

TITLE: RESIST INK COMPOSITION

This invention relates to a resist ink composition which is useful in the production of printed circuits for household and industrial appliances.

Heretofore, the screen printing method has been
5 widely adopted as a means of forming resist patterns on various printed circuits for household and industrial appliances. The screen printing method by its nature has low resolution. When screen printing is carried out with
10 a screen printing ink of relatively high viscosity, such adverse phenomena as breaks, screen marks, and pinholes can occur in the produced patterns. On the other hand, when screen printing is carried out with a screen printing ink of relatively low viscosity, such adverse phenomena as breeds, smudges, and sags can ensue. Because of these
15 defects, the screen printing technique can no longer keep abreast of the recent trend of printed circuits toward increasing density.

To solve these problems, dry film type photoresists and liquid developable resist inks have been
20 devised. To cite an example of dry film type photoresists, a dry film grade photosensitive resin composition which comprises urethane di(meth)acrylate, a linear high molecular compound possessing a glass transition point in a specific range, and a sensitizer is disclosed in the
25 specification of Japanese Patent Application Laid-open SHO 57(1982)-55,914. Generally a photoresist of the dry film type, however, tends to produce bubbles during thermocompression bonding, betrays imperfection in thermal resistance and fast adhesiveness, and poses problems such
30 as high price.

An example of a liquid developable resist ink is shown in UK Patent Application GB 2032939 A which discloses photopolymerizable coating compositions which comprise a solid or semi-solid reaction product of a

polyepoxide and an ethylenically unsaturated carboxylic acid, an inert inorganic filler, a photopolymerization initiator, and a volatile organic solvent. Another example of a liquid developable resist ink is given in the specification of Japanese Patent Application Laid-open SHO 58(1983)-62,636 (corresponding to Swiss Patent Application No. 6007/81-1 filed September 17, 1981) and which discloses a coating composition having a fine granular filler dispersed in a solution of a photo-sensitive epoxy resin mixed with a curing agent and possessing a viscosity in the range of 200 to 700 mPas so as to suit the curtain coating method. Since the liquid resist inks disclosed in the patent literature mentioned above and currently offered in the market require use of organic solvents as their developing agents, they pose problems of air pollution and the use of expensive solvents, and besides suffer from imperfection in resistance to solvents and resistance to acids.

A method which uses an alkaline aqueous solution as a developing liquid in the place of an organic solvent is disclosed in the specification of Japanese Patent Application SHO 57(1982)-164,595 (corresponding to US S.N. 225810 filed January 16, 1981). The method for the production of a printed circuit disclosed by this patent literature, unlike the conventional method which produces a film by applying a liquid polymer on a circuit blank and drying the applied liquid polymer, is a unique method which comprises causing the applied liquid polymer in its undried state to be exposed to light through a given resist pattern and cured in that pattern and then removing the uncured liquid polymer. Since this method uses a liquid prepolymer containing many reactive monomers, it is inferior to the conventional film-forming method in such characteristics as resistance to acids and resistance to chemicals. Further, since this method does not form a

film by drying, it is necessary to keep the surface of the applied liquid polymer at a distance from the resist pattern film. This separation impairs the resolution and necessitates provision of a special device and a consequent addition to the cost of production.

The object of this invention is to provide an improved liquid photosetting resist ink composition.

In accordance with this invention there is provided a photosetting and thermosetting liquid resist ink composition developable with a dilute alkaline aqueous solution, which comprises in combination a photosetting resin composition comprising:

(A) a resin curable by activated energy radiation, which resin has an acid value in the range of 45 to 165 mg KOH/g and is obtained by the reaction of (a) a saturated or unsaturated polybasic acid anhydride with (b) a product of the reaction of a novolak type epoxy compound and an unsaturated monocarboxylic acid in the proportion of 0.95 to 1.05 equivalent weight of said unsaturated monocarboxylic acid per one equivalent weight of said novolak type epoxy compound;

(B) a photopolymerization initiator;

(C) a diluent; and

(D) an epoxy compound containing at least two epoxy groups per molecule thereof as a thermosetting component.

The aforementioned resin (A) used in the compositions of this invention is obtained by causing a reaction product of a novolak type epoxy compound such as described below and an unsaturated monocarboxylic acid in the defined proportions, to react with a dibasic acid anhydride such as phthalic anhydride or an aromatic polycarboxylic acid anhydride such as trimellitic acid anhydride or pyromellitic acid anhydride. In this case, the resin proves particularly suitable when, in the

(12)

production thereof, the amount of the aforementioned acid anhydride used for the reaction exceeds 0.15 mol per each of the hydroxyl groups possessed by the reaction product
5 of the novolak type epoxy compound and the unsaturated carboxylic acid.

The acid value of the resin (A) so obtained should fall in the range of 45 to 160 mg KOH/g, preferably 50 to 140 mg KOH/g. If the acid value is
10 smaller than 45, the alkali solubility can be insufficient. Conversely, if the acid value is notably larger than 160, the resistance of the cured film to alkalis and the electric properties and other similar properties expected of the resist are inferior. Thus,
15 it is necessary to keep within the range mentioned above.

The novolak type epoxy compounds are represented by phenol novolak type epoxy resins and cresol novolak type epoxy resins. Compounds such as produced by causing epichlorohydrin to react with a
20 pertinent novolak resin by conventional methods can be used.

Typical examples of unsaturated monocarboxylic acids which can be used in the production of resin (A) include acrylic acid, methacrylic acid, crotonic acid,
25 and cinnamic acid. Among other unsaturated monocarboxylic acids cited, acrylic acid proves particularly suitable.

