

The invention relates to a mixture which is polymerizable by radiation, particularly by light, and which contains, as the essential constituents, a polymeric binding agent, a polymerization initiator which can be activated by radiation, and an acrylate or methacrylate, polymerizable by free radicals, of a polyhydric hydroxy compound having at least two urethane groups in the molecule.

Mixtures of this type are known and are predominantly used for the preparation of radiation-sensitive, particularly light-sensitive, recording materials, which are used, for example, for the preparation of printing plates, photoresists and relief images.

In DE-A 20 64 079, | photo-polymerizable mixtures are described which contain, as the polymerizable compounds, reaction products of acrylates or methacrylates of polyhydric alcohols, which contain at least one | free hydroxy group, for example of hydroxyethyl methacrylate, with diisocyanates. These mixtures tend to form relatively brittle light-hardened products. They also have a limited shelf life, since the monomers have a noticeable vapor pressure even at a slightly elevated temperature.

In DE-A 23 61 041, | mixtures are described which contain similar polymerizable compounds which have more than two urethane groups and in addition polyether units in the molecule. These mixtures yield only a limited crosslinkage density, and are relatively sensitive to atmospheric oxygen.

In DE-A 28 22 190, mixtures with higher molecular weight monomers containing urethane groups are described, which have many advantages for certain purposes, for example for the preparation of photo-resist layers which can be transferred dry. However, even these mixtures, owing to their lower content of polymerizable groups per molecular weight unit, yield products with limited crosslinkage densities.

Similar polymerizable oligourethanes are described in US-A 3,850,770 and 4,198,238 and in EP-A 9,967.

It is true that the light-sensitive or radiation-sensitive recording materials prepared with such polymerizable compounds have a number of outstanding properties, but these properties are accompanied, in most cases, by certain disadvantages. Thus, the higher molecular weight oligourethanes containing polyether groups give layers with outstanding mechanical properties in the exposed and unexposed state, whereas the crosslinkage density achieved with these substances is lower than in the case of certain low molecular weight monomers. Many monomers, particularly in combination with the preferred binding agents which can be developed in aqueous/alkaline media, give tacky layers. Further, the sensitivity of most of the known materials to atmospheric oxygen is greater than is desirable.

The object of the invention was to propose a mixture which is polymerizable by radiation and which has a high sensitivity to radiation and no tendency to

- 3 -

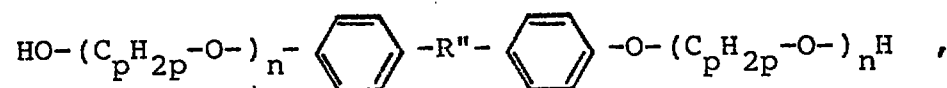
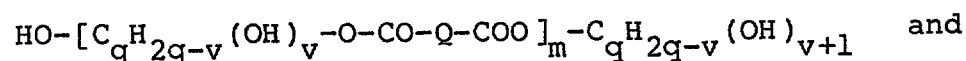
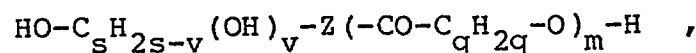
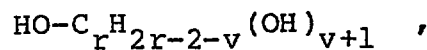
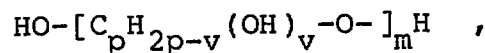
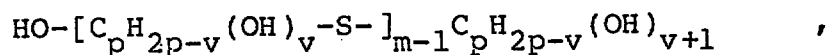
crystallization, but nevertheless gives layers with a surface which is not tacky. In particular, the mixture should develop its advantageous properties also in the presence of atmospheric oxygen, that is to say without
5 an oxygen-inhibiting covering layer, and should thus exhibit as good a reciprocity as possible.

The subject of the invention is a mixture which is polymerizable by radiation and which contains, as the essential constituents, a polymeric binding agent, a
10 polymerization initiator which can be activated by radiation, and an acrylate or methacrylate of a polyhydric hydroxy compound having at least two urethane groups in the molecule.

The mixture of this invention is characterized
15 in that the ester is a reaction product of glycerol dimethacrylate or glycerol diacrylate and a polyisocyanate which has been obtained by reacting a polyhydroxy compound having 2 to 6 OH groups with a diisocyanate, or a reaction product of glycerol dimethylacrylate or glycerol diacrylate
20 and a diisocyanate.

The polyhydroxy compound preferably has 2 or 3, in particular 2, OH groups. Preferably, it is a compound of one of the following formulas:

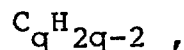
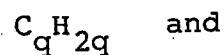
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wherein

R'' is O, S, CR₂ or SO₂,

Q is a phenylene group or one of the groups



R is a hydrogen atom or a methyl group,

Z is O or NR,

n is an integer from 0 to 20,

m is an integer from 1 to 40,

p is an integer from 2 to 20,

q is an integer from 2 to 10,

r is an integer from 4 to 20,

s is an integer from 2 to 10, and

v is an integer from 0 to 4,

p, q, and s being at least by 2 greater than v and

r being at least by 4 greater than v.

In general, the diisocyanate is a compound of the formula OCN-X-NCO , wherein X is a hydrocarbon radical, preferably a saturated aliphatic or cycloaliphatic hydrocarbon radical, having 2 to 20 carbon atoms.

5 The reaction products of the glycerol dimethacrylate are usually preferred over those of the glycerol acrylate.

The polyisocyanate obtained by reacting a polyhydroxy compound with a diisocyanate contains an average number of 2 to 40, preferably of 2 to 20, urethane groups per molecule.

