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Description

The instant invention relates to a radiation-polymerizable mixture which contains, as essential constituents,

- a) a compound which has at least two terminal ethylenically unsaturated groups and which can form a cross-linked polymer by means of chain polymerization by addition, initiated by free radicals,
- b) a polymeric binder, and
- c) a polymerization initiator which can be activated by radiation,

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

It is known to produce solder masks on printed circuit boards by the photoresist technique. As in the production of printed circuits, thermoplastic photopolymerizable layers are laminated onto the printed circuit board by means of pressure and heat and are hardened in imagewise fashion by exposure at those places where the printed circuit board is to be covered. The solder mask is obtained by washing away the unexposed layer areas.

Materials suitable for this purpose are, for example, described in DE-A No. 2,747,947. They comprise photopolymerizable layers which contain a certain amount of a bonded halogen to improve their flame-resistance. EP-A No. 15,004 describes a similar material which can be developed dry by mechanically separating exposed and exposed (sic) layer areas ("peel-apart process"). Finally, EP-A No. 2,040 describes a light-hardenable material for the same purpose, in which the light-sensitive compounds are identified as light-sensitive epoxy resins which are, however, not described in a more detailed way.

Photopolymerizable mixtures known and used for this purpose are transferred dry and with heating onto the printed circuit board to be masked and therefore must necessarily be thermoplastic. However, for use as solder masks this property is disadvantageous since the masks must withstand temperatures above 200°C without decomposition and without softening to too high a degree or even melting. Admittedly, the photopolymer layer is hardened to a considerable extent in the exposed areas by cross-linking polymerization, and this light-hardening can be further enhanced in a known way by re-exposure of the developed image stencil. However, the basic tendency of all known photopolymerizable layers to soften when heated remains.

In accordance with DE-A No. 3,114,931 a bis-epoxy compound was added to the photopolymerizable mixture used for producing the solder mask, and the light-hardened image

stencil was post-cured after developing by heat treatment, in order to overcome the above-stated disadvantage. This process produces highly heat-resistant solder masks. However, the photopolymerizable mixture produced in this way has the disadvantage that its shelf life is shorter than that of an otherwise identical mixture which does not contain an epoxy compound.

EP-A No. 73,444 discloses similar mixtures which in the unexposed state possess an improved shelf life. These mixtures contain compounds which are thermally cross-linkable with the binder, with the polymerization product of the ethylenically unsaturated compound, and/or with themselves. Preference is thereby given to compounds in which the cross-linking groups are epoxy groups or groups of the formula $-\text{CH}_2-\text{O}-\text{R}$, whereby R denotes a hydrogen atom or a lower alkyl, acyl or hydroxy-alkyl group, and the groups $-\text{CH}_2\text{OR}$ are bonded to a nitrogen atom of a low molecular weight, open-chain or cyclic acid amide or to an aromatic carbon atom of a compound which is capable of undergoing a condensation reaction with formaldehyde.

However, the mixtures described in the above publication still possess two significant drawbacks. Under particular soldering conditions, it can happen that - probably due to softening of the layer - threads or pellets of the solder alloy adhere to the surface of the solder mask after wave-soldering, which may possibly lead to short circuits.

In accordance with the former, not prepublished German Patent Application No. P 32 36 560.8, the formation of such so-called "tin cobwebs" can be reduced by roughening the photopolymeric layer by means of a pigmented polyester film. However, it is not possible to suppress the formation of these "cobwebs" completely.

In the fully cured state, the mixtures according to EP-A No. 73,444 furthermore possess an unsatisfactory resistance to solvents. As a consequence thereof, softening of the solder masks may (sic) during the cleaning of the soldered printed circuit boards. In addition, the dye-stuff is partially dissolved out of the layer if solvents, such as, for example, ethanol, are allowed to interact with the layer over a prolonged period.

It was the object of the present invention to provide photopolymerizable mixtures which are suitable for the production of thermally post-curable image stencils, the shelf lives of which are as good as those of the known mixtures, whereas their exposure products possess an increased hardness and improved resistance to solvents.

