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DESCRIPTION

The 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 crosslinked polymer by means of chain polymerization by addition which is 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, for the production of soldering stop masks.

One- and two-faced, but above all through-hole plated printed circuit boards are provided with a soldering stop mask before they are soldered. The application of such masks only leaves solder 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 heat-sensitive components employed in equipping the printed circuit boards are not damaged during the soldering. Last but not least soldering stop 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

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

To satisfy these quite complex requirements various processes and products in various presentation 5 forms have been used in the past.

It is clear from the above expositions that soldering stop masks must have a pattern which is oriented according to the given conducting paths. To apply soldering stop masks by the screen printing technique is a 10 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 15 printing process, come up against a limit which is inherent in the system, namely when the distances between the conducting paths are reduced, so that the relatively coarse image structures of the screen print can no longer cope with microconductor technology.

20 In recent years soldering stop masks have therefore been produced to an increasing extent by the photoresist technique. As in the production of printed circuits thermoplastic photopolymerizable layers are laminated here by means of pressure and heat to the printed 25 circuit board and hardened by imagewise exposure at those places where the printed circuit board is to be covered. The soldering stop mask is obtained by washing away the unexposed parts of the layer. This process makes possible higher image resolutions than the screen

(10)

printing process.

Suitable materials of this type have been described, for example, in DE-A-27 47 947. They are

- 5 photopolymerizable 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").

- 10 Finally, EP-A-2,040 describes a light-hardenable material for the same purpose in which the light-sensitive compounds used are light-sensitive epoxy resins which are not described in more detail.

- Photopolymerizable mixtures known and used for
- 15 this purpose are transferred dry and with heating onto the printed circuit board to be marked and they must therefore necessarily be thermoplastic. However, for use as soldering stop masks this property is disadvantageous since they must withstand without decomposition
- 20 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 areas by crosslinking polymerization, and this light-hardening can be further enhanced in a known way
- 25 by re-exposure of the developed image stencil. However, a basic softening tendency on heating of all known photopolymerizable layers remains.

It was the object of the invention to propose photopolymerizable mixtures which are suitable for the

production of photoresist layers which can be transferred dry, and which have the thermoplasticity required for the transfer, but which have, in the exposed and developed state, the resistance required under the conditions of
5 the soldering process.

According to the invention, a radiation-polymerizable mixture 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
10 chain polymerization by addition which is initiated by free radicals, b) a polymeric binder and c) a polymerization initiator which can be activated by radiation.

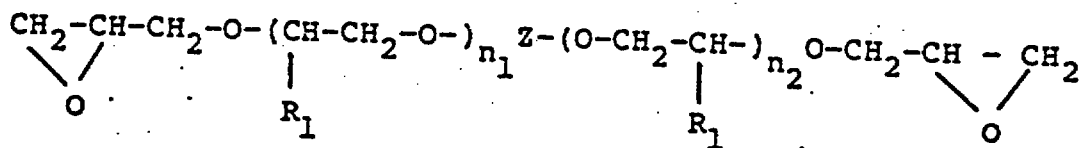
The mixture according to the invention contains in addition d) a compound which has two epoxy groups in
15 the molecule and a molecular weight of no more than 1,500. preferably less than 1,000.

Any form of electromagnetic radiation, the energy of which is sufficient to excite a suitable polymerization initiator, is possible for use as an actinic radiation to
20 which the mixture according to the invention is sensitive. Particularly suitable for this purpose are visible and ultraviolet 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
25 preferred.

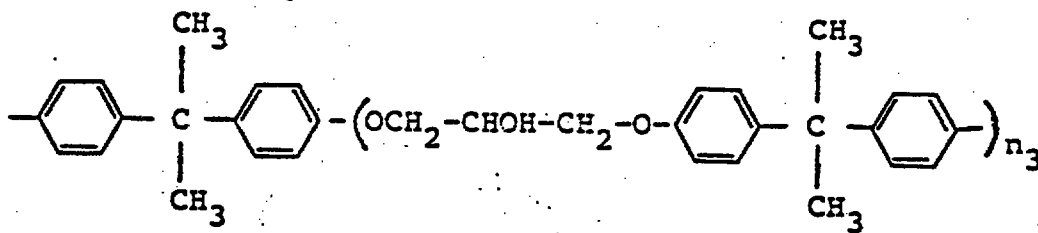
Suitable bis-epoxides are in particular bis-glycidyl ethers of dihydric alcohols and phenols, for example of bisphenol A, of polyethylene glycol and polypropylene glycol ethers of bisphenol A, of butane-1,4-diol, hexane-

