

The invention relates to a mixture which contains, as essential components,

- a) a compound which can undergo free radical polymerization, contains at least two terminal ethylenically unsaturated groups and has a boiling point of above 100°C under atmospheric pressure,
- b) a compound capable of initiating the polymerization of compound a) under the action of actinic radiation, and
- 10 c) a water-insoluble copolymer which is soluble in aqueous alkaline solutions.

Polymerizable mixtures of the stated type are known, and are used, inter alia, for the preparation of photopolymerizable printing plates and photoresist materials. A preferred field of use for such mixtures is the preparation of dry photoresist materials.

DE-A 20 64 080 describes mixtures of this type which contain, as binders, copolymers of methacrylic acid and alkyl methacrylates having at least 4 carbon atoms in the alkyl group, preferably terpolymers of methacrylic acid, methyl or ethyl methacrylate and an alkyl methacrylate having 4 to 15 carbon atoms in the alkyl group. These mixtures form flexible layers which adhere well but, when they are relatively thick, for example greater than 20 µm, tend to exhibit cold flow and, on prolonged storage in the form of coated, rolled up dry resist films, emerge at the edge and stick.

DE-A 23 63 806 describes similar mixtures which contain terpolymers of methacrylic acid, an alkyl methacrylate having at least 4 carbon atoms in the alkyl group and a further monomer whose associated homopolymer has a glass transition temperature of at least 80°C. Particular examples of such monomers are styrene, substituted styrenes and acrylonitrile. These mixtures have a considerably reduced cold flow but are completely

unsuitable, or can be used only to a limited extent, for certain applications, such as the tenting of holes in a base material, the so-called tenting technique. The tenting technique is being used to an increasing extent for the production of printed circuit boards. In processing according to the subtractive process, the drilled and brushed boards are chemically metallized in the holes and then reinforced over the entire surface, to the required thickness of the final layer, in an electrolytic copper-plating bath. The board is then laminated with a photoresist, after which it is exposed. During this procedure, the resist layer is cured in the areas of the wiring paths and soldering pads. The holes are covered on both sides by cured resist areas, which remain during development of the layer. The bared areas of the copper layer are etched away.

The tenting technique is also important for the covering of so-called holding or position holes. These are holes which have a diameter of up to 6 mm or more and are provided in the boards to permit handling during various treatment steps. In the semiadditive method, metal is deposited electrolytically in those areas not covered by the resist template. During this procedure, the position holes must also be covered since otherwise they would be narrowed by metal deposition and would therefore be rendered useless for further steps. The resist template is then removed, and the conductive copper underneath is etched away with an etching agent, the copper present in the holding holes and position holes also being removed.

The photoresist thus has to meet high requirements in the tenting technique. In the exposed state, it must be flexible and resistant to etching and plating baths and must be self-supporting in covering holes of 6 mm and more.

DE-B 25 17 656 describes other similar mixtures which contain, as a binder, a combination of two acidic polymers, under certain conditions one of these polymers being soluble in dilute aqueous sodium hydroxide

solution, and the other being insoluble. The methacrylic acid copolymers described therein are insoluble in the aqueous sodium hydroxide solution.

It was the object of the invention to propose
5 a radiation-polymerizable mixture which is suitable for the preparation of dry photoresist materials, can be developed readily and completely with aqueous alkaline solutions, forms layers having high flexibility and little cold flow, and is furthermore suitable for tenting
10 drilled holes of more than 1 mm diameter when laminated with drilled copper-clad boards of insulating material, and, in the form of the resulting self-supporting film after exposure, withstands further treatment steps, such as spray development, etching and electroplating, without
15 damage.

The present invention relates to a radiation-polymerizable mixture which contains, as essential components,

- a) a compound which can undergo free radical polymerization, contains at least two terminal ethylenically unsaturated groups and has a boiling point of above 100°C under atmospheric pressure,
- b) a compound which is capable of initiating the polymerization of compound a) under the action of actinic
25 radiation, and
- c) a water-insoluble copolymer which is soluble in aqueous alkaline solutions and comprises
 - c1) an α, β -unsaturated aliphatic carboxylic acid,
 - c2) an alkyl methacrylate having at least 4 carbon atoms
30 in the alkyl group and, if appropriate,
 - c3) a monomeric ethylenically unsaturated compound which is copolymerizable with c1) and c2) and whose homopolymer has a glass transition temperature of at least 80°C.

35 In the mixture according to the invention, the copolymer has a mean molecular weight in the range from about 50,000 to 200,000 and has been prepared by mass polymerization.