Typical examples of the aforementioned acid anhydride are dibasic acid anhydrides such as maleic anhydride, succinic anhydride, itaconic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, 5 hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, endomethylenetetrahydrophthalic anhydride, methylenendomethylenetetrahydrophthalic anhydride, chlorendic anhydride, and methyltetrahydrophthalic anhydride; aromatic polycarboxylic anhydrides such as 10 trimellitic anhydride, pyromellitic anhydride, and benzophenone-tetracarboxylic dianhydride; and polycarboxylic anhydride derivatives such as 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride.

15 Typical examples of the aforementioned photopolymerization initiator (B) include benzoin and alkyl ethers thereof such as benzoin, benzoin methyl ether, benzoin ethyl ether, and benzoin isopropyl ether; acetophenones such as acetophenone, 2-2-dimethoxy-2- 20 phenylacetophenone, 2,2-diethoxy-2-phenylacetophenone, 1,1-dichloroacetophenone, 1-hydroxycyclohexylphenylketone, and 2-methyl-1- 4-(methylthio)phenyl -2-morpholine-propan-1-one; anthraquinones such as 2-methylantraquinone, 2-ethylantraquinone, 2-tertiary-butylantraquinone, 25 1-chloroanthraquinone, and 2-amylantraquinone; thioxanthenes such as 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2-chlorothioxanthone, and 2,4-diisopropylthioxanthone; ketals such as acetophenone dimethylketal and benzyl dimethylketal; and benzophenones such as 30 benzophenone or xanthenes. The photopolymerization initiator (B) can be used in combination with one or more well-known conventional photopolymerization accelerators of benzoic acid type and tertiary amine type. The amount of the photopolymerization initiator (B) to be used 35 suitably falls in the range of 0.2 to 30 parts by weight, preferably 2 to 20 parts by weight, based on 100 parts by

weight of the resin (A).

As the diluent (C) mentioned above, a photopolymerizable monomer and/or an organic solvent can be used. Typical examples of photopolymerizable

- 5 monomers include water-soluble monomers (C-1) such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, N-vinylpyrrolidone, acryloyl morpholine, methoxytetraethylene glycol acrylate, methoxypolyethylene glycol acrylate, polyethylene glycol diacrylate, N,N-dimethyl
- 10 acrylamide, N-methylol acrylamide, N,N-dimethylaminopropyl acrylamide, N,N-dimethylaminoethyl acrylate, N,N-dimethylaminopropyl acrylate, and melamine acrylate, and methacrylates corresponding to the acrylates enumerated above; and water-insoluble monomers (C-2) such as
- 15 diethylene glycol diacrylate, triethylene glycol diacrylate, propylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, polypropylene glycol diacrylate, phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, cyclohexyl acrylate,
- 20 trimethylol propane diacrylate, trimethylol propane triacrylate, glycerindiglycidyl ether diacrylate, glycerin triglycidyl ether triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, isoborneolyl
- 25 acrylate, cyclopentadiene mono- or di-acrylate, methacrylates corresponding to the acrylates enumerated above, and mono-, di-, tri-, and higher polyesters of polybasic acids with hydroxyalkyl(meth)acrylates.

Examples of organic solvents (C-3) include

- 30 ketones such as methylethyl ketone and cyclohexanone; aromatic hydrocarbons such as toluene and xylene; cellosolves such as cellosolve itself and butyl cellosolve; carbitols such as carbitol, butyl carbitol; and acetic esters such as ethyl acetate, butyl acetate, cellosolve
- 35 acetate, butyl cellosolve acetate, carbitol acetate, and butyl carbitol acetate.

The diluents (C) enumerated above are used either singly or in the form of a mixture of two or more individual diluents. The amount of the diluent to be
5 used suitably falls in the range of 30 to 300 parts by weight, preferably 50 to 200 parts by weight, based on 100 parts by weight of the resin (A).

Here, the water-soluble monomer (C-1) and the water-insoluble monomer (C-2) are used for the purpose of
10 diluting the aforementioned resin (A), rendering the produced composition more easily applicable, and imparting photopolymerizability upon the composition. The solubility of the produced composition in the alkaline aqueous solution improves in proportion as the
15 ratio of the water-soluble monomer (C-1) incorporated increases. If it is used in an extremely large amount, however, the completely cured resist material is deprived of its waterproofness. Thus, the additional use of the water-insoluble (C-2) can be beneficial. If the amount
20 of the water-insoluble monomer (C-2) to be additionally used is too large, however, the composition produced becomes only sparingly soluble in the alkaline aqueous solution, and therefore it is preferred that not more than 100% by weight based on the amount of the resin (A)
25 of water-insoluble monomer (C-2) be used. Particularly, ample use of a hydrophilic monomer brings about a satisfactory effect at no sacrifice of the properties described afterwards.

The organic solvent (C-3) is used for the
30 purpose of dissolving and diluting the resin (A), allowing the resin to be applied in the form of a liquid, and enabling the applied layer of the liquid to form a film on drying.

