to prepare a resin composition, impregnating a fibrous substrate with said resin composition, superposing at  
25 least one sheet of the resin-impregnated substrate on a metallic foil, pressing the resulting assembly with heating at a temperature at least 70°C, preferably at least 100°C, higher than the reaction temperature for

- 1 the formation of the prepolymer to dissociate the urethane linkages and regenerate the isocyanate groups; and then reacting the said isocyanate groups with the epoxy groups of the epoxy compound.
- 5       The fibrous substrate which may be used in this invention includes fibrous materials which can be impregnated with resins, for example, fabrics such as polyester fibre, polyvinyl alcohol fiber, polyamide fiber, and the

- 1 like; cotton fabrics; fabrics of carbon fiber; paper;  
and the like. Metal foils which may be used in  
this invention include copper foil, aluminum foil, gold  
foil, nickel foil and the like, and may, optionally,  
5 have been subjected to surface-roughening treatment or  
coating with an adhesive.

This invention is explained in more detail  
below referring to Examples and the accompanying  
drawings in which Figs. 1 and 2 show infrared absorption  
10 spectra of the prepolymers obtained in Example 1. Said  
Examples are merely by way of illustration and not by  
way of limitation.

#### Example 1

- 15 In 950 g of methyl ethyl ketone (MEK) were  
dissolved 100 g of 2,4-tolylene diisocyanate, 850 g of  
diglycidyl ether having an average molecular weight of  
about 700, an epoxy equivalent of about 340 and an  
alcoholic hydroxyl equivalent of about 700 obtained by  
20 the reaction of Bisphenol A and epichlorohydrin, and  
2 g of 2-methylimidazole to obtain a solution of a con-  
centration of 50% by weight. This solution was heated  
to 70°C and stirred. Ten minutes after the start of  
heating and stirring, the infrared absorption spectrum  
25 of the solution was measured by a liquid film method by  
the use of KRS-5. The result of the measurement is  
shown in Fig. 1. Five hours after the start of heating

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1 and stirring, the infrared absorption spectrum of the  
solution was again measured by the same method as above,  
to obtain the result shown in Fig. 2. The absorption of  
isocyanate group at  $2250\text{ cm}^{-1}$  observed in Fig. 1, dis-  
and the absorption of the urethane linkage at  $1730\text{ cm}^{-1}$  in Fig. 2  
5 appeared in Fig. 2/is greater than that in Fig. 1.

The absorption of epoxy group at  $910\text{ cm}^{-1}$  shows no  
change. From these facts, it can be understood that the  
isocyanate group of 2,4-tolylene diisocyanate was masked  
by the alcoholic hydroxyl group of epoxy compound and  
10 a prepolymer stable at room temperature was formed.

Then, a varnish was prepared by adding 70 g of  
4,4'-diaminodiphenylsulfone to the solution. A prepreg  
was prepared by impregnating a glass cloth with the var-  
nish and drying it at  $130^{\circ}\text{C}$  for 5 minutes. Ten sheets  
15 of the prepreg were put on one another and the resulting  
assembly was placed between two copper foils having a  
thickness of  $35\text{ }\mu\text{m}$ , after which it was press-molded at  
 $170^{\circ}\text{C}$  for 2 hours under a pressure of  $40\text{ kg/cm}^2$  to  
obtain a double copper-clad laminate having a thickness  
20 of  $1.6\text{ mm}$ . This double copper-clad laminate had a high  
flexural strength at high temperatures and excellent  
heat resistance as shown in Table 2. The result of  
punching test was also good enough to show a high tough-  
ness, its soldering heat-resistance did not decrease  
25 even after boiling treatment, and its moisture resist-  
ance was excellent. When the prepreg was allowed to  
stand at room temperature for 30 days and thereafter

1 press-molded, there was obtained a copper-clad laminate  
having quite the same good appearance as the appearance  
obtainable by molding the prepreg just after its pre-  
paration. Further, as shown in Table 2, the perfor-  
5 mance of the copper-clad laminate were as excellent as  
those of the laminate obtained by molding just after the  
preparation of prepreg.