Layers which have good flexibility and toughness and can also be developed adequately in aqueous alkaline solutions are obtained using mixtures in which the copolymer has a molecular weight of 65,000 to 150,000.

5 The copolymer preferably contains, as the unsaturated aliphatic carboxylic acid c1, acrylic acid, methacrylic acid, crotonic acid, sorbic acid, maleic acid or itaconic acid, or half esters of the stated dicarboxylic acids. Methacrylic acid has proven very particularly
10 advantageous.

 The alkyl methacrylate c2 has preferably 4 to 20, in particular 6 to 12, carbon atoms in the alkyl group. Its homopolymer should preferably have a glass transition temperature of not more than 20°C.

15 Copolymers which consist only of the components c1 and c2 are suitable as binders when the unsaturated carboxylic acid c1 forms a homopolymer having a Tg value of above 80°C, preferably of at least 100°C. The glass transition temperature of these copolymers increases with
20 the acid content, even without the addition of a component c3. Copolymers having a higher glass transition temperature make it possible in turn to increase the monomer content in the layer without cold flow resulting. As a rule, these copolymers consisting of two components are preferred for many applications since they can be prepared
25 in a simple manner and their composition can be more easily reproduced than in the case of copolymers of three or more components.

 In many cases in which it is desired to vary the

glass transition temperature of the copolymer independently of its acid number, or in which other properties are to be influenced in a selective manner, it is, however, advantageous to employ a further monomer c3 which
5 forms homopolymers having Tg values of at least 80°C, preferably at least 100°C. Examples of suitable monomers of this type are:

Styrene or substituted styrenes, such as vinyltoluene, 4-chlorostyrene, propen-2-ylbenzene,
10 vinyl ethyl benzene or 2-methoxystyrene; vinyl-naphthalene or substituted vinyl-naphthalenes; vinyl heterocycles, such as N-vinylcarbazole, vinylpyridine or vinyloxazole; vinylcycloalkanes, such as vinylcyclohexane and 3,5-dimethylvinylcyclohexane; acrylamide, methacrylamide, N-substituted acrylamides and methacrylamides,
15 acrylonitrile, methacrylonitrile and aryl methacrylates.

Styrene or substituted styrenes, acrylamide, methacrylamide, acrylonitrile and methacrylonitrile are preferred, and styrene is particularly preferred.

20 It is of course also possible for several members of each of the components c1, c2 and c3 to be present.

The amount of component c1 is in general 20 to 60, preferably 30 to 55, mol %; the amount of component c2 is 25 to 80, preferably 35 to 65, mol %, depending on
25 the chain length, and the amount of component c3 is 0 to 30, preferably 3 to 20, mol %. The total amount of monomers with the associated Tg values of at least 80°C, i.e. of c1 and c3, is preferably at least 35 mol %. The acid number of the copolymer is preferably in the range of
30 170-250.

In order for the copolymers to meet the requirements in respect of processing in the dry resist method, it is necessary for their glass transition temperature Tg to be within a certain range. The Tg values of copoly-
35 mers can be calculated approximately from the Tg values of the homopolymers of the individual components, according to the following formula:

$$\frac{100}{Tg_{CP}} = \frac{m_A}{Tg_A} + \frac{m_B}{Tg_B} + \frac{m_C}{Tg_C} + \dots$$

In this formula,

T_{gcp} denotes the glass transition temperature of the copolymer (in Kelvin),
 $T_{gA} (B, C \dots)$ denotes the glass transition temperature of the homopolymer of A (B, C, etc.) (in Kelvin) and
5 $m_A (B, C \dots)$ denotes the amount of A (B, C, etc.) in the copolymer, in % by weight.

The T_g values of the copolymer in the mixture
10 according to the invention should in general be between 35 and 70°C, preferably between 40 and 60°C.

The copolymers are prepared by mass polymerization, i.e. without the addition of substantial amounts of solvents or dispersants, in the presence of a
15 polymerization initiator which forms free radicals.

The preparation is carried out in a conventional manner in flat containers, in order to permit better temperature monitoring. Peroxides or azo compounds, which form free radicals when heated, are used as initiators,
20 in a known manner. In order to obtain a uniform molecular weight distribution, it is advantageous to add a small amount of a chain regulator, for example a mercapto compound. It is also possible to add a small amount, for example less than 10% by weight of the monomer mixture,
25 of a solvent, for example water or a lower alcohol. The temperature can be between about 30 and 130°C.

The preparation process obviously has a substantial effect on the flexibility and resilience of the copolymer, i.e. the properties which are essential when
30 the mixture is used as a dry resist for the tenting technique.

