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Translation of European Patent Specification No. 0 073 444

Radiation-polymerisable composition and copying material
made therefrom

Specification

The invention relates to a radiation-polymerisable composition which contains as essential constituents

- a) a compound which has at least two terminal ethylenically unsaturated groups and which can form a crosslinked polymer by means of chain polymerisation by addition which is initiated by free radicals,
- b) a saturated polymeric binder which is insoluble in water and soluble in aqueous-alkaline solutions, and
- c) a polymerisation initiator which can be activated by radiation

and which is preferably used as a photoresist material which can be transferred dry for the production of solder masks.

Single and double-faced, but above all through-hole printed circuit boards are provided with a solder mask before they are soldered. The application of such masks only leaves the soldering pads exposed, whereby tin is saved on soldering. In addition, during the soldering process some of the soldering heat is kept away from the workpiece, so that the heat-sensitive components employed in assembling the printed circuit boards are not damaged during soldering. Last but not least, solder masks have the important function of covering all those areas of the circuit diagram which must not come into contact with the solder so as to avoid, for example, the possible

formation of conducting bridges between individual conducting paths, which are fatal for a circuit system. (39)

To satisfy these quite complex requirements various processes and products in various presentation forms have been used in the past.

It is clear from the above expositions that solder masks must have an image pattern which is oriented according to the given conducting paths. To apply solder masks by the screen printing technique is a method widely used in practice; by means of this method it is also possible to apply masks which have a relatively high layer thickness, and thereby to ensure especially that the conducting paths are well shielded and bedded in.

These masks which are produced by the screen printing process come up against a limit which is inherent in the system, namely when the distances between conducting paths are reduced so that the relatively coarse image structures of the screen print can no longer cope with fine line technology.

In recent years, solder masks have therefore been produced to an increasing extent by the photoresist technique. As in the production of printed circuits, thermoplastic photopolymerisable layers are laminated here by means of pressure and heat to the printed circuit board and cured by imagewise exposure at those places where the printed circuit board is to be covered. The solder mask is obtained by washing away the unexposed parts of the layer. This process makes possible higher image resolutions than the screen



printing process.

Suitable materials of this type are described, for example, in DE-A 27 47 947. They are photopolymerisable layers which contain a certain amount of bonded halogen to improve the flame-resistance. EP-A 15 004 describes a similar material which can be developed dry by mechanically separating exposed and unexposed layer areas ("peel-apart process"). Finally, EP-A 2040 describes a light-curable material for the same purpose, in which the light-sensitive compounds used are light-sensitive epoxy resins which are not described in more detail.

The photopolymerisable compositions known and used for this purpose are transferred dry and with heating onto the printed circuit board to be masked and they must therefore necessarily be thermoplastic. However, for use as solder masks this property is disadvantageous, since they must withstand without decomposition and without softening to too high a degree or even melting temperatures above 200 °C. Admittedly the photopolymer layer is hardened to a considerable extent in the exposed places by crosslinking polymerisation and this light-hardening can be further enhanced in a known way by re-exposure of the developed image stencil. However, basically a softening tendency on heating of all known photopolymerisable layers remains.

To overcome this disadvantage, EP-A2-63304 (date of priority: 13th April 1981; filing date: 5th April 1982, date of publication: 27th October 1982) proposed adding a bis-epoxy

(31)

compound to the photopolymerisable composition for the manufacture of the solder mask and post-curing, by heating the light-hardened image stencil after developing. For this purpose, the epoxy compound is dissolved in a customary manner in the coating mixture. This process produces very heat-stable solder masks. However, the photopolymerisable composition has the disadvantage that its shelf life is shorter than that of an otherwise identical composition which does not contain an epoxy compound.

10 The object of the invention was to propose photopolymerisable compositions which are suitable for the manufacture of thermally post-curable image stencils and which, in the unexposed state, have a long shelf life.

 According to the invention, a radiation-polymerisable composition
15 is proposed which contains

- a) a compound which has at least two terminal ethylenically unsaturated groups and which can form a crosslinked polymer by means of chain polymerisation by addition which is initiated by free radicals,
- b) a saturated polymeric binder which is insoluble in water and soluble
20 in aqueous-alkaline solutions, and
- c) a polymerisation initiator which can be activated by radiation.

 The composition according to the invention is characterised in that it additionally contains

- d) a compound which is thermally crosslinkable with the polymeric
25 binder b, with the polymerisation product of compound a and/or with itself and which, provided its crosslinking groups are epoxy groups, has at least three epoxy groups.

Those compounds are preferably suitable for use as compounds which are thermally crosslinkable with the binder the polymerisation product of the ethylenically unsaturated compound and/or with themselves which contain, as crosslinking groups, epoxy groups or groups of the formula $-\text{CH}_2-\text{O}-\text{R}$ in which R is a hydrogen atom or a lower alkyl, acyl or hydroxyalkyl group and in which the groups $-\text{CH}_2\text{OR}$ are bonded to a nitrogen atom of an open-chain or cyclic carboxamide or to an aromatic carbon atom of a compound capable of condensing with formaldehyde. The organic radicals R generally contain 1 to 4, preferably 1 or 2, carbon atoms.

