

Description

The present invention relates to a positive-working light-sensitive mixture, in particular a photo-resist mixture, essentially composed of a binder and a light-sensitive compound.

The preparation of positive-working photoresist mixtures is known (US-A-3,666,473, US-A-4,115,128, US-A-4,173,470 and US-A-4,550,069). They involve essentially combinations of an alkali-soluble novolak resin or a polyvinylphenol with a light-sensitive compound, usually a substituted o-quinone diazide compound. The resins and light-sensitive substances are dissolved in an organic solvent or solvent mixture and are applied as a thin layer or coating to a suitable layer support.

Although the novolak or polyvinylphenol components of these photoresist mixtures are soluble in aqueous-alkaline solutions, the light-sensitive o-quinone diazide compounds act on the resin as solution retarder. If, however, certain regions of the coated support are exposed to actinic radiation, the light-sensitive compound undergoes structural transformation due to the irradiation and the exposed regions of the coating become more soluble than the uncoated regions. Because of this solubility difference, the exposed regions of the photoresist dissolve in an alkaline developer solution so that a positive relief image is produced on the support.

In most cases, the exposed and developed support is treated with an etching solution, the photoresist layer protecting the unexposed regions of the support against the etchant.

The relief image produced on the support by the process described above is suitable for various application purposes, for example as a mask or image, for example during the production of semiconductor components in microelectronics.

Important properties for the commercial utilisation of a photoresist are the following: light sensitivity, development contrast, image resolution and

adhesion of the resist to the support.

High light sensitivity is important for a photoresist, in particular, if it is used for applications in which a plurality of exposures are necessary, for example in the production of multiple images in a repetitive process or in cases in which light having attenuated intensity is used, for example in the projection exposure technique in which the light passes through a series of objectives and monochromatic filters.

Development contrast is understood as meaning the difference between the percentage of the layer loss in the exposed regions after development and the percentage of the layer loss in the unexposed regions (dark-area erosion). Normally, a resist-coated support is developed after exposure until the layer has been essentially completely stripped in the exposed regions. The development contrast can therefore be determined by measuring the percentage of the layer loss in the unexposed regions after completely stripping the exposed layer regions.

Resolution of the resist is understood as meaning the ability of a resist system to reproduce the smallest line pairs, arranged at an equal distance from one another, and the associated gaps of a mask used for the exposure, with a high degree of edge steepness of the image in the developed exposed gaps.

For many technical applications, in particular for the production of semiconductor components in microelectronics, a photoresist must have a high degree of resolution if it is to reproduce very small lines and gap widths (in the order of magnitude of 1 μm).

The ability of a resist to reproduce very small dimensions in the order of magnitude of 1 μm and below is of greatest importance in the production of LSI (Large-Scale Integrated) circuits on silicon chips and similar components. If photolithographic processes are used, the circuit density on such a chip can only be increased by increasing the resolving power of the resist.

To achieve the necessary light sensitivity and the desired contrast, the concentration of light-sensitive

compounds in the photoresist mixture must be high enough to prevent a dissolution of the unexposed resist regions during the development. High concentrations of light-sensitive compounds can be achieved either by dissolving
5 a mixture of highly soluble and less readily soluble light-sensitive compounds in the photoresist solution or by supersaturating the photoresist solution with a light-sensitive compound.

Concentrations of light-sensitive compound in the
10 photoresist solution which are close to the saturation limit may, however, significantly reduce the shelf life of the photoresist solution since, in this case, the solution tends to be unstable or a precipitation of the light-sensitive compound before or during the use of the
15 photoresist mixture is possible. This problem is referred to in US-A-4,397,937 and US-A-4,526,856.

The condensation products of 1,2-naphthoquinone-diazide-4-sulphonic acid and aromatic diols or polyols are an important group of light-sensitive compounds.
20 Photoresist mixtures which contain these compounds are in general notable for good light-sensitivity and outstanding contrast when exposed in the middle-UV region. But here, too, there is the tendency to low solubility and to solution instability.

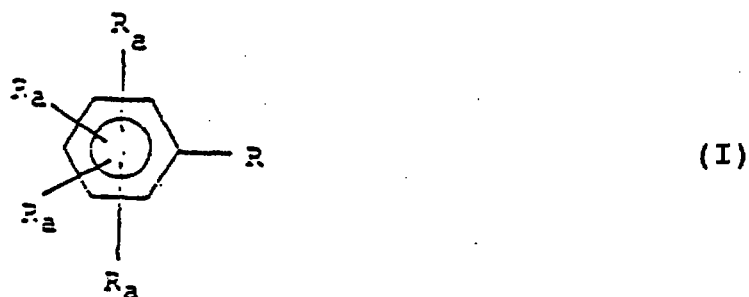
To improve the solubility, US-A-4,397,937 proposes using as light-sensitive compound a bisester of a
25 1-oxo-2-diazonaphthalenesulphonic acid and an asymmetrical primary or secondary aliphatic diol which is a mixture of geometrical isomers and diastereoisomers. As
30 1,2-naphthoquinone-diazide-sulphonic acids, use can be made both of the -4-sulphonic acids, the -5-sulphonic acids and mixtures of the two in which one hydroxyl group of the asymmetrical aliphatic diol is esterified with a
35 1,2-naphthoquinone-5-sulphonic acid, while the other hydroxyl group is esterified with a 1,2-naphthoquinone-diazide-4-sulphonic acid. However, only certain asymmetrical aliphatic diols are suitable.

In US-A-4,526,856, an attempt is made to avoid the problems which occur on increasing the concentration

of the light-sensitive compounds by altering the solvent system of the photoresist mixtures. In certain mixing ratios which are to be adhered to precisely, the use of a solvent mixture composed of cyclopentanone, or cyclopentanone and cyclohexanone, and an aliphatic alcohol results in good solution behaviour.

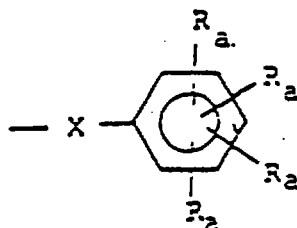
The object of the present invention was to propose a light-sensitive mixture which has excellent solution properties and an improved shelf life even at fairly high concentrations of the light-sensitive compound without exhibiting disadvantages in relation to the achievable light sensitivity. The light-sensitive mixture furthermore exhibits a higher contrast and a longer induction time, provided it is treated with a developer which is free of metal ions.

According to the invention, a light-sensitive mixture is proposed which contains a binder, which is insoluble in aqueous systems and soluble or at least swellable in aqueous-alkaline and organic solvents, and also a light-sensitive compound, characterised in that the light-sensitive compound is a condensation product of a phenolic compound of the formula I



in which

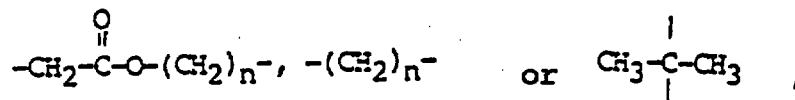
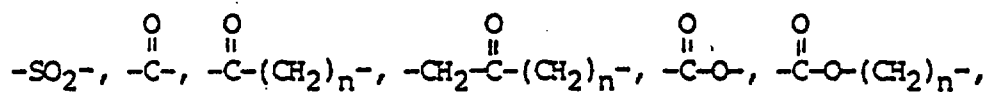
R is hydrogen, -X-R_b or



R_a is hydrogen, an OH group, halogen or a lower alkyl group, at least two and at most six R_a groups being