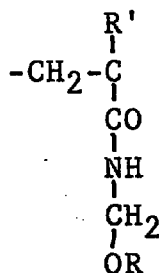
According to this invention, there is proposed a radiation polymerizable mixture which contains

- a) a compound which has at least two terminal ethylenically unsaturated groups which can form a cross-linked polymer by means of chain polymerization by addition, initiated by free radicals,

b) a polymeric binder, and

c) a polymerization initiator which can be activated by radiation.

The mixture of this invention is characterized in that it contains, as binder, a copolymer which comprises units of the formula



in which

R' denotes a hydrogen atom or a methyl group and
R denotes a hydrogen atom or a lower alkyl, acyl
or hydroxyalkyl group.

If R is an alkyl group, it generally contains 1 to 6, preferably 1 to 4, carbon atoms; if R is an acyl group, it generally contains 1 to 4, preferably 1 or 2, carbon atoms. In general, preference is given to compounds with R=alkyl.

In addition to the units of the above formula, the copolymer may include further units, whereby preference is

given to units which yield polymers of a low Tg value, in particular acrylic or methacrylic acid ester units.

Upon being heated in the presence of polymers with free hydroxyl groups or, preferably, free carboxyl groups, polymers containing the above described monomer units yield cross-linked products. Therefore, they can be present in a mixture with polymeric binders which carry such substituents. Binders which include both types of substituents in one molecule are preferably employed. Terpolymers of substituted acrylic or methacrylic acid amides, acrylic or methacrylic acid and alkyl esters of acrylic or methacrylic acid are particularly suitable. Special preference is given to methacrylic acid esters, in particular to those containing 4 to 12 carbon atoms in their alkyl groups. If acrylic acid esters are used, the alkyl group can be shorter.

Additionally, the polymers can contain minor amounts of interpolymerized hydroxyalkyl acrylates or hydroxyalkyl methacrylates.

The cross-linking density achieved during the heating of the mixture depends on the ratio of substituted acid amide groups to the carboxylic acid groups and/or OH-groups. The molar ratio of ROCH_2NH to COOH advantageously varies between 0.2:1 and 1.5:1, preferably between 0.5:1 and 1.1:1.

The proportion of carboxyl group-containing units in the copolymer is determined by the demand for a trouble-free, rapid development with aqueous-alkaline solutions which are preferably free from organic solvents, and for the highest possible degree of developer resistance of the exposed areas. To a minor extent, these properties are also influenced by the mean molecular weight and the chemical and molecular non-uniformity of the polymer. In general, the acid number should vary between 50 and 250, preferably between 100 and 220. In those cases where it is possible to use a developer which contains organic solvents, the acid number can be lower.

The preferred terpolymers usually contain about 15 to 60 % by weight, preferably about 20 to 50 % by weight, of substituted acid amide units. The proportion of acrylic or methacrylic acid units is selected in accordance with the above specified acid numbers; normally, it is about 10 to 35 % by weight. The amount of alkyl acrylate or alkyl methacrylate is within a range of 25 to 75 % by weight. Methacrylic acid in its free form or in the form of its alkyl ester is preferred over acrylic acid.

The proportion of binders in the polymerizable mixture is within a range of 40 to 90 % by weight, preferably of 55 to 85 % by weight, relative to the non-volatile constituents of the mixture.

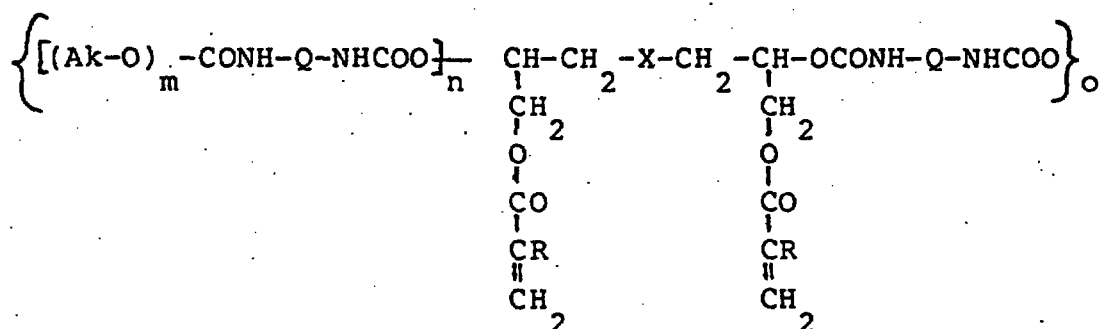
The binders are preferably prepared by means of a free-radical polymerization in organic solvents, for example, butanone or ethanol.