The crosslinkable compounds are usually contained in the composition in an amount of 0.5 to 30, preferably 1 to 8, % by weight, relative to its non-volatile constituents.

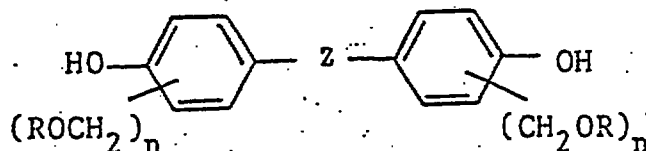
The crosslinkable compound should advantageously contain at least two crosslinking groups. The epoxy compounds must have at least three epoxy groups. To obtain a sufficiently long shelf life it is advantageous if the epoxy compound is virtually insoluble in the coating solvent, i.e. if it is present in the coating mixture at least for the largest part in a dispersed and undissolved state. The heterogeneous distribution in the prepared photopolymerisable layer which is brought about hereby evidently largely suppresses a premature crosslinking reaction. Compounds having less reactive epoxy groups, for example, high molecular weight epoxy compounds, can also be soluble in the coating mixture.

The compounds having crosslinking groups $-\text{CH}_2\text{OR}$ can be present not only in dissolved but also in dispersed form. Their reactivity at normal ambient temperature is evidently not sufficient for premature crosslinking in the layer. Of these compounds, in particular those are preferable in which $\text{R} = \text{H}$ or methyl. The derivatives of cyclic carboxamides, for example, of melamine, are also preferable.

In general, compounds having a relatively large number of crosslinking groups are particularly preferable.

It is in principle also possible to use crosslinkable compounds which are very reactive and soluble in the coating mixture. In this case, a premature reaction can be prevented by encapsulating these compounds in a covering substance which is insoluble in the coating solvent and which melts or softens below the post-heating temperature.

Suitable soluble crosslinkable compounds are, in particular, partially or completely etherified polyhydroxymethylmelamines, such as hexamethoxymethylmelamine; compounds of the following formula



in which $\text{Z} = \text{O}, \text{S}, \text{C}_1\text{-C}_8\text{-alkylene}$, for example CH_2 and $\text{C}(\text{CH}_3)_2$, or SO_2 , R denotes an H atom or a lower alkyl or acyl group and $n = 1$ or 2 ; or homopolymers and copolymers of glycidyl methacrylate.

Examples of suitable crosslinkable compounds are:

N-Methylol compounds of organic carboxamides

- N,N'-dimethylolurea, N,N'-dimethyloloxamide, N,N'-dimethylolmalonamide, N,N'-dimethylolsuccinamide, N,N'-dimethylolsebacamide, N,N',N''-trimethylolcitramide,
- 5 1,3-dimethylolimidazolidin-2-one, 1,3-dimethylol-4,5-dihydroxyimidazolidin-2-one, 1,3-dimethylolperhydropyrimidin-2-one, trimethylolmelamine, tetramethylolmelamine, hexamethylolmelamine, 1,3-dimethylol-5-methylperhydro-1,3,5-triazin-2-one, 1,3-dimethylol-5-allyl-
- 10 perhydro-1,3,5-triazin-2-one, 1,3-dimethylol-5-butylperhydro-1,3,5-triazin-2-one, 1,2-bis-[1,3-dimethylolperhydro-1,3,5-triazin-2-on-5-yl]ethane, tetramethylolhydrazine dicarboxamide, N,N'-dimethylolterephthalamide, N,N'-dimethylolbenzene-1,3-disulfonamide and tetramethylol-
- 15 glycoluril.

C-Methylol compounds of phenols, phenol-ethers and aromatic hydrocarbons

- 2,4,6-trimethylolphenol, 2,6-dimethylol-4-methylanisole, 2,6-dimethylol-4-methylphenol, 1,3-dimethylol-4,6-
- 20 diisopropylbenzene, 2,2-bis-(4-hydroxy-3,5-dimethylolphenyl)-propane, 3,3'-dimethylol-4,4'-dihydroxydiphenyl sulfone.

Instead of the methylol compounds mentioned, it is also possible to use, for example, the corresponding

25 methyl, ethyl or butyl ethers, or esters of acetic acid or propionic acid. Examples are: 4,4'-bis-methoxymethyldiphenyl ether, tris-methoxymethyldiphenyl ether, tetrakis-methoxymethyl hydrazine dicarboxamide, tetrakis-methoxymethyl-glycoluril, tetrakis-hydroxyethoxymethyl-

glycoluril, bis-acetoxymethyldiphenyl ether, hexamethoxymethylmelamine.