The mixtures according to the invention contain polymerizable compounds having at least two terminal ethylenic double bonds. The polymerizable compounds
35 generally used are esters of acrylic or methacrylic acid with polyhydric, preferably primary, alcohols. 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 of about 200 to 1,000, neopentylglycol, trimethylolethane and -propane, pentaerythritol and oxyethylated bisphenol A derivatives. Bisacrylates and bismethacrylates which contain urethane groups and are obtained by reacting 1 mole of a diol with 2 moles of a diisocyanate and 2 moles of a hydroxyalkyl acrylate or methacrylate are particularly suitable. Monomers of this type which contain urethane groups are described in DE-A 28 22 190. Similar monomers are described in DE-A 30 48 502.

A large number of substances can be used as polymerization initiators which can be activated by radiation, in particular actinic light, and are present in the mixture according to the invention. Examples are benzoin and its derivatives, trichloromethyl-s-triazines, carbonylmethyleneheterocycles containing trihalomethyl groups, for example 2-(p-trichloromethylbenzoylmethylene)-3-ethylbenzothiazoline, acridine derivatives, for example 9-phenylacridine, 9-p-methoxyphenylacridine, 9-acetylaminoacridine or benz(a)acridine; phenazine derivatives, for example 9,10-dimethylbenz(a)phenazine or 10-methoxybenz(a)phenazine, quinoxaline derivatives, for example 6,4',4''-trimethoxy-2,3-diphenylquinoxaline or 4',4''-dimethoxy-2,3-diphenyl-5-azaquinoxaline, or quinazoline derivatives. The initiators are generally employed in an amount of 0.01 to 10, preferably 0.05 to 4, % by weight, relative to the non-volatile components of the mixture.

The mixture according to the invention contains in general 30 to 70, preferably 40 to 60, % by weight of binder and 30 to 70, preferably 40 to 60, % by weight of polymerizable compounds, relative in each case to the total amount of non-volatile components.

The mixture can contain, as further conventional components, polymerization inhibitors, hydrogen donors, sensitometric regulators, dyes, pigments, plasticizers and thermally activatable crosslinking agents.

Suitable actinic radiation to which the mixture according to the invention is sensitive is any electromagnetic radiation whose energy is sufficient to initiate

polymerization. Visible and ultraviolet light, X-rays and electron radiation are particularly suitable. Laser radiation in the visible and UV range can also be used. Short-wavelength visible and near UV light is preferred.

5 Examples of suitable bases for recording materials produced using the mixture according to the invention are aluminum, steel, zinc, copper or screens or plastic films of, for example, polyethylene terephthalate. The surface of the base can be pretreated chemically or mechanically
10 in order to adjust the adhesion of the layer to the appropriate level.

 The mixture according to the invention is preferably used as a dry transferable photoresist material, and has proven particularly useful when the tenting technique is employed.
15 For this purpose, it can be applied in a conventional manner, as a pre-produced, transferable dry resist film, onto the workpiece to be processed, for example onto a base material for printed circuit boards. In general, the dry resist material is prepared by applying a solution of
20 the mixture in a solvent onto a suitable base, for example a polyester film, and drying it. The thickness of the resist layer can be about 10 to 80, preferably 20 to 60, μm . The free surface of the layer is preferably covered with a cover film of, for example, polyethylene
25 or polypropylene. The ready-prepared laminate can be stored as a large roll and can be cut, as required, into resist rolls of any width.

 The films can be processed using apparatuses conventionally employed in dry resist technology. In a commercial laminating apparatus, the cover film is peeled off and the photoresist layer is laminated with drilled, copper-plated base material. The board prepared in this manner is then exposed to an image-bearing transparency, and developed in a conventional manner after the base
35 film has been removed.

 Suitable developers are aqueous, preferably aqueous alkaline, solutions, for example solutions of alkali metal phosphates, carbonates or silicates, to which, if required, small amounts, for example up to 10%

by weight, of water-miscible organic solvents or wetting agents can be added.

The mixtures according to the invention can be employed for a very large range of uses. They are particularly advantageously used in the form of a dry resist film for the production of resists, i.e. protective layers against etching or plating resists, on metallic bases, for example copper.

