

The invention relates to a mixture which can be polymerized by radiation, particularly light, and which contains, as the essential constituents, a binder which is insoluble in water but soluble or swellable in aqueous-
5 alkaline solutions, a photoinitiator and a polyglycol dimethacrylate or diacrylate.

The mixture is suitable, in particular, as a photoresist for the production of printed circuits, electroplating resists and etched microstructures. The production of etched gravure printing forms and relief printing forms should be mentioned as a further field of application.
10

Negative-working photoresist lacquers which are applied in the form of a solution to the supports to be treated, are based essentially on the following types of compounds: polyvinyl cinnamates (U.S. Patent 2,690,966 and U.S. Patent 2,732,301), polyvinyl cinnamylidene esters (U.S. Patent 3,549,368), polystyrene cinnamyl ketone (U.S. Patent 2,566,302) and other polymers containing
20 cinnamoyl groups (German Patents 1,063,802 and 1,067,219 and German Offenlegungsschrift 2,111,415), allyl ester prepolymers (U.S. Patents 3,376,138, 3,376,139 and 3,462,267) and polyisoprenes (U.S. Patent 2,852,379 and British Patent 892,811).

25 Although some of these substances are used in industry as photoresist solutions, most of them have certain disadvantages. They require organic solvents for development or they have a relatively low sen-

sitivity to light. Others have a poor adhesion to metal surfaces or can only be processed to give relatively small layer thicknesses.

Negative-working liquid photoresist compositions
5 which depend on crosslinking by photo-initiated free-radical polymerization and which can be developed in an aqueous alkaline solution, are described, for example, in German Patent 2,060,575. However, the mixtures mentioned in that text are sensitive to oxygen. For this reason,
10 the layers must be provided with a polyvinyl alcohol covering layer. A further considerable problem is the tackiness of photopolymerizable layers, which can make contact exposure impossible. Thus the layers described in German Offenlegungsschrift 2,064,079 also exhibit a
15 tendency to adhesion or imprinting if they are exposed in direct contact with an original.

German Offenlegungsschrift 3,028,136 describes photopolymerizable mixtures which can advantageously be used as prefabricated, transferable photoresist layers, applied
20 to a plastic film as a temporary support. These layers are transferred to the final support by lamination under pressure and with the application of heat. For this purpose, they contain polymerizable compounds of a fairly high molecular weight, namely diacrylates or dimethacrylates of polyglycols, especially polyethylene glycols, having 14 to 23 glycol units,
25 in order to prevent evaporation of the monomer at the temperature of lamination. An influence of the type of the monomers on the tackiness of the layer does not become clear from this document.

The use of mixtures of this type as photoresist

solutions, which are applied as such by the user directly to the support to be treated and are dried, has not hitherto gained acceptance in practice, because the manual application of protective covering layers or films to the
5 photoresist layer by the user is too difficult.

German Offenlegungsschrift 2,614,860 describes a liquid, water-soluble mixture comprising (A) the ester of a hydroxyalkyl(meth)acrylate with a maleic acid anhydride/polybutadiene adduct, (B) among others, a di(meth)acrylate
10 of an oligoethylene or -propylene glycol having from 1 to 4 glycol units and (C) a benzoin ether, which is suitable for the manufacture of relief printing plates. In this case, tackiness of the unexposed layer does not present a problem, since the layer is liquid.

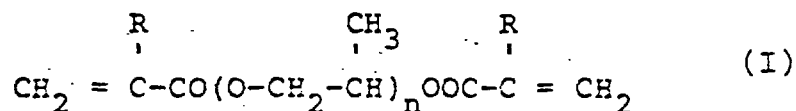
15 The object of the invention was to provide a mixture which can be polymerized by radiation and which is suitable for use as dry and liquid photoresist, produces layers with a non-tacky surface and has a low sensitivity towards oxygen.

