

AQUEOUS PHOTSENSITIVE RESIN COMPOSITION,
PREPARATION THEREOF AND PREPARATION OF
PRINTED CIRCUIT BOARD USING THE COMPOSITION

This invention relates to a method of preparing a printed circuit board by using an aqueous photosensitive resin composition and a method of preparing specific aqueous photosensitive resin compositions and specific aqueous photosensitive compositions.

Heretofore, in the preparation of a printed circuit board, generally a photosensitive film is coated on a laminated board which has been lined with an electrically conductive metal foil such as a copper foil. The coated board is then irradiated with actinic light through a negative and developed. Then, unnecessary portions of the metal foil, i.e., those not forming part of the circuit pattern, are etched and the photosensitive film is stripped. The result is a printed circuit on the laminated board. The board itself acts as an insulator. The photosensitive film used in such a method is fairly thick, and accordingly, causes problems such as decreased sharpness of the circuit pattern formed after the irradiation and development, difficulty of uniformly coating the photosensitive film on the metal foil and high cost of the photosensitive film. Another method of preparing a printed circuit board is to coat a liquid photosensitive resin composition directly on a substrate and dry it to form a photo-curable coating. Since the photosensitive resin composition used for this purpose is dissolved or dispersed in an organic solvent, the organic solvent will create a problem in the working environment and accordingly, this method is hardly acceptable.

The preparation of a printed circuit board by the electrodeposition technique has attracted a tremendous attention in recent years. Such a method not only requires expensive facilities, but also has a problem
5 that maintenance of the electrodeposition fluid is difficult.

It is an object of the present invention to provide a method of preparing a printed circuit board by using an aqueous photosensitive resin composition.
10 The resin image is sharp and has good resistance to an acidic etching solution after it has been irradiated with actinic light and developed with water or an aqueous alkaline solution. Furthermore, significant cost savings can be had over the electrodeposition
15 technique, and organic solvents are not required.

Another aspect of the present invention is that this method of preparing a photosensitive resin has no adverse effect on the working environment or natural environment, does not require safety precautions
20 against fire during the coating and drying steps, and does not require any solvent recovery system.

The present invention provides a method of preparing an aqueous photosensitive resin composition which comprises mixing or dispersing in water:

- 25 (a) a carboxyl group-containing resin having an acid value of 20 to 500, a number average molecular weight of 1,000 to 100,000 and a glass transition temperature (T_g) of not lower than 0°C , which resin is styrene maleic anhydride copolymer whose acid anhydride groups have been
30 ring-opened with water, an alcohol, ammonia or an amine,
(b) ammonia or an amine compound,
(c) a photo-curable unsaturated compound having at least two ethylenically unsaturated bonds, and
(d) a photopolymerization initiator.

35 The invention further provides an aqueous photosensitive resin composition which comprises:

(a) a carboxyl group-containing resin having an acid value of 20 to 500, a number average molecular weight of 1,000 to 100,000 and a glass transition temperature (T_g) of not lower than 0°C, which resin is styrene maleic

5 anhydride copolymer whose acid anhydride groups have been ring-opened with water, an alcohol, ammonia or an amine,

(b) ammonia or an amine compound,

(c) a photo-curable unsaturated compound having at least two ethylenically unsaturated bonds, and

10 (d) a photopolymerization initiator.

The invention yet further provides a method of preparing a printed circuit board which comprises:

(1) coating an aqueous photosensitive resin composition which comprises:

15 (a) a carboxyl group-containing resin having an acid value of 20 to 500, a number average molecular weight of 1,000 to 100,000 and a glass transition temperature (T_g) of not lower than 0°C,

(b) ammonia or an amine compound,

20 (c) a photo-curable unsaturated compound having at least two ethylenically unsaturated bonds, and

(d) a photopolymerization initiator on an insulating substrate having an electrically conductive metal layer thereon to form a photo-curable coating;

25 (2) drying the coating;

(3) imagewise irradiating the coating with actinic light;

(4) developing the coating thus obtained with water or an aqueous alkaline solution; and

30 (5) etching portions of the electrically conductive metal layer other than image portions with an acidic etching solution.