The thermosetting component (D) of the present
35 composition is an epoxy compound with two or more epoxy groups in the molecular unit thereof such as, for

example, a bis-phenol A type epoxy resin, a bis-phenol F type epoxy resin, a bis-phenol S type epoxy resin, a phenol-novolak type epoxy resin, a cresol-novolak type epoxy resin, a N-glycidyl type epoxy resin, or an alicyclic type epoxy resin. This component may optionally include additionally a small amount, for promotion of reaction, of an epoxy curing promoter such as, for example, an amine compound, an imidazole compound, a quaternary ammonium salt, or a methylol group-containing compound. When the composition is applied in a layer and the applied layer is then heated, the polymerization of the photosetting component is promoted and the copolymerization of the two components are facilitated so that the consequently produced resist coating acquires improvements in various properties such as resistance to heat, resistance to solvents, resistance to acids, resistance to plating, adhesiveness, electric properties, and hardness. The composition proves particularly useful for the formation of a solder resist.

The photosetting liquid resist ink composition of this invention as described above may further incorporate therein, as occasion demands, conventional fillers such as barium sulfate, siliconoxide, talc, clay, or calcium carbonate, conventional coloring pigments such as phthalocyanine blue, phthalocyanine green, titanium dioxide, or carbon black, a defoaming agent, an adhesiveness-imparting agent, a levelling agent, or other additives, or a conventional polymerization inhibitor such as hydroquinone, hydroquinone monoethyl ether, pyrogallol, tertiary butyl catechol, or phenothiazine.

A resist coating can be formed by applying a liquid resist ink composition of this invention on the entire surface of a printed-circuit substrate by the screen printing method, the roll coating method, or the curtain coating method, exposing the substrate to

activated energy radiation thereby curing the necessary part thereof, and dissolving the unexposed part of the applied layer with a dilute alkaline aqueous solution.

5 The aforementioned thermosetting component (D) may be admixed with the photosetting resin composition in advance of actual use thereof. However, since the mixture so formed is liable to increase in viscosity while awaiting actual application on a circuit blank, it
10 is desirable for the two components to be mixed immediately before actual use. Further, the aforementioned filler, colouring pigment, etc may be incorporated in the thermosetting component by being mixed with a solution of the thermosetting component in
15 an organic solvent. The amount of the thermosetting component to be used generally falls in the range of 10 to 150 parts by weight, preferably 30 to 50 parts by weight, based on 100 parts by weight of the photosetting resin composition. The aforementioned epoxy curing
20 promoter, if present, is used in an amount of 1 to 20 parts by weight, based on 100 parts by weight of the thermosetting component (epoxy compound).

Resist ink compositions of the present invention can produce a resist coating which excels in
25 photosetting property, adhesiveness, resistance to heat, resistance to solvents, resistance to acids, and resistance to plating. Moreover since they are developable with a dilute alkaline aqueous solution, the use in this step of organic solvents is avoided, in
30 contrast to conventional liquid resists and, therefore, the problems of pollution which organic solvents entail are avoided. As is clear from the examples below, the thermosetting component-containing ink composition of the present invention which is developable with a dilute
35 alkaline aqueous solution can be used not only in the

form of etching resist but also in the form of solder resist provided that an aftercuring step with heat is additionally incorporated in the procedure. Solder

- 5 resists can be formed which excel in curing property, adhesiveness, hardness, resistance to heat, resistance to solvents, resistance to plating, and electric properties.

Examples of light sources usable advantageously for the curing of the compositions of this invention
10 include low pressure mercury vapour lamps, medium-pressure mercury vapour lamps, high-pressure mercury vapour lamps, ultrahigh-pressure mercury vapour lamps, xenon lamps, and metal halide lamps. Also, a laser beam may be used as the source of activated energy radiation
15 during the exposure.

The invention is illustrated by the Examples which follow:

Example 1

The product of the reaction of (i) 1 equivalent
20 weight of a cresol-novolak type epoxy resin having an epoxy equivalent weight of 217 and possessing an average of 7 phenol ring residues and epoxy groups per molecule thereof with (ii) 1.05 equivalent weight of acrylic acid, was caused to react with 0.67 equivalent weight of
25 tetrahydrophthalic anhydride, by the conventional method, with phenoxyethyl acrylate as a solvent. The product of this reaction was a viscous liquid containing 35 parts by weight of phenoxyethyl acrylate. As a mixture, it showed an acid value of 63.4 mg KOH/g. Hereinafter,
30 this product will be referred to for convenience as "resin (A-1)".

Component (a)

	Resin (A-1)	40 parts by weight
	2-Hydroxyethyl acrylate	15 "
5	Benzyl-diethyl ketal	2.5 "
	1-Benzyl-2-methyl imidazole	1.0 "
	"Modaflow"* (levelling agent produced by Monsanto Chemical of the USA)	1.0 "
	Barium sulfate	26 "
10	Phthalocyanine green	0.5 "

Total of component (a)

85 parts by weight

* registered Trade Mark

Component (b)

- 15 Trimethylol propane triglycidyl ether 15 parts by weight

The component (a) above was kneaded in a test roll (roll mill) to prepare an ink. Then, the ink of this component (a) was mixed with the aforementioned component (b). The resulting mixture was applied with a curtain coater (made by Hiyama Manufacturing Co., Ltd.) on the entire surface of a copper-plated laminate consisting of a copper foil 35 μm in thickness and a glass epoxy substrate, and also on a printed circuit having a defined pattern formed thereon in advance by etching, to prepare test pieces.

Hereinafter, the test piece obtained by coating the copper-plated laminate will be referred to briefly as Test piece No. 1-E and the test piece obtained by coating the printed circuit as Test piece No. 1-S.