Moreover, the period of time taken until the  
flow of the resin in the prepreg became 1/5 of the ini-  
10 tial value was measured. The results are shown in Table  
1, which demonstrate that the flow of the resin in the  
prepreg was maintained more than 1/5 of the initial  
value, even after the lapse of 60 days.

A multi-layer board (6 layers) having a thick-  
15 ness of 2.2 mm was prepared from the prepreg. The pre-  
preg exhibited quite excellent moldability and process-  
ability in the many steps of multi-layer board prepara-  
tion including preparation of inner layer material,  
multi-layer forming, drilling, through-hole plating,  
20 preparation of surface circuit, etc. The 6-layer board  
thus obtained exhibited not only excellent soldering  
heat-resistance and bonding strength of copper foil to  
the prepreg, but also no formation of the so-called  
smear, namely the adhesion of resin to copper foils of  
25 inner layer, at the time of drilling, so that connect-  
ions of plated through.holes are very good.

1 Example 2

In 600 g of MEK were dissolved 100 g of diphenylmethane-4,4'-diisocyanate, 500 g of diglycidyl ether having an average molecular weight of about 950, an epoxy equivalent of about 480 and an alcoholic hydroxyl equivalent of about 50 obtained by the reaction of Bisphenol A and epichlorohydrin, 2 g of 2-phenylimidazole, to prepare a solution of a concentration of 50% by weight. In the same manner as in Example 1, the solution was stirred at 70°C for 6 hours and the infrared absorption spectrum was measured to find that the isocyanate group had been masked by the alcoholic hydroxyl group of the epoxy compound and a prepolymer stable at room temperature was formed. The solution was introduced into 5 kg of n-hexane, and the resulting prepolymer was recovered. A molding material was prepared by mixing together 190 g of the recovered prepolymer, 12 g of nadic anhydride, 500 g of powdery silica, 1 g of lithium chloride, 0.5 g of carbon black and 1 g of zinc stearate and kneading the resulting mixture on a hot roll at 70°C for 10 minutes. The spiral flow measured just after the kneading was 85 cm. After allowing this molding material to stand at room temperature for 30 days, its spiral flow was again measured to obtain a result of 82 cm which demonstrated that only a slight change took place. When this molding material was molded at 170°C for 5 minutes and then after-baked at

1 170°C for 16 hours, its glass transition point was as high as 210°C, demonstrating such excellent heat resistance that none of the conventional epoxy resin molded articles had.

5

### Example 3

In 600 g of MEK were dissolved 100 g of 4,4',4''-trimethyl-3,3',3''-triisocyanate-2,4,6-triphenyl isocyanurate (trimer of 2,4-tolylene diisocyanate), 10 500 g of diglycidyl ether having an average molecular weight of about 700, an epoxy equivalent of about 340, and an alcoholic hydroxyl equivalent of about 700 obtained by the reaction of Bisphenol A and epichlorohydrin and 2 g of 2-methylimidazole to prepare a solution of a concentration of 50% by weight. In the same 15 manner as in Example 1, the solution was stirred at 70°C for 4 hours and the infrared absorption spectrum was measured to find that the isocyanate group had been masked. In quite the same manner as in Example 1, a 20 glass cloth was impregnated with the solution, dried and pressed to obtain a double copper-clad laminate having a thickness of 1.6 mm. The performances of this double copper-clad laminate are shown in Table 1, which demonstrate that the laminate is particularly excellent in 25 heat resistance and is also excellent in moisture resistance and electrical properties. As shown in Table 1, this prepreg is excellent in storage stability and

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- 1 shows that the change of flow of resin with the lapse of time is very slight.