The carboxyl group-containing resin used in the present invention has an acid value of 20 to 500, a number
35 average molecular weight of 1,000 to 100,000, and a T_g of not less than 0°C. When the acid value is lower than 20, its affinity to water will be decreased even in the presence of an amine compound, and thus, it is

difficult to obtain the aqueous photosensitive resin composition of the present invention. On the other hand, when the acid value exceeds 500, it will be difficult to obtain a clear image by development with water or an aqueous alkaline solution because its affinity to water is too high. When the number average molecular weight is less than 1,000, the mechanical strength of the unexposed photosensitive resin coating will be decreased, and the coating may be easily damaged in the irradiation step. On the other hand, when the number average molecular weight exceeds 100,000, the viscosity of the photosensitive resin composition will be remarkably increased. As a result, the dissolving or mixing step is more difficult, and also the developing time will be increased. The Tg of the carboxyl group-containing resin of lower than 0°C tends to increase the stickiness of the photosensitive resin composition and causes a problem in the irradiation step.

Resins obtained by copolymerizing acrylic acid or methacrylic acid with an unsaturated monomer such as a (meth)acrylic acid ester, styrene, (meth)acrylonitrile or acrylamide and acid anhydride group-containing resins such as a styrene-maleic anhydride polymer whose acid anhydride groups have been ring-opened with water, an alcohol, ammonia or an amine can be included in preferred examples of the carboxyl group-containing resin used in the present invention to prepare a printed circuit board.

Although any conventional alcohols can be used to ring-open the acid anhydride groups of the resin, it is preferred to use a primary or secondary alcohol due to their reactivity. For example, methyl alcohol, ethyl alcohol, butyl alcohol, butoxy ethanol and ethyleneglycol monomethyl ether can be used. Also,

ammonia, primary amines and secondary amines can be used for this purpose. Examples of such amines include alkylamines such as diethylamine, monoethylamine, diisopropylamine and diisobutylamine; alkanolamines such as monoethanolamine and diethanolamine; alkylalkanol amines such as dimethylamino ethanol; and alicyclic amines such as cyclohexylamine.

Preferred carboxyl group-containing resins which can be used in the photosensitive composition of the present invention have a polymerizable unsaturated bond in the molecule. Such resins can be synthesized by any known method, for example, by esterifying part of the carboxyl groups of the carboxyl group-containing resin with glycidyl acrylate in the presence of a catalyst. Or, alcohols or amines having a polymerizable unsaturated bond can be used as the alcohol or the amine to ring-open the acid anhydride groups of the above described styrene- maleic anhydride polymer. Examples of such alcohols and amines suitable for such a purpose are hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, allyl alcohol and allylamine.

The photosensitive resin composition of the present invention also includes an amine compound or ammonia for the purpose of dissolving or dispersing the carboxyl group-containing resin in water. Any conventional amine compounds can be used for this purpose. Examples of such amine compounds include alkanolamines such as monoethanolamine, diethanolamine and triethanolamine; alkylamines such as triethylamine, diethylamine, monoethylamine, diisopropylamine and diisobutylamine; alkylalkanolamines such as dimethylaminoethanol; alicyclic amines such as

cyclohexylamine. Amine compounds having a polymerizable unsaturated bond in the molecule are particularly preferred for such a purpose and examples of such amine compounds include dimethylaminopropyl
5 acrylamide, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate and allylamine. To reduce generation of amine odor in the coating and drying steps, amine compounds having a boiling point of at least 100°C are preferred. The amount of the
10 amine compound which can be employed in the present invention is typically 0.2 to 2 mols per mol of the free carboxyl group of the carboxyl group-containing resin.

The photocurable unsaturated compounds which can be
15 used in the present invention comprise at least two ethylenically unsaturated bonds in the molecule. Examples of such compounds include (meth)acrylic acid esters, allyl compounds, vinyl ethers, vinyl esters and cinnamic acid esters containing at least two ethylenically unsaturated
20 bonds. Examples of the (meth)acrylic acid esters include epoxy (meth)acrylates obtained by the reaction of an epoxy resin having two or more functional groups and at least two equivalents of a carboxylic acid having an ethylenically
25 reaction of a polyvalent aliphatic isocyanate or a polyvalent aromatic isocyanate and at least two equivalents of a monoester of (meth)acrylic acid with a divalent alcohol; and (meth)acrylates of a polyvalent alcohol containing at least two ethylenically unsaturated bonds.
30 Examples of the allyl compound include diallyl esters of phthalic acid, adipic acid and malonic acid. Examples of the vinyl ethers include vinyl ethers of a polyvalent alcohol containing at least two ethylenically unsaturated bonds. Examples of the vinyl esters include divinyl
35 succinate. In addition, the so-called

mono-functional monomers having one ethylenically unsaturated bond can be used together with the above described photo-curable unsaturated compound. The amount of the photo-curable unsaturated compound which can be used in the present invention is typically 0.2 to 3 times the total weight of the carboxyl group-containing resin.