20 The invention relates to a mixture which can be polymerized by radiation and which contains, as the essential constituents,

a) 20 to 80 % by weight of a copolymer of methyl methacrylate and methacrylic acid or of methacrylic acid, alkyl meth-
25 acrylates and methyl methacrylate, styrene or acrylonitrile, which copolymer is insoluble in water but soluble in aqueous-alkaline solutions,

- b) 0.1 to 20 % by weight of a polymerization initiator which can be activated by radiation and
- c) 20 to 80 % by weight of an acrylate or methacrylate of a di- to tetrahydric alcohol, wherein 10 to 100 %
5 by weight, based on the total amount of polymerizable compounds, consist of a polyglycol diacrylate or dimethacrylate.

The mixture according to the invention is characterized in that the polyglycol dimethacrylate or diacrylate is
10 a compound of the formula



in which R is a hydrogen atom or a methyl group and n is a number from 4 to 10.

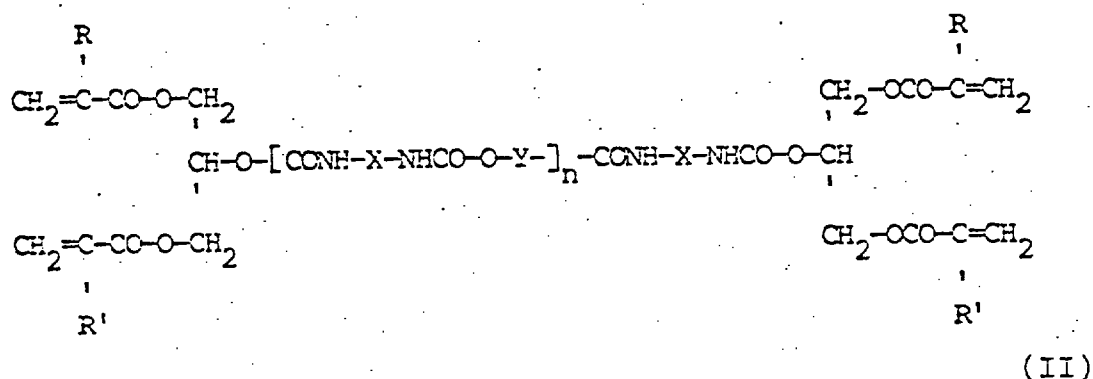
Suitable electromagnetic radiation, to which the mixture according to the invention is sensitive, is any
15 radiation having an energy corresponding to at least that

of short-wave visible light. Light of a wavelength within the range from 300 to 500 nm is preferred, but X-ray, electron and other corpuscular radiation and laser radiation are also suitable for initiating the polymerization. In every case the initiator system can be adjusted to, or sensitized for, the desired radiation in a known manner.

Amongst the compounds of the formula I, compounds which are particularly preferred are those in which R is a methyl group. The compounds are known per se and are available commercially.

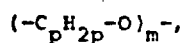
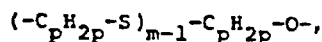
In addition to the polymerizable compound of the formula I, the mixture according to the invention can also contain up to 90 %, relative to the total content of polymerizable compounds, of other acrylates or methacrylates of dihydric to tetrahydric alcohols. It is particularly advantageous to add acrylates, and especially methacrylates, of polyhydric alcohols, particularly dihydric alcohols, containing urethane groups in the molecule.

Urethane compounds which are particularly preferred are those of the general formula II

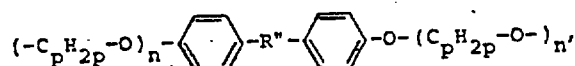
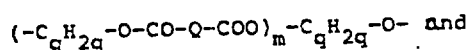
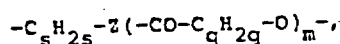
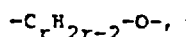


in which X denotes a hydrocarbon radical, preferably a

saturated aliphatic or cycloaliphatic radical, having 2 to 20 carbon atoms, Y denotes one of the groups



5



R and R' denote hydrogen atoms or methyl groups, R'' denotes O, S, CR₂ or SO₂, Q denotes a phenyl group or one of the groups C_qH_{2q} and C_qH_{2q-2}, Z denotes O or NR, n denotes a number from 0 to 20, m denotes a number from 1 to 40, p denotes a number from 2 to 20, q denotes a number from 2 to 10, r denotes a number from 4 to 20 and s denotes a number from 2 to 10.