OH groups,

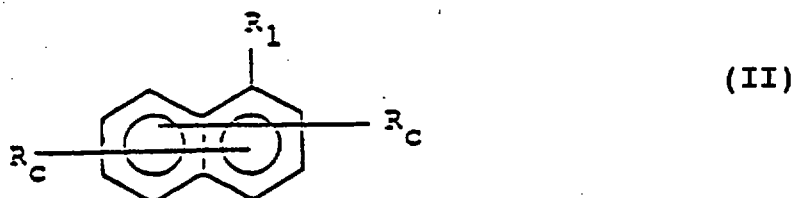
X is a C-C bond, -O-, -S-,



n is 1 or 2 and

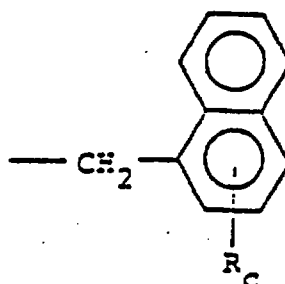
R_b is hydrogen or a substituted or unsubstituted alkyl or aryl group,

or of the formula II



in which

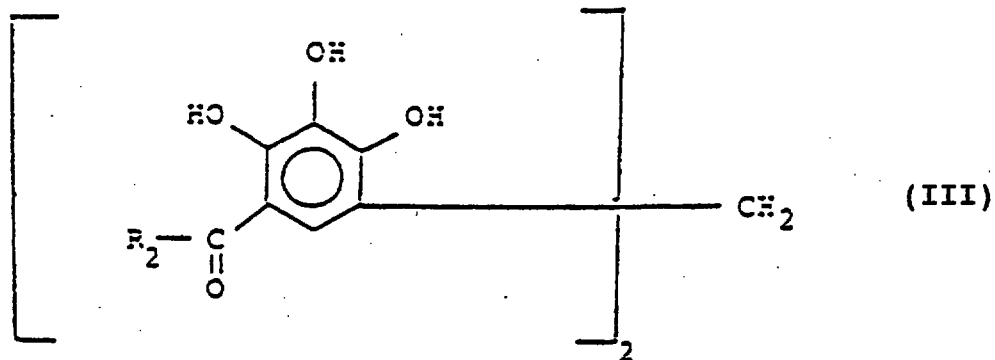
R₁ is hydrogen or



and

R_c is hydrogen or an OH group, at least two R_c groups being OH groups,

or of the formula III



in which

R₂ is hydrogen or a substituted or unsubstituted alkyl

or aryl group,
with a mixture of a 1,2-naphthoquinone-diazide-5-sul-
phonic acid chloride (diazo compound) and an organic acid
halide of the formula IV

5



(IV)

in which

W is $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{V} \end{array}$ or $-\text{SO}_2-\text{V}$, V being a halogen, and
10 R₃ is a substituted or unsubstituted alkyl or aryl
group.

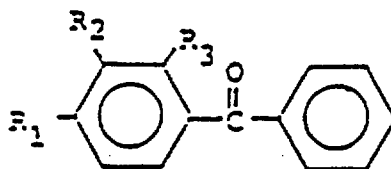
In addition, according to the invention, a
process for producing a recording material is proposed,
in which a suitable support is coated with a photoresist
15 mixture essentially composed of a binder and a light-
sensitive compound of the type described above, the
coated support is imagewise exposed by means of UV
radiation, and finally, the exposed layer parts are
removed from the support with an aqueous-alkaline devel-
20 oper.

According to the invention, the precipitation of
the light-sensitive compounds and the instability and
short shelf life of photoresist solutions associated
therewith is counteracted as a result of the fact that a
25 mixed ester of phenolic compounds with 1,2-naphtho-
quinone-diazide-5-sulphonic acid and an organic acid
which is not sensitive to light are used. When these
mixed esters of diazo compound and organic acid are used
with an alkali-soluble binder, the service life and shelf
30 life of the mixtures increase, the light-sensitivity and
the development contrast not being reduced in comparison
with other light-sensitive mixtures which only contain
esters of the diazo compound.

In addition, the photoresists according to the
35 invention have a higher development contrast than known
systems and exhibit longer "induction times" when

developed with a developer solution which is free of metal ions.

The light-sensitive compounds according to the invention are obtained by condensation of phenolic compounds with a mixture of the diazo compound and an organic acid halide. The molar ratio of diazo compound to organic acid halide in the mixture is between 1:2 and 19:1, preferably between 2:3 and 19:1, in particular between 7:8 and 9:1. For example, 1 mol of 2,3,4-trihydroxybenzophenone is condensed with a mixture of 1.4 mol of diazo compound and 1.6 mol of methanesulphonyl chloride. The light-sensitive compound obtained comprises units of the formula



in which R₁, R₂ and R₃ may, independently of one another, each be a 1,2-naphthoquinone-diazide-4-sulphonyloxy group (diazo compound) or a methanesulphonyloxy group.

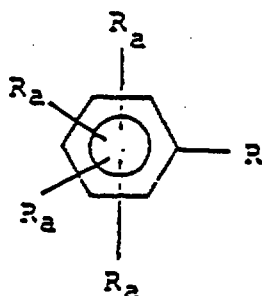
According to the invention, light-sensitive compounds are proposed which are obtained by condensation of phenolic compounds with mixtures of diazo compound and organic acid halides. The diazo component and the acid halide component of the mixture can be condensed simultaneously or consecutively with the phenolic compound.

The mixture of diazo compound and organic acid halide reacts with the phenolic compounds preferably in stoichiometric ratios. However, the phenolic compounds do not have to be completely esterified; less than stoichiometric quantities of diazo compound and organic acid halide can also be reacted with the phenolic compounds.

The total quantity of the mixture of diazo compound and organic acid halide reacted with the phenolic compounds should be so dimensioned that a light-sensitive compound is obtained which ensures an adequate solubility of the light-sensitive mixture in alkaline media after the exposure.

The phenolic compounds which are suitable for the condensation with the mixture of diazo compound and organic acid halide correspond to the formulae I), II) or III) described below:

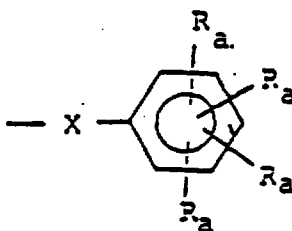
5 I)



(I)

in which

R is hydrogen, -X-R_b or

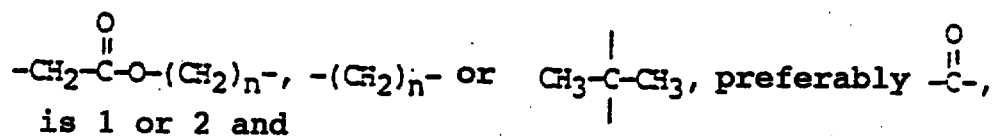
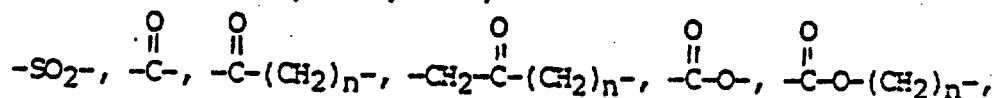


10

R_a is hydrogen, an OH group, halogen, in particular chlorine or bromine, or a lower alkyl group preferably containing 1 to 4 carbon atoms, particularly preferably hydrogen and OH groups, at least two and at most six R_a groups being OH groups,

15

X is a C-C bond, -O-, -S-,



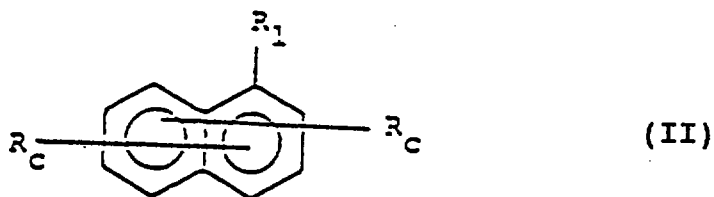
n is 1 or 2 and

20

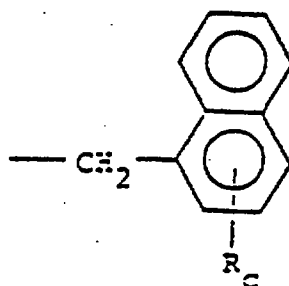
R_b is hydrogen or a substituted or unsubstituted alkyl or aryl group, the alkyl group preferably having 1 to 20, in particular 1 to 12, carbon atoms, the aryl group preferably being a phenyl

or naphthyl group and the alkyl or aryl group having as substituents optionally lower alkyl groups containing 1 to 4 carbon atoms, lower alkoxy groups containing 1 to 4 carbon atoms or halogen atoms, in particular chlorine or bromine; particularly preferred is an unsubstituted phenyl group;

II)



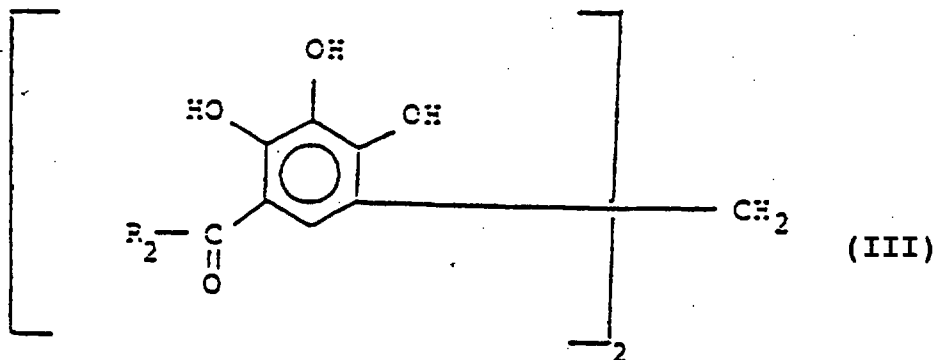
in which
R₁ is hydrogen or



and

R₀ is hydrogen or an OH group, at least two R₀ groups being OH groups; or

III)



in which

R₂ is hydrogen or a substituted or unsubstituted alkyl or aryl group, the alkyl group preferably having 1 to 20 carbon atoms, being capable of being straight or branched and optionally having halogen atoms or lower alkoxy groups containing

1 to 4 carbon atoms as substituents; the aryl group preferably has 1 to 10 carbon atoms, preferably being mononuclear and optionally having lower alkyl or alkoxy groups containing 1 to 4 carbon atoms or halogen atoms as substituents. In this connection, compounds in which R_2 is an aryl group, in particular a phenyl group, are preferred.