Example 2

Component (a)

	Resin (A-1)	30 parts by weight
5	N-vinyl pyrrolidone	15 "
	Trimethylol propane triacrylate	10 "
	2-Ethyl anthraquinone	2.0 "
	2,4-Diethyl thioxanthone	1.5 "
10	2-Phenyl-4-methyl-5-hydroxymethyl imidazole	1.0 "
	Phthalocyanine green	0.5 "
	"Modaflow"*	1.0 "
	Calcium carbonate	24 "
15	Total of component (a)	85 parts by weight
	* registered Trade Mark	

Component (b)

	Epikote*828 (epoxy resin made by Shell Oil)	7 parts by weight
20	Glycerin diglycidyl ether	8 "
	Total of component (b)	15 parts by weight
	* registered Trade Mark	

25 Test pieces were prepared by following the procedure of Example 1, except that the components indicated above were used instead. The test pieces will be referred to as Test piece No. 2-E and No. 2-S, respectively.

Example 3

The product of (i) the reaction of 1 equivalent weight of a phenol-novolak type epoxy resin having an epoxy equivalent weight of 178 and possessing an average of 3.6 phenyl ring residues and epoxy group per molecule thereof with (ii) 0.95 equivalent weight of acrylic acid, was caused to react with 0.78 equivalent weight of hexahydrophthalic anhydride, by the conventional method, with diethylene glycol acrylate as a solvent. The product of this reaction was a viscous liquid containing 35 parts by weight of diethylene glycol diacrylate. As a mixture, it showed an acid value of 72.8 mg KOH/g. It will be referred to briefly as "resin (A-2)".

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Component (a)

Resin (A-2)	40 parts by weight
2-Hydroxypropyl acrylate	10 "
Pentaerythritol triacrylate	10 "
2-Ethyl anthraquinone	2.0 "
20 2-Dimethylaminoethyl benzoate	1.5 "
"AC-300" (defoaming agent produced by Kyoeisha Yushi K.K.)	1.0 "
Phthalocyanine green	0.5 "
25 Talc	20 "
Total of component (a)	85 parts by weight

Component (b)

"Epikote"* 828 15 parts by weight
 * registered Trade Mark

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An ink was prepared by kneading the component (a) shown above in a test roll (roll mill). Then, the component (a) and the component (b) was mixed. The

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resulting mixture was applied by the screen printing method on the entire surface of a copper-plated laminate, and also on a printed circuit having a stated pattern
5 formed by etching in advance to prepare test pieces. These test pieces will be referred to as Test piece No. 3-E and No. 3-S, respectively.

Example 4

The product of the reaction of (i) 1 equivalent
10 weight of a cresol novolak type epoxy resin having an epoxy equivalent weight of 217 and possessing an average of 7 phenol ring residues and epoxy group with (ii) 1.05 equivalent weight of acrylic acid, was caused to react with 0.95 equivalent weight of tetrahydrophthalic
15 anhydride by the conventional method. The product of the reaction was diluted with cellosolve acetate to an involatile content of 70%. The diluted product will be referred to as "resin (A-3)".

Component (a)

20	Resin (A-3)	50 parts by weight
	Trimethylol propane triacrylate	4 "
	Pentaerythritol triacrylate	4 "
	2-Ethyl anthraquinone	3 "
	2-Dimethylaminoethyl benzoate	2 "
25	2-Phenyl-4-benzyl-5-hydroxymethyl imidazole	0.5 "
	"AC-300"	1.0 "
	Phthalocyanine green	0.5 "
30	Calcium carbonate	10 "
Total of component (a)		75 parts by weight

Component (b)

"Epiclon"* EXA-1514 bis-phenol S type epoxy resin made by		
5	Dai-Nippon Ink & Chemicals, Inc.	10 parts by weight
	Trimethylol propane triglycidyl ether	4 "
	Cellosolve acetate	6 "
	Calcium carbonate	5 "
10	Total of component (b)	25 parts by weight
	* registered Trade Mark	

The components (a) and (b) indicated above were separately kneaded in a test roll (roll mill) to prepare inks.

- 15 Then the component (a) and the component (b) were mixed. The resulting mixture was applied by the screen printing method on the entire surface of a copper-plated laminate and also on a printed circuit substrate having a defined pattern formed thereon by etching in
- 20 advance and then dried in a hot-air circulation type drier oven at 70°C for 30 minutes to produce test pieces. The test piece produced by applying the ink on the copper-plated laminate will be referred to as "Test piece 4-E" and the test piece produced by applying the ink on
- 25 the printed circuit having the stated pattern formed by etching in advance as "Test piece 4-S".

Example 5

Component (a)

Resin (A-3)			50 parts by weight
30	"Aronics M-5400" (acryl monomer made by Toa Gosei Chemical Industry Co Ltd	3	"
	Tetramethylol methane tetraacrylate	2.5	"

	Benzoin isopropyl ether	3 parts by weight
	1-Benzyl-2-methyl imidazole	1.0 "
	"AC-300"	1.0 "
5	Phthalocyanine green	0.5 "
	Talc	10 "

Total of component (a) 70 parts by weight

Component (b)

10	"Eikote" 1001	15 parts by weight
	Glycerin diglycidyl ether	5 "
	Butyl cellosolve	6 "
	Talc	4 "

15 Total of component (b) 30 parts by weight

Inks were prepared and test pieces were produced by following the procedure of Example 4, except that the components indicated above were used instead. The test pieces thus obtained will be referred to as

20 "Test piece No. 5-E and 5-S", respectively.