Amongst the compounds of the formula II, preferred compounds are those in which n is a number from 0 to 20, in particular from 0 to 10.

R and R' are preferably methyl groups.

Amongst the diol components used for the preparation of the polymerizable urethanes, polyether diols, particularly saturated representatives thereof, are preferred. Y is thus preferably the group $(-C_{pH_{2p}}-O)_m$ in which preferred values of p are 2 to 10, particularly 2 to 4. If unsaturated diols are used, they preferably have 4 to 10 carbon atoms per diol unit.

For certain purposes, for example for achieving specific mechanical properties or higher sensitivity to

light, it can also be advantageous to use polyester diols. These can be synthesized in a known manner from dicarboxylic acid and diol units or from hydroxycarboxylic acid units. In this respect, preferred hydroxycarboxylic acids are those in which $q = 3$ to 6 .

The polyester diols formed from hydroxycarboxylic acids are usually prepared from lactones by ring opening by means of a molecule of an H-active compound $\text{HO}-\text{C}_s\text{H}_{2s}-\text{Z}-\text{H}$. In this formula, s preferably has a value of 2 to 6 and Z is preferably an oxygen atom.

In general, polyester diols having molecular weights within the range from about 500 to 3,000 are very suitable.

The preparation of the polymerizable diurethanes or polyurethanes is effected in a manner which is known per se, for example as described in U.S. Patent 3,297,745 or German Offenlegungsschriften 2,064,079 and 2,822,190.

For the preparation of the glycerol diester, 1 mole of glycidyl acrylate or glycidyl methacrylate is reacted with 1 mole of acrylic acid or methacrylic acid. 2 moles of this reaction product are then reacted with 1 mole of a diisocyanate. The diisocyanate used is either a monomer or is a product from the reaction of an excess of a monomeric diisocyanate with a diol component. In the latter case, the diol component $\text{HO}-\text{Y}-\text{H}$ is previously reacted with the desired excess of diisocyanate. As a rule, polymer-homologous mixtures are obtained in this reaction. The non-uniformity of the molecular weights of the diisocyanates obtained therefrom results in products

which have a high viscosity and are virtually non-crystallizable.

The compounds of the formula II and their preparation and use are described in detail in published European
5 Patent Application 54 700.

The total quantity of polymerizable compounds in the mixture according to the invention is generally 20 to 80, preferably 30 to 70, % by weight of the non-volatile constituents of the mixture.

10 A large number of substances are suitable as photoinitiators, for example benzoin, benzoin ethers or polynuclear quinones, for example 2-ethylanthraquinone; acridine derivatives, for example 9-phenylacridine, 9-p-methoxyphenylacridine, 9-acetylaminoacridine or benz(a)-
15 acridine; phenazine derivatives, for example 9,10-dimethylbenz(a)phenazine, 9-methylbenz(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, and qui-
20 nazoline derivatives.

In general, the photoinitiators are added in an amount of 0.1 to 20 % by weight, relative to the non-volatile constituents of the photopolymerizable mixture.

The binders used are natural or synthetic poly-
25 mers which are insoluble in water and are soluble or at least swellable in aqueous-alkaline solutions, since layers containing such binders can be developed using the preferred aqueous-alkaline developers. Binders of this type can, for example, contain the following groups:

-COOH-, $-PO_3H_2$, $-SO_3H$, $-SO_2NH_2$, $-SO_2-NH-CO-$ and the like.