Examples which may be mentioned of compounds which are insoluble in the coating solution are:

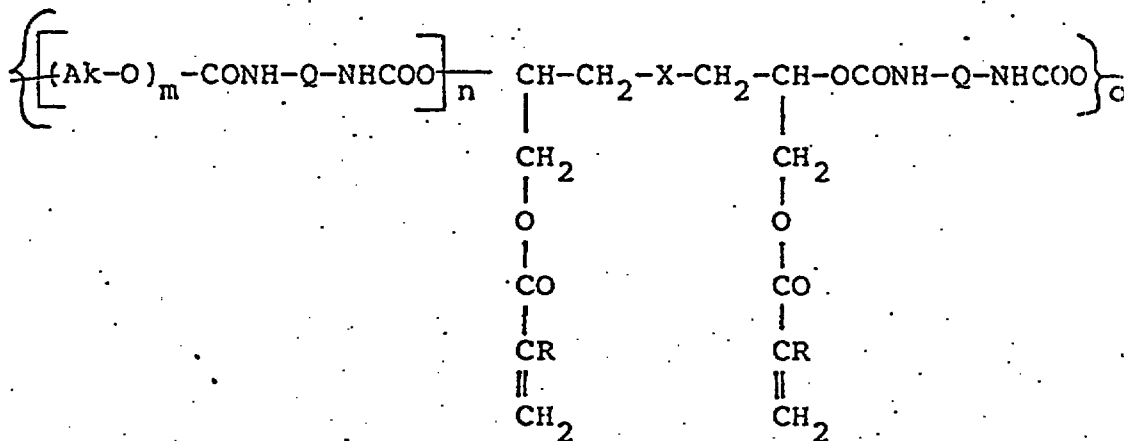
- 5 triglycidyl isocyanurate, hexamethylolmelamine and dimethylolurea.

Any form of electromagnetic radiation the energy of which is sufficient to trigger polymerisation is possible for use as an actinic radiation to which
10 the composition according to the invention is sensitive. Particularly suitable are visible and ultra-violet light, X-ray, γ and electron radiation. Laser radiation in the visible and in the UV region can also be used. Short-wave visible and near UV light is
15 preferred.

Polymerisable compounds a) used are in general esters of acrylic acid or of methacrylic acid with polyhydric, preferably primary, alcohols. The alcohol should contain 2 to
20 4 hydroxyl groups, since the crosslinking action desired is achieved by polyunsaturated compounds. The composition can also contain minor quantities of esters of monohydric alcohols or of alcohols which have more than four hydroxyl groups. Examples of suitable polyhydric alcohols are ethylene glycol, propylene glycol, butane-1,4-
25 diol, butane-1,3-diol, diethylene glycol, triethylene glycol, polyethylene glycols or polypropylene glycols having molecular weights from about 200 to 1000, neopentylglycol, trimethylolethane, trimethylolpropane, pentaerythritol and oxy-

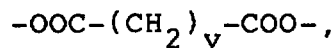
ethylated bisphenol A derivatives. Low-molecular bis-acrylates and bis-methacrylates which contain urethane groups and which are obtained by reacting 2 moles of a hydroxyalkyl acrylate or hydroxyalkyl methacrylate with 1 mole of an aliphatic or cycloaliphatic diisocyanate, for example 2,2,4-trimethylhexamethylene diisocyanate, are also suitable. Monomers of this type containing urethane groups are described in US-A 4,088,498. Similar suitable monomers are described in DE-A 28 22 190 and in EP-A2-54 700 (date of priority: 22nd December 1980; filing date: 27th October 1981; date of publication: 30th June 1982)

Mixtures of various monomers are advantageously used. Here it has proved particularly suitable to combine monomers of the abovementioned type with higher-molecular monomers which contain urethane groups and are of the general formula



in which Q is a bivalent mononuclear or binuclear aromatic radical which is unsubstituted or substituted by lower alkyl groups and which can contain a lower alkylene group as a connecting member,

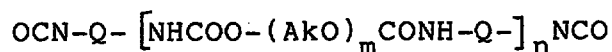
X is one of the groups -O-Ph-X'-Ph-O- and



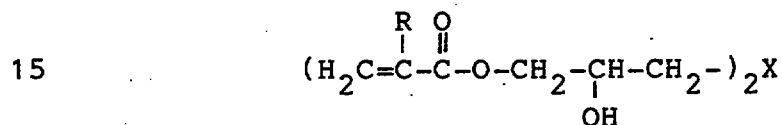
in which Ph is an optionally substituted phenylene group, X' is an alkylene group having 1-4 carbon atoms and y is a number from 2 to 12,

- 5 R is a hydrogen atom or a methyl group,
 Ak is an alkylene radical having 2-4 carbon atoms,
 m is a number from 4 to 50,
 n is a number from 1 to 6 and
 o is a number from 4 to 20.

- 10 These polyether ester urethanes are prepared in a known manner by reacting oligomeric diisocyanates of the formula



with bis-acrylate diols of the formula



The preparation and use of these compounds is described in EP-A1-48913 (date of priority: 29th September 1980; filing date: 19th September 1981; date of publication: 7th April 1982).

- 20 These polyurethanes in general have reduced specific viscosities (RSV) of 0.15 to 1.4 dl/g, measured on 1% strength solutions in dimethylformamide at 25 °C.