Example 6

Component (a)

	Resin (A-3)	45 parts by weight
25	"M-310" (acryl monomer made by Toa Gosei Chemical Industry Co Ltd)	3 "
	"M-5400" (acryl monomer made by Toa Gosei Chemical Industry Co Ltd)	3 "
	Benzoin isopropyl	3 "
	2-Dimethylaminoethyl benzoate	1.5 "
30	2-Phenyl imidazole	1.0 "
	"AC-300"	1.0 "

	Phthalocyanine green	0.5 parts by weight
	Cellosolve acetate	7 "
5	Barium sulfate	15 "

	Total of component (a)	80 parts by weight
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Component (b)

	"Epikote"* 828	10 parts by weight
	Trimethylolpropane triglycidyl ether	4 "
10	Barium sulfate	6 "

	Total of component (b)	20 parts by weight
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* registered Trade Mark

Inks were prepared and test pieces were
 15 produced by following the procedure of Example 4, except
 that the components indicated above were used instead.
 The test pieces so produced will be referred to as "Test
 piece 6-E" and "Test piece 6-S", respectively.

Example 7

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Component (a)

	Resin (A-3)	50 parts by weight
	Cellosolve acetate	10 "
	Benzyl diethyl ketal	3.0 "
	2-Ethyl-4-methyl imidazole	0.5 "
25	"AC-300"	1.0 "
	Phthalocyanine green	0.5 "
	Talc	20 "

	Total of component (a)	85 parts by weight
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Component (b)

	"Epikote" 1001	10 parts by weight
5	Trimethylolpropane triglycidyl ether	5 "
	Total of component (b)	15 parts by weight
	* registered Trade Mark	

Inks were prepared and test pieces were produced by following the procedure of Example 4, except that the components indicated above were used instead. The test pieces will be referred to as "Test piece No. 7-E and No. 7-S", respectively.

Comparative Experiment 1

15	"NK ester EA-800" (bis-phenol A type epoxy acrylate resin made by Shin Nakamura Kagaku K.K.)	40 parts by weight
	Trimethylol propane triacrylate	16 "
	Isobutyl methacrylate	20 "
20	"Darocure"* 1173 (photopolymerization initiator made by Merck)	3.5 "
	Barium sulfate	30 "
	Phthalocyanine green	0.5 "
	Total	100 parts by weight
25	* registered Trade Mark	

To prepare an ink composition for comparison, the components indicated above were kneaded in a test roll (roll mill) to prepare an ink.

This ink was applied by the screen printing method on the entire surface of a copper-plated laminate, and also on a printed circuit having a defined pattern formed thereon by etching in advance, to produce test pieces. The test pieces will be referred to as "Comparison 1-E" and "Comparison 1-S", respectively.

Comparative Experiment 2

5	"XP-4200" (urethane acrylate resin made by Nippon Synthetic Chemical Industry Co Ltd)	35 parts by weight
	Neopentyl glycol diacrylate	20 "
	2-Hydroxypropyl methacrylate	16 "
	"Darocure"* 1173	3.5 "
	Talc	35 "
10	Phthalocyanine green	0.5 "

Total 100 parts by weight

* registered Trade Mark

Test pieces were produced by following the procedure of Comparative Experiment 1, except that the components indicated above were used for an ink composition for control. The test pieces will be referred to as "Comparison 2-E" and "Comparison 2-S", respectively.

20 Comparative Experiment 3

25	"V-90" (bis-phenol A type epoxy acrylate resin solid at room temperature made by Showa Highpolymer Co Ltd)	50 parts by weight
	Dipentaerythritol hexaacrylate	5 "
	Carbitol acetate	40 "
	Benzoin isopropyl ether	3.5 "
	Phthalocyanine green	0.5 "
30	"AC-300"	1.0 "

Total 100 parts by weight

To prepare an ink composition for comparison the components indicated above were kneaded in a test roll (roll mill) to prepare an ink.

Then, this ink was applied by the screen plating method on the entire surface of a copper-plated laminate, and also on a printed circuit having a defined pattern formed by etching in advance, and then dried in a hot-air circulation type drier oven at 70°C for 30 minutes. The test pieces so produced will be referred to as "Comparison 3-E" and "Comparison 3-S", respectively.

10 Comparative Experiment 4

	"ZX-673" (novolak type epoxy acrylate resin solid at room temperature made by Toto Chemical Co Ltd)	35	parts by weight
15	"ECN 1280" (cresol-novolak type epoxy resin produced by Ciba Geigy)	8	"
	Dipentaerythritol hexaacrylate	6	"
	Carbitol	30	"
	2-Ethyl anthraquinone	3.5	"
20	"AC-300"	1.0	"
	Phthalocyanine green	0.5	"
	2-Ethyl-4-methyl imidazole	1.0	"
	Barium sulfate	15	"
25	Total	100	parts by weight

Test pieces were produced by following the procedure of Comparative Experiment 3, except that the components indicated above were used instead. The test pieces so produced will be referred to as "Comparison 4-E" and "Comparison 4-S", respectively.

Test Examples 1-3 (Photosetting property, developability, and dryness by finger touch)

On each of the test pieces, 1-E through 7-E and Comparison 1-E through Comparison 4-E, obtained in Examples 1-7 and Comparative Experiments 1-4, a resist

pattern film applied fast on glass was placed through the medium of a spacer 0.5 mm in thickness so as to be kept untouched, irradiated for a varying time with the light from a parallel exposure device (Model HMW-590, made by Orc Manufacturing Co Ltd) to test for photosetting property. The resist pattern film, after being cured by the exposure, was developed with an aqueous 1% sodium carbonate solution as a developer to test for developability. The results are collectively shown in Table 1.