The following may be mentioned as examples of these:

maleate resins, polymers formed from β -methacryloyloxyethyl
N-(p-tolylsulfonyl)-carbamate and copolymers of these and
5 similar monomers with other monomers, styrene/maleic
anhydride copolymers, methyl methacrylate/methacrylic
acid copolymers and copolymers formed from methacrylic
acid, alkyl methacrylates and methyl methacrylate and/or
styrene, acrylonitrile and other compounds, such as are
10 described in German Offenlegungsschriften 2,064,080 and
2,363,806.

In general, the quantity of the binder is 20 to
80, preferably 30 to 70, % by weight of the constituents
of the mixture.

15 In addition to monomers, binders and photoiniti-
ators, the photopolymerizable mixture also contains, if
appropriate, stabilizers and/or inhibitors for preventing
polymerization of the monomers in the dark, hydrogen do-
nors, compounds for decreasing sensitivity to oxygen,
20 wetting agents, plasticizers, sensitometric regulators,
dyes and colorless or colored pigments.

The hydrogen donors used are principally alipha-
tic polyethers. If desired, this function can also be
taken over by the binder or by the polymerizable monomer,
25 if these compounds contain labile hydrogen atoms.

The compounds added to decrease sensitivity to
oxygen can advantageously be the disulfides described in
German Offenlegungsschrift 2,944,866.

The preparation of the light-sensitive materials

using the mixture according to the invention is carried out in a known manner. The mixture is taken up in a solvent and the solution or dispersion is applied to the intended support by casting, spraying, dipping or application with rollers, in the form of a film which is subsequently dried.

The nature of the support depends on the end use of the light-sensitive material.

Besides copper, steel, chromium-plated copper or 10 steel, zinc, nickel, aluminum or aluminum alloys, it is also possible to use layers of silicon dioxide, or doped oxide layers, which have been grown or deposited by heat, plastic films (polyethylene terephthalate or cellulose acetate) or screen printing supports (Perlon gauze or 15 nickel screens).

The mixture according to the invention produces photopolymerizable layers which have a high sensitivity to light. The layers exhibit no tendency to adhesion or imprinting even at layer thicknesses of up to 150 μm .
20 They can be developed with aqueous-alkaline solutions and exhibit an excellent resistance to developer. The ratio of the layer thickness of the photopolymerizable layer to the degree of resolution is 1:1 to 1:2. The shoulders of the exposed portions of the layer, and thus also the metal 25 buildup, are virtually straight and vertical at layer thicknesses of up to 110 μm .

The copying materials are provided with an image in a known manner, for example by contact exposure under a transparent original. The customary sources of light,

such as carbon arc lamps, xenon lamps, high-pressure mercury vapor lamps doped with metal halides, and the like are used in this process. An image can also be provided by means of laser light, for example using an argon ion
5 laser.

The copying materials which have been exposed are developed in a known manner by washing out the unexposed areas of the layer by means of a developer. Suitable developers are aqueous solutions which can contain buffer
10 salts, for example ammonium phosphates, silicates, hydroxides or carbonates or alkali metal phosphates, silicates, hydroxides or carbonates; wetting agents, dyes, optionally organic solvents which are miscible with water and other customary additives, and also aqueous solutions
15 of wetting agents.

The mixtures according to the invention are suitable for the production of dry resist films, relief images, screen printing stencils and color proofing films. They can also be used as fast-curing coating compositions, dental
20 filling compositions and adhesives and for the preparation of rigid, heat-stable moldings.

The mixtures are used particularly advantageously in a dissolved form for the production of etch resist layers or electroplating resist layers on metallic sup-
25 ports. They are suitable, above all, for use on copper supports, such as are used, for example, for the production of printed circuits and gravure printing forms. They can also be employed advantageously as prefabricated dry resist films for the same uses.

In these use forms, the excellent adhesion of the exposed portions of the layers proves adequate not only during development, but also during subsequent etching and reinforcement of the support by electroplating, in
5 the course of which the layers exhibit good resistance.