Any form of electromagnetic radiation, the energy of which is sufficient to trigger polymerization, is possible for use as actinic radiation, to which the mixture 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 long-wave UV light is preferred.

Polymerizable compounds used are in general esters of acrylic acid or of methacrylic acid with polyhydric, preferably primary, alcohols. The alcohol should contain 2 to about 4 hydroxyl groups since the crosslinking action desired is achieved by polyunsaturated compounds. The mixture can also contain minor quantities of esters of monohydric alcohols or of alcohols which have more hydroxyl groups. Examples of suitable polyhydric alcohols are ethylene glycol, propylene glycol, butane-1,4-diol, butane-1,3-diol, diethylene glycol, triethylene glycol, polyethylene glycols or polypropylene glycols having molecular weights from about 200 to about 1,000, neopentylglycol, trimethylolethane, trimethylolpropane, pentaerythritol and oxyethylated 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 Patent No. 4,088,498. Similar suitable monomers are described in DE-A Nos. 2,822,190 and 3,048,502.

Mixtures of differing monomers can also be used. It is, for example, possible to combine monomers of the above-mentioned 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

-OOC-(CH₂)_y-COO-,

whereby 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,

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.

These polyether ester urethanes are prepared in a known manner by reacting oligomeric diisocyanates with bis-acrylic acid ester diols.

The preparation and use of these compounds has been described in EP-A No. 48,913.

These polyurethanes in general have reduced specific viscosities (RSV) of about 0.15 to 1.4 dl/g, measured on 1 % strength solutions in dimethyl formamide at 25 °C. Products having RSV values within a range from 0.2 to 0.9 dl/g are preferable.

The total amount of polymerizable compounds is in general between 10 and 60, preferably between 15 and 45 percent by weight, relative to the non-volatile proportions of the mixture. Of this amount, 2 to 20, preferably 5 to 10 percent by weight, relative to the same basis, can be composed of polyurethanes of the general formula given above.

Apart from the above-described cross-linkable polymers, the mixtures according to the invention can contain other known, preferably saturated, binders. Water-insoluble binders which are soluble or at least swellable in

aqueous-alkaline solutions are preferably used. The mixtures can furthermore contain low molecular-weight, thermally cross-linkable mixtures of the type described in EP-A No. 73,444, in particular methoxymethyl melamines. These compounds can be added in amounts of 0.5 to 30 percent by weight, preferably of 5 to 25 percent by weight, relative to the non-volatile constituents of the mixture.

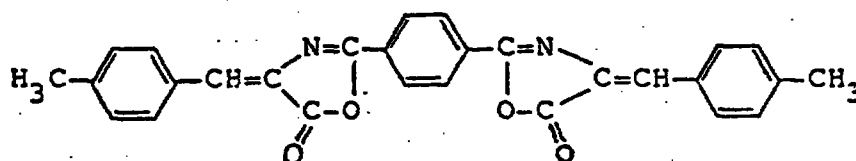
A large number of substances can be used as photoinitiators in the mixture according to the invention. Examples are benzoin and its derivatives, polynuclear quinones, trichloromethyl-s-triazines, acridine derivatives, for example, 9-phenylacridine, 9-p-methoxyphenylacridine, 9-acetylamino-acridine or benz(a)acridine; phenazine derivatives, for example, 9,10-dimethylbenzo(a)phenazine, 9-meth-benzo(a)phenazine (sic) or 10-methoxybenzo(a)phenazine; quinoxaline derivatives, for example 6,4', 4"-trimethoxy-2,3-diphenylquinoxaline, 4'4"-dimethoxy-2,3-diphenyl-5-azaquinoxaline and quinazoline derivatives. The acridine, phenazine and quinoxaline derivatives are preferred. The photoinitiators are in general used in an amount of 0.01 to 10 % by weight, preferably of 0.05 to 2 % by weight.