#### Example 4

- 5 In 850 g of MEK were dissolved 100 g of 2,4-tolylene diisocyanate, 750 g of diglycidyl ether having an average molecular weight of about 950, an epoxy equivalent of about 480 and an alcoholic hydroxyl equivalent of about 500 obtained by the reaction of
- 10 Bisphenol A and epichlorhydrin, and 2 g of 2-methylimidazole to prepare a solution of a concentration of 50% by weight. In the same manner as in Example 1, the solution was stirred at 70°C for 5 hours and the infrared absorption spectrum was measured to find that the
- 15 isocyanate group had been masked. A varnish was prepared by adding to this solution 50 g of a polyvinyl compound obtained by thermal polymerization of p-vinylphenol and having an average molecular weight of about 8,000 and a hydroxyl equivalent of about 120. In quite
- 20 the same manner as in Example 1, a glass cloth was impregnated with this varnish, dried and pressed to obtain a double copper-clad laminate having a thickness of 1.6 mm. As shown in Table 2, this double copper-clad laminate was excellent in heat resistance, toughness,
- 25 moisture resistance, etc. As shown in Table 1, the change of flow of resin in this prepreg with the lapse of time was very small.

1 Example 5

In 600 g of MEK were dissolved 100 g of diphenylmethane-4,4'-diisocyanate, 500 g of diglycidyl ether having an average molecular weight of about 950, an epoxy equivalent of about 480, and an alcoholic hydroxyl equivalent of about 500 obtained by the reaction of Bisphenol A and epichlorohydrin, and 2 g of 2-phenylimidazole, to prepare a solution of a concentration of 50% by weight. In the same manner as in Example 1, the solution was stirred at 70°C for 6 hours and the infrared absorption spectrum was measured to find that the isocyanate group had been masked and a prepolymer stable at room temperature was formed. The solution was poured into n-hexane and the resulting prepolymer was recovered. A molding material was prepared by mixing together 200 g of this prepolymer, 70 g of a phenol novolac having a softening point of about 100°C, and a hydroxyl equivalent of about 100 synthesized by quite the same method as in Example 1, 500 g of powdery silica, 1 g of lithium chloride, 2 g of carbon black and 4 g of zinc stearate and kneading the resulting mixture on a hot roll at 70°C for 10 minutes. The spiral flow just after the kneading was 82 cm. When this molding material was allowed to stand at room temperature for 30 days and thereafter its spiral flow was measured, the result was 80 cm, demonstrating that only a slight change took place. When this molding material was

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1 molded at 170°C for 5 minutes and then after-baked at  
170°C for 16 hours, the glass transition point of the  
molded product was as high as 220°C and the molded pro-  
duct showed such excellent resistance that none of the  
5 conventional epoxy resin molded articles had.

#### Example 6

In 600 g of MEK were dissolved 100 g of  
4,4',4''-trimethyl-3,3',3''-triisocyanate 2,4,6-triphenyl  
10 isocyanurate (trimer of 2,4-tolylene diisocyanate),  
500 g of diglycidyl ether having an average molecular  
weight of about 700, an epoxy equivalent of about 340,  
and an alcoholic hydroxyl equivalent of about 700  
obtained by the reaction of Bisphenol A and epichloro-  
15 hydrin, and 2 g of 2-methylimidazole, to prepare a solu-  
tion of a concentration of 50% by weight. In the same  
manner as in Example 1, the solution was stirred at 70°C  
for 10 hours and the infrared absorption spectrum was  
measured to find that the isocyanate group had been  
20 masked. A varnish was prepared by adding to this solu-  
tion 40 g of 4,4'-diaminodiphenylmethane to obtain a  
homogeneous solution and then further adding thereto a  
solution of 100 g of N,N'-4,4'-diphenylmethane-bismale-  
imide in 400 g of dimethylformamide. In quite the same  
25 manner as in Example 1, a glass cloth was impregnated  
with the varnish, dried and pressed to obtain a copper-  
clad laminate. As shown in Table 2, this copper-clad

- 1 laminate was quite excellent in heat resistance and was also excellent in toughness, moisture resistance, etc. As shown in Table 1, the change of flow of resin in this prepreg with the lapse of time was very slight.