When the urethane monomers of the formula II, which are the preferred additive, are used, the mixture according to the invention is distinguished by a particularly low sensitivity towards oxygen, this sensitivity being
10 still pronounced even in the case of thin layers. After the solution has dried, the layers are not tacky and do not become imprinted by the original when in vacuum contact. It is surprising that this property is only achieved by the polypropylene glycol esters of the formula I de-
15 scribed above. If these monomers are replaced by the same or an equivalent quantity of polyethylene glycol bisacrylate or bismethacrylate, a tacky layer is obtained.

The mixture can be applied in layer thicknesses of about 0.5 to 150 μm . Even in this thickness, it ex-
20 hibits a high sensitivity to light and can, in spite of this, be developed rapidly with alkaline solutions, while having a good resistance to developer. It can therefore be employed for the production of electroplating resists. The shoulders of the exposed portions of the layers and thus
25 also the buildup of metal are virtually straight and vertical at layer thicknesses up to 110 μm .

In some cases it can be advantageous to render the layer even more resistant by baking prior to etching.

The examples which follow illustrate embodiments

of the mixture according to the invention and the use thereof for the preparation of photopolymerizable copying materials. Unless otherwise indicated, percentages and quantitative ratios are to be understood as meaning units of weight. The numerical data given in the case of poly-
5 glycols refer to the molecular weights of these compounds.

Example 1

A solution of

66 parts by weight of a terpolymer formed from n-hexyl methacrylate, methacrylic acid and styrene
10 (60:30:10), having an average molecular weight of approx. 35,000 and an acid number of about 200,
42 parts by weight of polypropylene glycol 420 dimethacrylate,
1.3 parts by weight 9-phenylacridine and
15 0.2 part by weight of a blue dyestuff obtained by coupling a 2,4-dinitro-6-chlorobenzenediazonium salt with 2-methoxy-5-acetylamino-N-cyanoethyl-N-hydroxy-ethylaniline, in
240 parts by weight of butanone and
20 30 parts by weight of ethanol
was spin-coated onto a phenoplast laminate sheet clad with a 35 μm thick copper foil such that, after drying at 100°C, a layer thickness of 80 μm was obtained. The sheet was exposed for 6 seconds using
25 a 5 kW metal halide lamp, at a distance of 110 cm between the lamp and the vacuum copying frame. The original used was an exposure wedge having 13 steps with density increments of 0.15, as well as a line original having line widths and spacings down to 80 μm .

After exposure, the layer was developed for 100

seconds with 0.8 % strength sodium carbonate solution in a spray developing apparatus. Five to six fully cross-linked wedge steps were obtained.

The sheet was then rinsed for 30 seconds with tap water, slightly etched for 30 seconds in a 15 % strength solution of ammonium peroxydisulfate, rinsed again with water, immersed in 10 % strength sulfuric acid for 30 seconds and then electroplated successively in the following electrolyte baths:

10 1) 50 minutes in a "Glanzkupfer-Bad (Bright copper bath) PC" type copper electrolyte bath made by Schlötter, Geislingen/Steige,
current density: 2.5 amperes/dm²
metal build-up: approx. 25 μm
15 temperature: room temperature

 2) 55 minutes in a LA lead-tin bath made by Schlötter, Geislingen/Steige
current density: 2 amperes/dm²
metal build-up: 55 μm
20 temperature: room temperature

The sheet exhibited no undercutting or damage at all.

The overhang, or the inclination of a shoulder of the resist layer, was 7 μm at a resist web width of 138 μm,
25 that is to say the upper edge of the resist shoulder projected 7 μm over the lower edge.

It was then possible to remove the coating from the sheet in a 5 % strength KOH solution at 50°C, and the copper exposed could then be removed by etching in the

customary etching media.

If the monomer is replaced by polyethylene glycol 400 dimethacrylate, by trimethylolethane triacrylate or by a reaction product formed from 1 mole of 2,2,4-trimethyl-
5 hexamethylene diisocyanate and 2 moles of hydroxyethyl methacrylate, layers are obtained, from which, after exposure, the film original can only be removed with damage caused to the resist layer by tearing off portions of the layer.