The mixtures preferably contain at least one dyestuff to make the developed resist stencil more visible. For this purpose a combination of at least two dyestuffs is advantageously used, of which one dyestuff changes color on irradiation and is destroyed at temperatures

above 200 °C, i.e., becomes colorless. The other dye-stuff should be able to survive not only irradiation but also temperatures above 200 °C without change. It is intended to make the solder mask clearly visible during soldering and thereafter.

Suitable examples of dyestuffs which change color on exposure are triphenylmethane dyestuffs and certain azo dyestuffs, as described in DE-A No. 2,807,933 (= US-A No. 4,241,166).

Suitable light- and heat-resistant dyestuffs are oxazonone dyestuffs, for example a dyestuff of the formula



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

The mixtures according to the invention can also contain, in addition to monomers, binders, photoinitiators and dyestuffs, a series of other customary additives, for example, inhibitors to prevent the thermopolymerization of the monomers, hydrogen donors, sensitometric regulators, pigments, plasticizers, and flame retardants.

The mixture according to the invention is preferably used as a photoresist, in particular as a solder mask.

For this purpose, the mixture can be applied in a known manner from a solution or as a prefinished transferable dry resist film to the workpiece to be processed, for example a printed circuit board. The mixture is preferably processed into a dry resist material. In general a solution of the mixture 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 μm , preferably 20 to 120 μm . The free surface of the layer is preferably covered with a top 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 equipment customary in dry resist technology. In a commercially available laminating device the top film is peeled off and the solder mask 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

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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 layers, after being freed from the support film, are developed in a known manner. Suitable developers are aqueous, preferably 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 at temperatures between 80 °C and 150 °C for approximate treatment times of 10 to 60 minutes.

The board which is ready for soldering can be equipped with electronic component parts, the connectors of which are bent across the corresponding lines of the circuit in those areas which are 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 wave soldering in a commercially available wave soldering machine.

The soldering fluxes used are known eutectic mixtures which permit soldering temperatures of about 230 °C 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-sided, through-hole plated printed circuit boards are soldered by dipping them into liquid metal baths.

The mixtures according to the invention produce solder mask 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 photopolymerizable layers exhibit, 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 μm the exposed layers can be developed perfectly and completely by means of aqueous-alkaline solutions.

The exposed and developed layers can be thermally cured without an excessive impairment of the flexibility of

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the mask or of its adhesion to the substrate and without alteration of the position and dimensions of the areas laid bare by developing. The cured masks are resistant to atmospheric, thermal and, in particular, chemical influences for prolonged time periods.

Even after the prolonged action of, for example, ethanol for a period of 24 hours, no softening of the masks is observed, nor are any components, such as, for example, dyestuff, dissolved out of the layer. After the solvent treatment, the adhesion of the solder mask both to the circuit paths and to the printed circuit board basis is still excellent. This solvent resistance is of great importance, for alcohol-containing solutions are used to remove the soldering flux. The solder masks obtained from the mixtures according to this invention are particularly suitable for protecting sensitive electronic conductor structures from atmospheric attack in an effective and lasting way.

Although, in the above descriptive section, the invention has been preferably described with regard to its use in 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 also the case in other photoresist applications, for example in the production of electroplating stencils, which are to be resistant to aggressive baths and/or to elevated temperatures.

Processing of the mixture is preferably performed by means of the dry photoresist technique, as described above. However, the mixture is also well suited for being processed by means of the liquid resist technique, i.e. by applying a solution of the components to the final layer support, both in the production of printed circuit boards and of solder masks.

The mixture according to the invention is suitable also for the manufacture of offset printing plates, for example using aluminum, steel or chromium as support materials, which plates 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 the print run.

The examples which follow illustrate particular embodiments of the mixture according to the invention. Unless otherwise indicated, percentages and quantity ratios are to be understood as units by weight. The quantities in the formulations are given in parts by weight (p.b.w.).