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Bis-epoxides of the general formula



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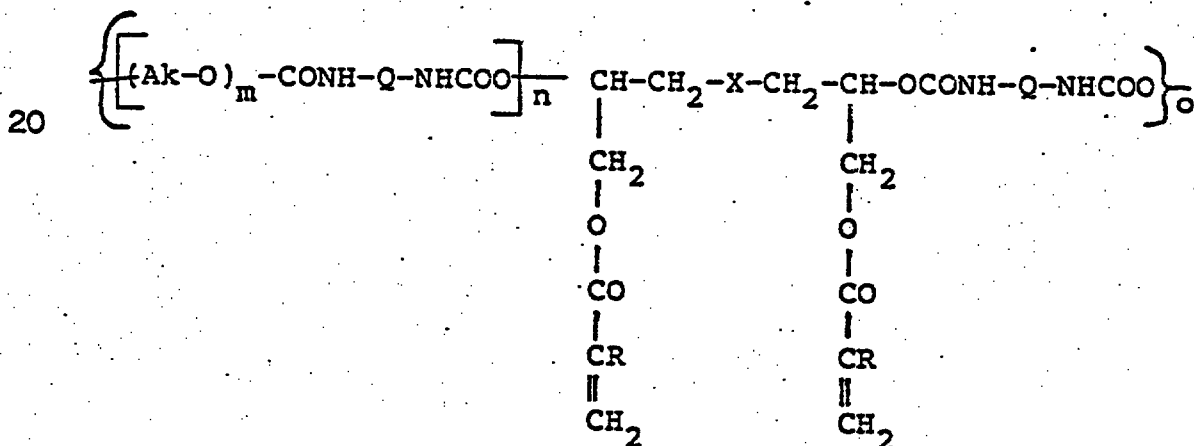
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hydroxyl groups. Examples of suitable polyhydric alcohols are ethylene glycol, propylene glycol, butane-1,4-diol, butane-1,3-diol, diethylene glycol, triethylene glycol, polyethylene glycols having molecular weights from about 200 to 1000, neopentylglycol, trimethylolethane, trimethylolpropane, pentaerythritol and bisphenol A bis-hydroxyethyl ether. 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 containing such urethane groups are described in US-A-4,088,498.

Mixtures of various monomers are advantageously used. Here it has proved particularly suitable to combine monomers of the abovementioned type with high-molecular urethanes which comprise groups of the general formula



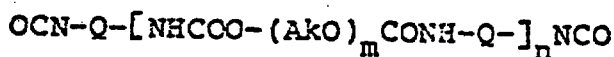
in which Q is a bivalent mononuclear or binuclear aromatic radical which is unsubstituted or substituted by

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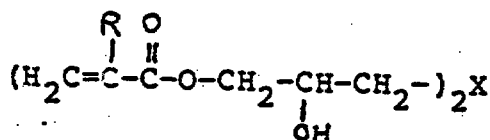
lower alkyl groups and which can contain a lower alkylene group as a connecting member, X is one of the groups -O-Ph-X'-Ph-O- and -OOC-(CH₂)_y-COO-.

- 5 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, 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 of the formula



- 15 with bis-acrylic acid ester diols of the formula



The preparation and use of these compounds has been described in EP-A-48,913.

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

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

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 polymerizable compounds is in general between 20 and 50, preferably 25 to 45, % by weight, relative to the non-volatile constituents of the mixture. Of this amount 2 to 20, preferably 5 to 10, % by weight, can be composed of polyurethanes of the general formula given above.

The mixtures according to the invention also contain a polymeric, preferably saturated, binder. Water-insoluble binders which are soluble or at least swellable in aqueous-alkaline solutions are preferably used. The binders can contain, as groups which impart solubility in alkali, phosphonic acid, sulfonic acid, sulfonamide, carboxylic acid anhydride and, preferably, carboxyl groups. Preferred binders are copolymers 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, relative to the non-volatile constituents of the mixture.