5

#### Comparative Example 1

- In 460 g of MEK were dissolved 200 g of 2,4-tolylene diisocyanate, 260 g of phenol, and 2 g of 2-methylimidazole to prepare a solution of a concentration of 50% by weight. In the same manner as in Example 1, the solution was stirred at 70°C for 5 hours and the infrared absorption spectrum was measured to find that the isocyanate group had been masked. Then, a varnish was prepared by adding, to this solution, 400 g of 15 diglycidyl ether having an average molecular weight of about 380, an epoxy equivalent of about 190, and an alcoholic hydroxyl equivalent of zero obtained by the reaction of Bisphenol A and epichlorohydrin. In quite the same manner as in Example 1, a glass cloth was 20 impregnated with this varnish, dried and pressed to obtain a double copper-clad laminate having a thickness of 1.6 mm. However, many voids were formed in this double copper-clad laminate, and accordingly it was quite inferior in mechanical strength, soldering heat- 25 resistance, etc. and could not be used practically.

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1 Comparative Example 2

In 700 g of MEK were dissolved 100 g of 2,4-tolylene diisocyanate, 600 g of diglycidyl ether having an average molecular weight of about 950, an epoxy  
5 equivalent of about 480, and an alcoholic hydroxyl equivalent of about 500 obtained by the reaction of Bisphenol A and epichlorohydrin, and 1 g of 2-methylimidazole to prepare a varnish of a concentration of 50% by weight.

10 Without heating nor stirring this varnish, glass cloth was impregnated with this varnish, dried and press-molded in the same manner as in Example 1 to obtain a copper-clad laminate. As shown in Table 2, this copper-clad laminate was so poor in moisture  
15 resistance that, when boiled for 30 minutes and then allowed to float on molten solder at 260°C, blisters occurred in 20 seconds or less. This is probably because the isocyanate group was not masked beforehand, and hence, many free isocyanate groups remained in the final  
20 cured product. Further, as shown in Table 1, this prepreg showed a very great change with the lapse of time of flow of resin, and therefore, the flow reached 1/5 of the initial value in 5 hours.

25 Comparative Example 3

In 550 g of MEK were dissolved 100 g of 2,4-tolylene diisocyanate, 450 g of monoglycidyl ether of

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1 Bisphenol A having a molecular weight of about 280, an  
epoxy equivalent of about 280, a phenolic hydroxyl  
equivalent of about 280, and 1 g of 2-methylimidazole,  
to prepare a solution of a concentration of 50% by  
5 weight. In the same manner as in Example 1, the solu-  
tion was heated and stirred at 70°C for 10 hours and then  
the infrared absorption spectrum was measured to find  
that the isocyanate group had been masked. Then, a  
varnish was prepared by adding 30 g of 4,4'-diamino  
10 diphenylsulfone to this solution, with which a glass  
cloth was impregnated, dried and press molded to obtain  
a copper-clad laminate in the same manner as in Example  
1. As shown in Table 2, this copper-clad laminate was  
quite poor in water resistance, so that when boiled for  
15 30 minutes and then allowed to float on molten solder at  
260°C, blisters appeared in 20 seconds or less. This is  
probably because the isocyanate was masked with phenolic  
hydroxyl group, and hence, the urethane linkage had a  
lower dissociation temperature, so that the masked iso-  
20 cyanate group was partially changed into free isocyanate  
group during the impregnation of glass cloth and drying,  
and the free isocyanate group remained in the cured pro-  
duct to result in a decrease in water resistance.