Example 1

Coating solutions were prepared from:

52 p.b.w. of one of the following terpolymers

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- a) N-butoxymethyl-methacrylamide, methacrylic acid, hexylmethacrylate (25:25:50),
- b) N-butoxymethyl methacrylamide, methacrylic acid, decyl methacrylate (23:30:47),
- c) N-butoxymethyl methacrylamide, acrylic acid, hexyl methacrylate (47:18:35) or
- d) (comparison) styrene, methacrylic acid, hexyl methacrylate (10:30:60),

17.6 p.b.w. of polyethylene glycol-400-dimethacrylate,

4 p.b.w. of hexamethoxymethyl melamine

0.8 p.b.w. of 9-phenyl acridine,

0.04 p.b.w. of a blue azo dyestuff obtained by coupling 2,4-dinitro-6-chloro-benzene diazonium salt with 2-methoxy-5-acetyl-amino-N,N-diethyl aniline, and

0.12 p.b.w. of 1,4-bis-(4-tert.butoxy-phenylamino)-5,8-dihydroxyanthraquinone, in

90 p.b.w. of butanone and

50 p.b.w. of ethanol.

Each of these solutions was coated onto a 25 μm thick biaxially oriented thermoset polyethylene terephthalate film by means of a coating apparatus. After passing through a drying zone the resist layers had a thickness of 100 μm each and were covered with a polypropylene film. The dry resist films thus produced were then cut, by means of a slit, into manageably sized resist rolls having a width of 30 cm and a web length of 50 m.

After the top films had been stripped off, the resist layers were laminated, by means of a customary laminating appliance, to a phenoplast laminate board clad with a 35 μm thick copper foil and were exposed for 20 seconds using a commercially available exposure device (5 kW metal halide lamp). The original employed was a 13-step exposure wedge having density increments of 0.15. Thereafter, the plates were developed with a 0.8 % strength soda solution in a spray processor.

The following table indicates the development times t and the number of fully crosslinked wedge steps; the numbers in parentheses give the total number including the ghost steps.

	a)	b)	c)	d) (comparison)
Wedge steps	10 (11)	9 (10)	6 (8)	8
t (seconds)	110	200	105	105

For soldering tests, test boards of rigid epoxy glass fabric with about 65 μm thick conducting paths having a tinned surface and plated-through holes were used. The widths and mutual distances of the conducting paths were between 200 and 1,000 μm , the hole diameters were 0.6 to 4 mm.

The solder resist layers described above were laminated onto these boards at 115 °C, using a commercially available laminating device.

The boards were then exposed for 20 seconds through an original which covered the pads to be soldered, developed with a 0.8 % strength soda solution and blown dry. Subsequently, the printed circuit boards treated in this way were cured during 60 minutes in a drying cabinet at 150 °C. Thereafter, the cooled-down boards were wetted with the soldering flux TL 33-16, produced by Alpha Grillo, and then passed, at a speed of 1 m/min, through a commercially available wave soldering bath having a temperature of 250 °C.

None of the soldered boards showed any signs of chipping-off. No tin remainders were left on the solder resist areas of boards a), b) and c), whereas so-called "tin cobwebs" were clearly visible on layer d).

After soldering, each board was cleaned for one minute in a mixture composed of 65 percent by weight of 1,1,2-trichloro-1,2,2-trifluoroethane and 35 percent by weight

of 2-propanol, and for 1 minute in pure 1,1,2-trichloro-1,2,2-trifluoroethane in an ultrasonic bath.

Before and after the solvent treatment, the respective hardness of the solder mask was determined.

The hardness tests were performed by means of the indentation hardness test according to Buchholz, which is described in DIN 53 153.

In this test, the penetration of a disk knife, under a specified load, into the layer to be tested, is measured by means of a suitable apparatus. The softer the material to be tested, the longer is the indentation. The hardness number then corresponds to

$$\frac{100}{\text{indentation length (mm)}}$$

Furthermore, the ratio of the hardness values determined before and after the solvent treatment is a measure for the softening or swelling behavior of the layer under the influence of organic solvents.

Additionally, portions of the soldered boards were immersed in ethanol for 24 hours, in order to test their resistance to solvents and thus their degree of curing.

