

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 photo-resist 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.

5 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
10 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
15 after completely stripping the exposed layer regions.
20

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.
25

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).
30

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.
35

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 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 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 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. 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.

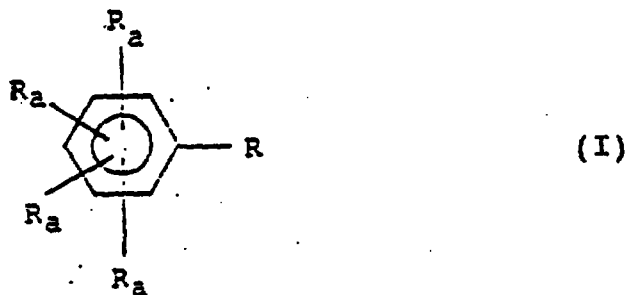
To improve the solubility, US-A-4,397,937 proposes using as light-sensitive compound a bisester of a 1-oxo-2-diazonaphthalenesulphonic acid and an asymmetrical primary or secondary aliphatic diol which is a mixture of geometrical isomers and diastereoisomers. As 1,2-naphthoquinone-diazide-sulphonic acids, 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 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.

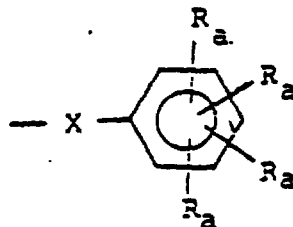
The object of the present invention was to propose a light-sensitive mixture which has excellent solution properties and an improved shelf life even at fairly high concentrations of the light-sensitive compound without exhibiting disadvantages in relation to the achievable light sensitivity and the contrast.

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



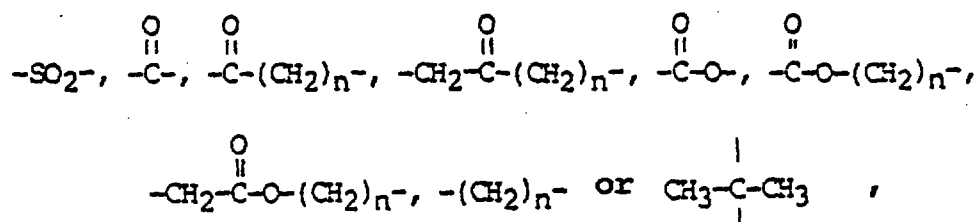
in which

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,

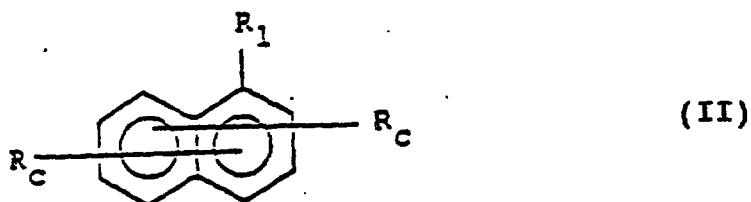
X is a C-C bond, -O-, -S-,



n is 1 or 2 and

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

5 or of the formula II

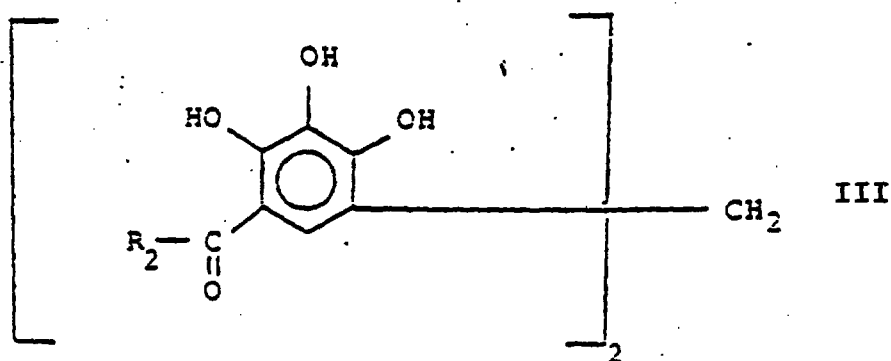


in which

R₁ is hydrogen or

and

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



in which

15 R₂ 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



(IV)

in which

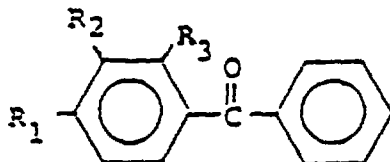
W is $\overset{\text{O}}{\parallel}\text{-C-V}$ or $\text{-SO}_2\text{-V}$, V being a halogen, and
5 R₃ is a substituted or unsubstituted alkyl or aryl group.