Products having RSV values within a range from 0.2 to 0.9 dl/g are preferable.

- 25 Preferred average values are 8-20 for m, 2-4 for n, 5-12 for o and 2-6 for y.

X' is an alkylene group in which the free valencies are preferably located at one C atom. Preferred

groups are methylene, 1,1-ethylene and 2,2-propylene groups. R is preferably a methyl group.

The total amount of polymerisable compounds a) is between 20 and 50, preferably between 25 and 45, % by weight, relative to the non-volatile proportions of the composition. Of this amount 2 to 20, preferably 5 to 10, % by weight, relative to the same basis, can be composed of polyurethanes of the general formula given above.

The compositions according to the invention also contain a polymeric, saturated, water-insoluble binder which is soluble in aqueous-alkaline solutions. The binders can contain as groups which impart solubility in alkali, phosphonic acid, sulfonic acid, sulfonamide, carboxylic anhydride and preferably carboxyl groups. Preferred binders are mixed polymers of methacrylic acid and alkyl methacrylates and, if appropriate, also styrene or other comonomers, as they have been described in DE-A 20 64 080 and in DE-A 23 63 806. The binders are used in an amount of 40 to 80, preferably 50 to 70, % by weight of the non-volatile constituents of the composition.

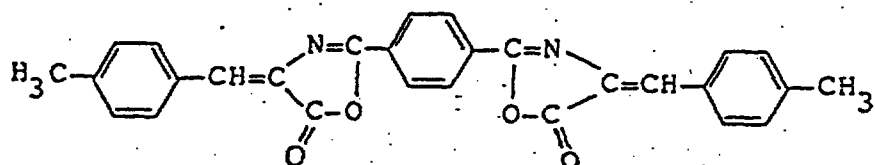
A large number of substances can be used as photoinitiators in the composition according to the invention. Examples are benzoin and its derivatives, polynuclear quinones, trichloromethyl-s-triazines, acridine derivatives, for example 9-phenylacridine, 9-p-methoxyphenylacridine, 9-acetylamino-acridine or benz(a)acridine; phenazine derivatives, for example, 9,10-dimethylbenzo(a)phenazine, 9-methylbenzo(a)-phenazine or 10-methoxybenzo(a)phenazine, quinoxaline deri-

vatives, for example, 6,4',4"-trimethoxy-2,3-diphenyl-
quinoxaline or 4',4"-dimethoxy-2,3-diphenyl-5-azaquinox-
aline, and quinazoline derivatives. The acridine, phen-
azine and quinoxaline derivatives are preferred. The
5 photoinitiators are in general used in an amount of 0.01
to 10, preferably 0.05 to 2 % by weight.

The compositions preferably contain at least one dye-
stuff to make the developed resist stencil more
visible. For this purpose a combination of at least
10 two dyestuffs is advantageously used, of which one
dyestuff changes its colour on irradiation and is des-
troyed, i.e. becomes colourless, at temperatures above 200 °C.
The other dyestuff should be able to survive not only
irradiation but also temperatures above 200°C without
15 change. It should make the solder mask clearly
visible during soldering and thereafter.

Suitable examples of dyestuffs which change colour
on exposure are triphenylmethane dyestuffs and certain azo
dyestuffs, as described in DE-A 28 07 933.

20 Suitable dyestuffs which are resistant to light
and heat are oxazolone dyestuffs, for example, a
dyestuff of the formula



25 or anthraquinone dyestuffs, for example 1,4-bis-(4-tert.-
butoxy-phenylamino)-5,8-dihydroxy-anthraquinone.

Compositions according to the invention can also con-

tain, in addition to monomers, binders, photoinitiators and dyestuffs, a number of other customary additives, for example, inhibitors to prevent the thermopolymerisation of the monomers, hydrogen donors, sensitometric regulators, pigments and plasticisers.

The composition according to the invention is preferably used as a photoresist, in particular as a solder mask. For this purpose, the composition can be applied in a known manner from a solution or as a pre-finished transferable dry resist film to the workpiece to be processed, for example, a printed circuit board.

The composition is preferably processed into a dry resist material. In general a solution of the composition in a solvent is applied to a suitable support, for example, a polyester film, and dried. The layer thickness of the resist layer can be about 10 to 150, preferably 20 to 120, μm . The free surface of the layer is preferably covered with a covering film, for example, of polyethylene or polypropylene. The finished laminate can be stored in the form of a full width roll which in the case of demand can be cut into resist rolls of any width desired.

Even after months of storage at 20°C , the resist rolls remain unchanged and can be processed without problems, and the cut edges remain completely free of resist outflows which lead to sticking. Resist layers stored for more than 2 months at 40°C in a drying cabinet show no differences, compared to freshly prepared layers, in respect of laminatability,

developability and soldering resistance.

The films can be processed by means of the equipment customary in dry resist technology. In a commercially available laminating device the covering film is peeled off and the solder resist layer is laminated onto the printed circuit board which is to be protected and which has been provided, for example, with metallized bores. The board thus prepared is then exposed through an original which protects those parts of the board from irradiation which must be left free for the soldering process.