According to another embodiment of the present invention, an aqueous photosensitive resin composition can be obtained by using a carboxyl group-containing resin and/or an amine compound which has a photopolymerizable unsaturated bond instead of or together with the above described photo-curable unsaturated compound. Such an aqueous photosensitive resin composition can form an image when coated, dried on a substrate and then developed with water or an aqueous alkaline solution after irradiation with actinic light, and can form a photo-curable coating having good resistance to an acidic etching solution. Any conventional photopolymerization initiators can be used as the photopolymerization initiator in the photosensitive composition of the present invention.

For example, benzophenones such as benzophenone, benzophenone methyl ether and Michler's ketone; benzoin such as benzoin, alpha-methylbenzoin, alpha-phenylbenzoin, alpha-allylbenzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin n-butyl ether and benzoin isobutyl ether; acetophenones such as acetophenone, 2,2-diethoxyacetophenone, p-tert-butyltrichloroacetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-2-phenylacetophenone and N,N-diethylaminoacetophenone; benzil; ketals such as benzyl dimethyl ketal; anthraquinones such as 2-

methylantraquinone, 2-ethylantraquinone, 2-amylan-
thraquinone and 2-aminoanthraquinone; and
thioxanthenes such as 2,4-dimethylthioxanthone, 2,4-
diisopropylthioxanthone and 2-chlorothioxanthone can
5 be preferably used. The amount of this
photopolymerization initiator to be added in the
photosensitive resin composition is typically 0.10 to
10% by weight based on the total weight of the
photosensitive composition.

10 It is preferred to employ an appropriate
polymerization inhibitor in the photosensitive resin
composition of the present invention. Any
conventional inhibitors can be used as such a
polymerization inhibitor. Preferred examples of
15 polymerization inhibitors are phenols such as 2,4-
dimethyl-6-tert-butylphenol and 2,6-di-tert-butyl-p-
cresol; hydroquinones such as hydroquinone,
methylhydroquinone, 1,4-benzoquinone and hydroquinone
monomethyl ether; and catechols such as tert-
20 butylcatechol and pyrogallol. The amount of the
polymerization inhibitors which can be used is
typically 0.001 to 5% by weight based on the total
weight of the photosensitive resin composition.

5 Any conventional appropriate surfactants may be
added to improve the dispersibility resins in water.
For this purpose, anionic, cationic or nonionic
surfactants can be used. If desired or necessary, the
resin may be mixed with a known filler such as barium
sulfate, silicon oxide, talc, clay and barium
30 carbonate; a known coloring agent such as
phthalocyanin green and titanium oxide; a dye; a
leveling agent; an adhesion promotor; thixotropic
agent; and a plasticizer.

The amount of water which can be employed in the

photosensitive resin composition is 30 to 90% by weight based on the total weight of the photosensitive resin composition, and the total amount of the carboxyl group-containing resin, the amine compound, the photo-curable unsaturated compound, the photopolymerization initiator and, if desired, other additives which can be employed in the photosensitive resin composition is 10 to 70% by weight based on the total weight of the photosensitive resin composition. The aqueous photosensitive resin composition used in the present invention can easily be prepared by the following methods which are given for illustrative purposes and are not meant to limit the invention.

(1) A carboxyl group-containing resin or an acid anhydride group-containing resin is mixed with water containing an amine compound and heated to dissolve or disperse the resin in water. Then a photo-curable unsaturated compound and a photopolymerization initiator are added to the resulting solution or dispersion, and the solution or dispersion is mixed and dispersed.

(2) After a carboxyl group-containing resin or an acid anhydride group-containing resin is dissolved in a photo-curable unsaturated compound under heating, a photopolymerization initiator is added to the resulting solution and then the water containing an amine compound is blended in.