10

Any radiation, the energy of which corresponds to at least that of short wavelength visible light is suitable as the electromagnetic radiation to which the mixture according to the invention is sensitive. Light of a wavelength in the range from 300 to 500 nm is preferred, but X-radiation, electron radiation and other corpuscular radiation, as well as laser radiation, are suitable for initiating the polymerization. In any case, the initiator system can be adapted to, or sensitized for, the desired radiation in a known manner.

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Among the polyol components used for the preparation of the polymerizable urethanes, the polyether polyols, par-

particularly the saturated representatives, i.e., the compounds of the formula $\text{HO}-[\text{C}_p\text{H}_{2p-v}(\text{OH})_v-\text{O}]_m\text{H}$, are preferred. Values from 2 to 10, particularly from 2 to 4, are preferred for p. If unsaturated polyols are used, these preferably have 4 to 10 carbon atoms per polyol unit.

For certain purposes, for example for attaining certain mechanical properties or higher light sensitivities, it can also be advantageous to use polyester polyols. These can be synthesized, in a known manner, from dicarboxylic acid units and polyol units, or from hydroxycarboxylic acid units. In this context, hydroxycarboxylic acids having $q = 3$ to 6 are preferred.

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

The number of units in the polyester diols and polyether diols depends on the nature of these compounds and the remaining units of the molecule,

on the nature of the binding agent and on the particular intended application. Polymerizable compounds having relatively long polyoxyethylene chains in the molecule are very hydrophilic and are very rapidly developed with aqueous developers. Even when less hydrophilic binding agents are used, monomers with such polyether groups are generally very suitable. In contrast, in the case of monomers which contain polyoxyalkylene groups

having higher alkylene radicals or polyester groupings, the use of binding agents which are more hydrophilic is necessary if the material is to be developed without the addition of organic solvent to the developer. In most cases, compounds with $m = 2$ to 25, particularly 3 to 15, are preferred.

Examples of suitable diisocyanates are tolylene diisocyanates, xylylene diisocyanates, naphthylene diisocyanates, hexamethylene diisocyanate, cyclohexylene diisocyanate, diphenylmethane diisocyanate, isophorone diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate and the reaction product of 2 moles of tolylene diisocyanate or diphenylmethane diisocyanate and 1 mole of polytetrahydrofuran.

Examples of suitable monomeric or polymeric diols are ethylene glycol, propylene glycol, 1,4-butanediol, 2-ethyl-1,6-hexanediol, 1,10-decanediol, 1,4-bis-hydroxymethylcyclohexane, diethylene glycol, triethylene glycol, polyethylene glycols having molecular weights of from 200 to about 1500, and the reaction products of 4,4'-dihydroxydiphenyl ether, 4,4'-dihydroxy-diphenyl sulfide, 4,4'-dihydroxy-diphenylmethane, 4,4'-dihydroxy-diphenylpropane or 4,4'-dihydroxy-diphenylsulfone with 0 to 40 moles of alkylene oxide, polypropylene glycols, polytetrahydrofuran, polybutylene glycols, thiodiethylene glycol and dithiotriethylene glycol.

Examples of suitable polyester components are polycaprolactone, polybutyrolactone, polyethylene terephthalate, polypropylene adipate, polybutylene adipate and polyethylenebutylene sebacate.

- 8 -

Polyester polyols having molecular weights in the range of about 500 to 3,000 are generally very suitable.

Apart from the preferred diols, compounds having 2 to 6 aliphatic hydroxy groups can generally be used .

5 Examples of monomeric compounds are glycerol, trimethylolpropane, pentaerythritol, dipentaerythritol and sorbitol. Suitable polymeric polyhydroxy compounds are polyester polyols, such as the lactone polyesters described in

10 US-A 3,169,945, the polyester condensation polymers having terminal hydroxy groups described in US-A 3,641,199, the hydroxy group containing polyesters described in US-A

15 3,931,117, block copolymers of polyethers and polyesters having terminal hydroxy groups, caprolactone polyols and polysiloxane polyols.

The preparation of the polymerizable diurethanes or polyurethanes is effected in a manner which is in itself known, for example as described in US-A 3,297,745, 5 DE-A 20 64 079 and DE-A 28 22 190.

For the preparation of the glyceroldiester, 1 mole of glycidyl acrylate or glycidyl methacrylate is 10 first reacted with 1 mole of acrylic acid or methacrylic acid. One mole of this reaction product is then reacted with 1 equivalent of polyisocyanate. In this process, the polyisocyanate, preferably diisocyanate, is either monomeric or a reaction product of an excess of monomeric diisocyanate with a polyol 15 component. In the latter case, the polyol component is previously reacted with the desired excess of a diisocyanate. As a rule, polymer-homologous mixtures are obtained thereby. The non-uniformity of the molecular weights of the monomers obtained therefrom 20 leads to products which are highly viscous and virtually non-crystallizable.

In addition to the new monomers described above, the mixture according to the invention can contain smaller quantities, that is to say less than 50%, preferably less than 20%, relative to the total monomer content, of known monomers, particularly acrylates 25 or methacrylates of polyhydric alcohols, which optionally can also contain urethane groups. The total quantity of polymerizable compounds is generally 20 to 80, preferably 30 to 70, % by weight of the non-volatile

constituents of the mixture.

A number of substances are suitable as photo-initiators, for example benzoin, benzoin ether, polynuclear quinones, for example 2-ethyl-anthraquinone;

5 acridine derivatives, for example 9-phenyl-acridine, 9-p-methoxyphenyl-acridine, 9-acetylamino-acridine and benz(a)acridine; phenazine derivatives, for example 9,10-dimethyl-benz(a)phenazine, 9-methyl-benz(a)phenazine and 10-methoxy-benz(a)phenazine; quinoxaline derivatives,
10 for example 6,4',4"-trimethoxy-2,3-diphenyl-quinoxaline and 4',4"-dimethoxy-2,3-diphenyl-5-aza-quinoxaline, and quinazoline derivatives.