The phenolic compounds according to the formula (I) preferably include:

Benzene compounds carrying hydroxyl groups, such as, for example,

1,2-dihydroxybenzene,
1,3-dihydroxybenzene,
15 1,4-dihydroxybenzene,
1,2,3-trihydroxybenzene,
1,2,4-trihydroxybenzene,
1,3,5-trihydroxybenzene;

Dihydroxybenzophenones, such as, for example,

20 2,2'-dihydroxybenzophenone,
2,3'-dihydroxybenzophenone,
2,4-dihydroxybenzophenone,
2,4'-dihydroxybenzophenone,
2,5-dihydroxybenzophenone,
25 3,3'-dihydroxybenzophenone,
4,4'-dihydroxybenzophenone;

Trihydroxybenzophenones, such as, for example,

2,2',6-trihydroxybenzophenone,
2,3,4-trihydroxybenzophenone,
30 2,4,4'-trihydroxybenzophenone,
2,4,6-trihydroxybenzophenone,
2,4,5-trihydroxybenzophenone;

Tetrahydroxybenzophenones, such as, for example,

2,2',3,4-tetrahydroxybenzophenone,
35 2,2',4,4'-tetrahydroxybenzophenone,
2,2',4,6'-tetrahydroxybenzophenone,
2,2',5,6'-tetrahydroxybenzophenone,
2,3',4,4'-tetrahydroxybenzophenone,
2,3',4,6-tetrahydroxybenzophenone,

- 2,4,4',6-tetrahydroxybenzophenone,
3,3',4,4'-tetrahydroxybenzophenone;
Pentahydroxybenzophenones;
Hexahydroxybenzophenones;
- 5 Dihydroxy- and trihydroxyphenyl alkyl ketones, such as,
for example,
2,4-dihydroxyphenyl alkyl ketones,
2,5-dihydroxyphenyl alkyl ketones,
3,4-dihydroxyphenyl alkyl ketones,
10 3,5-dihydroxyphenyl alkyl ketones,
2,3,4-trihydroxyphenyl alkyl ketones,
3,4,5-trihydroxyphenyl alkyl ketones,
2,4,6-trihydroxyphenyl alkyl ketones,
alkyl groups containing 1 to 12 carbon atoms which are
15 optionally branched preferably being used, such as, for
example, methyl, ethyl, butyl, n-hexyl, heptyl, decyl,
dodecyl;
Dihydroxyphenyl arylalkyl ketones;
Trihydroxyphenyl arylalkyl ketones;
- 20 Dihydroxydiphenyls;
Trihydroxydiphenyls, such as, for example,
2,2',4-trihydroxydiphenyl;
Tetrahydroxydiphenyls, such as, for example,
2,2',4,4'-tetrahydroxydiphenyl;
- 25 Dihydroxydiphenyl ethers;
Dihydroxydibenzyl ethers;
Dihydroxydiphenylalkanes, preferably having lower
alkylene chains, such as, for example, methylene,
ethylene, propylene;
- 30 Dihydroxybenzoic acid;
Trihydroxybenzoic acids;
Alkyl dihydroxy- and trihydroxybenzoates, the alkyl group
preferably having 1 to 12 carbon atoms, in particular 1
to 8 carbon atoms, such as, for example,
35 n-butyl 2,4-, 2,5-, 3,4- and 3,5-dihydroxybenzoate,
2,4,4-trimethylpentyl 2,4-dihydroxybenzoate;
Phenyl dihydroxy- and trihydroxybenzoates;
Dihydroxy-, trihydroxy- and tetrahydroxydiphenyl
sulphides, such as, for example, 4,4'-dihydroxydiphenyl

sulphide;

Dihydroxydiphenyl sulphones;

Dihydroxy- and trihydroxyphenyl naphthyl ketones, such as, for example,

5 2,3,4-trihydroxyphenyl 1-naphthyl ketone;
and similar compounds.

The compounds of the formula (I) in which at least one R_a group is a halogen atom or a lower alkyl group include, for example,

10 2,4-dihydroxy-3,5-dibromobenzophenone,
5-bromo-2,4-dihydroxybenzoic acid and its esters,
2,4,2',4'-tetrahydroxy-3,5,3',5'-tetrabromodiphenyl,
4,4'-dihydroxy-2,2'-dimethyl-5,5'-di-tert-butylidiphenyl,
4,4'-dihydroxy-2,2'-dimethyl-5,5'-di-tert-butylidiphenyl
15 sulphide, 2,4,2',4'-tetrahydroxy-3,5,3',5'-tetrabromodi-
phenyl sulphone and similar compounds.

The benzophenones containing hydroxyl groups, in particular the trihydroxybenzophenones, are preferably used as phenolic compounds of the formula (I).

20 The phenolic compounds of the formula (II) preferably include the following compounds:

Dihydroxynaphthalenes, such as, for example,

1,2-dihydroxynaphthalene,
1,4-dihydroxynaphthalene,
25 1,5-dihydroxynaphthalene,
1,6-dihydroxynaphthalene,
1,7-dihydroxynaphthalene,
1,8-dihydroxynaphthalene,
2,3-dihydroxynaphthalene,
30 2,6-dihydroxynaphthalene,
2,7-dihydroxynaphthalene;

Dihydroxydinaphthylmethanes, such as, for example,
2,2'-dihydroxydinaphthylmethane etc.

35 The dihydroxynaphthalenes are preferably used. In this connection, the hydroxyl groups may be located either on one ring or on both rings of the naphthalene molecule.

The phenolic compounds of the formula (III) preferably include the following compounds:
bis(3-benzoyl-4,5,6-trihydroxyphenyl)methane,

bis(3-acetyl-4,5,6-trihydroxyphenyl)methane,
bis(3-propionyl-4,5,6-trihydroxyphenyl)methane,
bis(3-butyryl-4,5,6-trihydroxyphenyl)methane,
bis(3-hexanoyl-4,5,6-trihydroxyphenyl)methane,
5 bis(3-heptanoyl-4,5,6-trihydroxyphenyl)methane,
bis(3-decanoyl-4,5,6-trihydroxyphenyl)methane and
bis(3-octadecanoyl-4,5,6-trihydroxyphenyl)methane.

The organic acid halides which are used to
prepare the mixed esters in addition to the 1,2-naphtho-
10 quinone-5-sulphonyl chlorides, correspond to the
formula IV



(IV)

in which

15
$$W \text{ is } \begin{array}{c} O \\ || \\ -C-V \end{array} \text{ or } -SO_2-V, V \text{ being halogen, in particular} \\ \text{chlorine or bromine, and}$$

$$R_3 \text{ is a substituted or unsubstituted alkyl or aryl}$$

20
$$\text{group; in this connection, the alkyl groups}$$

$$\text{preferably have 1 to 20 carbon atoms, are}$$

$$\text{straight-chain or branched-chain and optionally}$$

$$\text{have halogen atoms, in particular bromine or}$$

25
$$\text{chlorine, or lower alkoxy groups containing 1 to}$$

$$\text{4 carbon atoms as substituents; the aryl groups}$$

$$\text{preferably have 6 to 10 carbon atoms, are}$$

$$\text{preferably mononuclear and optionally have lower}$$

$$\text{alkyl or alkoxy groups containing 1 to 4 carbon}$$

$$\text{atoms or halogen atoms, preferably bromine or}$$

30
$$\text{chlorine, as substituents; phenyl groups are}$$

$$\text{preferred; very particularly preferred are alkyl}$$

$$\text{groups, in particular lower alkyl groups contain-}$$

$$\text{ing 1 to 6 carbon atoms.}$$

The organic acid halides of the above formula
include, for example,
35 Alkylsulphonyl halides, such as, for example
methanesulphonyl chloride,
ethanesulphonyl choride,

propanesulphonyl chloride,
n-butane sulphonyl chloride,
dodecanesulphonyl chloride;
Arylsulphonyl chlorides, such as, for example,
5 benzene sulphonyl chloride,
naphthalenesulphonyl chlorides;
Acyl halides, such as, for example,
acetyl chloride,
butanoyl chloride,
10 valeroyl chloride,
benzoyl chloride,
benzoyl bromide,
naphthoyl chloride.