(3) An acid anhydride group-containing resin and an alcohol or an amine compound are reacted with a photocurable unsaturated compound to ring-open the acid anhydride groups. Then, a photopolymerization initiator and

subsequently, water containing an amine compound are mixed into the reaction solution and the solution.

5 (4) An acid anhydride group-containing resin and an alcohol or an amine compound having a polymerizable unsaturated bond are reacted, if desired, in a photo-curable unsaturated compound to ring-open the acid anhydride groups to introduce an unsaturated group in the resin. Then, a photopolymerization initiator and subsequently, water containing an amine compound are blended into the reaction solution.

10 (5) An acid anhydride group-containing resin and a primary or a secondary amine are reacted in water to ring-open the acid anhydride groups, and then an amine compound to render the resin easily dissolved or dispersed in water, a photo-curable unsaturated compound and a photopolymerization initiator are added to the reaction solution, and the solution or dispersion is mixed. These components which are to be added later may be previously added in the reaction system and the ring-opening reaction may be carried out in the presence of these components. Or, an amine compound having a polymerizable unsaturated bond may be used as the amine compound to ring-open the acid anhydride groups and/or as the amine compound to render the resin easily dissolved or dispersed in water.

30 The aqueous photosensitive resin composition of the present invention can be prepared by the methods

as described above without using any volatile organic solvent. However, a small amount, at most 20% by weight, based on the total weight of the water, of a volatile organic solvent such as ethanol may be used to lower the viscosity of the photosensitive resin composition.

The preparation of a printed circuit board in accordance with the present invention using an aqueous photosensitive resin composition can be typically carried out in the following manner.

The aqueous photosensitive resin composition is coated on a substrate having an electrically conductive metal layer such as a copper foil. Coating can be done by any conventional device such as an ordinary curtain coater, roll coater, screen coater or electrostatic coater. Any conventional dryer may be used, if needed. In this case, since the aqueous photosensitive resin composition of the present invention contains no volatile organic solvent or contains a very small amount of such an organic solvent, no special measures for protecting the working environment from fire or explosion are required, and neither is a solvent recovery system.

As with any other conventional photosensitive resist materials, the resist image-forming step is carried out by the irradiation of the coating with actinic light having a wavelength of 200 to 600 nm. Preferred light sources include a high pressure mercury lamp, a metal halide lamp, a xenon lamp, a carbon arc lamp and a chemical lamp. The developing step after the irradiation can easily be carried out by an ordinary procedure using water or a dilute aqueous alkaline solution, for example, a 1% by

weight sodium hydroxide solution.

The etching step for forming a circuit can be carried out with an ordinary acidic etching solution such as an aqueous hydrochloric acid solution of cupric chloride. A dilute aqueous alkaline solution such as a 3% by weight sodium hydroxide solution can be used to strip the resist coating after the etching.

Surprisingly, the aqueous photosensitive resin composition of the present invention can form an image when coated and dried on a substrate, irradiated with actinic light and developed with water or an aqueous alkaline solution despite its ability to dissolve or disperse in water and the presence of an amine compound. In addition, the irradiated coating has a good resistance to an acidic etching solution. Since it does not contain any organic solvent at all or contains only a very small amount of an organic solvent, there is no need to provide safety precautions against fire in the coating and drying steps. Furthermore, it has no adverse effect on the working environment or natural environment which might be caused by organic solvents.

The examples which follow are given for illustrative purposes and are not meant to limit the invention described herein. "Part" means "part by weight" unless otherwise expressly stated.

Example 1

One hundred parts of an aqueous acrylic resin ("CARBOSET XL-27", a product of B.F. Goodrich Co., U.S.A., acid value = 80, molecular weight = 40,000) as the carboxyl group-containing resin, 14.4 parts of triethylamine as the amine compound and 330 parts of

water were mixed and heated at 70°C to obtain a homogeneous and clear solution. Thirty three parts of trimethylolpropane triacrylate as the photopolymerizable unsaturated compound, 15 parts of 2,2-dimethoxy-2-phenylacetophenone as the polymerization initiator and 0.5 part of hydroquinone monomethyl ether as the polymerization inhibitor were added to the solution, and then the mixture was cooled to room temperature with agitation to form an opaque, creamy aqueous photosensitive resin.

The resin was coated on a laminated board having an 18 micron copper foil layer using a doctor blade, and dried at 100°C for 5 minutes to give a dried film having a thickness of about 20 microns.