In general, the photoinitiators are added in a quantity of from 0.1 to 20 percent by weight relative
15 to the non-volatile constituents of the photopolymerizable mixture.

A number of soluble organic polymers can be used as the binding agent. The following may be mentioned as examples: polyamides, polyvinyl esters, polyvinyl
20 acetals; polyvinyl ethers, polyacrylates, polymethacrylates, polyesters, alkyd resins, polyacrylamide, polyvinyl alcohol, polyethylene oxide, polydimethylacrylamide, polyvinylpyrrolidone, polyvinylmethylformamide and polyvinylmethylacetamide, and copolymers of the monomers
25 which form the homopolymers listed.

Natural substances or modified natural substances, for example gelatines and cellulose ethers, are also suitable as binding agents.

Binding agents which are particularly advant-

ageously used are those which are soluble, or at least swellable, in aqueous/alkaline solutions, since layers with such binding agents can be developed with the preferred aqueous/alkaline developers. Binding agents of this type can, for example, contain the following groups: $-\text{COOH}$, $-\text{PO}_3\text{H}_2$, $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{NH}_2$, $-\text{SO}_2-\text{NH}-\text{CO}-$ and the like. The following may be mentioned as examples of these binding agents: maleinate resins, polymers of β -methacryloyloxy-ethyl N-(p-tolyl-sulfonyl)-carbamate and copolymers of these and similar monomers with other monomers, styrene/maleic anhydride copolymers, copolymers of methyl vinyl ether and maleic anhydride or maleic acid esters or half esters, methyl methacrylate/methacrylic acid copolymers and copolymers of methacrylic acid, alkyl methacrylates and methyl methacrylate and/or styrene, acrylonitrile, etc., as described in DE-A 2,064,080 and 2,363,806. Copolymers of styrene and maleic anhydride or maleic acid esters or half esters, optionally in combination with copolymers of methylvinyl ether and maleic acid half esters, are particularly preferred.

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

In addition to monomers, binding agents and photoinitiators, the photopolymerizable mixture also optionally contains stabilizers or inhibitors for preventing the polymerization of the monomers in darkness, hydrogen donors, surfactants, plasticizers, sensitometric regulators, dyestuffs and colorless pigments or colored pigments.

Aliphatic polyethers are used, in the main, as

hydrogen donors. This function can also optionally be assumed by the binding agent or by the polymerizable monomer if these substances have labile hydrogen atoms.

- It can be advantageous to largely remove the
- 5 photopolymerizable layer of the photopolymerizable copying material prepared from the mixture from the action of the atmospheric oxygen, during the light polymerization, that is to say, in particular to prevent the subsequent diffusion of the atmospheric oxygen in the layer.
- 10 This is normally particularly important if - for example in the case of exposure by projection or with laser radiation - the procedure is carried out without a vacuum copying frame. When the mixture is used in the form of thin copying layers, it is advantageous to apply a
- 15 suitable covering film which has a low permeability to oxygen. This can be self-supporting and can be withdrawn before the development of the copying layer. Polyester films, for example, are suitable for this purpose. The covering film can also be composed of a
- 20 material which dissolves in the developer liquid or can be removed, at least at the non-hardened points, during the development. Materials suitable for this purpose are, for examples, waxes, polyvinyl alcohol, polyphosphates, sugar, etc.
- 25 The mixtures according to the invention give photopolymerizable layers with a high light-sensitivity. This is also the case when a covering layer which acts as a screen to oxygen is dispensed with. Even without a covering layer, the layers show no tendency to

tackiness and are stable, in the exposed state, to alkaline developers and acid alcoholic rinsing liquors.

In addition, the new polymerizable urethanes with polyglycol units promote the aqueous/alkaline development, without adversely affecting the resistance to overdevelopment.

Printing plates having photopolymerizable layers which contain such polymerizable urethanes can be developed by dipping them in a cell filled with developer.

The preparation of the light-sensitive materials using the mixture according to the invention is effected in a known manner. Thus, the mixture can be taken up in a solvent and the solution or dispersion can be applied as a film, on the support provided, by pouring, spraying, dipping or application with rollers, and can subsequently be dried.

The type of support depends on the intended use of the light-sensitive materials. For the preparation of lithographic printing plates, aluminum which preferably carries an anodically produced porous oxide layer is generally used. The aluminum is advantageously roughened, mechanically, chemically or electrolytically, before the anodic oxidation process. The anodic oxidation process is effected in a known manner, for example in sulfuric acid and/or phosphoric acid, preferably under conditions such that an oxide layer having a layer weight of about 0.5 to 10 g/m² is obtained.

Before the application of the light-sensitive layer, the oxide layer is advantageously subjected to a pretreatment to improve the printing behavior, particu-

larly the hydrophilia, for example using silicates or polyvinyl phosphonic acid.

In addition to aluminum and aluminum alloys, steel, zinc, copper, nickel, chromium-plated steel or chromium-plated copper, silicon dioxide layers which have thermally grown or been separated on silicon, or doped oxide layers, plastic films, for example composed of polyethylene terephthalate or cellulose acetate, or screen printing supports, for example perlon gauze or nickel screens, can also be used.

10 The images are produced on the recording materials in a known manner, for example by contact exposure using a transparent original. The customary light sources, such as carbon arc lamps, xenon lamps, mercury high pressure lamps doped with metal halides, and the like, are used in this process. The images can also be produced using laser light, for example using an argon ion laser.