Preferred are lower alkylsulphonyl halides and
15 lower alkylacyl halides containing 1 to 6 carbon atoms,
and benzenesulphonyl halides and benzoyl halides. The
acid halides may optionally be substituted.

The light-sensitive mixtures according to the
invention, in particular photoresists, are prepared by
20 mixing the light-sensitive compounds with alkali-soluble
resins, solvents and, optionally, further additives.
Suitable alkali-soluble resins are, for example, novolaks
and polyvinylphenols.

Alkali-soluble novolaks which can be used for the
25 preparation of light-sensitive mixtures are known. A
process for producing these novolaks is described in
"Chemistry and Application of Phenolic Resins", by
A. Knop and W. Scheib, Springer Verlag, New York, 1979,
Chapter 4.

30 To prepare the light-sensitive mixtures according
to the invention, the novolak or the polyvinylphenol and
the light-sensitive compound are dissolved in a solvent.
Solvents suitable for this purpose are, for example
glycol ethers such as, for example, ethylene glycol
35 monomethyl ether and ethylene glycol monoethyl ether or,
alternatively, their acetates such as propylene glycol
methyl ether acetate; esters such as, for example, ethyl
acetate and butyl acetate; ketones such as, for example,
methyl ethyl ketone, cyclopentanone and cyclohexanone,

and aromatic hydrocarbons such as, for example, toluene and xylene. Mixtures of these solvents may also be used. The precise choice of the solvent or solvent mixture depends in the individual case on, inter alia, the particular coating process, the desired layer thickness, the drying conditions, the solubility of the individual components and the evaporation rate of the solvent after coating the support with the photoresist mixture.

Before application to a layer support, additives such as, for example, colorants, dyes, flow agents, plasticisers, adhesion promoters, development accelerators and surfactants, for example nonionic surfactants, may also be added to the light-sensitive mixture according to the invention.

In a preferred embodiment, the content of solid constituents of the light-sensitive mixture is about 15 to 99% by weight for the novolak or the polyvinylphenol, and about 1 to 85% by weight for the light-sensitive compound. In particular, the mixture contains the binder in a proportion of about 50 to 97% by weight, and very particularly preferably, of about 65 to 93% by weight, relative to the weight of the solid constituents. The proportion of light-sensitive compound is, in particular, about 3 to 50% by weight and, very particularly preferably, about 7 to 35% by weight, relative to the weight of the solid constituents of the mixture. To prepare the light-sensitive mixture, the binder and [sic] the light-sensitive compound are mixed with the solvent in such a way that the solvent is present in a proportion of about 40 to 90% by weight, preferably of about 60 to 85% by weight, and in particular of about 65 to 80% by weight, relative in all cases to the weight of the entire mixture.

Dyes which may be used as additives for the photoresist mixtures according to the invention are, for example methyl violet 2B (C.I. 42 535), crystal violet (C.I. 42 555), malachite green (C.I. 42 000), Victoria blue B (C.I. 44 045) and neutral red (C.I. 50 040). These dyes are added in a quantity of 1 to 10% by weight,

relative to the combined weight of binder and light-sensitive compound. The dye additives reduce the back scattering of light from the support and therefore contribute to an improved resolution.

5 Flow agents may be used in a quantity of up to 5% by weight, relative to the combined weight of binder and light-sensitive compound.

10 Suitable plasticisers are, for example, tri-(β -chloroethyl)phosphate, stearic acid, dicamphor, polypropylene, acetal resins, phenoxy resins and alkyd resins, which can be added in proportions of 1 to 10% by weight, relative to the combined weight of binder and light-sensitive compound. The plasticiser additives improve the coating properties of the mixture and make
15 possible the application in a smooth and uniformly thick layer to the layer support.

20 Suitable adhesion promoters for improving the adhesion of the mixture to the support are, for example, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, p-methyl-disilanemethyl methacrylate, vinyltrichlorosilane and γ -aminopropyltriethoxysilane, in a proportion of up to 4% by weight, relative to the combined weight of binder and light-sensitive compound.

25 As development accelerators, for example, picric acid, nicotinic acid or nitrocinnamic acid may be added in a proportion of up to 20% by weight, relative to the combined weight of binder and light-sensitive compound. These accelerators have the effect that the solubility of the light-sensitive layer increases both in the exposed
30 and in the unexposed regions. They are therefore used in those applications in which the development rate is of primary importance. While the exposed regions of the photoresist layer are dissolved more rapidly by the developer as a result of the addition of accelerators,
35 the development accelerators at the same time bring about, however, a greater loss of photoresist layer from the unexposed regions, with the result that a certain degree of contrast is possibly lost.

 As nonionic surfactants, for example, nonyl-

phenoxy poly(ethyleneoxy) ethanol, octylphenoxy(ethyleneoxy) ethanol, and dinonylphenoxy poly(ethyleneoxy) ethanol can be used in a proportion of up to 10% by weight, relative to the combined weight of binder and light-sensitive compound.

According to the invention, a light-sensitive recording material is furthermore proposed which is essentially composed of the light-sensitive mixture described above and a support, and a process for producing a photoresist stencil using the recording material:

The light-sensitive mixture can be applied to a support by one of the processes standard in photoresist technique, such as immersion, spraying and spinning-on. In the case of spinning-on, for example, the percentage of solids in the resist solution can be adjusted so that a coating is produced in the desired thickness depending on the spinning device used in the individual case and on the period of time scheduled for the spinning-on operation. Examples of suitable support materials are: silicon, aluminium or polymeric resins, silicon dioxide, doped silicon dioxide, silicon nitride, tantalum, copper, polycrystalline silicon (polysilicon), ceramic and aluminium/copper alloys.

The light-sensitive mixtures prepared according to the process described are suitable, in particular for application to silicon wafers which carry a layer of thermally grown silicon dioxide such as those used in the production of microprocessors and other semiconductor components used in microelectronics. An aluminium wafer having an aluminium oxide layer can also be used. The support may also be composed of various polymeric resins, in particular of transparent polymers such as, for example, polyesters.

After the light-sensitive mixture has been applied to the layer support, the support is subjected to pre-drying at 80 to 105°C. This heat treatment is continued until the solvent is essentially completely evaporated and a thin layer of about 1 μm is left behind on the layer support.

The coated support is then imagewise exposed in a known manner to actinic radiation, in particular UV radiation, through suitable masks, negatives, stencils, etc.

5 The imagewise exposed recording materials are immersed in an aqueous-alkaline developer solution, the solution preferably being intensely agitated by blowing nitrogen through it.

10 After removing the developed wafer from the developer solution, a heat post-treatment or a baking treatment may be carried out in order to increase the adhesion and the chemical resistance of the layer to etching solutions and other substances. The heat treatment after development may comprise an oven curing of the
15 layer and support at temperatures below the softening point of the layer.

 For industrial application, in particular in the production of semiconductor components on silicon supports having a silicon dioxide layer, the developed
20 supports may be treated with a buffered etching solution based on hydrofluoric acid. The photoresist mixtures according to the invention are resistant to such acid-based etching solutions and ensure an effective protection of the unexposed areas, coated with the
25 photoresist mixture, of the support.

 The light-sensitive mixtures according to the invention are preferably suitable as photoresist mixtures. They may, however, also be used as light-sensitive mixtures for printing plate production and for colour
30 proof films.

Preparation of light-sensitive compounds

 The preparation of light-sensitive compounds based on naphthoquinone diazides is described, by way of example, in US-A-3,046,118, US-A-3,106,645 and
35 US-A-4,397,937. The light-sensitive compounds for the light-sensitive mixture according to the invention are prepared by condensing the 1,2-naphthoquinone-2-diazide-5-sulphonyl chloride and the organic acid halide with a phenolic compound of the type I to III containing more

than one hydroxyl group in the presence of an acid-binding substance. The light-sensitive compounds obtained in this way may optionally also be purified.

5 Solvents suitable for carrying out the reaction are, for example, acetone, 1,4-dioxane, tetrahydrofuran, methylene chloride, pyridine, etc.

10 The acid-binding substance may be inorganic, for example sodium carbonate, or organic, for example a sodium salt of a weak organic acid, a tertiary amine, for example triethylamine, or a pyridine (derivative).