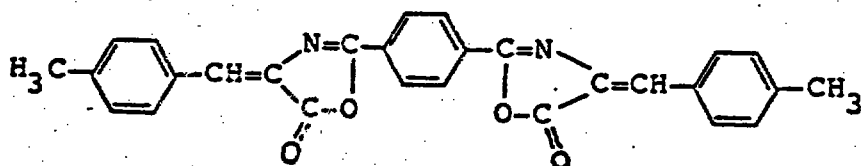
A large number of substances can be used as photoinitiators in the mixture according to the invention. Examples are acridine derivatives, for example 9-phenylacridine, 9-p-methoxyphenylacridine, 9-acetylamino-

acridine or benzo(a)acridine; phenazine derivatives, for example 9,10-dimethylbenzo(a)phenazine, 9-methylbenzo(a)-phenazine or 10-methoxybenzo(a)phenazine, quinoxaline derivatives, for example 6,4',4"-trimethoxy-2,3-diphenyl-5 quinoxaline or 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, preferably 0.05 to 2, % by weight.

10 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 at least one dyestuff changes its colour on irradiation and is destroyed at temperatures above 200°C, ie, becomes colorless. 15 The other dyestuff should be able to survive not only irradiation but also temperatures above 200°C without change. It should make the soldering stop mask clearly visible during soldering and thereafter.

20 Suitable examples of dyestuffs which change color on exposure are triphenylmethane dyestuffs and certain azo dyestuffs, as described in DE-A-28 07 933 (= US-A-4,241,166).

Suitable light- and heat-resistant dyestuffs are 25 oxazolone dyestuffs, for example a dyestuff of the formula



17

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

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 and plasticizers.

The mixture according to the invention is processed in a known way to give a dry resist material. In general a solution of the mixture in a solvent is applied to a suitable layer 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.

20 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 pulled off and the soldering stop 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 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, preferably aqueous-alkaline, solutions, for example of alkali metal phosphates, alkali metal carbon-
5 ates 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 may be added.

Fully prepared printed circuit boards, covered by
10 the process steps just described, must then be subjected to a heat treatment before the soldering process. It is assumed that in this treatment parts of the binder react with the epoxide to give an interpenetrating network which is responsible for the good mechanical, thermal and chemi-
15 cal properties of the soldering stop masks. This thermal treatment is in general carried out between 80°C and 150°C for approximate treatment times of 10 to 40 minutes.

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

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

The soldering fluxes 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.

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

The mixtures according to the invention produce soldering stop 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
10 exposed and post-cured state. The photopolymerizable 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
15 above 100 μm the exposed layers can be developed acceptably and completely by means of aqueous-alkaline solutions.

The exposed and developed layers can be thermally cured without excessively impairing the flexibility of the mask or its adhesion to the substrate and without
20 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. Already after exposure of the resist layer a high-contrast image is obtained in the layer. The
25 light-cured mask retains its high-contrast coloration even after the soldering. Soldering stop masks obtained from the mixtures according to the invention are particularly suitable for protecting sensitive electronic conductor structures from atmospheric attack in an effective and

permanent manner.

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. Parts by weight are related to parts by volume as the g is related to the ml.

Example 1

A solution was prepared from:

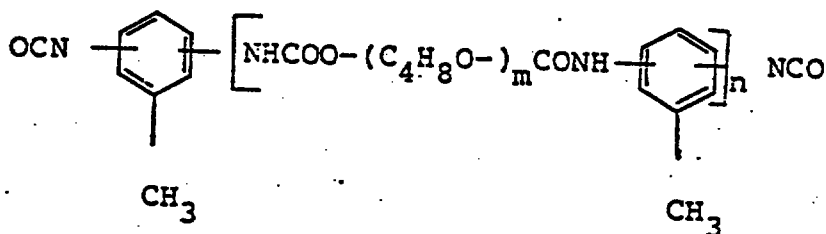
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| 10 | 26 | parts by weight of a terpolymer from n-hexyl methacrylate, methacrylic acid and styrene (60:30:10) having an average molecular weight of about 35,000 and an acid number of 195. |
| 12.8 | | parts by weight of polyethylene glycol-400-dimethacrylate. |
| 3.2 | | parts by weight of the elastomer described below. |
| 1.2 | | parts by weight of 2,2-bis-(4-glycidoxy-phenyl)-propane. |
| 0.2 | | part by weight of 9-phenyl-acridine. |
| 20 | 0.02 | part by weight of 2,4,6-trinitro-2'-acetylamino-4'-diethylamino-5'-methyl-azobenzene and |
| 0.06 | | part by weight of 1,4-bis-(4-tert.-butoxy-phenyl-amino)-anthraquinone in |
| 107.5 | | parts by weight of butanone and |
| 25 | 6.0 | parts by weight of ethanol. |

The elastomer used was prepared as follows:

A. In a 1 liter four-necked flask, equipped with a stirrer, 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 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-
 5 ethylammonium chloride. After about 2 hours a clear solution was obtained which was kept at 80°C for a further 14 hours. After this time the content of free glycidyl methacrylate was less than 0.5 %.