15 The development of the exposed recording materials is effected in a known manner, by washing out the unexposed regions of the layer with a developer. The composition of the developer depends on the nature and solubility of the light-sensitive layer. Suitable developers are organic solvents or solvent mixtures, water, 20 which can contain small quantities of organic solvents or surfactants, and in particular alkaline aqueous solutions, which can contain buffer salts, for example alkali metal phosphates or silicates, organic solvents, 25 surfactants, dyestuffs and other customary additives. Developers which are free of organic solvents are preferred.

The mixtures according to the invention are particularly suitable in the form of a presensitized copying

material on a suitable support for the photomechanical preparation of offset printing plates. They are also suitable for the preparation of dry-resist films, relief images, screenprinting templates and color-proofing films, and it is possible to use them as liquid resists, in addition. They are also useful as rapidly hardening coating compositions, teeth filling compositions and adhesives, and for the preparation of hard moldings stable to heat.

10 The examples which follow illustrate embodiments of the mixture according to the invention and their use for the preparation of photopolymerizable copying materials. Percentage data and proportions are to be understood as weight units, if not otherwise indicated.

15 Example 1

Electrochemically roughened and anodically oxidized aluminum which had an oxide layer of 2 g/m^2 and which had been pretreated with an aqueous solution of polyvinylphosphonic acid was used as the support for printing plates.

20 The support described above was spin-coated with a solution composed of
2 parts by weight of a styrene/maleic anhydride copolymer which was partly esterified with alkanol and which had an average molecular weight of
25 20,000 and an acid number of about 200,
2 parts by weight of the diurethane described below,
0.125 part by weight of 9-phenyl-acridine and
0.05 part by weight of a blue dyestuff, obtained by coupling 2,4-dinitro-6-chloro-benzene diazonium

salt with 2-methoxy-5-acetylamino-N-cyanoethyl-N-hydroxyethyl-aniline in

- 25 parts by weight of butanol and
- 12 parts by weight of butyl acetate.

5 The plate was then dried in a circulating air-drying cabinet for 2 minutes at 100°C. A layer weight of 3.7 - 4 g/m² was obtained.

10 The printing plate obtained was exposed for 40 seconds, under a 13-step intensity wedge with density increments of 0.15, by means of a 5 kW metal halide lamp, with a distance of 110 cm between lamp and vacuum copying frame.

The plate was then developed manually, using a developer of the following composition:

- 15 3.0 parts by weight of sodium metasilicate x 9 H₂O,
- 0.03 part by weight of a non-ionic surfactant (coconut fatty alcohol polyoxyethylene ether having approx. 8 oxyethylene units),
- 0.003 part by weight of anti-foaming agent,
- 20 0.02 part by weight of nitrilotriacetic acid,
- 0.053 part by weight of strontium chloride x 6 H₂O, and
- 96.894 parts by weight of completely demineralized water.

5 completely crosslinked wedge steps were obtained.

25 Preparation of glycerol dimethacrylate

1282.5 g (9 moles) of glycidyl methacrylate were added dropwise, during the course of 3 hours and whilst stirring, to a mixture of 860.9 g (10 moles) of methacrylic acid, 21.4 g of benzyltriethylammonium chloride

and 5 g of p-methoxy-phenol at 75 - 85°C. The mixture was further stirred for 2 hours at 80°C, and the solution was then poured into dilute sodium bicarbonate solution and stirred for some time. The organic phase was separated off and again washed with sodium bicarbonate solution. The product was dried over sodium sulfate and, after filtration, was stabilized with 15 g of p-methoxy-phenol. Small portions of approx. 150 g each were fractionally distilled at 0.07 mbar and a bath temperature of about 140°C. Boiling point (0.08 mbar) 115°C. Yield: 1541 g = 75 % of theory.

Partial polymerization occurs on distillation.

Analysis:

	calculated:	C: 57.89	H: 7.02
15	found:	C: 57.7	H: 7.05
	calculated:	OH number: 245.8; Br number: 491.6; ester number: 140	
	found:	OH number: 247; Br number: 489; ester number: 135	

20 Synthesis of the diurethane

336.4 g (2 moles) of hexamethylene diisocyanate and 4 g of benzoquinone in 350 g of butanone were initially introduced into a three-necked flask fitted with a stirrer, a reflux condenser with a mounted CaCl_2 drying tube, and a dropping funnel. After the addition of a catalyst solution composed of 0.85 g of iron (III) acetylacetonate and 0.06 g of triethylamine in 40 ml of butanone, 913 g (4 moles) of glycerol dimethacrylate in 900 g of butanone were added dropwise to the mixture at 80°C,

during the course of 2.5 hours.

The mixture was further stirred for 2 hours at 80°C, 8 ml of ethanol were then added, and the mixture was again stirred for 1 hour at 80°C. The approx.

- 5 50 % strength solution of the diurethane in butanone was directly employed for the preparation of the coating solution.

Example 2

- 10 0.04 parts by weight of amorphous highly porous silicic acid having an average particle size of 8 μ m was added to the coating solution given in Example 1, and the support was spin-coated with this mixture such that a layer weight of 4 g/m² was obtained.

- 15 The plate was further processed in a manner identical to that in Example 1.

5 completely crosslinked wedge steps were obtained.

- 20 The printing plate attained a print run of 170,000 sheets in a conventional damping unit, and a print run of 70,000 sheets in an alcohol damping unit.