The resist films, freed from the support film, are developed in a known manner. Suitable developers are aqueous-alkaline solutions, for example, of alkali metal phosphates, alkali metal carbonates or alkali metal silicates, to which, if desired, small amounts, for example, up to 10 % by weight, of wetting agents or organic solvents which are miscible with water can be added.

Fully prepared printed circuit boards, covered by the process steps just described, must then be subjected to a heat treatment before the soldering process. It is assumed that in this treatment an interpenetrating network is formed which is responsible for the good mechanical, thermal and chemical properties of the solder masks. This thermal treatment is in general carried out between 80°C and 150°C for approximate treatment times of 10 to 60 minutes.

The board which is ready for soldering can be assembled with electronic components, the connectors of which are bent across the corresponding lines of the circuit in those areas which have been laid bare in the developing process.

The conducting side of the board can then be treated with a suitable, commercially available soldering flux and subjected to flow soldering in a commercially available flow soldering machine.

The soldering metals used are known eutectic mixtures which permit soldering temperatures of about 230° to 260°C . A known mixture contains, for example, 63 % by weight of tin and 37 % by weight of lead.

Solder masks according to the invention can be used successfully also in processes in which double-faced, through-hole printed circuit boards are soldered by dipping into liquid metal baths.

The compositions according to the invention produce solder resist layers which are distinguished by a high flexibility and mechanical strength in the unexposed and exposed state and by a high heat resistance in the exposed and post-cured state. The photopolymerisable layers have in combination with the preferred photoinitiators a high sensitivity to light and a satisfactory curing or crosslinking throughout the layer is obtained even in the case of thick layers. Even in the case of thicknesses above $100\text{ }\mu\text{m}$ the exposed layers can be developed perfectly and completely by means of aqueous-alkaline solutions.

The exposed and developed layers can be therm-

ally cured without excessively impairing the flexibility of the mask or its adhesion to the substrate and without altering the position and dimensions of the areas laid bare by developing. The cured masks are resistant to atmospheric, thermal and chemical influences for relatively long time periods. Solder masks obtained from the compositions according to the invention are particularly suitable for protecting sensitive electronic conductor structures from atmospheric attack in an effective and permanent manner.

Although, in the above descriptive section, the invention has been preferably described in its use for the manufacture of solder masks, it is not restricted to this use. It is applicable to any case where the object is to produce imagewise stencils of particularly high thermal, mechanical and chemical resistance. This is the case also in other photoresist applications, for example in the production of electroplating resists, which are intended to be resistant to aggressive baths and/or at elevated temperatures. The composition according to the invention is particularly suitable also for the manufacture of offset printing plates, for example, on aluminum, steel or chromium as support material, which are intended to be baked in a known manner, after developing, to consolidate the image stencil. This process is described in GB-A 1,154,749. However, in this mode of application heating should be carried out for a shorter time and at higher temperatures, in general for 2 to 20 minutes at temperatures within a

range of 200 to 250°C. This can considerably increase also the print run of photopolymerisable offset printing plates.

The examples which follow illustrate particular embodiments of the composition according to the invention. Unless otherwise indicated, percentages and quantity ratios are to be understood as units by weight. Parts by weight (p.b.w.) relate to parts by volume (p.b.v.) as the gram relates to the milliliter.

10 Example 1

The following crosslinkable compounds

- a) 0.6 part by weight of 2,2-bis-(4-glycidoxyphenyl)-propane (0.00316 mole of epoxy groups = 7 mole%, relative to COOH groups in the binder),
- 15 b) 0.21 part by weight of hexamethoxymethylmelamine (0.00316 mole of methoxymethyl groups = 7 mole%, relative to COOH groups in the binder),
- c) 0.21 part by weight of condensed-on hexamethoxymethylmelamine ($\approx$ 0.003 mole of methoxymethyl groups $\approx$ 7 mole%, relative to COOH groups in the binder),
- 20 d) 0.28 part by weight of tetramethylol-bisphenol-A (0.00316 mole of hydroxymethyl groups = 7 mole%, relative to COOH groups in the binder),
- e) 0.16 part by weight of hexamethylolmelamine (0.00316 mole of hydroxymethyl groups = 7 mole%, relative to COOH groups in the binder),
- 25 f) 0.31 part by weight of triglycidyl isocyanurate (0.00316 mole of epoxy groups = 7 mole%, relative to COOH groups in the binder),