In this application, the outstanding resilience and toughness of the photoresist layers produced from the mixture according to the invention show themselves to full advantage, both in the unexposed and in the exposed state. The photopolymerizable layer laminated with copper possesses such firm cohesion that the self-supporting areas of the layer covering the holes remain undamaged when the base film is separated off and are not torn away by this film. Using layers of the mixture according to the invention it is possible to cover holes of 6 mm diameter and more, the layer remaining undamaged during removal of the film, development, electroplating and/or etching. In spite of the high molecular weight of the copolymers, layers of the mixtures according to the invention can be developed completely using pure aqueous, slightly alkaline developer solutions. The binders exhibit better miscibility with further proportions of the conventional monomers than corresponding binders having a low molecular weight; the addition of a plasticizer is not necessary. In the same form, the mixtures possess good resistance to developers, etching solutions and electroplating baths. The mixture according to the invention is particularly suitable for use in the dry resist method. It is also suitable for other applications in which flexibility and toughness of a photosensitive layer are important, for example for the preparation of photoresist solutions, of printing plates, relief images, screens for screen printing and color proofing films.

The examples below illustrate preferred embodiments of the mixture according to the invention and its use. If not stated otherwise, percentages and amounts

are understood as being in weight units. Parts by weight (pbw) bear the same relation to parts by volume (pbv) as that of the gram to the cubic centimeter.

Example 1

5 A solution of
6.5 pbw of the terpolymer described below,
8.8 pbw of a polymerizable diurethane prepared by reacting 1 mole of triethylene glycol,
2 moles of 2,2,4-trimethylhexamethylene diisocyanate
10 and 2 moles of hydroxyethyl methacrylate,
0.25 pbw of 9-phenylacridine and
0.025 pbw of a blue dye obtained by coupling
2,4-dinitro-6-chlorobenzenediazonium salt with
2-methoxy-5-acetylamino-N,N-diethylaniline in
15 15 pbw of butanone and
15 pbw of ethanol
was applied, by spin-coating, to a biaxially oriented,
heat-set 25 μ m thick polyethylene terephthalate film so
that, after drying at 100°C, a layer weight of
20 45 g/m^2 was obtained.

The terpolymer was prepared as follows:

A monomer mixture consisting of n-hexyl methacrylate,
methacrylic acid and styrene in a weight ratio of 60:30:10
was mixed with 0.05% by weight of azoisobutyronitrile,
25 0.02% by weight of tert.-butyl perisononanoate and 0.5%
by weight of tert.-dodecylmercaptan, and the mixture was
introduced, for polymerization, into flat hollow chambers
made of steel sheet. The mixture was heated to 50°C in
a water bath or air bath until it solidified. In order
30 to achieve a sufficiently high final conversion, the mixture
was further heated to 100°C and kept at this temperature
for some time. After cooling, the hollow chambers were opened,
and the polymer blocks removed were comminuted mechanically.
A polymer having a kinematic
35 viscosity ν of 32 mm^2/s (15% strength in ethanol) was
obtained; the mean molecular weight $\bar{M}_w$ was 128,000,
measured by light scattering. The acid number was 195
and the conversion greater than 97%.

The dry resist film prepared in this manner was

laminated at 115°C, using a commercial laminating apparatus, with a phenoplast laminate board to which a 35 µm thick copper foil is laminated, and exposed for 8 seconds to a 5 kW metal halide lamp, the distance between the lamp and the vacuum frame being 110cm. The transparency used was a line transparency with line widths and spacings down to 80 µm.

After exposure, the polyester film was removed and the layer developed for 120 seconds with 1% strength sodium carbonate solution in a spray-developing apparatus.

The board was then 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 plated in the following electrolytic baths:

1. for 60 minutes in a copper-plating bath from Schloetter, Geislingen/Steige, type "Glanzkupfer-Bad"
current density: 2.5 A/dm²
thickness of metal layer: about 30 µm
temperature: room temperature
2. for 15 minutes in a lead-tin bath LA from Schloetter, Geislingen/Steige
current density: 2 A/dm²
thickness of metal layer: 15 µm
temperature: room temperature

The board did not exhibit any undercutting or damage.

It was then possible to strip the board in 5% strength KOH solution at 50°C, and the bared copper could be etched away in the conventional etching media.

In another experiment, the photoresist layer was laminated with a copper clad test board having holes with a diameter between 1 and 6 mm, and the resist was exposed through a photographic negative corresponding to the holes (diameter of the transparent areas 1.4 to 6.4 mm). Thereafter, the unexposed parts of the layer were washed out with 1% strength sodium carbonate solution, and the bared copper was etched away with ammonia/cupric chloride solution. After the etching

procedure, all drilled holes were found to be covered with cured photoresist.