Example 3

- 1 A coating solution was prepared from
1 part by weight of a methyl-methacrylate/methacrylic acid copolymer having a molecular weight of 30,000
25 and an acid number of 117,
1 part by weight of the copolymer given in Example 1,
2 parts by weight of a diurethane obtained from
2 moles of glycerol dimethacrylate and 1 mole of
2,2,4-trimethyl-hexamethylene diisocyanate,

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0.125 part by weight of 9-phenyl-acridine,
0.07 part by weight of the dyestuff given in Example 1
and
0.04 part by weight of the silicic acid given in Example
5 2 in
28 parts by weight of butanone and
12 parts by weight of butyl acetate,
and the aluminum support described in Example 1 was
spin-coated with this solution such that a dry layer
10 weight of 5 g/m² was obtained.

Exposure, development and assessment were effected
as in Example 1.

4 completely crosslinked wedge steps were ob-
tained.

15 Example 4

The support given in Example 1 was spin-coated
with a solution of the following composition such that a
layer weight of 1.8 g/m² was obtained after drying:

2 parts by weight of the copolymer given in Example 1,
20 1.6 parts by weight of the oligourethane described
below,
0.5 part by weight of 9-phenyl-acridine and
0.05 part by weight of the dyestuff given in Example 1
in
25 25 parts by weight of butanone,
12 parts by weight of butyl acetate and
20 parts by weight of ethylene glycol monomethyl ether.

Exposure and development were effected as in
Example 1.

7 completely crosslinked wedge steps were obtained.

It was also possible to develop the printing plate in a developing cell. For this purpose, it was hung, after exposure, in a cell filled with the developer described in Example 1. The plate was developed after approx. 2 minutes. It had only to be sprayed off with water.

Synthesis of the oligourethane

10 336.4 g (2 moles) of hexamethylene diisocyanate
in 660 g of butanone were initially introduced into a
three-necked flask fitted with a stirrer, a reflux condenser
with a mounted drying tube, and a dropping funnel.

After the addition of a mixture acting as a
15 catalyst and being composed of
0.07 g of iron (III) acetylacetonate and
0.005 g of triethylamine in
5 ml of butanone,
400 g (1 mole) of polyethylene glycol 400, dissolved in
20 330 g of butanone, were added dropwise to the mixture at
70°C, during the course of 1.5 hours. The mixture was
then warmed to 70°C for 2 hours. 4 g of benzoquinone
and 5 ml of the catalyst solution described above were
added to the mixture, and a solution of 456.5 g (2 moles)
25 of the glycerol dimethacrylate described in Example 1,
in 330 g of butanone, was added dropwise at 70°C, during
the course of 1 hour. After the end of the addition,
the mixture was stirred for a further 2.5 hours at 70°C,
20 ml of ethanol were then added, and the mixture was

- 21 -

again heated to 70°C for 1 hour.

After the solvent had been distilled off, the mixture was extracted by shaking with 5 l of water.

The formation of an emulsion was prevented by the addition of approx. 200 ml of 15 % strength NaCl solution. After the mixture had been taken up in 500 ml of ethyl acetate, it was again washed out with 5 l of water.

The organic phase was separated off, diluted with a further 2.1 l of ethyl acetate and dried over sodium sulfate.

10 An oleaginous product was precipitated by the addition of 1.4 l of gasoline (boiling range 40 - 80°C), and this product was taken up in 2 l of ethyl acetate and again precipitated with 1.1 l of gasoline.

After stabilization with 2.4 g (approx. 0.3 %) of p-methoxyphenol, the remaining solvent was removed at a bath temperature of approx. 40°C.

Yield: 674 g = 56.5 % of theory.

The molecular weight distribution of the product obtained was determined by gel chromatography against the diurethane described in Example 1, as a comparison.

20 The evaluation gave a proportion of about 15 % for homologues having 4 urethane groups, of about 24 % for homologues having 6 urethane groups, and of about 58.5 % for homologues having more than 6 urethane groups.

Example 5

25 A plate coated as in Example 4 was provided with a polyvinyl alcohol covering layer of 4 g/m² after drying.

Samples of this plate were exposed for 5, 10, 20 or 40 seconds in each case, under a 13-step intensity wedge

with density increments of 0.15, by means of a metal halide lamp, and were thereafter developed with the developer solution described in Example 1.

In a further experiment, samples of the same plate, after exposure, were heated in a circulating air drying cabinet for 5 seconds at 100°C and then developed.

The following table shows that the layer has a strictly reciprocal behavior and that the subsequent heating step results in a significant increase in the completely crosslinked wedge steps. The number of almost completely crosslinked wedge steps is given in brackets.

Wedge steps	Exposure time (seconds)			
	5	10	20	40
without subsequent heating	3 (4)	5	7 (8)	9 (10)
with subsequent heating	9 (10)	10 (11)	12 (13)	13

A comparison of the completely crosslinked wedge steps of the printing plate exposed for 40 seconds and having a covering layer (9 (10)) with those of the corresponding plate without a covering layer (7; Example 4) shows that the layer has only little sensitivity to oxygen.

Layers having other monomers (for example trimethylolethane triacrylate) crosslink substantially less under the action of oxygen (that is to say without a covering layer) than with the covering layer. (4 wedge steps without a covering layer and 9 wedge steps with a covering layer, for an exposure time of 40 seconds).