Example 1

23.0 g of 2,3,4-trihydroxybenzophenone and 37.6 g of 1,2-naphthoquinone diazide-5-sulphonyl chloride (diazo compound) are mixed together in 165 ml of acetone. 20.5 g of methanesulphonyl chloride are added. Then 34.0 g of triethylamine are slowly added dropwise, the internal temperature being kept at 30°C. The reaction mixture is then filtered, washed with 165 ml of acetone and taken up in 3.5 litres of 1N hydrochloric acid. The reaction product is filtered off, washed with water and dried in a circulating-air oven at a temperature below 40°C. The yield is 67.8 g, corresponding to 99.7% of theory.

The product obtained in this way may optionally also be purified.

25 The preparation process described is not the only possible one. Any person skilled in the art can arrive at comparable products without difficulty by varying the solvents, bases or reaction conditions used. A number of further light-sensitive compounds are cited in Table 1.

Table 1

Light-sensitive ⁽¹⁾ compound	Triester with the diaz compound (%)	3,4-bisester with the diazo compound (%)	Methanesulphonyl triester (%)	(Diazo) nitrogen content (%)
A	30.5	3.0	16.6	6.20
B	30.1	4.2	13.8	6.38
C	29.0	4.7	11.2	6.28
D	12.2	1.6	9.3	6.09
E	12.8	1.7	7.9	6.09
F	13.1	0.8	9.9	5.99
G	12.2	1.0	9.6	6.11
H	14.3	1.9	10.3	6.20
I	12.7	0.7	6.6	6.60
J	10.3	0.7	6.4	6.36
K	12.8	1.9	6.9	6.47
L	13.2	1.9	9.2	6.53
M	12.4	1.7	6.8	6.40
N	12.7	1.8	7.6	6.50
O	14.9	-	7.6	6.38
P	11.9	0.7	7.7	6.41

⁽¹⁾ To prepare the light-sensitive compounds A, B and C, the diazo compound is first reacted with 2,3,4-trihydroxybenzophenone and the methanesulphonyl chloride is then added. On the other hand, to prepare the light-sensitive compounds M and O, the methanesulphonyl chloride is reacted with 2,3,4-trihydroxybenzophenone and the diazo compound is then added. To prepare the light-sensitive compounds D to L and N and P, the diazo compound and the methanesulphonyl chloride are simultaneously condensed with 2,3,4-trihydroxybenzophenone.

Example 2

To prepare a light-sensitive compound, 1,2,3-tri-hydroxybenzene is condensed with a mixture of 90 mol-% diazo compound and 10 mol-% methanesulphonyl chloride in a molar ratio of 1:3. 0.74 g of the resultant light-sensitive compound are introduced into 24.26 g of a solution of 28.4% novolak and 71.6% of a solvent mixture composed of cellosolve acetate, butyl acetate and xylene, and the lithographic properties of the light-sensitive mixture obtained in this way are measured. With an absorbtivity of 0.740 l/g.cm at 398 nm, the measurement reveals a dark-area erosion of 0.004 $\mu\text{m}/\text{min}$; the light-sensitivity is 31.0 mJ/cm², determined at 405 nm with a broad-band exposure in the 350-450 nm range; the contrast value is 2.50. When stored at room temperature, the light-sensitive solution remains stable for at least 2 weeks. On the other hand, it is not possible to prepare a stable solution from an unmodified light-sensitive compound, obtained by condensing 1,2,3-trihydroxybenzene and diazo compound in a molar ratio of 1:3, in conjunction with the novolak and solvent mixture used above.

As a comparison, 2,3,4-trihydroxybenzophenone is condensed with 1,2-naphthoquinone-diazide-5-sulphonyl chloride in a molar ratio of 1:1.4. The light-sensitive compound obtained has a content of trisester with the diazo compound of 36 to 40% by weight, a content of 3,4-bisester with the diazo compound of 18 to 20% by weight and a content of 2,3,4-trihydroxybenzophenone of 9 to 10% by weight. In Table 3 below, this light-sensitive compound is denoted by "X".

The solubility of the light-sensitive compounds is tested by dissolving the individual light-sensitive compounds in various concentrations in a solvent and observing the solutions for several days. The light-sensitive compound G does not crystallise out even at a concentration of 30% in acetone. On the other hand, the light-sensitive compound X crystallises out overnight at concentrations of 30% and 15%. Even at a concentration of

light-sensitive compound X of 5%, a slight flocculation still occurs.

Examples 3 to 15

5 Light-sensitive mixtures are prepared by the process already described. For this purpose the different light-sensitive compounds are dissolved in a filtered solution of binder and propylene glycol methyl ether acetate (PGMEA) or a solvent mixture composed of cello-

10 solve acetate, butyl acetate and xylene (CBX).
The composition of the individual mixtures emerges from Table 2.

15 The light-sensitive mixtures are filtered through an Alsop filter 175 and then through a Fluoropore filter having filter apertures of 0.2 μm (manufactured by Millipore Corporation). They are stored for seven days at a constant temperature of 50°C with light excluded. Whether a visible precipitate has formed is then checked. If so, the solution concerned has not passed the stability test. In addition, the solution stability of the
20 light-sensitive mixtures is investigated at room temperature. In this procedure, whether visible crystallising-out, precipitation or a colour change has taken place is checked from time to time.

Table 2

Example No.	Light-sensitive compound (% by wt.)	Binder solution	Diazo compound contrast of the light-sensitive mixture
3	A 9.12	24% novolak/76% PGMEA	0.565%
4	B 8.88	24% novolak/76% PGMEA	0.565%
5	C 9.00	24% novolak/76% PGMEA	0.565%
6	D 9.29	24% novolak/76% PGMEA	0.565%
7	E 9.3	24% novolak/76% PGMEA	N/A
8	F 9.3	24% novolak/76% PGMEA	N/A
9	G 9.3	24% novolak/76% PGMEA	N/A
10	N 9.3	24% novolak/76% PGMEA	N/A
11	O 9.3	24% novolak/76% PGMEA	N/A
12	P 9.3	24% novolak/76% PGMEA	N/A
13	N 8.825	25.6% novolak/74.4% CBX	N/A
14	O 8.825	25.6% novolak/74.4% CBX	N/A
15	P 8.825	25.6% novolak/74.4% CBX	N/A

The light-sensitive mixtures according to the invention are notable for an outstanding solution stability and colour stability. In the case of the mixtures of Examples 3 to 15, no visible precipitation can be detected after storage for 7 days at 50°C. In the case of the samples of Examples 3 to 10, 12, 13 and 15, no precipitate can be detected even after seven months when stored at room temperature. In the case of the sample according to Example 11, a precipitate can be detected after four months and in the case of the sample according to Example 14, a precipitate can be detected after six months. Compared with light-sensitive mixtures containing light-sensitive compounds of the type X (cf. Table 3), the mixtures according to the invention have an extremely clear, light colour.

The possibility of preparing a solution of a particular light-sensitive compound may be affected by the choice of solvent system. It happens that a light-sensitive compound is sparingly soluble in one solvent system while it can be dissolved without difficulties in another solvent system. It is, however, generally the case that, in solvent systems in which both the unmodified and the corresponding modified light-sensitive compound are soluble, the unmodified light-sensitive compound tends to precipitate more rapidly.

Examples 16 to 41

Light-sensitive mixtures are prepared from the light-sensitive compounds by dissolving the light-sensitive compound to be tested in each case in a filtered stock solution of binder and solvent. Then the mixtures are filtered and spun onto silicon wafers in a dry layer thickness of 2.0 μm . The wafers are dried for 30 minutes at 90°C.

The initial thickness of the photoresist layers is determined with a Rudolph thickness measuring instrument. Exposure is then carried out with different doses of UV light (350-450 nm). The photoresists are developed for 1 minute at 25°C using an alkaline developer E1, E2 or E3 which has been diluted with deionised water. The

remaining layer thickness is measured and in this way the layer loss occurring for a particular energy dose is determined.

5 The light-sensitivity is measured using a characteristic curve according to R.W. Wake and M.C. Flanigan, "A Review of Contrast in Positive Photoresists", SPIE vol. 539, Advances in Resist Technology and Processing II (1985, page 291), the layer thickness loss after a development time of 1 minute being plotted against the
10 logarithm of the UV exposure dose. The respective light-sensitivity value is obtained in mJ/cm^2 by interpolating this curve to a layer thickness loss of $1 \mu\text{m}$.

 The slope of the linear part of the curve indicates the contrast.

15 The results obtained on testing the light-sensitivity, the contrast and the dark-area erosion of several photoresist mixtures containing the light-sensitive compounds according to the invention are shown in summarised form in Table 3 and are compared with
20 photoresist mixtures which contain the light-sensitive compound X.