In the case of the test pieces from the comparative experiments, since they were not developable with an alkaline aqueous solution, they were developed with "Eterna IR" (modified 1,1,1-trichloroethane made by Asahi Chemical Industry Co Ltd).

The test pieces produced in Examples 4-7 and Comparative Experiments 3-4 were tested for dryness with a finger tip. On each of these test pieces, a resist film was attached fast directly, irradiated for a varying time with the light, and tested for photosetting property and developability. The results are also shown in Table 1.

Table 1

Property		Example							Comparative Experiment			
		1-E	2-E	3-E	4-E	5-E	6-E	7-E	C.1-E	C.2-E	C.3-E	C.4-E
Developability*) Photosetting property	Exposure time to ultraviolet light (in seconds)	-	-	-	o	⊙	Δ	⊙	-	-	Δ	Δ
		Δ	o	Δ	⊙	⊙	⊙	x	x	x	x	x
		o	⊙	⊙	⊙	⊙	⊙	Δ	x	Δ	Δ	x
		⊙	⊙	⊙	⊙	⊙	⊙	⊙	Δ	Δ	o	x
		⊙	⊙	⊙	⊙	⊙	⊙	⊙	o	o	o	o
		⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	o
Spray time (in seconds)	30	o	Δ	Δ	x	x	x	x	Δ	x	x	x
	60	⊙	o	o	Δ	Δ	Δ	Δ	o	Δ	x	x
	90	⊙	⊙	o	o	o	o	⊙	o	o	Δ	Δ
	120	⊙	⊙	⊙	⊙	⊙	⊙	⊙	o	o	o	o
	180	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	o

*) The developing liquid was an aqueous 1% sodium carbonate solution in the case of examples and Eterna IR (modified 1,1,1-trichloroethane) in the case of comparative experiments.

The marks indicated in Table 1 as results of rating of properties are based on the following scales.

Driness by finger tip --- A given test piece was left standing in a constant temperature and constant humidity bath at 25°C and 65% RH for 1 hour, touched with a finger tip to test for tack, and rated on the following four-point scale, wherein

◎ --- Total absence of perceivable tack

○ --- Slightly perceivable tack

△ --- Conspicuously perceivable tack

x --- Adhesion of ink to finger tip

Photosetting property --- A given test piece was exposed to ultraviolet light, developed with a "dilute alkaline aqueous solution" as a developing liquid for 1 minute under the condition of spray pressure of 2 kg/cm², visually examined with respect to condition of coating, and rated on the following four-point scale, wherein

◎ --- Total absence of discernible change

○ --- Slight change of surface

△ --- Conspicuous change of surface

x --- Complete separation of coating

Developability --- A given test piece, while being developed under spray pressure of 2 kg/cm², was examined for developability under a microscope at stated intervals and rated by the following four-point scale, wherein

◎ --- Complete development to fine portions

○ --- Occurrence of thin undeveloped portions on substrate surface

Δ --- Heavy occurrence of undeveloped portions
 x --- Substantial absence of development

Test Example 4 (Coating property):

5 The test pieces, 1-E through 7-E and Comparison
 1-E through Comparison 4-E, produced by applying relevant
 inks on copper-plated laminates in Examples 1-7 and
 Comparative Experiments 1-4 were exposed to light and
 developed. Then, with an etching machine (made by Tokyo
 10 Kakoki K.K.), the test pieces had their copper foils
 etched to test for resistance to etching, peelability,
 and other coating properties. The results are shown in
 Table 2.

Table 2

	Conditions		Film properties after development				
	Exposure time to ultraviolet light (in seconds)	Developing time*1) (in seconds)	Adhesive-ness	Hard-ness	Resistance to etching liquid		Peelability *2)
					Copper chloride	Iron chloride	
Example	1-E	60		H	◎	◎	◎
	2-E	"	○	H	◎	◎	○
	3-E	"	○	F	◎	◎	△
	4-E	30	○	2H	◎	◎	△
	5-E	"	○	H	◎	◎	○
	6-E	"	○	2H	◎	◎	○
	7-E	90	○	F	○	○	△
Comparative Experiment	1-E	180	x	F	△	△	△
	2-E	120	△	HB	○	○	x
	3-E	120	○ ~ △	B	△	△	○
	4-E	180	△	F	○	○	△

*1) The developing liquid was a weakly alkaline aqueous solution (aqueous 1% sodium carbonate solution) in the case of examples and Eterna IR in the case of comparative experiments.

*2) The peeling liquid was a strongly alkaline aqueous solution (an aqueous 5% sodium hydroxide solution at 50°C) in the case of the Examples and methylene chloride in the case of comparative experiments.

The marks indicated in Table 2 as results of rating of properties are based on the following scales.

- Adhesiveness --- In a given test piece, cross cuts were
- 5 inserted after the pattern of a checkerboard in accordance with the testing method of JIS D-0202. The test piece was then subjected to a peeling test with a "Cellophane" (registered Trade Mark) tape and examined visually with
- 10 respect to separation of cut squares and rated on the following four-point scale, wherein
- ◎ --- Total absence of change (100/100)
 - o --- Slight peeling along cut edges (100/100)
 - Δ --- 50/100 to 90/100
 - 15 x --- 0/100 to 50/100

- Pencil hardness --- In accordance with the testing method of JIS K-5400 using a pencil hardness tester, a given test piece was placed under a load of 1 kg. This property was reported by the
- 20 highest hardness which inflicted no dent on the coating. The pencils used for this test were "Mitsubishi* Hi-Uni" (made by Mitsubishi Pencil Co Ltd) (*registered Trade Mark)

- Resistance to etching liquid --- A given test piece,
- 25 after development, was subjected to etching of 35- μ m copper foil under the conditions of spray pressure of 1.7 kg/cm² and liquid temperature of 50°C until complete etching. The time for complete etching was clocked. The coating
- 30 exposed to the etching liquid was visually examined with respect to condition of coating and rated on the following four-point scale, wherein

- ◎ --- Total absence of change
- o --- Slight rise of coating along the edges
- Δ --- Separation of coating along the edges
- 5 x --- Complete separation of the whole coating

Peelability --- A given test piece, after etching, was sprayed with the peeling liquid under conditions of spray pressure of 2 kg/cm² and liquid temperature of 40°C. The time required for complete separation was clocked.