Example 6

The support given in Example 1 was whirler-coated with solutions of the following composition such that a layer weight of 2.5 g/m² was obtained after drying:

- 5 2 parts by weight of the copolymer given in Example 1,
 1.6 parts by weight of one of the following compounds
- a) oligourethane obtained from 2 moles of glycerol dimethacrylate, 2 moles of hexamethylene diisocyanate and 1 mole of polyethylene glycol 200,
 - 10 b) analogous oligourethane having 1 mole of polyethylene glycol 300,
 - c) analogous oligourethane having 1 mole of polyethylene glycol 600,
 - d) analogous oligourethane having 1 mole of polyethylene glycol 1000,
 - 15 e) analogous oligourethane having 1 mole of diisopropylene glycol,
 - f) analogous oligourethane having 1 mole of polyisopropylene glycol 400,
 - 20 0.5 part by weight of 9-phenyl-acridine and
 - 0.05 part by weight of the azo dyestuff from Example 1 in
 - 23 parts by weight of butanone,
 - 12 parts by weight of butyl acetate and
 - 12 parts by weight of ethylene glycol monomethyl ether.

25 The plates were exposed for 40 seconds and were developed with the developer solution given in Example 1.

The following number of completely crosslinked wedge steps were obtained:

574

Monomer	Development time (seconds)	Wedge steps
a	15	5 (6)
b	10	6 (7)
5 c	5	8 (9)
d	5	4 (5)
e	45	3 (4)
f	30	4

Example 7

- 10 Coating solutions were prepared from
- 2 parts by weight of the copolymer given in Example 1,
- 2 parts by weight of one of the following monomers
- a) 2,2-bis-[4-(2-acryloyloxy-propoxy)-phenyl] propane,
- 15 b) trimethylolethane triacrylate,
- c) reaction product of 1 mole of 2,2,4-trimethyl-hexamethylene diisocyanate and 2 moles of hydroxyethyl methacrylate,
- d) reaction product of 1 mole of triethylene glycol, 2 moles of 2,2,4-trimethyl-hexamethylene diisocyanate and 2 moles of hydroxyethyl methacrylate,
- 20 e) diurethane from Example 1,
- f) oligourethane from Example 4,
- 25 0.125 part by weight of 9-phenyl-acridine and
- 0.05 part by weight of the azo dyestuff from Example 1 in
- 27 parts by weight of butanone and
- 12 parts by weight of butyl acetate,
- and electrolytically roughened and anodically oxidized aluminum was

spin-coated with the solutions such that a dry layer weight of 3.5 g/m² was obtained. The plates were exposed for 10, 20 and 40 seconds, and were then manually developed for 90 seconds with the developer given in

5 Example 1.

In another experiment, the plates were stored in a circulating air drying cabinet for 1 hour at 100°C, and were thereafter exposed for 40 seconds and developed for 90 seconds. The results are summarized in the follow-

10 ing table:

	Monomer	Developing time (seconds)	Exposure time (seconds)			
			10	20	40	40 (1 hour 100°C)
15			Wedge steps			
	a	30	2 (3)	3 (4)	4 (5)	3
	b	20	2	3	4	0
	c	20	3 (4)	3 (4)	4 (5)	2 (3)
	d	25	2	4	5	5
20	e	20	1	3	5	5
	f	5	2 (3)	4 (5)	6 (7)	6 (7)

It is clear that the four comparative monomers exhibit disadvantages in comparison with the compounds (e, f) described in this application, both with respect to development time and reciprocity and with respect to volatility (100°C test).

Example 8

A biaxially stretched and heat-set polyethylene terephthalate film of 25 μ m thickness was spin-coated

with a solution of

- 6.5 parts by weight of a terpolymer of n-hexyl methacrylate, methacrylic acid and styrene (60:30:10) having an average molecular weight of approx. 35,000,
- 5.6 parts by weight of the diurethane described in Example 1,
- 0.2 part by weight of 9-phenyl-acridine and
- 0.02 part by weight of the azo dyestuff from Example 1 in
- 10 25 parts by weight of butanone and
- 3 parts by weight of ethanol,
- such that a layer weight of 33 g/m² was obtained, after drying at 100°C.

The dry-resist film thus prepared was laminated at 120°C, using a commercial laminating device, onto a laminated phenoplast plate backed with copper film of 35 µm thickness, and was exposed for 20 seconds with a commercial exposure device. A lined original with line widths and intervals down to 80 µm was used as the original.

After the exposure, the polyester film was removed and the layer was developed for 90 seconds in a spray-development apparatus, using the developer solution described in Example 1.

The plate 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 successively electroplated in the following electrolyte

baths:

1) For 30 minutes in a copper electrolyte bath of Schlötter, Geislingen/Steige, "Glanzkupfer-Bad" type

current density: 2.5 A/dm^2

5 metal deposit: approx. $15 \text{ }\mu\text{m}$

temperature: room temperature

2) for 10 minutes in a nickel bath of the "Norma" type of Schlötter, Geislingen/Steige

current density: 4 A/dm^2

10 metal deposit: $10 \text{ }\mu\text{m}$

temperature: 50°C

The plate shows no undercuttings or damage.

It was then possible to remove the layers from the plate in 5 % strength KOH solution at 50°C and to
15 etch away the exposed copper in the customary etching media.

Example 9

A laminated phenoplast plate backed with copper film of $35 \text{ }\mu\text{m}$ thickness was spin-coated with the resist solution described in Example 8 and the plate was
20 dried (30 g/m^2).

The plate was exposed, developed and electroplated analogously to Example 8, the following procedure being carried out instead of the nickel plating:

25 15 minutes in a pewter bath LA of Schlötter, Geislingen/Steige

current density: 2 A/dm^2

metal deposit: $15 \text{ }\mu\text{m}$

temperature: room temperature

88

This plate also showed no undercuttings or damage, and it was possible to remove the layers with KOH solution and to etch the plate with customary etching agents.