Table 3

Example No.	Light sensitive compound (% by wt.)	Binder solvent	Absorbitivity (1/g·cm)	Developer ⁽¹⁾	Developer concentration (ratio to H ₂ O)	Dark-area erosion (μm/min)	Light- ⁽²⁾ sensitivity (mJ/cm ²)	Contrast
16	X 3.9	30% novolak 70% CBX	0.741	E2	1:1.5	4	43.1	1.48
17	D 4.9	30% novolak 70% CBX	0.727	E2	1:1	3	43.2	1.90
18	X 3.9	30% novolak 70% CBX	0.745	E1	1:5	8	27.6	2.27
19	D 4.9	30% novolak 70% CBX	0.736	E1	1:4	4	33.6	2.55
20	X 6.9	30% novolak 70% CBX	1.30	E1	1:4	4	14.2	3.04
21	D 8.8	30% novolak 70% CBX	1.35	E1	1:2	4	15.1	4.03
22	X 6.9	30% novolak 70% CBX	1.30	E3	1:1.5	6	26.3	2.21
23	D 6.9	30% novolak 70% CBX	1.30	E3	1:1.5	7	26.1	2.29
24	X 6.87	25.6% novolak 74.4% CBX	1.31	E3	1:1.5	8	24.1	2.23
25	D 7.16	30% novolak 70% CBX	1.33	E3	1:1.5	9	25.2	2.37

Continuation of Table 3

Example No.	Light sensitive compound (% by wt.)	Binder solvent	Absorbitivity (l/g.cm)	Developer ⁽¹⁾	Developer concentration (ratio to H ₂ O)	Dark-area erosion (μm/min)	Light ⁽²⁾ sensitivity (mJ/cm ²)	Contrast
26	X 7.12	30% novolak 70% CBX	1.31	E3	1:1.5	2	38.7	2.04
27	D 7.12	25.6% novolak 74.4% CBX	1.31	E3	1:1.5	8	25.8	2.38
28	D 8.66	30% novolak 70% CBX	1.32	E3	1:1	9	21.2	4.00
29	X 8.8	30% novolak 70% CBX	1.35	E3	1:1	15	29.9	3.71
30	D 8.8	30% novolak 70% CBX	1.35	E3	1:1	5	27.5	4.18
31	X 8.82	25.6% novolak 74.4% CBX	1.33	E3	1:1	5	29.9	3.74
32	D 8.82	30% novolak 70% CBX	1.35	E3	1:1	8	27.4	4.09
33	X 8.82	25.6% novolak 74.4% CBX	1.36	E3	1:1	6	29.5	4.02
34	D 9.24	30% novolak 70% CBX	1.32	E3	1:1	6	30.6	4.42
35	X 9.24	30% novolak 70% CBX	1.32	E2	1:1	6	31.8	4.54

Continuation of Table 3

Example No.	Light sensitive compound (% by wt.)	Binder solvent	Absorbitivity (1/g.cm)	Developer ⁽¹⁾	Developer concentration (ratio to H ₂ O)	Dark-area erosion (μm/min)	Light ⁽²⁾ sensitivity (mJ/cm ²)	Contrast
36	E 9.24	30% novolak 70% CBX	1.34	E3	1:1	5	31.0	4.50
37	F 9.24	30% novolak 70% CBX	1.33	E3	1:1	5	31.4	4.41
38	G 9.24	30% novolak 70% CBX	1.32	E3	1:1	6	31.5	4.57
39	N 8.82	24.6% novolak 74.4% CBX	1.36	E3	1:1	8	30.0	4.17
40	O 8.82	24.6% novolak 74.4% CBX	1.35	E3	1:1	9	30.9	3.89
41	P 8.82	24.6% novolak 74.4% CBX	1.35	E3	1:1	7	31.2	3.88

⁽¹⁾ E1 is an inorganic aqueous-alkaline developer, E2 is an inorganic buffered aqueous-alkaline developer and E3 is an aqueous-alkaline developer which is free of metal ions and contains a quaternary ammonium salt.

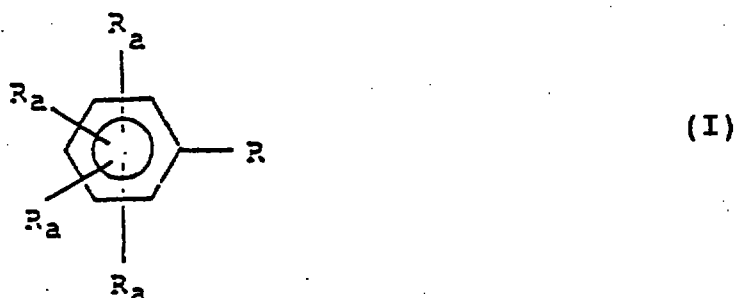
⁽²⁾ Exposure to broad-band illumination, measured at 365 nm.

From Table 3 it emerges that, when developed with an aqueous-alkaline developer, the photoresist mixtures according to the invention have higher contrast values than the mixtures containing the light-sensitive compound X (comparison examples), the light-sensitivity values of the mixtures being approximately equal.

If the mixtures according to the invention are developed with a developer which is free of metal ions, it is found that the induction time is up to 50% longer than if comparison mixtures are used. (The induction time is a limit value and indicates the period of time which elapses before the exposure resist regions become soluble in the developer. It can be determined by plotting the layer loss against the logarithm of the respective exposure energy).

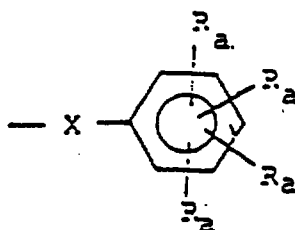
Patent claims

1. Light-sensitive mixture, containing a binder, which is insoluble in aqueous systems and soluble or at least swellable in aqueous-alkaline and organic solvents, and also a light-sensitive compound, characterised in that the light-sensitive compound is a condensation product of a phenolic compound of the formula I



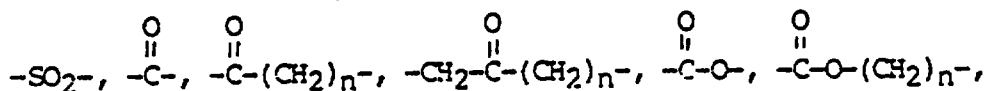
in which

- 10 R is hydrogen, -X-R_b, or

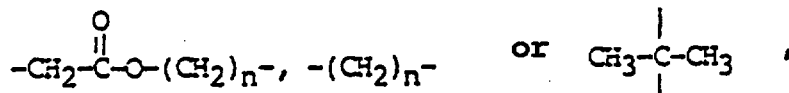


R_a is hydrogen, an OH group, halogen or a lower alkyl group, at least two and at most six R_a groups being OH groups,

X is a C-C bond, -O-, -S-,



15

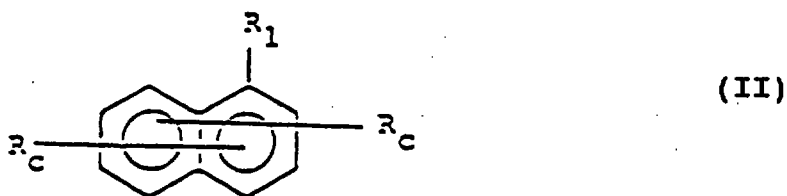


n is 1 or 2 and

R_b is hydrogen or a substituted or unsubstituted alkyl or aryl group,

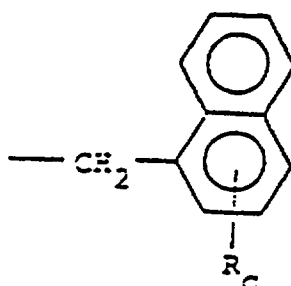
or of the formula II





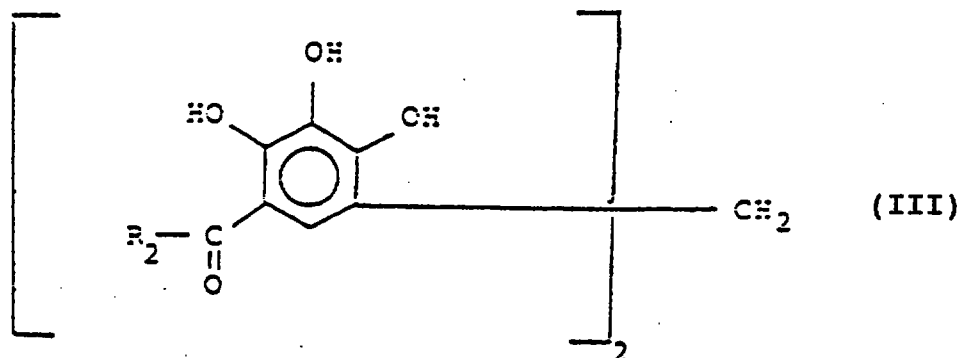
in which

R_1 is hydrogen or



and

- 5 R_c is hydrogen or an OH group, at least two R_c groups being OH groups,
or of the formula III



in which

- 10 R_2 is hydrogen or a substituted or unsubstituted alkyl or aryl group,
with a mixture of a 1,2-naphthoquinone-diazide-5-sulphonic acid chloride (diazo compound) and an organic acid halide of the formula IV

15



(IV)

in which



W is $\overset{\text{O}}{\parallel}\text{-C-V}$ or $\text{-SO}_2\text{-V}$, V being a halogen, and
R₃ is a substituted or unsubstituted alkyl or aryl
group.