10

- ◎ --- Separation obtained within 30 seconds
- o --- Separation obtained after 30 to 60 seconds
- Δ --- Separation obtained after 1 to 3 minutes
- x --- Separation obtained after more than 3 minutes

15 Test Example 5 (Coating properties as solder resists)

The test pieces, 1S through 7S and Comparison 1-S through Comparison 4-S, produced in Examples 1-7 and Comparative Experiments 1-4 were exposed to light, developed, and heated at 140°C for 60 minutes. The completely cured solder resists consequently formed were tested for coating properties. The results are shown in Table 3.

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Table 3

Conditions		Coating properties after after-heating										
	Exposure time to ultra-violet light (sec.)	Developing time (sec.)	Adhesiveness	Hardness	Resistance to heat of soldering			Resistance to solvents	Resistance to acids	Resistance to plating	Insulation resistance (Ω)	
					1st cycle	2nd cycle	3rd cycle				Normal state	After absorption of moisture
Example	1-S 60	60	◎	5H	◎	◎	○	◎	◎	○	¹³ 4.2x10	¹² 7.8x10
	2-S "	"	◎	6H	◎	◎	○	◎	◎	○	¹³ 6.7x10	¹² 5.6x10
	3-S "	"	◎	4H	◎	◎	◎	◎	◎	◎	¹³ 6.3x10	¹² 8.8x10
	4-S 30	90	◎	7H	◎	◎	◎	◎	◎	◎	¹⁴ 1.2x10	¹³ 2.7x10
	5-S "	"	◎	5H	◎	◎	○	◎	◎	◎	¹³ 8.9x10	¹³ 1.4x10
	6-S "	"	◎	7H	◎	◎	◎	◎	◎	◎	¹⁴ 1.1x10	¹² 9.5x10
	7-S 90	"	◎	3H	◎	◎	○	◎	◎	◎	¹³ 5.5x10	¹² 4.6x10
Comparative Experiment	1-S 180	60	△	4H	○	x	x	△	x	x	¹³ 2.3x10	¹¹ 7.1x10
	2-S 120	90	◎	2H	△	x	x	○	△	△	¹² 8.7x10	¹¹ 5.6x10
	3-S "	120	○	2H	○	x	x	○	△	△	¹² 4.9x10	¹⁰ 6.9x10
	4-S 180	"	◎	4H	◎	○	x	◎	○	○	¹³ 4.2x10	¹² 5.3x10

The marks indicated in Table 3 as results of rating of properties are based on the following scales. The scales used for rating adhesiveness and hardness were the same as those of Table 2.

Resistance to heat of soldering --- In accordance with the testing method of JIS C-6481, a given test piece was left flowing on a solder bath for 1, 3 and 6 cycles each of 10 seconds. After the floating, the test piece was examined with respect to "blister" and adhesiveness and rated synthetically.

- 10 ◎ --- Total absence of change
- --- Very slight perceivable change
- 15 Δ --- Peeling on not more than 10% of coated surface
- x --- Peeling on entire coated surface

Resistance to solvents --- A given test piece was immersed in methylethyl ketone at 20°C for 1 hour, then examined with respect to condition of coating and adhesiveness, and rated synthetically on the following four-point scale, wherein

- 20 ◎ --- Total absence of change
- --- Very slight perceivable change
- 25 Δ --- Conspicuous change
- x --- Swelled and separated coating

Resistance to acids --- A given test piece was immersed in an aqueous solution of 10% by weight of hydrochloric acid at 20°C for 30 minutes and then examined with respect to condition of coating and adhesiveness and rated synthetically on the following four-point scale, wherein

- © --- Total absence of perceivable change
- o --- Very slight perceivable change
- Δ --- Conspicuous change
- 5 x --- Swelled and separated coating

Resistance to gold plating --- In a bath of "Autronex CI" (gold plating liquid made by Sel-Rex Corp. of the USA), a given test piece was subjected to gold plating at a current density of 1 A/dm² for 12 minutes to have gold deposited thereon in a thickness of 2 μm. The coating was subjected to a peeling test using a "Cellophane" (registered Trade Mark) tape, visually examined with respect to separation of coating, and rated on the following four-point scale, wherein

- © --- Total absence of separation
- o --- Very slight separation
- Δ --- Separation of 10 to 50% of the whole coating
- 20 x --- Separation of the whole coating

Insulation resistance --- In accordance with the method of JIS Z-3197, a given test piece was tested for insulation in normal state and, after 500 hours' standing for absorption of moisture under the conditions of 55°C and 95% RH, tested for insulation with the aid of "TR-8601" (product of Takeda Riken Co Ltd). The results obtained in 1 minute at DC 500 V were reported.