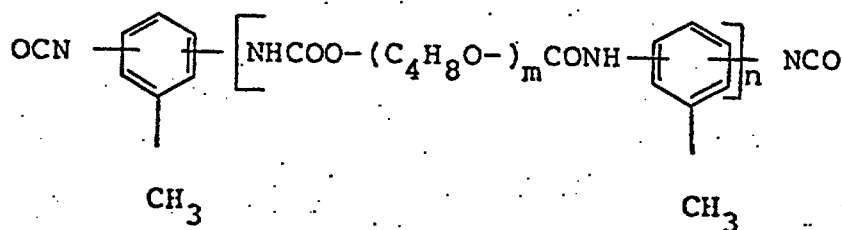
- g) 1.2 parts by weight of 2,2-bis-(4-glycidoxyphenyl)-
propane (0.00632 mole of epoxy groups = 14 mole%,
relative to COOH groups in the binder),
- h) 0.41 part by weight of hexamethoxymethylmelamine
5 (0.00632 mole of methoxymethyl groups = 14 mole%,
relative to COOH groups in the binder),
- i) 0.41 part by weight of condensed-on hexamethoxymethyl-
melamine ($\approx$ 0.006 mole of methoxymethyl groups $\approx$
14 mole%, relative to COOH groups in the binder),
- 10 k) 0.55 part by weight of tetramethylol-bisphenol-A
(0.00632 mole of hydroxymethyl groups = 14 mole%,
relative to COOH groups in the binder),
- l) 0.32 part by weight of hexamethylolmelamine (0.00632
mole of hydroxymethyl groups = 14 mole%, relative
15 to COOH groups in the binder),
- m) 0.19 part by weight of dimethylolurea (0.00316 mole
of hydroxymethyl groups = 7 mole%, relative to
COOH groups in the binder), and
- n) 0.41 part by weight of bis-methoxymethyldiphenyl ether
20 (0.00316 mole of methoxymethyl groups = 7 mole%,
relative to COOH groups in the binder,
- were added in the amounts indicated to a solution each of
13 parts by weight of a terpolymer of n-hexyl meth-
acrylate, methacrylic acid and styrene (60:30:10)
25 having an average molecular weight of about
35,000 and an acid number of 195,
- 6.4 parts by weight of polyethylene glycol 400
dimethacrylate,
- 1.6 parts by weight of the elastomer described below,

- 0.2 part by weight of 9-phenylacridine,
 0.01 part by weight of a blue dyestuff obtained by
 coupling the diazonium salt of 2,4-dinitro-6-
 chlorobenzene with 2-methoxy-5-acetylamino-N,N-
 5 diethylaniline and
 0.03 part by weight of 1,4-bis-(4-tert.butoxyphenyl-
 amino)-5,8-dihydroxyanthraquinone in
 30.0 parts by weight of butanone and
 5.0 parts by weight of ethanol.

10 The elastomer used was prepared as follows:

A. In a 1 liter four-necked flask, equipped with a stir-
 rer, a thermometer, a reflux condenser and a drying tube,
 426 parts by weight of glycidyl methacrylate and 216 parts
 by weight of adipic acid were mixed by stirring and the
 15 mixture was heated carefully to an internal temperature
 of 80°C after the addition of 19.7 parts by weight of
 p-methoxy-phenol and 6.4 parts by weight of benzyl-tri-
 ethylammonium chloride. After about 2 hours a clear
 solution was obtained which was kept at 80°C for a fur-
 20 ther 14 hours. After this time, the content of free gly-
 cidyl methacrylate was less than 0.5 %.

B. 143 parts by weight of an oligomeric diisocyanate of
 the formula



having an average molecular weight of about 2,000 and an isocyanate group content of 4.1 % by weight (Adiprene[®] L 100), dissolved in 300 parts by volume of methyl ethyl ketone, were placed into a 1 liter four-necked flask equipped with a stirrer, thermometer, dropping funnel, condenser and drying tube, and 0.87 part by weight of benzoquinone and 0.85 part by volume of a solution were added which had been prepared by dissolving 6.3 parts by weight of iron(III) acetylacetonate and 0.45 part by weight of triethylamine in methyl ethyl ketone and adding methyl ethyl ketone to 100 parts by volume. A solution of 31.33 parts by weight of the reaction product obtained in accordance with A in 300 parts by volume of methyl ethyl ketone was poured into the dropping funnel and added dropwise in the course of 40 minutes to the solution in the flask which was heated at 70°C and stirred. After two hours' further stirring at 30°C 10 parts by volume of ethanol were added to the clear reaction mixture. Distilling off the solvent produced from the viscous solution a non-tacky rubber-like mass which gave clear solutions in numerous organic solvents, such as tetrahydrofuran, acetone or toluene. The reduced specific viscosity of the product was 0.72 dl/g (measured on a 1 % strength solution in dimethylformamide at 25°C).

110 cm wide webs of a biaxially oriented and heat-set 25 µm thick polyethylene terephthalate film were coated in a continuous manner with the solutions indicated by means of a slot die. After passing through a drying zone the resist layers each had a thickness of 100 µm

and were covered with a polypropylene film. The dry resist films thus produced were then cut, by means of a roll slitter into manageably sized resist rolls having a width of 45 cm and a web length of 50 m.

Test boards of rigid epoxy glass fabric and having approximately 65 μm thick conducting paths with a tinned surface and plated-through holes were used in the laminating experiments. The conducting paths' widths and distances were between 200 and 1,000 μm , and the hole diameters were 0.6 to 4 mm.