#### 25 Comparative Example 4

In 850 g of MEK were dissolved 100 g of 4,4'-  
diaminodiphenylsulfone which was conventionally used as

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1 a curing agent for epoxy resins, 750 g of diglycidyl  
ether having an average molecular weight of about 950,  
an epoxy equivalent of about 480 obtained by the reac-  
tion of Bisphenol A and epichlorohydrin, and 2 g of 2-  
5 methylimidazole, to prepare a varnish of a concentration  
of 50% by weight. In the same manner as in Example 1,  
a glass cloth was impregnated with this varnish, dried  
and press-molded to obtain a copper-clad laminate.

The performance of this copper-clad laminate are shown  
10 in Table 2, which demonstrates that, as compared with  
the cured product obtained by the curing process of this  
invention, it is much inferior in heatresistances such  
as hot flexural strength.

15 Comparative Example 5

A molding material was prepared by mixing  
together 100 g of 4,4',4"-trimethyl-3,3',3"-triiso-  
cyanate 2,4,6-triphenyl isocyanurate, 130 g of polygly-  
cidyl ether of cresol novolac having an average molecu-  
20 lar weight of about 1,400, an epoxy equivalent of about  
230, and an alcoholic hydroxyl equivalent of zero, 2 g  
of 2-methylimidazole, 450 of powdery silica, 1 g of  
lithium chloride, 0.5 g of carbon black and 1 g of zinc  
stearate and kneading the resulting mixture on a hot  
25 roll at 70°C for 10 minutes. The spiral flow measured  
just after the kneading was 88 cm. However, when the  
molding material was allowed to stand at room tempera-

- 1 ture for 6 hours and thereafter the spiral flow was again measured, it was as small as 5 cm.

5

Table 1

| No.                                                 | Period of time take until the flow of resin in prepreg became 1/5 of the initial value |
|-----------------------------------------------------|----------------------------------------------------------------------------------------|
| 10 Example 1<br>Example 3<br>Example 4<br>Example 6 | More than 60 days<br>More than 60 days<br>More than 60 days<br>More than 60 days       |
| Comparative Example 2                               | 0.2 days (5 hours.)                                                                    |
| 15 Comparative Example 3                            | 25 days                                                                                |
| Comparative Exmample 4                              | More than 60 days                                                                      |

Note: 1) The flows were measured according to JIS C 6487.

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- 2) The prepregs were stored in an atmosphere at a temperature of 23°C at a humidity of 60%.

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Table 2 Performances of laminates

| Item of test                     | Unit     | Conditions of treatment and measurement             | Performances       |
|----------------------------------|----------|-----------------------------------------------------|--------------------|
|                                  |          |                                                     | Example 1-1        |
| Insulation resistance            | $\Omega$ | A                                                   | $3 \times 10^{14}$ |
|                                  |          | D - 2/100                                           | $2 \times 10^{12}$ |
| Dielectric constant (1 MHz)      | -        | A                                                   | 4.5                |
|                                  |          | D - 48/50                                           | 4.7                |
| Dielectric tangent (1 MHz)       | -        | A                                                   | 0.012              |
|                                  |          | D - 48/50                                           | 0.014              |
| Flexural strength                | kg/mm    | A                                                   | 55                 |
|                                  |          | E-1/150 at 150°C                                    | 32                 |
|                                  |          | E-1/200 at 200°C                                    | 16                 |
| Soldering heat-resistance        | -        | 260°C, 60 sec float                                 | No change          |
|                                  |          | D-0.5/100 treatment followed by 260°C, 60 sec float | No change          |
|                                  |          | D-2/100 treatment followed by 260°C, 60 sec float   | No change          |
| Flexural strength of copper foil | kg/cm    | A                                                   | 1.8                |
|                                  |          | E-1/150 at 150°C                                    | 1.5                |
| Chemical resistance              | -        | Boiling in trichlene* for 5 minutes                 | No change          |
| Punching quality                 | -        | A                                                   | Good               |

Note: Example 1-1: In Example 1, the sample molded just after prepreg preparation.

Example 1-2: In Example 1, the sample molded after allowing prepreg to stand at room temperature for 60 days.