Test Example 6 (Resolution)

30 Methods used for the formation of a circuit pattern were tested with respect to resolution. The method of non-contact exposure (using Test piece 2-S of Example 2), the method of contact exposure (using Test piece 5-S of Example 5), and the

method of screen printing (using Comparison Test piece 1-S of Comparative Experiment 1) were tried. In the case of the method of non-contact exposure, the surface of the substrate and the exposure film (mask) were separated by a gap of 500 μm .

As an instrument for measuring the resolution, a tool maker's microscope (Model STM, 150 magnifications, made by Olympus Optical Co., Ltd.) was used. A ridge, Wb, and a groove, Wa, in the cross section of a circuit pattern(ink) formed by exposure and development on a substrate (glass epoxy substrate or glass epoxy substrate coated with a copper foil) 2 as schematically illustrated in the accompanying drawing were measured. The measured values were compared with the corresponding dimensions of the pattern in the mask. The results are shown in Table 4.

Table 4

Method of pattern formation	Part of measurement	Surface of substrate	Width of exposure film pattern (μm)				
			250	200	150	100	75
Non-contact exposure	Groove Wa	G-E *1)	203.6	154.6	102	51.8	-
		Cu *2)	209.6	158.8	105.8	48	-
	Ridge, Wb	G-E	291	242.4	192.4	151.8	-
		Cu	290.2	239.8	189.8	140.8	-
Contact exposure	Groove, Wa	G-E	256.1	202.7	147.6	92.2	662
		Cu	245.4	194.1	144.2	95.4	697
	Ridge, Wb	G-E	247.4	196.6	153.5	108.2	834
		Cu	254.3	203.3	152.8	104.3	822
Screen printing	Groove, Wa	G-E	-	-	-	-	-
		cu	91.7	37.4	-	-	-
	Ridge, Wb	G-E	-	-	-	-	-
		Cu	412.7	352.3	-	-	-

*1) G-E: Pattern exposed on glass epoxy substrate

*2) Cu: Pattern exposed on copper foil

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CLAIMS:

1. A photosetting and thermosetting liquid resist ink composition developable with a dilute alkaline aqueous solution, which comprises in combination a photosetting resin composition comprising:

(A) a resin curable by activated energy radiation, which resin has an acid value in the range of 45 to 165 mg KOH/g and is obtained by the reaction of (a) a saturated or unsaturated polybasic acid anhydride with (b) a product of the reaction of a novolak type epoxy compound and an unsaturated monocarboxylic acid in the proportion of 0.95 to 1.05 equivalent weight of said unsaturated monocarboxylic acid per one equivalent weight of said novolak type epoxy compound;

(B) a photopolymerization initiator;

(C) a diluent; and

(D) an epoxy compound containing at least two epoxy groups per molecule thereof as a thermosetting component.

2. A composition according to Claim 1, wherein said resin (A) is produced by the reaction of said saturated or unsaturated polybasic acid anhydride of an amount of not less than 0.15 mol per each of the hydroxyl groups possessed by said product of the reaction of a novolak type epoxy compound and an unsaturated monocarboxylic acid.

3. A composition according to Claim 1 or Claim 2, wherein said novolak type epoxy compound is a product of the reaction of a phenol novolak type or cresol novolak type resin and epichlorohydrin.



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4. A composition according to any preceding claim, wherein said unsaturated monocarboxylic acid is acrylic acid or methacrylic acid.

5. A composition according to any preceding claim, wherein said acid anhydride is a dibasic acid anhydride, an aromatic polycarboxylic anhydride, or a polycarboxylic anhydride.

6. A composition according to any preceding claim, wherein said photopolymerization initiator is used in combination with a photopolymerization accelerator.

7. A composition according to any preceding claim, wherein said photopolymerization initiator is used in a proportion in the range of from 0.2 to 30 parts by weight, based on 100 parts by weight of said resin (A).

8. A composition according to any preceding claim, wherein said diluent is a photopolymerizable monomer or an organic solvent and is used in a proportion in the range of from 30 to 300 parts by weight, based on 100 parts by weight of said resin (A).

9. A composition according to Claim 8, wherein said photopolymerizable monomer is a water-soluble monomer of an α, β -unsaturated compound possessing a hydrophilic group.

10. A composition according to Claim 9, wherein said water-soluble monomer is selected from hydroxyalkyl acrylates and methacrylates, acrylamides, aminoalkyl acrylates or methacrylates, polyethylene glycol mono- and di-acrylates or methacrylates, and N-vinyl pyrrolidone.

(42)



11. A composition according to Claim 8, wherein said photopolymerizable monomer is a polyol polyacrylate or polymethacrylate or a polyester of a polybasic acid with a hydroxyalkyl acrylate or methacrylate.

12. A composition according to any preceding claim, which further comprises an inorganic filler, a pigment, a defoaming agent, a levelling agent, and/or a polymerization inhibitor.

13. A composition according to any preceding claim, wherein said epoxy compound as a thermosetting component is present in combination with an epoxy curing promoter.

14. A composition according to any preceding claim, wherein said epoxy compound as a thermosetting component is in an organic solvent solution and additionally contains a filler.

15. A composition according to any preceding claim, wherein said epoxy compound as a thermosetting component is used in a proportion in the range of from 10 to 150 parts by weight, based on 100 parts by weight of said photosetting resin composition.

16. A photosetting and thermosetting liquid resist ink composition according to Claim 1 and substantially as described in any one of the Examples herein.

17. A resist pattern on a substrate formed using a liquid resist ink composition according to any preceding claim.