For comparison, the binder according to the invention was replaced by an analogous binder having a molecular weight of about 33,000 [η (15% strength in ethanol) = 11 mm²/sec] according to DE-A 23 63 806, this binder having been prepared by polymerization in 33% strength solution in butanone. A tacky photoresist layer which was difficult to process was obtained. Because the low molecular weight binder has a poorer action with regard to the production of a solid layer, layer substance emerged at the cut edges when resist rolls were stored, particularly at elevated temperatures. On lamination with a base material provided with holes, a ring having a smaller layer thickness formed around each drilled hole. A layer of this type could not be used for the tenting technique.

The dry resist layers described in DE-A 23 63 806, Example 4 and in DE-A 28 22 190, Example 1, both of which contain the above binder, are also unsuitable for covering drilled holes having a diameter of more than 1 mm.

Example 2

Comparable results were achieved when, instead of the urethane stated in Example 1, the following monomer mixtures were employed:

- a) 5.8 pbw of the urethane from Example 1 and
1.5 pbw of triethylene glycol dimethacrylate
- b) 5.8 pbw of the urethane from Example 1 and
1.5 pbw of polyethylene glycol-400 dimethacrylate.

The advantage of these photoresist layers is their shorter development time.

	Layer of Example		
	1	2a	2b
Development time (s)	95	75	75

Example 3

In the coating solution described in Example 1, the binder described there was replaced with the same amounts of the following terpolymers:

- 5 a) terpolymer of n-hexyl methacrylate, methacrylic acid and styrene (60:30:10) having a mean molecular weight ($\bar{M}_w$) of about 185,000, a kinematic viscosity ν (15% strength in ethanol) of 74 mm²/s and an acid number of 195,
- 10 b) terpolymer of n-hexyl methacrylate, methacrylic acid and styrene (60:35:5) having an $\bar{M}_w$ of 74,000, a kinematic viscosity ν (15% strength in ethanol) of 23 mm²/s and an acid number of 228,
- 15 c) terpolymer of n-hexyl methacrylate, methacrylic acid and styrene (60:35:5), having an $\bar{M}_w$ of 94,000, a kinematic viscosity ν (15% strength in ethanol) of 32 mm²/s and an acid number of 228,
- d) terpolymer of n-hexyl methacrylate, methacrylic acid and methyl methacrylate (60:35:5), having a kinematic viscosity ν (15% strength in ethanol) of 36 mm²/s and an acid number of 228, and
- 20 e) copolymer of n-hexyl methacrylate and methacrylic acid (65:35), having a kinematic viscosity ν (15% strength in ethanol) of 34 mm²/s and an acid number of 228.

25 In all cases, satisfactory covering of the drilled holes (tenting) was achieved.

Example 4

A coating solution was prepared from:

- 4 pbw of the terpolymer described in
- 30 Example 1,
- 4 pbw of a diurethane obtained by reacting 1 mole of 2,2,4-trimethylhexamethylene diisocyanate with 2 moles of hydroxyethyl methacrylate,
- 0.17 pbw of 9-phenylacridine,
- 35 0.02 pbw of a blue dye obtained by coupling 2,4-dinitro-6-chlorobenzenediazonium salt with 2-methoxy-5-acetylamino-N-cyanoethyl-N-hydroxyethyl-aniline and
- 0.01 pbw of 5-nitro-2-[2-methyl-4-(N-ethyl-



Patent Claims

1. A radiation-polymerizable mixture which contains, as essential components,
 - a) a compound which can undergo free radical polymerization, contains at least two terminal ethylenically unsaturated groups and has a boiling point of above 100°C under atmospheric pressure,
 - b) a compound which is capable of initiating the polymerization of compound a) under the action of actinic radiation, and
 - c) a water-insoluble copolymer which is soluble in aqueous alkaline solutions and comprises
 - c1) an α,β -unsaturated aliphatic carboxylic acid,
 - c2) an alkyl methacrylate having at least 4 carbon atoms in the alkyl group and, if appropriate,
 - c3) a monomeric ethylenically unsaturated compound which is copolymerizable with c1) and c2) and whose homopolymer has a glass transition temperature of at least 80°C,

wherein the copolymer has a mean molecular weight in the range from about 50,000 to 200,000 and has been prepared by mass polymerization.

2. A radiation-polymerizable mixture as claimed in claim 1, wherein the copolymer contains units c3 of styrene or a substituted styrene.



3. A radiation-polymerizable mixture as claimed in claim 1, wherein the polymerizable compound is an acrylate or methacrylate of a polyhydric alcohol.
4. A radiation-polymerizable mixture as claimed in claim 1, wherein the copolymer contains 20 to 60 mole % of units of an α,β -unsaturated carboxylic acid.
5. A radiation-polymerizable mixture as claimed in claim 1, wherein the α,β -unsaturated carboxylic acid is acrylic acid or methacrylic acid.

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