\* "trichlene" signifies "trichloroethylene".

Table 2 (Cont'd)

| Performances       |                    |                    |                    |
|--------------------|--------------------|--------------------|--------------------|
| Example 1-2        | Example 3          | Example 4          | Example 6          |
| $4 \times 10^{14}$ | $5 \times 10^{14}$ | $2 \times 10^{14}$ | $7 \times 10^{14}$ |
| $2 \times 10^{12}$ | $3 \times 10^{12}$ | $6 \times 10^{12}$ | $5 \times 10^{12}$ |
| 4.5                | 4.3                | 4.6                | 4.4                |
| 4.7                | 4.5                | 4.8                | 4.5                |
| 0.013              | 0.007              | 0.012              | 0.008              |
| 0.014              | 0.008              | 0.014              | 0.009              |
| 55                 | 52                 | 54                 | 52                 |
| 33                 | 40                 | 38                 | 45                 |
| 17                 | 22                 | 20                 | 38                 |
| No change          | No change          | No change          | No change          |
| No change          | No change          | No change          | No change          |
| No change          | No change          | No change          | No change          |
| 1.8                | 1.6                | 1.6                | 1.7                |
| 1.5                | 1.4                | 1.4                | 1.5                |
| No change          | No change          | No change          | No change          |
| Good               | Fair               | Good               | Good               |

Table 2 (Cont'd)

| Performances          |                       |                       | Testing method |
|-----------------------|-----------------------|-----------------------|----------------|
| Comparative Example 2 | Comparative Example 3 | Comparative Example 4 |                |
| 1 x 10 <sup>14</sup>  | 2 x 10 <sup>14</sup>  | 1 x 10 <sup>14</sup>  | JIS C-6481     |
| 2 x 10 <sup>10</sup>  | 3 x 10 <sup>10</sup>  | 2 x 10 <sup>12</sup>  |                |
| 4.6                   | 5.1                   | 4.8                   | JIS C-6481     |
| 5.3                   | 5.5                   | 4.9                   |                |
| 0.009                 | 0.022                 | 0.028                 | JIS C-6481     |
| 0.035                 | 0.038                 | 0.035                 |                |
| 53                    | 52                    | 56                    | JIS C-6481     |
| 34                    | 5                     | 6                     |                |
| 16                    | 3                     | 3                     |                |
| No change             | No change             | No change             | JIS C-6481     |
| Blistered             | Blistered             | No change             |                |
| Blistered             | Blistered             | No change             |                |
| 1.2                   | 1.6                   | 1.8                   | JIS C-6481     |
| 1.0                   | 0.3                   | 0.6                   |                |
| No change             | Swollen               | No change             | JIS C-6481     |
| Very poor             | Good                  | Good                  | D-617          |

1           It is apparent from the Examples and the  
Comparative Examples that, according to the process of  
this invention, there can be obtained the B-stage com-  
pounds such as heat resistant varnish, prepreg, molding  
5 material and the like quite stable at room temperature,  
and that the final cured product is excellent in tough-  
ness, heat resistance, moisture resistance, adhesive-  
ness, etc. Therefore, it is very useful as copper-clad  
laminate as well as in other various uses such as  
10 electrical insulating material, cast article, structural  
material, and the like.

The carboxylic acid anhydrides referred to  
herein for use in the final curing stage are of course  
anhydrides of polycarboxylic acids, that is compounds  
containing at least two carboxylic acid groups.