A negative film was tightly contacted with the dried film with rays from a high pressure mercury lamp at an exposure energy of 400 mJ/cm², and then, developed by spraying with a 1% by weight aqueous sodium carbonate solution at 25°C to give a resist film with a clear image showing a line width as small as 50 microns.

The copper-lined laminated board having the resist film was soaked in an etching solution containing 40 parts of anhydrous cupric chloride, 30 parts of concentrated hydrochloric acid and 50 parts of water at room temperature for 20 minutes. With the exclusion of the area of the resist film, the copper foil was etched and removed. There was no damage to the resist film. Furthermore, the laminated board obtained after the etching was soaked in a 3% by weight aqueous sodium hydroxide solution at room temperature for one minute. As a result, the resist film could be easily stripped to give a circuit board.

Example 2

The procedure of Example 1 was repeated except that 22.3 parts of dimethylaminopropyl acrylamide were employed instead of the triethylamine to obtain an opaque, creamy, aqueous photosensitive resin composition.

When the subsequent coating, drying, irradiation with light and development were carried out under the same conditions as in Example 1, a resist image which had reproduced clearly to a line width of 30 microns was obtained. In the same manner as in Example 1, etching and stripping of the resist film after the etching could be carried out without any problem.

Example 3

A mixture containing 150 parts of a styrene-maleic anhydride copolymer ("SMA-1000", styrene/maleic anhydride = 1/1, a product of Sartomer Co., U.S.A.), 150 parts of trimethylolpropane triacrylate, 54 parts of butyl alcohol, 8 parts of dimethylolpropane triacrylate, 47 parts of N-butylbenzene sulfonamide as the plasticizer and 0.5 part of hydroquinone monomethyl ether was heated and agitated at 80°C for 2 hours to obtain a viscous substance. Four parts of a surfactant ("EMULGEN 903", a product of Kao K.K., Japan), 20 parts of 2,2-dimethoxy-2-phenylacetophenone and 35 parts of ethyl alcohol as the solvent were added to the viscous substance, and then the mixture was cooled to room temperature. Furthermore, 55 parts of dimethylaminopropyl acrylamide were added in 300 parts of water to prepare a solution. This solution was added to the

above obtained mixture with constant and vigorous agitation to yield an aqueous photosensitive resin.

The resin was coated on a laminated board having a 18 micron thick copper foil layer using a doctor blade, and then dried at 100°C for 5 minutes to give a dried film having a thickness of about 20 microns.

A negative film was contacted with the dried film, irradiated with rays from a high pressure mercury lamp at an exposure energy of 400 mJ/cm², and then developed with tap water at 25°C to give a resist film having a clear image which showed a line width of 50 microns.

When the copper-lined laminated board having the resist film was soaked in an etching solution containing 40 parts of anhydrous cupric chloride, 30 parts of concentrated hydrochloric acid and 50 parts of water at room temperature for 20 minutes, the copper foil was etched and removed except the area of the resist film, and there was no damage in the resist film. Furthermore, when the laminated, etched board was subsequently soaked in a 3% by weight aqueous sodium hydroxide solution at room temperature for one minute, the resist film could be easily striped to give a circuit board.

Example 4

The procedure of Example 3 was repeated except that 85 parts of hydroxyethyl acrylate to ring-open the acid anhydride groups to introduce a double bond in the resin were employed instead of the butyl alcohol to prepare an aqueous photosensitive resin composition. When the subsequent coating, drying, irradiation with actinic light and development with

tap water were carried out under the same conditions as in Example 3, a resist image which had reproduced an image clearly to a line width of 30 microns was obtained. In the same manner as in Example 3, the resist film could be etched and stripped without any problem.