Example 10

- 5 A cleaned support composed of an insulating material with a 35 μm copper coating was whirler-coated with a solution of
- 6.5 parts by weight of the terpolymer given in Example 8,
5.6 parts by weight of the oligourethane from Example 4,
10 0.2 part by weight of 9-phenyl-acridine and
0.02 part by weight of the azo dyestuff from Example 1 in
25 parts by weight of butanone and
3 parts by weight of ethanol,
such that a dry layer thickness of 4 μm was obtained.
- 15 The layer was dried in a circulating air drying cabinet for 2 minutes at 100°C. It was then exposed for 40 seconds by means of a 5 kW lamp. The lined original described in Example 8 was used as the original. After the exposure, the plate was developed in a spray
20 processor for 45 seconds, using 0.8 % strength sodium carbonate solution.

The plate was rinsed, etched and then electroplated as follows:

- 1) for 8 minutes in the "Glanzkupferbad" described in
25 Example 8
current density: 2.5 A/dm²
metal deposit: approx. 4 μm
temperature: room temperature
- 2) for 2 minutes in the nickel bath "Norma" described in

Example 8

current density: 4 A/dm²

metal deposit: approx. 2 μm

temperature: 50°C

5 It showed no undercuttings.

It was possible to remove the layers from the plate in 5 % strength KOH solution at 50°C and to etch away the exposed copper in the customary etching media.

Example 11

10 The support given in Example 1 was spin-coated with solutions of the following composition, such that layer weights of 2.2 g/m² were obtained:

- 2 parts by weight of a styrene/maleic anhydride copolymer (1:1, molecular weight 50,000), which had
- 15 been reacted with hydroxyethyl methacrylate (molecular weight of the reacted product about 80,000),
- 2 parts by weight of one of the following monomers
- a) diurethane obtained from 2 moles of glycerol dimethacrylate and 1 mole of hexamethylene diisocyanate,
- 20 b) oligourethane obtained from 2 moles of glycerol dimethacrylate, 2 moles of hexamethylene diisocyanate and 1 mole of polytetrahydrofuran-diol (commercial product with a molecular
- 25 weight of 1000),
- c) oligourethane obtained from 2 moles of glycerol dimethacrylate, 2 moles of hexamethylene diisocyanate and 1 mole of polycaprolactonediol (molecular weight 830),

- d) oligourethane obtained from 2 moles of glycerol dimethacrylate, 2 moles of hexamethylene diisocyanate and 1 mole of polyethylene glycol 400,
- 5 e) oligourethane obtained from 2 moles of glycerol dimethacrylate, 2 moles of hexamethylene diisocyanate and 1 mole of 4,4'-dihydroxydiphenylsulfone,
- f) analogous oligourethane with 1 mole of bisphenol A,
- 10 g) analogous oligourethane with 1 mole of the reaction product of 1 mole of bisphenol A and 2 moles of ethylene oxide,
- h) analogous oligourethane with 1 mole of the reaction product of 1 mole of bisphenol A and 8
- 15 moles of ethylene oxide,
- i) analogous oligourethane with 1 mole of the reaction product of 1 mole of bisphenol A and 16 moles of ethylene oxide
- k) diurethane obtained from 1 mole of hexamethylene
- 20 diisocyanate and 2 moles of the reaction product of 1 mole of glycidyl methacrylate and 1 mole of acrylic acid,
- l) diurethane obtained from 2 moles of glycerol diacrylate and 1 mole of hexamethylene diisocyanate, or
- 25 m) tetraurethane obtained from 2 moles of glycerol dimethacrylate and 1 mole of the reaction product of 2 moles of tolylene diisocyanate and 1 mole of polytetrahydrofurandiol (molecular

weight about 2000),

- 0.7 part by weight of 9-phenyl-acridine,
 0.07 part by weight of the azo dyestuff from Example 1,
 32 parts by weight of butanone,
 5 12 parts by weight of butyl acetate and
 12 parts by weight of ethylene glycol monomethyl
 ether.

The plates were exposed, as in Example 1, for
 40 seconds, and were developed with the developer so-
 lution given in Example 1.

The wedge step number and development time are
 given in the following table:

	Monomer	Development Time (seconds)	Wedge steps
15	a	7	7 (8)
	b	7	10 (11)
	c	7	9 (10)
	d	5	10
	e	5	2 (3)
20	f	> 30	2
	g	> 30	3 (4)
	h	7	8 (9)
	i	7	11
	k	5	7 (8)
25	l	5	5 (6)
	m	7	10 (11)

Example 12

If the binding agent given in Example 11 is re-
 placed by a styrene/monoallyl maleate copolymer (molecular
 weight ~ 64,000) and the recipe is otherwise identical,

6 (7) completely crosslinked wedge steps are obtained for the monomer 'a' from Example 11 and 8 (9) completely crosslinked wedge steps are obtained for the monomer 'c'. The development time is shorter than 5 seconds in both cases.

Example 13

Coating solutions of

- | | | |
|----|------|--|
| 5 | 1.6 | parts by weight of the copolymer given in Example 1, |
| 10 | 0.4 | part by weight of a copolymer of methylvinyl ether and maleic acid monobutyl ester, having an acid number of about 260, |
| 15 | 2 | parts by weight of one of the following monomers
a) reaction product of 2 moles of glycerol dimethacrylate and 1 mole of hexamethylene diisocyanate,
b) reaction product of 3 moles of glycerol dimethacrylate, 3 moles of hexamethylenediisocyanate and 1 mole of trimethylolethane,
c) reaction product of 3 moles of glyceroldimethacrylate, 3 moles of hexamethylene diisocyanate and 1 mole of trimethylolpropane, |
| 20 | 0.7 | part by weight of 9-phenyl-acridine, |
| 25 | 0.07 | part by weight of the azo dyestuff from Example 1 in |
| 30 | 12 | parts by weight of butanone, |
| 12 | 12 | parts by weight of butyl acetate and |
| 12 | 12 | parts by weight of ethylene glycol monomethyl ether |

(62)

were prepared and spin-coated onto electrolytically roughened and anodically oxidized aluminum, such that a layer weight of 2.5 g/m^2 was obtained after drying.