10 Example 2

A copper-clad sheet of insulating material was coated, dried, exposed and developed as in Example 1. The sheet was then electroplated as follows:

1) 100 minutes in the copper electrolyte bath described in Example 1
15

current density: 2.5 amperes/dm²

metal build-up: approx. 50 µm

temperature: room temperature

2) 10 minutes in a "Norma" type nickel bath made
20 by Schlötter, Geislingen/Steige

current density: 4 amperes/dm²

metal build-up: approx. 10 µm

temperature: 50°C

3) 12 minutes in a "Autronex CC" type gold bath
25 made by Blasberg, Solingen

current density: 1 ampere/dm²

metal build-up: approx. 5 µm

temperature: 40°C

This sheet also exhibited no undercutting

or damage.

Example 3

The resist solution described in Example 1 was spin-coated onto a phenoplast laminate sheet, clad with a copper foil 35 μm thick, and was dried (layer thickness 108 μm). The sheet was exposed for 8 seconds and was then developed for 140 seconds with 0.8 % strength sodium carbonate solution. 6 fully crosslinked wedge steps were obtained.

10 After being pretreated as described in Example 1, the sheet was electroplated as follows:

180 minutes in the nickel bath described in Example 2

current density: 4 amperes/ dm^2

15 metal build-up: 180 μm

temperature: 50°C

This plate also exhibited no undercutting or damage at all; it was possible to remove its coating with KOH solution and to etch it with customary etching agents.

20 An overhang of the resist shoulder on one side of 13 μm was found, the resist web width being 138 μm .

Example 4

100 ml of the photoresist solution from Example 1 were diluted with 25 ml of butanone and 25 ml of ethylene glycol monoethyl ether.

Using a Mettenheimer cylindrical spraying apparatus, a resist layer was applied to a brass sheet 0.2 mm thick which had been previously nickel-plated to a thick-

ness of 10 μm . Immediately after application, the resist layer was dried for 10 minutes using an infrared lamp (1,200 watts) at a distance of 20 cm from the layer. The layer thickness was 70 μm . It was exposed for 50 seconds with a 400 watt lamp and was then developed with 0.8 % strength sodium carbonate solution. The development time was 80 seconds and the layer had a resistance time of 7 minutes. The resolution was about 65 μm .

The test sheet was passivated for 3 minutes in a 2 % strength potassium dichromate solution and, after being rinsed with water (30 seconds), was nickel-plated for 2 hours or for 3 hours at 3 amperes/dm². This deposited 70 μm or 110 μm , respectively, of nickel.

The nickel stencil was removed and the resist stencil was then dissolved off with acetone.

Example 5

A solution of the following composition was spin-coated onto a phenoplast laminate support clad with a copper foil 17 μm thick, such that, after drying, a layer thickness of 5 μm was obtained:

- 6.5 parts by weight of the copolymer described in Example 1,
- 3.4 parts by weight of polypropylene glycol 420 dimethacrylate,
- 0.3 part by weight of 9-phenylacridine,
- 0.075 part by weight of the blue dyestuff from Example 1 and
- 0.025 part by weight of crystal violet in
- parts by weight of butanone and

20 parts by weight of ethanol.

The sheet was exposed for 20 seconds with a 5 kW metal halide lamp. The original used was a gravure screen (width of cell walls 36 μm) as well as an Itek test original (elements of 2 - 500 μm). The sheet was developed for 35 seconds with 0.8 % strength sodium carbonate solution.

After being developed, the resolution was about 10 μm and the width of cell walls of the gravure screen was 48 μm .

After being etched with iron(III) chloride solution at 40°C (65 seconds), the cell wall widths obtained were 12 μm measured at the upper edge, and 33 μm measured at the lower edge.

Examples 6 - 13

Solutions were prepared as in Example 5, containing, instead of the quantity of polypropylene glycol 420 dimethacrylate (PPG-420-DMA) used in that example, mixtures of this dimethacrylate with other difunctional and/or polyfunctional methacrylates or acrylates.