The results are compiled in the table below:

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	a)	b)	c)	d) (comparison)
Buchholz hard- ness before/after cleaning	80/79	82/83	not tested	72/48
After 24 hours in ethanol	solder mask on printed circuit board unchanged			dyestuff dissolved out of solder mask

Example 2

The following coating solutions were prepared:

52 p.b.w. of one of the following terpolymers:

- a) N-butoxymethyl methacrylamide, acrylic acid, hexamethacrylate (sic) (25:22:52)
- b) N-butoxymethyl methacrylamide, methacrylic acid, ethyl acrylate (31:32:37)

4 p.b.w. of an elastomeric reaction product of glycidyl methacrylate, adipic acid and an oligomeric diisocyanate, obtained by reacting tolylene diisocyanate with a polytetramethylene ether diol (see DE-A No. 30 36 694)

17.6 p.b.w. of polyethylene glycol-400-dimethacrylate,

4 p.b.w. of hexamethoxymethyl melamine,

0.8 p.b.w. of 9-phenyl acridine,

0.04 p.b.w. of the blue dyestuff described in Example 1, and

0.12 p.b.w. of the anthraquinone dyestuff described in Example 1, in

80 p.b.w. of butanone and

50 p.b.w. of ethanol.

As described in Example 1, 100 μ m thick solder resist layers were prepared from these solutions. The layers were processed as described in Example 1. The results are compiled in the table below:

	a)	b)
Exposure time (sec)	20	20
Wedge steps	6 (8)	7 (10)
t (sec)	65	120
24 hours in ethanol	Solder mask on printed circuit board unchanged	

Example 3

The following coating solutions were employed as described in Example 1:

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a)

- 39 p.b.w. of a styrene/methacrylic acid/hexyl methacrylate terpolymer (10:30:60)
- 13 p.b.w. of a N-methoxymethyl methacrylamide/hexyl methacrylate copolymer (50:50),
- 8 p.b.w. of the elastomer described in Example 2,
- 22 p.b.w. of polyethylene glycol-400-dimethacrylate,
- 5 p.b.w. of hexamethoxymethyl melamine,
- 1 p.b.w. of 9-phenylacridine,
- 0.05 p.b.w. of the blue dyestuff described in Example 1, and
- 0.15 p.b.w. of the anthraquinone dyestuff described in Example 1, in
- 210 p.b.w. of butanone.

b)

- 52 p.b.w. of a N-butoxymethyl methacrylamide/methacrylic acid/Hexyl methacrylate terpolymer (36:28:36)
- 6.4 p.b.w. of the elastomer described in Example 2,

17.6 p.b.w. of polyethylene glycol-400-dimethacrylate,

4 p.b.w. of hexamethoxymethyl melamine;

0.8 p.b.w. of 9-phenylacridine

0.04 p.b.w. of the blue dyestuff described in Example 1, and

0.12 p.b.w. of the anthraquinone dyestuff described in Example 1, in

90 p.b.w. of butanone and

70 p.b.w. of ethanol.

Here, too, solder masks possessing a very good solvent resistance were obtained, without any tin cobwebs being left after soldering. The results are compiled in the table which follows:

	a)	b)
Exposure time (sec)	20	20
Wedge steps	7 (9)	9
t (sec)	120	80
Buchholz hardness	59/60	86/79
before/after cleaning		
24 hours in ethanol	Solder mask on printed circuit board unchanged	

Example 4

A coating solution was prepared from:

- 2 p.b.w. of the terpolymer described in Example 1a,
- 2 p.b.w. of a diurethane prepared from 2 moles of glycerol dimethacrylate and 1 mole of hexamethylene diisocyanate,
- 0.7 p.b.w. of 9-phenylacridine, and
- 0.07 p.b.w. of a blue azo dyestuff obtained by coupling 2,4-dinitro-6-chloro-benzene diazonium salt with 2-methoxy-5-acetylamino-N-cyanoethyl-N-hydroxyethyl aniline, in
- 30 p.b.w. of butanone,
- 12 p.b.w. of butyl acetate and
- 12 p.b.w. of ethylene glycol monomethyl ether.

Electrochemically roughened and anodically oxidized aluminum which had an oxide layer of 2 g/m² and which had been pretreated with an aqueous solution of polyvinylphosphonic acid was spin-coated with this solution, in such a manner that a dry layer weight of 4 g/m² was obtained. Then the plate was provided with a top layer of polyvinyl alcohol, which had a weight of 4 g/m². The printing plate was cut into two, and the two halves were

exposed for 2 seconds by means of a 5 kW metal halide lamp, under a 13-step continuous tone wedge and halftone step wedges having 60 and 120 lines/cm, respectively.