5 The plates were exposed for 40 seconds and were developed with the developer solution given in Example 1.

The following number of completely cross-linked wedge steps were obtained:

Monomer	Development time (seconds)	Wedge steps
a	10	6 (7)
b	30	6 (7)
c	35	5 (7)

Example 14

15 A silicon wafer bearing a $1 \mu\text{m}$ thick silicon dioxide layer was spin-coated with a coating solution of

6.5 parts by weight of the terpolymer given in Example 8,

5.0 parts by weight of the diurethane from Example 1,

0.7 part by weight of 9-phenylacridine and

20 0.125 part by weight of a blue dyestuff, obtained by coupling 2,4-dinitro-6-chloro-benzene diazonium salt with 2-methoxy-5-acetylamino-N,N-diethyl aniline, in

30 parts by weight of butanone and

25 28 parts by weight of ethylene glycol monomethyl ether such that a layer weight of 1 g/m^2 was obtained after drying for 10 minutes at 80°C .

By means of an exposure equipment the sample was exposed for 6 seconds through a test original having structures

of down to 1.5 μm (irradiation strength 8.4 mW/cm^2) and developed in a 0.8 % strength sodium carbonate solution for 45 seconds. Then etching was carried out for 10 minutes at 23 $^{\circ}\text{C}$, in a mixture of 70 g of ammonium fluoride, 31 ml of 40 % strength hydrofluoric acid and 105 ml of de-ionized water. Thereafter decoating took place for 2 minutes at 110 $^{\circ}\text{C}$, in a mixture of 300 ml of 98 % strength sulfuric acid and 50 ml of 35 % strength hydrogen peroxide solution.

Images with sharp edges were obtained of structures down to 1.5 μm .



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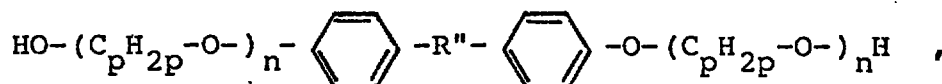
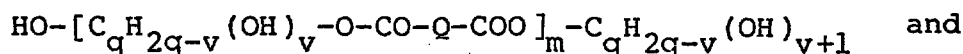
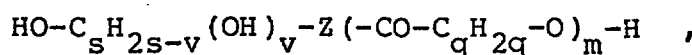
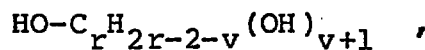
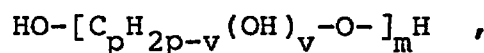
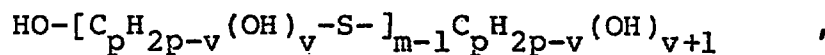
(15)

WHAT IS CLAIMED IS:

1. A mixture which is polymerizable by radiation and which contains, as the essential constituents,
- a) a polymeric binding agent,
 - b) a polymerization initiator which can be activated by radiation and
 - c) an acrylate or methacrylate of a polyhydric hydroxy compound having at least two urethane groups in the molecule,

characterized in that the ester is a reaction product of glycerol dimethacrylate or glycerol diacrylate and a polyisocyanate which has been obtained by reacting a polyhydroxy compound having 2 to 6 OH groups with a diisocyanate, or a reaction product of glycerol dimethacrylate or glycerol diacrylate and a diisocyanate.

2. A mixture which is polymerizable by radiation as claimed in Claim 1, characterized in that the polyhydroxy compound is a compound of one of the following general formulas

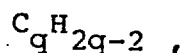
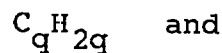




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wherein

R" is O, S, CR₂ or SO₂,
Q is a phenylene group or one of the groups



R is a hydrogen atom or a methyl group,
Z is O or NR,
n is an integer from 0 to 20,
m is an integer from 1 to 40,
p is an integer from 2 to 20,
q is an integer from 2 to 10,
r is an integer from 4 to 20,
s is an integer from 2 to 10,
v is an integer from 0 to 4,

p, q, and s being at least by 2 greater than v,
and r being at least by 4 greater than v.

3. A mixture which is polymerizable by radiation as claimed in Claim 1, characterized in that the ester contains 2 to 40 urethane groups.

4. A mixture which is polymerizable by radiation as claimed in Claim 1, characterized in that the ester is a methacrylic acid ester.

5. A mixture which is polymerizable by radiation as claimed in Claim 1, characterized in that the diisocyanate is a compound of the formula OCN-X-NCO, wherein X means a hydrocarbon radical having 2 to 20 carbon atoms.

6. A photopolymerizable recording material comprising a layer support and a photopolymerizable layer which, as the essential components, contains

- a) a polymeric binding agent,
- b) a polymerization initiator which can be activated by radiation and
- c) an acrylate or methacrylate of a polyhydric hydroxy compound having at least two urethane groups in the molecule,

characterized in that the ester is a reaction product of glycerol dimethacrylate or glycerol diacrylate and a polyisocyanate which has been obtained by reacting a polyhydroxy compound having 2 to 6 OH groups with a diisocyanate, or a reaction product of glycerol dimethacrylate or glycerol diacrylate and a diisocyanate.