24

Example No.	PPG-420-DMA (parts by wt.)	Monomer added (parts by wt.)	Tackiness ¹⁾	Optimum exposure time (seconds)	Resolution (μm) at a layer thickness of 5 μm
6	2.55	Dipropylene glycol dimethacrylate (0.85)	++	25	12
7	2.55	Polypropylene glycol 420 diacrylate (0.85)	+	20	10
8	2.55	Diurethane obtained from 2 moles of glycerol dimethacrylate and 1 mole of hexamethylene diisocyanate (0.85)	++	15	10
9	1.7	Above diurethane (1.7)	++	15	12
10	2.55	Oligourethane obtained from 2 moles of glycerol dimethacrylate, 2 moles of hexamethylene diisocyanate and 1 mole of polyethylene glycol 400 (0.85)	++	15	10
11	1.7	Above oligourethane (1.7)	++	15	10
12	2.55	Polyethylene glycol 400 dimethacrylate (PEG-400-DMA) (0.85)	++	25	10
13	1.7	PEG-400-DMA (1.7)	+	13	10

1) ++ layer completely dry and tack-free;
+ slight imprints

Example 14

- A solution of
- 6.5 parts by weight of the terpolymer described in Example 1,
 - 5 1.6 parts by weight of polyethylene glycol 400 dimethacrylate,
 - 1.6 parts by weight of polypropylene glycol 420 dimethacrylate,
 - 0.1 part by weight of 9-phenylacridine,
 - 10 0.01 part by weight of the azo dye from Example 1,
 - 0.0045 part by weight of the azo dye 5-nitro-2-[2-methyl-4-(N-ethyl-N-cyanoethyl)-aminobenzeneazobenzothiazole] and
 - 0.8 part by weight of the elastomer described below in
 - 15 38 parts by weight of butanone

was spin-coated onto a biaxially stretched and heat-set polyethylene terephthalate film 25 μm thick such that, after drying at 100°C, a layer weighing 40 g/m² was obtained.

- 20 The dry resist film thus prepared was laminated at 120°C, using a commercially available laminating apparatus, onto a preheated phenoplast laminated sheet, clad with a copper foil 35 μm thick, and was exposed for 4 seconds with a commercially available exposure apparatus.
- 25 The original used was a line original having line widths and spacings down to 80 μm .

After exposure, the polyester film was removed and the layer was developed for 90 seconds with 0.8 % strength sodium carbonate solution in a spray developing

apparatus.

The sheet was then subjected to further treatment as described in Example 1 and was electroplated, but was treated for 20 minutes at 1 ampere/dm² in the lead/tin bath, and the metal build-up obtained was 10 μm.

The sheet exhibited no undercutting or damage at all. The color of the resist was unchanged. It was then possible to remove the coating from the sheet in 5 % strength KOH solution at 50°C and to remove the copper exposed by etching in the customary etching media.

After the lead/tin electroplating, especially in baths having a high content (300 g/l) of fluoboric acid, a resist layer containing 3.2 parts by weight of polyethylene glycol 400 dimethacrylate instead of the mixture of monomers described above exhibited a pronounced golden discoloration, associated with a certain degree of embrittlement.

The elastomer used was prepared as follows:

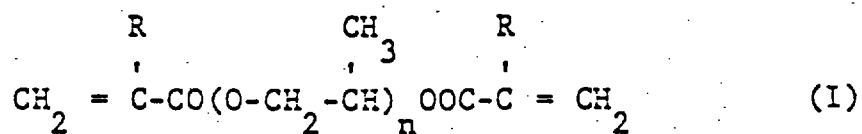
A. 426 parts by weight of glycidyl methacrylate and 216 parts by weight of adipic acid were mixed by stirring in a 1 liter four-necked flask, equipped with a stirrer, a thermometer, a reflux condenser and a drying tube, 19.7 parts by weight of p-methoxyphenol and 6.4 parts by weight of benzyltriethylammonium chloride were added and the mixture was heated cautiously to an internal temperature of 80°C. A clear solution was obtained after approx 2 hours; this solution 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 formed from tolylene diisocyanate and poly-1,4-butanediol, having an average molecular weight of about 2,000 and containing 4.1 % by weight of isocyanate groups (Adiprene L 100), dissolved in 300 parts by volume of methyl ethyl ketone, was placed in a 1 liter four-necked flask equipped with a stirrer, a thermometer, a dropping funnel, a condenser and a drying tube, and 0.87 part by weight of benzoquinone and 0.85 part by volume of a solution obtained by dissolving 6.3 parts by weight of iron(III) acetylacetonate and 0.45 part by weight of triethylamine in methyl ethyl ketone and making up the mixture to 100 parts by volume with methyl ethyl ketone, were added. A solution, in 300 parts by volume of methyl ethyl ketone, of 31.33 parts by weight of the reaction product obtained in accordance with A was charged to the dropping funnel and was added dropwise in the course of 40 minutes to the solution in the flask, which was heated at 70°C and stirred. After stirring for a further two hours at 30°C, 10 parts by volume of ethanol were added to the clear reaction mixture. Distilling off the solvent from the viscous solution gave a non-tacky rubber-like mass which dissolved to give a clear solution in numerous organic solvents, e.g. tetrahydrofuran, acetone or toluene. The reduced specific viscosity of the product was 0.72 dl/g (measured on a 1 % strength solution in dimethylformamide at 25°C).



Claims

1. A mixture which can be polymerized by radiation and which contains, as the essential constituents,
 - a) 20 to 80 % by weight of a copolymer of methyl methacrylate and methacrylic acid or of methacrylic acid, alkyl methacrylates and methyl methacrylate, styrene or acrylonitrile, which copolymer is insoluble in water but soluble in aqueous-alkaline solutions,
 - b) 0.1 to 20 % by weight of a polymerization initiator which can be activated by radiation and
 - 10 c) 20 to 80 % by weight of an acrylate or methacrylate of a di- to tetrahydric alcohol, wherein 10 to 100 % by weight, based on the total amount of polymerizable compounds, consist of a polyglycol diacrylate or dimethacrylate, characterized in that the polyglycol diacrylate or dimethacrylate is a compound of the
15 formula I



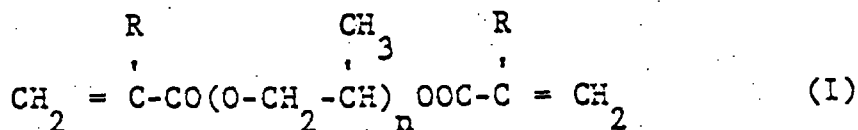
in which R is a hydrogen atom or a methyl group and n is a number from 4 to 10.



2. A polymerizable mixture as claimed in Claim 1, which contains a compound of the formula I, in which R is a methyl group.

5 3. A copying material which can be polymerized by radiation and has a support and a polymerizable layer which contains, as the essential constituents,

- 10 a) 20 to 80 % by weight of a copolymer of methyl methacrylate and methacrylic acid or of methacrylic acid, alkyl methacrylates and methyl methacrylate, styrene or acrylonitrile, which copolymer is insoluble in water but soluble in aqueous-alkaline solutions,
- 15 b) 0.1 to 20 % by weight of a polymerization initiator which can be activated by radiation and
- c) 20 to 80 % by weight of an acrylate or methacrylate of a di- to tetrahydric alcohol, wherein 10 to 100 % by weight, based on the total amount of polymerizable compounds, consist of a polyglycol diacrylate or
- 20 dimethacrylate, characterized in that the polyglycol diacrylate or dimethacrylate is a compound of the formula I



25 in which R is a hydrogen atom or a methyl group and n is a number from 4 to 10.



4. A polymerizable copying material as claimed in Claim 3, wherein the polymerizable layer has a thickness of 0.5 to 150 μm .