# Claims

1. A crosslinked resin obtained by reacting one equivalent of an isocyanate compound having isocyanate groups in the molecule with an epoxy compound having at least one alcoholic hydroxyl group and at least two epoxy groups in the molecule in an amount corresponding to 0.5 to 5 epoxy equivalents per isocyanate equivalent and at least one alcoholic hydroxyl equivalent per isocyanate equivalent to first react isocyanate groups of the isocyanate compound with alcoholic hydroxyl groups of the epoxy compound, thereby forming an epoxy prepolymer having urethane linkages stable at room temperature; subsequently heating the resulting prepolymer at a temperature at least 70°C higher than the reaction temperature for the formation of the prepolymer to dissociate the urethane linkages and regenerate the isocyanate groups; and then reacting the said isocyanate groups with the epoxy groups of the epoxy compound.
2. A crosslinked resin as claimed in claim 1, wherein the epoxy compound having at least two epoxy groups and at least one alcoholic hydroxyl group is at least one compound selected from glycidyl ethers obtained by reaction between Bisphenol A or F or hydrogenated Bisphenol A and  $\beta$ -methyl-substituted or unsubstituted epichlorohydrin, and brominated products of these epoxy compounds.
3. A crosslinked resin as claimed in claim 1, wherein the epoxy compound is a diglycidyl ether obtained by



1 reaction between Bisphenol A and epichlorohydrin, and  
having an average molecular weight of 400 to 1,000.

4. A crosslinked resin as claimed in any one of claims  
1 to 3, wherein the isocyanate compound is an isocyanate  
5 compound having an isocyanurate ring in the molecule.

5. A crosslinked resin as claimed in any one of claims  
1 to



1     3, wherein the isocyanate compound is a trimer of 2,4-  
tolylene diisocyanate, 2,5-tolylene diisocyanate, 2,6-  
tolylene diisocyanate or 3,5-tolylene diisocyanate, a  
trimer of hexane-1,6-diisocyanate or a copolymer of  
5     2,4-tolylene, 2,5-tolylene, 2,6-tolylene or 3,5-tolylene  
diisocyanate and hexane-1,6-diisocyanate.

6.     A crosslinked resin as claimed in any one of claims  
1 to 5, wherein the dissociation of the urethane link-  
ages of the epoxy prepolymer to regenerate the iso-  
10     cyanate groups and the reaction between the regenerated  
isocyanate groups and the epoxy groups has been carried  
out in the presence of at least one curing agent select-  
ed from the group consisting of amine compounds, polycar-  
boxylic acid anhydrides, phenol novolac compounds and  
15     polyvinyl-phenol compounds.

7.     A crosslinked resin as claimed in claim 6, wherein  
the curing agent is an amine.

8.     A crosslinked resin as claimed in claim 7, wherein  
the amine is an aromatic amine.

20     9.     A crosslinked resin as claimed in claim 8, wherein  
the aromatic amine is diaminodiphenyl ether, diamino-  
diphenylsulfone, diaminodiphenylmethane or methylenebis  
(o-chloroaniline).

10.     A crosslinked resin as claimed in any one of claims  
25     1 to 5, wherein the dissociation of the urethane linkages  
of the epoxy prepolymer to regenerate the isocyanate  
groups and the reaction between the regenerated isocyanate  
groups and the epoxy groups has been carried out in the  
presence of a bisimide compound.



- 1 11. A crosslinked resin as claimed in claim 10, wherein  
the bisimide is N,N'-4,4'-diphenylmethane-bismale-  
mide, N,N'-4,4'-diphenyl ether-bismaleimide or N,N'-4,  
4'-diphenylsulfone-bismaleimide.
- 5 12. A crosslinked resin as claimed in any one of claims  
6 to 9, wherein the dissociation of the urethane link-  
ages of the prepolymer is regenerate the isocyanate  
groups and the reaction between the regenerated iso-  
cyanate groups and the epoxy groups has been carried out  
10 in the presence of a bisimide compound and at least one  
member selected from the group consisting of amine  
compounds, carboxylic acid anhydrides, phenol novolac  
compounds and polyvinyl-phenol compounds.
13. A crosslinked resin as claimed in any one of claims  
15 1 to 12 wherein the amount of epoxy compound corresponds  
to 0.5 to 2.6 epoxy equivalents per isocyanate equivalent.
14. A crosslinked resin as claimed in any one of claims  
1 to 13, wherein the prepolymer has been heated to a  
temperature at least 100°C higher than the reaction temp-  
20 erature for the formation of the prepolymer.
15. A process for producing a crosslinked epoxy resin  
which comprises reacting one equivalent of an isocyanate  
compound having isocyanate groups in the molecule with  
an epoxy compound having at least one alcoholic hydroxyl  
25 group and at least two epoxy groups in the molecule in  
an amount corresponding to 0.5 to 5 epoxy equivalents  
per isocyanate equivalent and at least one alcoholic  
hydroxyl equivalent per isocyanate equivalent to first