Example 5

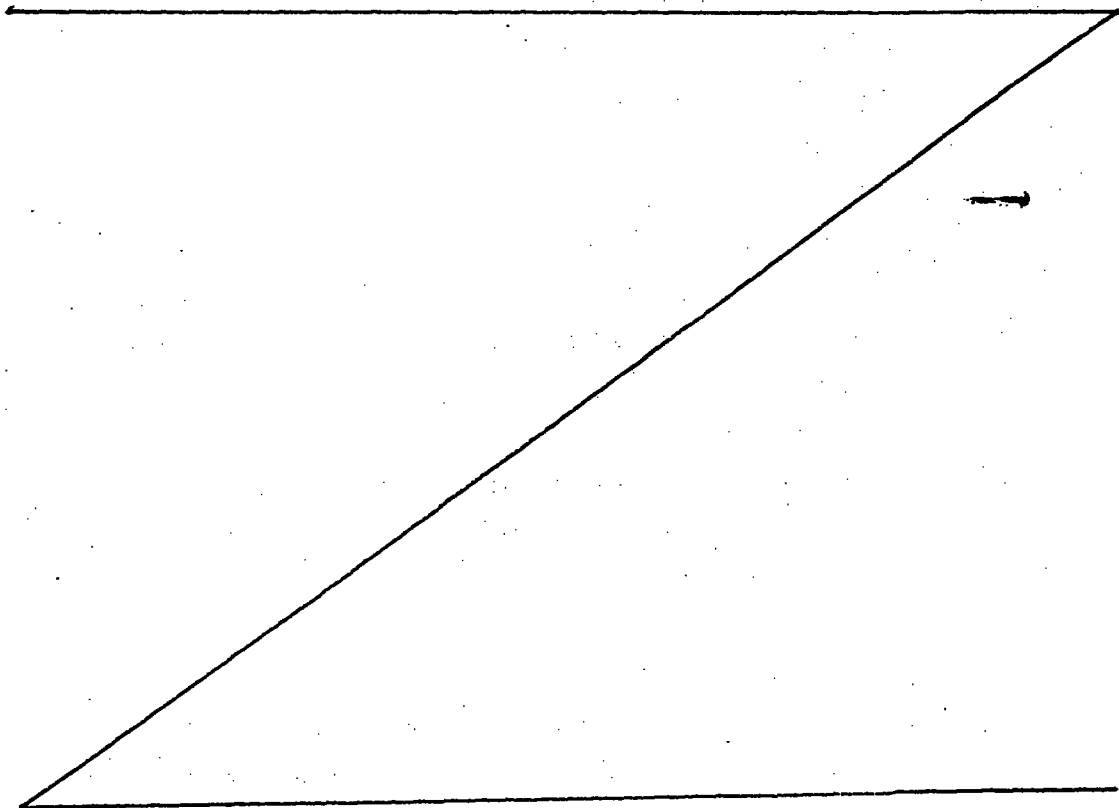
A mixture containing 150 parts of a styrene-maleic anhydride copolymer ("SMA-2000", styrene/maleic anhydride = 2/1, a product of Sartomer Co., U.S.A.), 150 parts of trimethylolpropane triacrylate, 28 parts of allylamine for ring-opening of the acid anhydride groups in the above described copolymer to introduce a photopolymerizable unsaturated bond in the resin, 77 parts of dimethylaminoethyl methacrylate, 47 parts of N-butylbenzene sulfonamide as the plasticizer, 0.5 part of hydroquinone monomethyl ether as the polymerization inhibitor, 20 parts of 2,2-dimethoxy-2-phenylacetophenone and 300 parts of water was agitated at room temperature for 3 hours, and then the mixture was heated and agitated at 80°C for one hour to obtain an aqueous photosensitive resin composition.

The composition was coated on a laminated board having a 18 micron thick copper foil layer using a doctor blade, and then dried at 100°C for 5 minutes to give a dried film having a thickness of about 20 microns.

A negative film was tightly contacted with the dried film, and irradiated with rays from a high pressure mercury lamp at an exposure energy of 200

mJ/cm², and then developed by spraying with a 1% by weight aqueous sodium carbonate solution at 25°C to give a resist film having a clear image with a line width of 30 microns.

5 When the copper-lined laminated board formed with
a resist film was soaked in an etching solution
containing 40 parts of anhydrous cupric chloride, 30
parts of concentrated hydrochloric acid and 50 parts
10 of water at room temperature for 20 minutes, the
copper foil was etched and removed except the area of
the resist film which did not show any damage.
Furthermore, when the laminated, etched board was
soaked in a 3% by weight aqueous sodium hydroxide
15 solution at room temperature for one minute, the
resist film could be easily stripped to give a circuit
board.