The 100 μm thick solder resist layers were laminated at 120°C by means of a commercially available laminating device onto these boards.

15 The boards were then exposed, through an exposure original which covered the pads and holes to be soldered, for 10 seconds by means of a commercially available exposure device having a 5 kW metal halide light, developed in a commercially available spray processor for 20 100 seconds with a 0.8 % strength sodium carbonate solution and blown dry. The printed circuit boards thus prepared were then cured for 60 minutes at 150°C in a drying cabinet. The cooled boards were then wetted with the soldering flux TL 33-16 from Messrs. Alpha Grillo 25 and then passed with a speed of 0.5 m/min through a commercially available flow soldering bath at 250°C.

This process produced boards having a dust-dry, very impact-resistant and scratch-proof surface. Even narrow conducting paths were tightly shielded by the

cured solder resist layer.

To determine the shelf life, samples of the dry resist materials described above were stored at 40°C in a drying cabinet. Each day one sample was removed and
5 laminated, exposed and developed, all three steps being carried out as described above.

In the Table below, the shelf life of various resist layers is indicated by the number of days after which the layer could still be completely developed:

10	Layer	a	b	c	d	e	f	g	h	i	k	l	m
	Shelf life (days at 40°C)	10	>80	>67	>77	>70	39	5	>72	>61	>70	>70	>61

15 It should be noted that a baking time of 60 minutes is not absolutely necessary. Thus, adequate soldering resistance is shown, for example, by layers b and c after only 30 minutes and by layer f after only
15 minutes.

20 The baking time can also be shortened by a longer exposure time.

Examples 2 - 7

In the Table which follows, 6 examples are summarised which do not differ from Example 1 in tech-
25 nical procedure but have differences in formulation.

Variations in properties of the resists caused thereby are briefly noted in the Table. 13 parts by weight of the terpolymer specified in Example 1 were used as the binder in all 6 examples. Moreover, the polyurethane
30 monomer specified in Example 1 as well as the photoinitiator

and dyestuffs were added in the same amounts as used there. The thixotropic urethane monomers additionally used in Examples 4 and 5 prevent edge outflow of the unexposed resist layer.

Ex- ample	Low molecular monomer (PEG 400 DMA*) part by weight	Low molecular weight additional monomer, part by weight	Condensed-on hexamethoxy- methyl- melamine part by weight	Comments	Shelf life days at 40°C
2	-	PPG 420 DMA** 6.4	0.21	Slightly more brittle layer than with PEG 400 DMA	> 76
3	4.8	PPG 420 DMA** 1.6	0.21	High light sensitivity, no edge outflow, long shelf life	> 76
4	4.8	Oligo-urethane of PEG 300, hexamethylene diisocyanate and glycerol dimethacrylate 1.6	0.21	No edge outflow	> 76
5	4.8		0.21		
6	5.2	-	0.8	High crosslinking rate Long shelf life	> 168
7	4.8	-	1.6		

* Polyethylene glycol 400 dimethacrylate.

** Polypropylene glycol 420 dimethacrylate

(51)

Example 8

The following amounts of low molecular weight monomers and crosslinkable compounds:

- a) 6.4 parts by weight of PEG 400 DMA and
5 0.2 part by weight of hexamethoxymethylmelamine,
- b) 5.2 parts by weight of PEG 400 DMA and
0.2 part by weight of hexamethoxymethylmelamine
- c) 5.2 parts by weight of PEG 400 DMA and
0.8 part by weight of hexamethoxymethylmelamine and
- 10 d) 6.4 parts by weight of PEG 400 DMA and
0.24 part by weight of triglycidyl isocyanurate,
were added to a solution each of
- 13 parts by weight of the terpolymer specified in
Example 1,
- 15 1.6 parts by weight of the elastomer of Example 1,
0.2 part by weight of 9-phenylacridine,
0.03 part by weight of 1,4-bis-(4-tert.butoxy-
phenylamino)-5,8-dihydroxyanthraquinone and
0.01 part by weight of the blue dyestuff specified in
20 Example 1 in
- 30 parts by weight of butanone and
5 parts by weight of ethanol.

Resist rolls having a width of 45 cm and a web length
of 50 m were prepared with solutions of the composition
25 given, as described in Example 1.

The dry resist films were laminated at 120°C
with a commercially available laminating device onto
laminated phenoplast boards covered with a 35 µm thick
copper foil and in each case exposed for 10 seconds by

means of a 5 kW metal halide light. The original used was a line original with line widths and distances down to 80 μm .

After exposure, the polyester film was peeled off, and the layers were developed for 180 seconds with 0.8% strength sodium carbonate solution in a spray developing device.

The boards were then rinsed for 30 seconds with tap water, incipiently etched for 30 seconds in a 15% strength ammonium peroxydisulfate solution, rinsed again with water, dipped for 30 seconds in 10% strength sulfuric acid and then electroplated in the following electrolyte baths:

1) 120 minutes in a copper electrolyte bath from Messrs. Schlötter, Geislingen/Steige, "bright copper"® bath" type

Current density: 2.5 A/dm^2

Metal build-up: about 100 μm

Temperature: room temperature

2) 2 minutes in a nickel bath of the "Norma"® type from Messrs. Schlötter, Geislingen/Steige

Current density: 4 A/dm^2

Metal build-up: 2 μm

Temperature: 50°C

The boards did not display any undercutting or damage.