Thereafter, development was performed using a developer of the following composition:

3.0 p.b.w. of sodium metasilicate x 9 H₂O

0.03 p.b.w. of a non-ionogenic surfactant (coconut fatty alcohol polyoxyethylene ether having about 8 oxyethylene units),

0.003 p.b.w. of an anti-foam agent, and

96.967 p.b.w of deionized water.

5 (6) fully cross-linked wedge steps were obtained. After the development, one of the two halves of the lithographic printing plate was baked for 5 minutes at 230 °C.

Comparative printing tests resulted in a higher print run of the baked printing plate.

Example 5

A phenoplast laminate board clad with a 35 μ m thick copper foil was spin-coated with the coating solution described in Example 4, in a way such that a dry layer weight of 7 g/m² was obtained.

The plate was exposed for 40 seconds through a line original having line widths and distances of down to 80 μ m and then developed for 60 seconds with 0.8 % strength sodium carbonate solution. Thereafter, etching was performed with ammoniacal copper chloride solution (pH 8.5) at 48 °C and the resist stencil was removed with a 5 % strength aqueous solution of KOH at 50 °C.

The copper structures were perfectly reproduced.

Example 6

A biaxially oriented and thermoset, 25 μ m thick polyethylene terephthalate film was spin-coated with a solution of

13 p.b.w. of the terpolymer described in Example 1a,

6.4 p.b.w. of polyethylene glycol-400-dimethacrylate,

0.2 p.b.w. of 9-phenylacridine,

0.01 p.b.w. of azo dyestuff 5-nitro-2-[2-methyl-4-(N-ethyl-N-cyanoethyl)amino-phenylazo-]benz-thiazole, and

0.02 p.b.w. of the blue dyestuff described in Example 4, in

18 p.b.w. of butanone and

18 p.b.w. of ethanol,

such that a dry layer weight of 40 g/m^2 was obtained after drying at 100°C .

In a commercially available laminating device, the dry resist film thus prepared was laminated, at 120°C , onto a preheated phenoplast laminate board clad with a $35 \text{ }\mu\text{m}$ thick copper foil and exposed for 4 seconds in a commercially available exposing apparatus. The original used was a line original having line widths and distances of down to $80 \text{ }\mu\text{m}$.

After the exposure, the polyester film was peeled off and the layer was developed with a 0.8 % strength solution of sodium carbonate for 90 seconds in a spray developing apparatus. Then the board was rinsed for 30 seconds with tap water, etched for 30 seconds in a 15 % strength ammonium peroxydisulfate solution, rinsed again with water, dipped for 30 seconds into 10 % strength sulfuric acid and then electroplated in the following electrolyte baths:

1. 50 minutes in a copper electrolyte bath from Messrs. Schloetter, Geislingen/Steige, "Glanz kupfer-Bad PC" (Bright Copper Bath PC) type
Current density: 2.5 A/dm^2
Metal build-up: about $25 \text{ }\mu\text{m}$
Temperature: room temperature

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2. For 15 minutes in a lead tin bath LA from Messrs.
Schloetter, Geislingen/Steige,
Current density: 2 A/dm²
Metal build-up: 15 /um
Temperature: room temperature

The board did not display any undercuttings or damage.

It was then possible to decoat the board in a 5 %
strength solution of KOH at 50 °C and to remove the
bared copper by etching in customary etching media.

Example 7

In analogy with Example 6, a resist layer was prepared
using the following coating solution:

- 6.5 p.b.w. of the terpolymer described in Example 1a,
5.6 p.b.w. of a reaction product obtained from 1 mole
of trimethyl hexamethylene diisocyanate
and 2 moles of hydroxyethyl methacrylate,
0.2 p.b.w. of 9-phenylacridine, and
0.035 p.b.w. of the blue dyestuff described in Example
4, in
14 p.b.w. of butanone and

9 p.b.w. of ethanol.