CLAIMS

1. A method of preparing an aqueous photosensitive resin composition which comprises mixing or dispersing in water:
 - 5 (a) a carboxyl group-containing resin having an acid value of 20 to 500, a number average molecular weight of 1,000 to 100,000 and a glass transition temperature (Tg) of not lower than 0°C, which resin is a styrene-maleic anhydride copolymer whose acid anhydride groups have been
 - 10 ring-opened with water, an alcohol, ammonia or an amine, (b) ammonia or an amine compound,
 - (c) a photo-curable unsaturated compound having at least two ethylenically unsaturated bonds, and
 - (d) a photopolymerization initiator.
- 15 2. A method according to claim 1, wherein the carboxyl group-containing resin has a photopolymerizable unsaturated bond.
3. A method according to claim 1 or 2 wherein the amine compound has a photopolymerizable unsaturated bond.
- 20 4. A method according to claim 1, 2 or 3 wherein the styrene-maleic anhydride copolymer has been ring-opened with a primary or secondary alcohol.
5. A method according to claim 1, 2 or 3 wherein the styrene-maleic anhydride copolymer has been ring-opened
- 25 with a primary or secondary amine.
6. A method according to claim 4 or 5, wherein the alcohol, or amine has a polymerizable unsaturated bond.
7. A method according to any one of the preceding claims, wherein the amine compound is used in an amount of
- 30 0.2 to 2 mols per mol of the free carboxyl group of the carboxyl group-containing resin.
8. A method according to any one of the preceding claims, wherein the photo-curable unsaturated compound is used in an amount of 0.2 to 3 times the total weight of the
- 35 carboxyl group-containing resin.
9. A method of preparing an aqueous photosensitive resin composition which is as defined in any one of the



preceding claims, save that the photo-curable unsaturated compound is replaced by an amine compound and/or a carboxyl group-containing resin which has a photopolymerizable unsaturated bond.

5 10. A method according to any one of the preceding claims, wherein the photopolymerization initiator is used in an amount of 0.1 to 10% by weight of the total weight of the photosensitive resin composition.

10 11. A method according to any one of the preceding claims, wherein the aqueous photosensitive resin composition comprises 30 to 90% water by weight based on the total weight of composition.

15 12. A method according to any one of the preceding claims, wherein the aqueous photosensitive resin composition further comprises a polymerization inhibitor in an amount of 0.001 to 5% by weight of the total weight of the composition.

20 13. A method according to any one of the preceding claims, wherein the water contains a volatile organic solvent in an amount of not greater than 20% by weight based on the weight of the water.

14. A method according to claim 1 substantially as hereinbefore described in any one of Examples 3 to 5.

25 15. An aqueous photosensitive resin composition which comprises:

- (a) a carboxyl group-containing resin having an acid value of 20 to 500, a number average molecular weight of 1,000 to 100,000 and a glass transition temperature (T_g) of not lower than 0°C, which resin is a styrene-maleic anhydride copolymer whose acid anhydride groups have been ring-opened with water, an alcohol, ammonia or an amine,
- (b) ammonia or an amine compound,
- (c) a photo-curable unsaturated compound having at least two ethylenically unsaturated bonds, and
- 35 (d) a photopolymerization initiator.

16. A composition according to claim 15 wherein the



components of the composition are as defined in any one of claims 2 to 13.

17. A composition according to claim 15 substantially as hereinbefore described in any one of
5 Examples 3 to 5.

18. A method of preparing a printed circuit board which comprises:

- (1) coating an aqueous photosensitive resin composition which comprises:
 - 10 (a) a carboxyl group-containing resin having an acid value of 20 to 500, a number average molecular weight of 1,000 to 100,000 and a glass transition temperature (T_g) of not lower than 0°C,
 - 15 (b) ammonia or an amine compound,
 - (c) a photo-curable unsaturated compound having at least two ethylenically unsaturated bonds, and
 - 20 (d) a photopolymerization initiator on an insulating substrate having an electrically conductive metal layer thereon to form a photo-curable coating;
- (2) drying the coating;
- 25 (3) imagewise irradiating the coating with actinic light;
- (4) developing the coating thus obtained with water or an aqueous alkaline solution; and
- (5) etching portions of the electrically conductive metal layer other than image portions with an
30 acidic etching solution.

19. A method according to claim 18 wherein the composition is as defined in any one of claims 15 to 17.

20. A method according to claim 18 substantially as hereinbefore described in any one of the foregoing
35 Examples.