It was then possible to strip the boards in 5% strength KOH solution at 50°C , and to remove the copper laid bare in customary etching media.

Example 9

The following coating solutions were spin-coated onto electrochemically roughened and anodized aluminum having an oxide layer of 2 g/m^2 and which had been pretreated with an aqueous solution of polyvinylphosphonic acid:

- a) 2 parts by weight of a copolymer of styrene and monobutyl maleate (1:1, molecular weight about 68,000),
- 10 2 parts by weight of a diurethane of 2 moles of glycerol dimethacrylate and 1 mole of hexamethylene diisocyanate,
- 0.7 part by weight of 9-phenylacridine and
- 0.07 part by weight of a blue dyestuff obtained by
- 15 coupling the diazonium salt of 2,4-dinitro-6-chlorobenzene with 2-methoxy-5-acetylamino-N-cyanoethyl-N-hydroxyethylaniline in
- 24 parts by weight of butanone,
- 10 parts by weight of butyl acetate and
- 20 10 parts by weight of ethylene glycol monomethyl ether,
- b) a coating solution as a, which additionally contained 0.027 part by weight of partially condensed-on hexamethoxymethylmelamine.

25 The plates were then dried for 2 minutes at 100°C in a circulating air drying cabinet. A layer weight of 2.5 g/m^2 was obtained.

The printing plates obtained were then exposed for 40 seconds by means of a 5 kW metal halide light at

a distance of 110 cm between light and vacuum copying frame under a 13-step exposure wedge having density increments of 0.15. The plates were then developed manually with a developer of the following composition:

- 5 3.0 parts by weight of sodium metasilicate x 9 H₂O,
- 0.03 part by weight of a non-ionic wetting agent
 (coconut fatty alcohol polyoxyethylene ether
 containing about 8 oxyethylene units),
- 0.003 part by weight of an antifoam agent,
- 10 0.02 part by weight of nitrilotriacetic acid,
- 0.053 part by weight of strontium chloride x 6 H₂O and
- 96.894 parts by weight of fully demineralized water.

7 to 8 fully crosslinked wedge steps were obtained.

- The plate coated with solution b was baked for 10
- 15 minutes at 230°C after developing and gave a considerably
 increased print run.

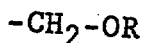
Claims

1. A radiation-polymerizable mixture containing
a) a compound which has at least two terminal ethylene-
5 nically unsaturated groups and which can form a cross-
linked polymer by means of chain polymerization by
addition which is initiated by free radicals, b) a
saturated polymeric binder which is insoluble in water
and soluble in aqueous-alkaline solutions and c) a
10 polymerization initiator which can be activated by
radiation, which contains in addition d) a compound
which is thermally crosslinkable with the polymeric
binder b, with the polymerization product of compound a
and/or with itself and which, provided its crosslinking
15 groups are epoxy groups, has at least three epoxy groups.

2. A radiation-polymerizable mixture as claimed in
claim 2, which contains the crosslinkable compound in
an amount of 0.5 to 30 % by weight.

20 3. A radiation-polymerizable mixture as claimed in
claim 1, wherein the crosslinkable compound contains,
as crosslinking groups, epoxy groups or groups of the
formula

25



in which R is a hydrogen atom or an alkyl, acyl or
hydroxyalkyl group having from 1 to 4 carbon atoms, and
the groups $-\text{CH}_2\text{OR}$ are bonded to a nitrogen atom of an
30 open-chain or cyclic acidamide or to an aromatic carbon



atom of a compound capable of condensing with form-
aldehyde.

4. A radiation-polymerizable mixture as claimed in
5 claim 1, wherein the crosslinkable compound contains at
least two crosslinking groups.
5. A radiation-polymerizable mixture as claimed in
claim 1, which contains as crosslinkable compound an
10 epoxy compound which is insoluble in the coating
solvent used.
6. A radiation-polymerizable mixture as claimed in
claim 1, wherein the compound having at least two ter-
15 minal ethylenically unsaturated groups contains as
unsaturated groups acrylate or methacrylate groups.
7. A photopolymerizable copying material having a
flexible transparent temporary support and a trans-
20 ferable thermoplastic photopolymerizable layer con-
taining a) a compound which has at least two terminal
ethylenically unsaturated groups and which can form a
crosslinked polymer by means of chain polymerization
by addition which is initiated by free radicals,
25 b) a saturated polymeric binder which is insoluble
in water and soluble in aqueous-alkaline solutions
and c) a polymerization initiator, wherein the layer
additionally contains d) a compound which is thermally
crosslinkable with the polymeric binder b, with the
30 polymerization product of compound a and/or with itself
and which, provided its crosslinking groups are epoxy
groups, has at least three epoxy groups.