2. Light-sensitive mixture according to Claim 1, characterised in that the molar ratio of diazo compound reacted with the phenolic compound to the reacted organic acid halide ranges in each case from 1:2 to 19:1.

3. Light-sensitive mixture according to Claim 1 or 2, characterised in that

R is -X-R_b ,

R_a is hydrogen and OH groups,

X is $\overset{\text{O}}{\parallel}\text{-C-}$ and

R_b is aryl, especially phenyl, in the phenolic compound of the formula I,

R₁ is hydrogen and

R_c represents OH groups

in the phenolic compound of the formula II, and

R₂ is phenyl or alkyl having 1 to 20 carbon atoms in the phenolic compound of the formula III and, furthermore,

R₃ is alkyl having preferably 1 to 6 carbon atoms or phenyl

in the organic acid halide of the formula IV.

4. Light-sensitive mixture according to one or more of Claims 1 to 3, characterised in that the binder is a novolak or a polyvinylphenol.

5. Light-sensitive mixture according to one or more of Claims 1 to 4, characterised in that the mixture contains a solvent or solvent mixture.

6. Light-sensitive mixture according to one or more of Claims 1 to 5, characterised in that the mixture additionally contains dyes, flow agents, plasticisers, adhesion promoters, development accelerators and/or nonionic surfactants.

7. Light-sensitive mixture according to one or more of Claims 1 to 6, characterised in that the binder is



present in a concentration from 15 to 99 % by weight, relative to the solid constituents of the light-sensitive mixture.

5 8. Light-sensitive mixture according to one or more of Claims 1 to 7, characterised in that the light-sensitive compound is present in a concentration from 1 to 85 % by weight, relative to the solid constituents of the light-sensitive mixture.

10 9. Recording material, essentially consisting of a support and a light-sensitive layer, characterised in that the light-sensitive layer corresponds to the light-sensitive mixture according to one or more of Claims 1 to 8.

15 10. Recording material according to Claim 9, characterised in that the support is a silicon wafer coated with a thermally grown silicon dioxide layer.

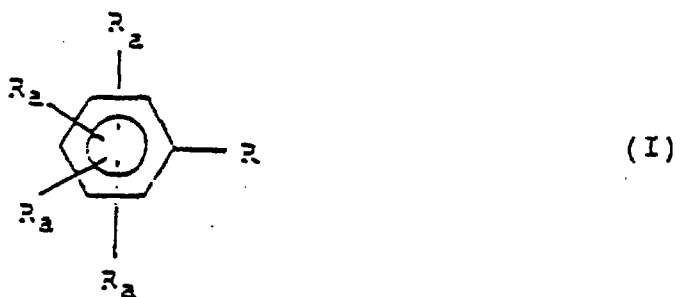
20 11. Process for producing a photoresist stencil, using a recording material according to Claim 9 or 10, characterised in that the light-sensitive mixture is applied to the support, the recording material is subjected to pre-drying at 80 to 105°C, imagewise exposed and then developed and also, if desired, subjected to a heat treatment.



As printed

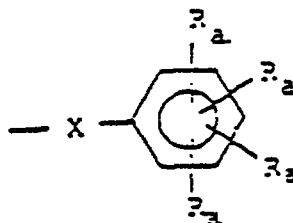
Claims

1. Light-sensitive mixture, containing a binder, which is insoluble in aqueous systems and soluble or at least swellable in aqueous-alkaline and organic solvents, and also a light-sensitive compound, characterised in that the light-sensitive compound is a condensation product of a phenolic compound of the formula I



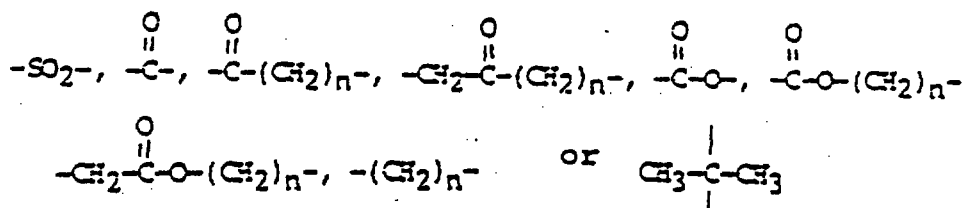
in which

R is hydrogen, -X-R_b or



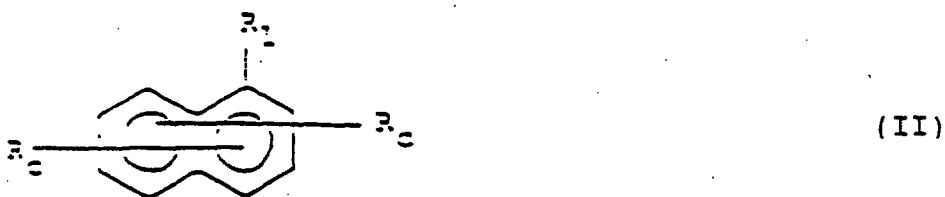
R_a is hydrogen, an OH group, halogen or a lower alkyl group, at least two and at most six R_a groups being OH groups,

X is a C-C bond, -O-, -S-,



n is 1 or 2 and

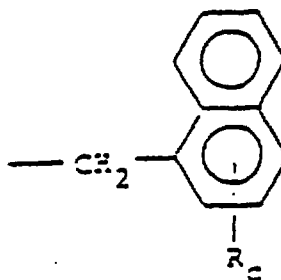
R_b is hydrogen or a substituted or unsubstituted alkyl or aryl group, or of the formula II



in which

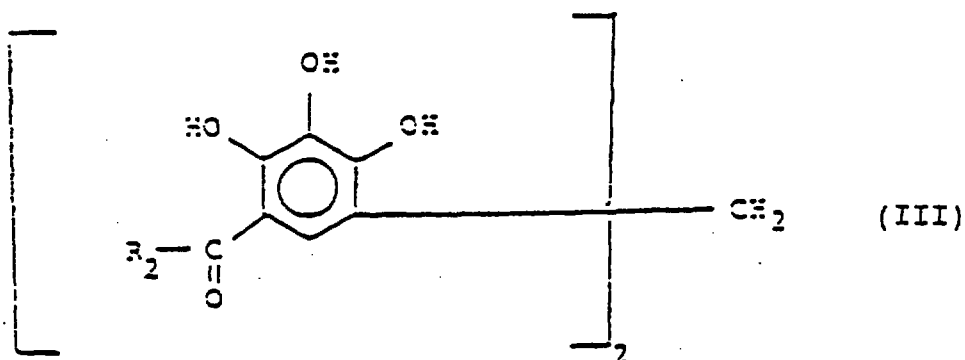
R₁ is hydrogen or





and

R_c is hydrogen or an OH group, at least two R_c groups being OH groups, or of the formula III



in which

R_2 is hydrogen or a substituted or unsubstituted alkyl or aryl group, with a mixture of a 1,2-naphthoquinone-diazide-5-sulphonic acid chloride (diaz compound) and an organic acid halide of the formula IV

W- R_3 (IV)

in which

W is



or -SO₂-V, V being a halogen, and

R_3 is a substituted or unsubstituted alkyl or aryl group.

2. Light-sensitive mixture according to Claim 1, characterised in that the molar ratio of diazo compound reacted with the phenolic compound to the reacted organic acid halide ranges in each case from 1:2 to 19:1.
3. Light-sensitive mixture according to Claim 1 or 2, characterised in that
 - R is -X- R_b ,
 - R_b is hydrogen and OH groups,
 - X is



and

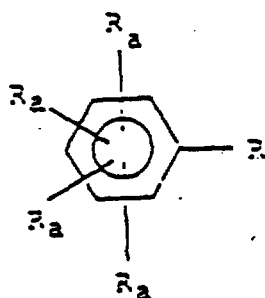


R_b is aryl, especially phenyl,
in the phenolic compound of the formula I,
 R_1 is hydrogen and
 R_c represents OH groups
in the phenolic compound of the formula II, and
 R_2 is phenyl or alkyl having 1 to 20 carbon atoms
in the phenolic compound of the formula III and, furthermore,
 R_3 is alkyl having preferably 1 to 6 carbon atoms or phenyl
in the organic acid halide of the formula IV.