B. 143 parts by weight of an oligomeric diisocyanate of
 10 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
 15 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
 20 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
 25 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. Dis-
5 tilling 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
10 in dimethylformamide at 25°C).

A 110 cm wide web of a biaxially stretched and heat-set 25 µm thick polyethylene terephthalate film was coated in a continuous manner with a solution of this composition by means of a slot die. After passing through
15 a drying zone the resist layer had a thickness of 70 µm and it was covered with a polypropylene film. The dry resist film thus produced was stored on a full width roll. The full width roll was then cut, by means of a
slitter, into manageably sized resist rolls having a width
20 of 45 cm and a web length of 50 m. By selecting an optimal winding tension it was ensured that layer upon layer of the roll was positioned evenly over the support core and that the roll did not slide off laterally, ie. did not telescope.

25 Even after months of storage at 20°C the cut edges of these rolls were unchanged and completely free of resist outflows which lead to sticking. The cut edges were still tack-free after storage for more than three weeks at 40°C in a drying cabinet.

Epoxy resin glass fabrics of size 24 x 36 cm and backed with a 35 μm thick copper foil were used in the laminating experiments. A conductor diagram having conducting paths' widths of down to 200 μm and conducting paths' distances of down to 180 μm was produced on these boards in a known manner by exposure by means of a commercially available negative dry resist and an exposure mask featuring a circuit diagram. The conducting paths, laid bare after the developing, were then reinforced by means of electroplating as follows:

1. 40 minutes in a copper electrolyte bath from Messrs. Schlötter, Geislingen/Steige, of the [®] Glanzkupfer-Bad (Bright Copper Bath) type

Current density 2.5 A/dm²

15 Metal coating about 20 μm

2. 15 minutes in a lead tin bath from Messrs. Schlötter, Geislingen/Steige, of the [®] LA type

Current density 1.0 A/dm²

Metal coating 10 μm

20 After stripping off the photoresist stencil and etching away the base copper, test boards having approximately 65 μm thick conducting paths with a tinned surface which are referred to as "Sn boards" in the text below, were obtained.

In a further experiment boards were produced on which only the additional copper reinforcement was carried out and the base copper was etched away. These boards are referred to in the text below as "Cu boards".

The 70 μm thick soldering stop resist layer was laminated at 120°C by means of a commercially available

laminating device onto these boards.

The boards were then exposed, through an exposure original which covered the pads and holes to be soldered, for 12 seconds by means of a commercially available exposure device having a 5 kW metal halide light, then developed in a commercially available spray processor for 2 minutes with a 0.8 % strength sodium carbonate solution and blown dry. The printed circuit boards thus prepared were then cured for 20 minutes at 120°C in a drying cabinet. The cooled boards were then wetted with the water-soluble soldering flux[®] ALPHA 709 from Messrs. Alpha Grillo and then passed with a speed of 0.25 m/min through a commercially available flow soldering bath at 240°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 soldering stop layer, and ground sections prepared showed neither defects nor inclusions of air at the upper and lower edges of the conducting paths.

Wrinkled surfaces ("orange peels") formed on the soldering stop mask in the case of the Sn boards, due to a fusing of the tin surface during soldering. However, even in these cases a perfectly safe and acceptable adhesion of the soldering stop mask was obtained.

The Cu boards were treated as follows:

The steps laminating, exposing, developing and post-curing were carried out in the same way as above. The laid-bare holes of the printed circuit boards were then provided with a thin lead-tin layer with the aid of

the so-called hot-air leveling process. In this hot-air leveling or in the hot tinning the printed circuit boards were immersed into a hot lead-tin bath at 250°C and blown dry with hot air at the same temperature during the extracting. During this blowing, holes which might have become sealed were opened up. A wafer-thin lead-tin layer remained in the holes and around them as a protection from corrosion. After this treatment the soldering stop mask showed no impairment.