1 react isocyanate groups of the isocyanate compound with  
alcoholic hydroxyl groups of the epoxy compound, thereby  
forming an epoxy prepolymer having urethane linkages  
stable at room temperature; subsequently heating the  
5 resulting prepolymer at a temperature at least 70°C  
higher than the reaction temperature for the formation of  
the prepolymer to dissociate the urethane linkages and  
regenerate the isocyanate groups; and then reacting the  
said isocyanate groups with the epoxy groups of the epoxy  
10 compound.

16. A process as claimed in claim 15, wherein the  
dissociation of the urethane linkages to regenerate the  
isocyanate groups and the reaction between the regenera-  
ted isocyanate groups and the epoxy groups are carried  
15 out in the presence of at least one member selected from  
the group consisting of amine compounds, polycarboxylic  
acid anhydrides, phenol novolac compounds and poly-  
vinyl-phenol compounds.

17. A process as claimed in claim 15, wherein the  
20 dissociation of the urethane linkages to regenerate the  
isocyanate groups and the reaction between the rege-  
nerated isocyanate groups and the epoxy groups are  
carried out in the presence of a bisimide compound.

18. A process as claimed in claim 15, wherein the dis-  
25 sociation of the urethane linkages to regenerate the  
isocyanate groups and the reaction between the regene-  
rated isocyanate groups and the epoxy groups are carried  
out in the presence of a bisimide compound and at least



(5)

- 1 one member selected from the groups consisting of amine compounds, polycarboxylic acid anhydrides, phenol novolac compounds and polyvinyl phenol compounds.
19. A process for producing a laminate which comprises
  - 5 reacting one equivalent of an isocyanate compound having isocyanate groups in the molecule with an epoxy compound having at least one alcoholic hydroxyl group and at least two epoxy groups in the molecule in an amount corresponding to 0.5 to 5 epoxy equivalents per iso-
  - 10 cyanate equivalent and at least one alcoholic hydroxyl equivalent per isocyanate equivalent to first react isocyanate groups of the isocyanate compound with alcoholic hydroxyl groups of the epoxy compound, thereby forming an epoxy prepolymer having urethane linkages stable at room
  - 15 temperature, optionally adding to the prepolymer a bisimide compound and/or at least one member selected from the group consisting of amine compounds, polycarboxylic acid anhydrides, phenol novolac compounds, and polyvinyl-phenol compounds to prepare a resin composition,
  - 20 impregnating a fibrous substrate with said resin composition, superposing at least one sheet of the resin-impregnated substrate on a metallic foil, pressing the resulting assembly with heating at a temperature at least
  - 25 formation of the prepolymer to dissociate the urethane linkages and regenerate the isocyanate groups; and then reacting the said isocyanate groups with the epoxy groups of the epoxy compound.



\* C L M S \*

- 1 20. A process as claimed in any one of claims 15 to 19, wherein the prepolymer or resin composition is heated to a temperature at least 100°C higher than the reaction temperature for the formation of the prepolymer.
- 5 21. A process as claimed in any one of claims 15 to 20, wherein the amount of epoxy compound corresponds to 0.5 to 2.6 epoxy equivalents per isocyanate equivalent.
22. A crosslinked resin obtainable by the process of any one of claims 15 to 21.
- 10 23. A crosslinked resin, substantially as described in any one of Examples 1 to 6 herein.
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