Exposure, development and electroplating were performed as described in Example 6.

This plate did not display any undercuttings or damage, either.



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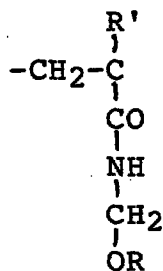
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Claims:

1. A radiation-polymerizable mixture which contains

- a) a compound which has at least two terminal ethylenically unsaturated groups and which can form a cross-linked polymer by means of chain polymerization by addition, initiated by free radicals,
- b) a polymeric binder, and
- c) a polymerization initiator which can be activated by radiation,

characterized in that it contains, as a binder, a copolymer with units of the formula



R' denoting a hydrogen atom or a methyl group, and R being a hydrogen atom, a lower alkyl group, acyl group or hydroxyalkyl group.



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2. A radiation-polymerizable mixture as claimed in Claim 1, wherein the copolymer furthermore includes units with lateral carboxyl groups.
3. A radiation-polymerizable mixture as claimed in Claim 2, wherein the copolymer is a terpolymer of
 - a) methacrylic acid or acrylic acid,
 - b) an acryl- or methacrylamide with ROCH_2 -groups at the nitrogen, and
 - c) an alkyl acrylate or alkyl methacrylate.
4. A radiation-polymerizable mixture as claimed in Claim 3, wherein the terpolymer comprises 10 to 35 per cent by weight of units formed by acrylic or methacrylic acid, 15 to 60 per cent by weight of units formed by substituted acryl- or methacryl- amide and 25 to 75 per cent by weight of units formed by an alkyl acrylate or alkyl methacrylate.
5. A radiation-polymerizable mixture as claimed in Claim 4, wherein component c) is an alkyl methacrylate which has 4 to 12 carbon atoms in its alkyl group.
6. A radiation-polymerizable mixture as claimed in Claim 1, wherein 40 to 90 per cent by weight of binder, 10 to 60 per cent by weight of polymerizable compound and 0.01 to 10 per cent by weight of initiator are contained.



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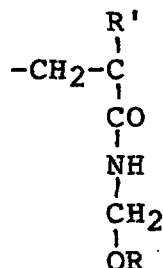
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7. A radiation-polymerizable mixture as claimed in Claim 1, wherein additionally a low molecular weight compound is contained which at an elevated temperature reacts with cross-linking with the binder or the polymerizable compound.
8. A radiation-polymerizable mixture as claimed in Claim 5, wherein the terpolymer is a copolymer of methacrylic acid, N-butoxymethyl methacrylamide and hexyl methacrylate.
9. A radiation-polymerizable copying material comprised of a flexible, transparent temporary layer support and a transferable thermoplastic radiation-polymerizable layer which contains
 - a) a compound which has at least two terminal ethylenically unsaturated groups and which can form a cross-linked polymer by means of chain polymerization by addition, initiated by free radicals,
 - b) a polymeric binder, and
 - c) a polymerization initiator which can be activated by radiation,characterized in that the layer contains, as a binder, a copolymer with units of the formula



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R' denoting a hydrogen atom or a methyl group, and R being a hydrogen atom, a lower alkyl group, acyl group or hydroxyalkyl group.

10. A process for producing a solder mask, in which a dry solid photopolymerizable photoresist layer, containing as the essential constituents

- a) a compound which has at least two terminal ethylenically unsaturated groups and which can form a cross-linked polymer by means of chain polymerization by addition, initiated by free radicals,
- b) a polymeric binder, and
- c) a polymerization initiator which can be activated by radiation,

and being present on a transparent temporary layer support, is laminated onto the surface of a printed circuit by applying pressure and heat, is exposed imagewise with the exception of the solder pads, the temporary layer support is peeled off, the unexposed layer areas are

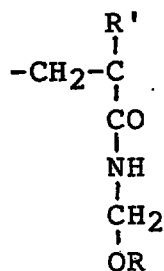


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washed out with a developer, and the resulting solder mask is heated to an elevated temperature, characterized in that the photoresist layer contains, as a binder, a copolymer with units of the formula



R' denoting a hydrogen atom or a methyl group, and R being a hydrogen atom, a lower alkyl group, acyl group or hydroxyalkyl group.