10 Example 2

The solution described in Example 1 was used in an analogous manner to produce a 100 μ m thick resist layer, laminated onto printed circuit boards, exposed, developed and post-cured. The boards thus prepared did not have wrinkly surfaces after soldering.

Example 3

The procedure used in Example 1 was followed, but 3.2 parts by weight of the elastomer described below were used instead of the elastomer used there. This solution was used to produce as in Example 1 a dry resist film, which was then laminated, exposed and developed. In all these processing steps virtually the same results as in Example 1 were obtained. The elastomeric polyurethane used was prepared as follows:

25 177 parts by weight of the oligomeric diisocyanate given under B in Example 1 were initially introduced in 250 parts by volume of methyl ethyl ketone with the addition of 1 part by weight of 1,4-benzoquinone, 0.05 part by weight of iron(III) acetylacetonate and 2 parts

(26)

by volume of a 1 % strength solution of triethylamine in methyl ethyl ketone, into a 1 liter three-necked flask equipped with a thermometer, dropping funnel, condenser, drying tube, and magnetic stirrer.

5 After this solution had been heated to 60°C, a solution of 45.3 parts by weight of 2,2-bis-[4-(2-methacryloyloxypropoxy)-phenyl]-propane, a commercial product (calculated C: 67.97 %, observed C: 67.9 %; calculated H: 7.03, observed H: 7.1; calculated OH number: 219, observed OH
10 number: 216; calculated Br number: 62.5, observed Br number: 65), in 150 parts by volume of methyl ethyl ketone was added dropwise in the course of 30 minutes, and the reaction product was maintained for 2 hours at 65 - 70°C; 5 parts by volume of alcohol were then added. After the
15 solvent had been distilled off, a dry, elastic rubber, soluble in, and recoverable from, ethyl ketone and other organic solvents, such as toluene and tetrahydrofuran, was obtained. The product had a reduced specific viscosity of 0.68 dl/g (measured on a
20 1 % strength solution of dimethylformamide at 25°C).

Examples 4 to 7

In the table which follows four examples are summarized which do not differ from Examples 1 and 2 in the techniques used to carry them out, but there are
25 differences in the recipes used. Where these cause the resist to have differing properties this is briefly noted in the table. The quantities given are in parts by weight. The binder used was in all four examples
26 parts by weight of the terpolymer indicated in

Example 1. Furthermore, the dyestuffs indicated in
Example 1 were added in the same quantities as there.

(27)

Ex-ample	Low-molecular monomer	Quan-tity	Polyurethane monomer	Quan-tity	Bis-epoxide	Quan-tity	9-Phenyl-acridine	Remarks
4	Bis-urethane dimethacrylate*)	18	as Example 1	3.2	as Example 1	1.2	0.2	good adhesion to metal
5	Polypropylene glycol dimethylacrylate	14	"	3.2	"	1.2	0.2	comparable to Example 1 high light sensitivity
6	Polyethylene glycol 400 dimethacrylate	12.8	"	3.2	**)	1.5	0.2	flexible resist layer orange peel effect
7	"	12.8	"	3.2	as Example 1	1.2	0.1	long shelf life slightly lower light sensitivity

*) Prepared from 1 mole of 2,2,4-trimethylhexamethylene diisocyanate and 2 moles of β -hydroxyethylmethacrylate

**) Reaction product from bisphenol A and epichlorohydrin, having an epoxy equivalent weight of 450

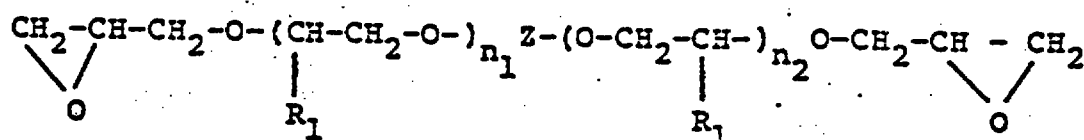
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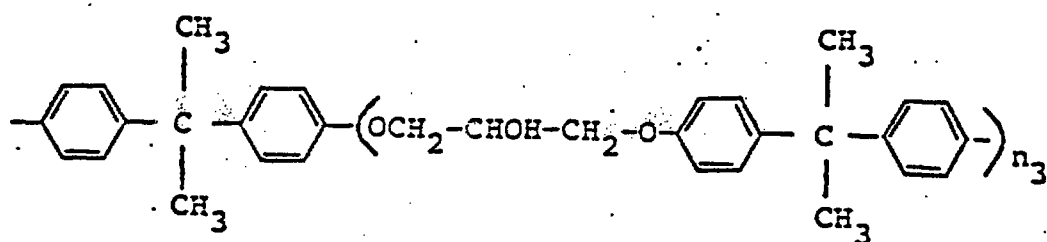
PATENT CLAIMS:

1. A radiation-polymerizable mixture containing
 - 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,
 - b) a polymeric binder and
 - c) a polymerization initiator which can be activated by radiation,
 characterized in that it contains in addition
 - d) a compound which has two epoxy groups in the molecule and a molecular weight of no more than 1,500.
2. A radiation-polymerizable mixture, which contains the compound having two epoxy groups in a quantity of 1.5 to 10 % by weight.
3. A radiation-polymerizable mixture as claimed in claim 1, wherein the compound having two epoxy groups is a bis-glycidyl ether of a dihydric alcohol or phenol.
4. A radiation-polymerizable mixture as claimed in claim 3, wherein the compound having two epoxy groups corresponds to the general formula



in which Z denotes an alkylene or hydroxyalkylene group having 2 to 6 carbon atoms or a group

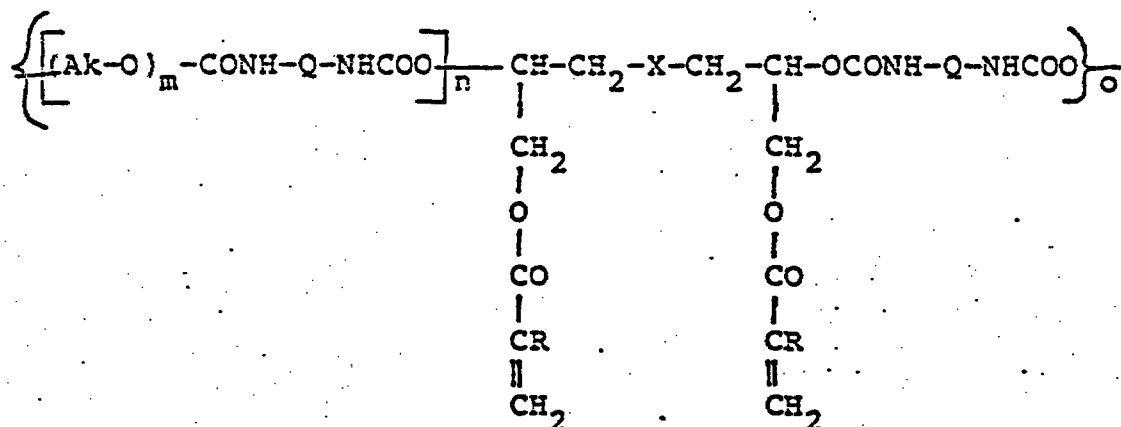
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R_1 denotes a hydrogen atom or a methyl group, n_1 and n_2 denote numbers from 0 to 10 and n_3 denotes 0 or a number from 1 to 4.

5. A radiation-polymerizable mixture as claimed in claim 1, wherein the polymerizable compound contains acrylate or methacrylate groups as unsaturated groups.

6. A radiation-polymerizable mixture as claimed in claim 5, wherein the polymerizable compound used is a mixture of an acrylate or methacrylate of a dihydric or polyhydric primary alcohol and a polyurethane 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,

$\bar{X}$ is one of the groups $\text{---O---Ph---X'---Ph---O---}$ and $\text{---OOC---(CH}_2\text{)}_y\text{---COO---}$,

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, 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.

7. A radiation-polymerizable mixture as claimed in claim 1, wherein the polymeric binder is water-insoluble and soluble or at least swellable in aqueous-alkaline solutions.

8. A radiation-polymerizable mixture as claimed in claim 1, which additionally contains two dyestuffs of which one changes its color on irradiation and is destroyed at temperatures above 200°C with loss of color and the other is not changed on irradiation and at temperatures above 200°C.

9. A photopolymerizable copying material having a flexible transparent temporary support and a transferable thermoplastic photopolymerizable layer, containing

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,

b) a polymeric binder and

c) a photopolymerization initiator

characterized in that the layer additionally contains

d) a compound which has two epoxy groups in the molecule and a molecular weight of no more than 1,500.