4. Light-sensitive mixture according to one or more of Claims 1 to 3, characterised in that the binder is a novolak or a polyvinylphenol.
5. Light-sensitive mixture according to one or more of Claims 1 to 4, characterised in that the mixture contains a solvent or solvent mixture.
6. Light-sensitive mixture according to one or more of Claims 1 to 5, characterised in that the mixture additionally contains dyes, flow agents, plasticisers, adhesion promoters, development accelerators and/or nonionic surfactants.
7. Light-sensitive mixture according to one or more of Claims 1 to 6, characterised in that the binder is present in a concentration from 15 to 99 % by weight, relative to the solid constituents of the light-sensitive mixture.
8. Light-sensitive mixture according to one or more of Claims 1 to 7, characterised in that the light-sensitive compound is present in a concentration from 1 to 85 % by weight, relative to the solid constituents of the light-sensitive mixture.
9. Recording material, essentially consisting of a support and a light-sensitive layer, characterised in that the light-sensitive layer corresponds to the light-sensitive mixture according to one or more of Claims 1 to 8.
10. Recording material according to Claim 9, characterised in that the support is a silicon wafer coated with a thermally grown silica layer.
11. Process for producing a photoresist stencil, using a recording material according to Claim 9 or 10, characterised in that the light-sensitive mixture is applied to the support, the recording material is subjected to pre-drying at 80 to 105° C, imagewise exposed and then developed and also, if desired, subjected to a heat treatment.

Revendications As Printed

1. Composition photosensible contenant un liant insoluble dans des systèmes aqueux, soluble ou au moins apte à gonfler dans des solvants organiques et aqueux-alcalins, ainsi qu'un composé photosensible, caractérisée en ce que le composé photosensible est un produit de condensation obtenu à partir d'un composé de type phénol de formule I

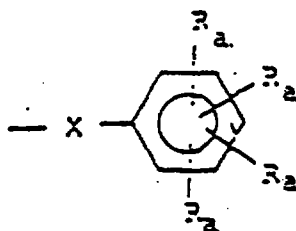


(I)



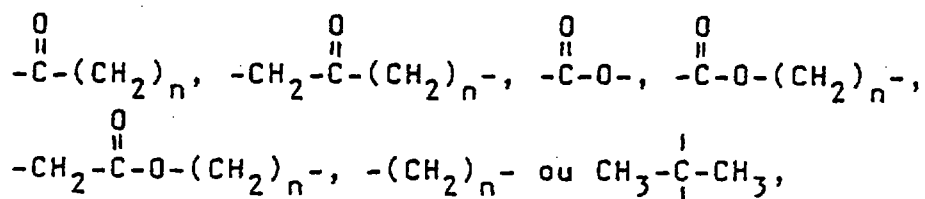
dans laquelle

R représente un atome d'hydrogène, -X-R_b ou



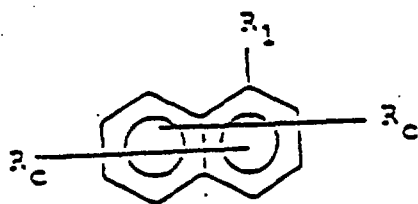
R_a représente un atome d'hydrogène ou d'halogène, le groupe OH ou un groupe alkyle inférieur, au moins deux et au maximum six groupes R_a étant des groupes OH,

X représente une liaison C-C-, -O-, -S-, -SO₂-,



n est 1 ou 2 et

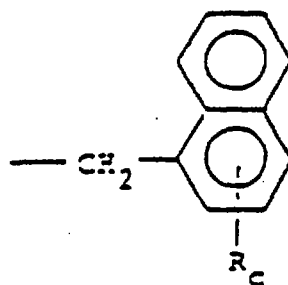
R_b représente un atome d'hydrogène ou un groupe alkyle ou aryle éventuellement substitué; ou de formule II



(II)

dans laquelle

R₁ représente un atome d'hydrogène ou

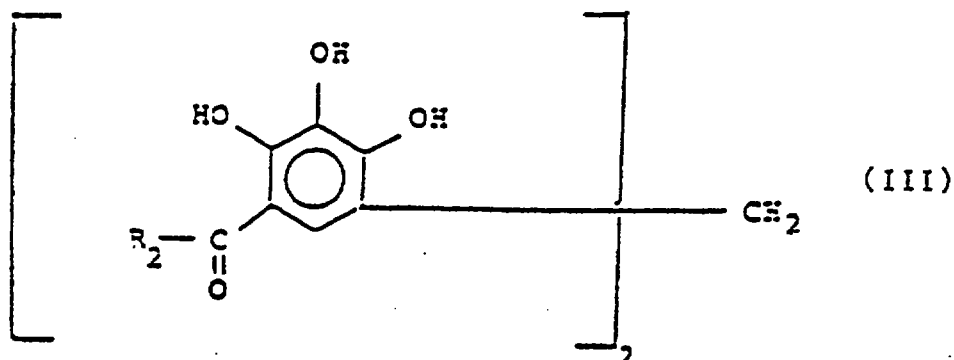


et

R_c représente un atome d'hydrogène ou le groupe OH, au moins deux groupes R_c représentant



des groupes OH;
ou de formule III



dans laquelle

R₂ représente un atome d'hydrogène ou un groupe alkyle ou aryle éventuellement substitué;
avec un mélange d'un chlorure de 1,2-naphtoquinonediazide-5-sulfonyle (composé diazo) et d'un
halogénure d'acide organique de formule IV

W-R₃ (IV)

dans laquelle

W représente



ou -SO₂-V, V représentant un halogène, et
R₃ représente un groupe alkyle ou aryle éventuellement substitué.

2. Composition photosensible selon la revendication 1, caractérisée en ce que le rapport molaire du composé diazo, mis en réaction avec le composé de type phénol, à l'halogénure d'acide organique mis en réaction, va de 1:2 à 19:1.
3. Composition photosensible selon la revendication 1 ou 2, caractérisée en ce que, dans le composé de type phénol de formule I
 - R représente -X-R_b,
 - R_a représente un atome d'hydrogène ou le groupe OH,
 - X représente



R_b représente un groupe aryle, en particulier phényle;
dans le composé de type phénol de formule II

R₁ représente un atome d'hydrogène,

R_c représente le groupe OH;

et dans le composé de type phénol de formule III

R₂ représente le groupe phényle ou un groupe alkyle ayant de 1 à 20 atomes de carbone;
et dans l'halogénure d'acide organique de-formule IV

R₃ représente un groupe alkyle ayant de préférence de 1 à 6 atomes de carbone, ou le groupe phényle.



4. Composition photosensible selon une ou plusieurs des revendications 1 à 3, caractérisée en ce que le liant est une Novolaque ou un polyvinylphénol.
5. Composition photosensible selon une ou plusieurs des revendications 1 à 4, caractérisée en ce que la composition contient un solvant ou un mélange de solvants.
6. Composition photosensible selon une ou plusieurs des revendications 1 à 5, caractérisée en ce que le mélange contient en outre des colorants, agents d'étalement, plastifiants, agents favorisant l'adhérence, accélérateurs de développement et/ou surfactifs non ioniques.
7. Composition photosensible selon une ou plusieurs des revendications 1 à 6, caractérisée en ce que le liant est présent à une concentration de 15 à 99 % en poids, par rapport aux constituants solides de la composition photosensible.
8. Composition photosensible selon une ou plusieurs des revendications 1 à 7, caractérisée en ce que le composé photosensible est présent à une concentration de 1 à 85 % en poids, par rapport aux constituants solides de la composition photosensible.
9. Matériau de reprographie, essentiellement constitué d'un support et d'une couche photosensible, caractérisé en ce que la couche photosensible correspond à la composition photosensible selon une ou plusieurs des revendications 1 à 8.
10. Matériau de reprographie selon la revendication 9, caractérisé en ce que le support est une plaquette de silicium revêtue d'une couche de dioxyde de silicium produite thermiquement.
11. Procédé pour la préparation d'un masque de photoresist avec utilisation d'un matériau de reprographie selon la revendication 9 ou 10, caractérisé en ce que la composition photosensible est appliquée sur le support, le matériau de reproduction est soumis à un pré-séchage à 80-105° C, exposé selon l'image et ensuite développé et éventuellement soumis à un traitement thermique.