10 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 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 developer.
15

20 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 mixed ester of phenolic compounds with 1,2-naphthoquinone-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
25 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.

30 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 1:1 and 39:1, preferably between 4:1 and 19:1, in particular
35 between 85:15 and 93:7. For example, 1 mol of 2,3,4-tri-

hydroxybenzophenone is condensed with a mixture of 2.7 mol of diazo compound and 0.3 mol of methanesulphonyl chloride in a mixing ratio of 9:1. 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-diazone-4-sulphonyloxy group (diazo compound) or a methanesulphonyloxy group.

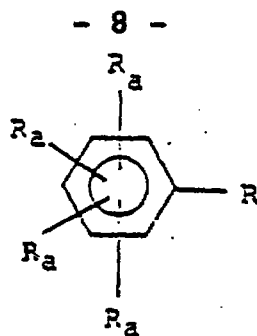
According to the invention, light-sensitive compounds are proposed which are obtained by condensation of phenolic compounds with mixtures of diazo compound and organic acid halides. The diazo component and the acid halide component of the mixture can be condensed simultaneously or consecutively with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

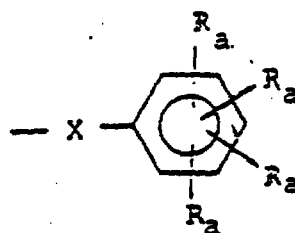
The phenolic compounds which are suitable for the condensation with the mixture of diazo compound and organic acid halide correspond to the formulae I), II) or III) described below:

I)



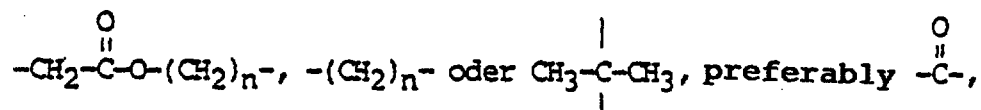
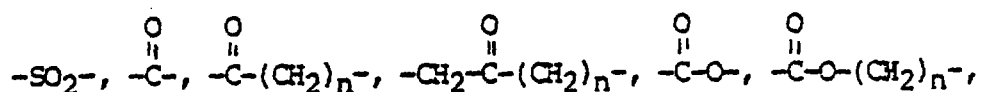
in which

R is hydrogen, $-X-R_b$ or



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,

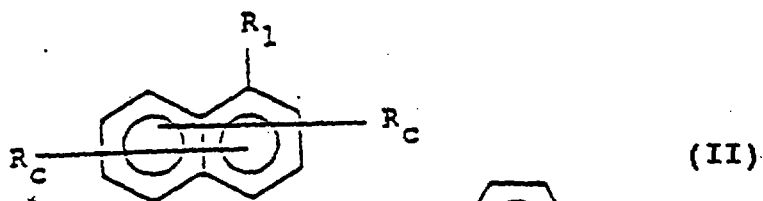
X is a C-C bond, -O-, -S-,



n is 1 or 2 and

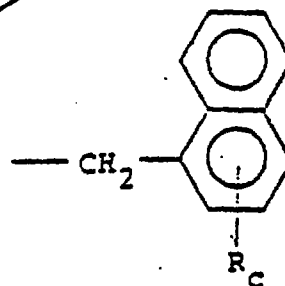
R_b is hydrogen or a substituted or unsubstituted alkyl or aryl group, the alkyl group preferably having 1 to 20, in particular 1 to 12, carbon atoms, the aryl group preferably being a phenyl or naphthyl group and the alkyl or aryl group having as substituents optionally lower alkyl groups containing 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

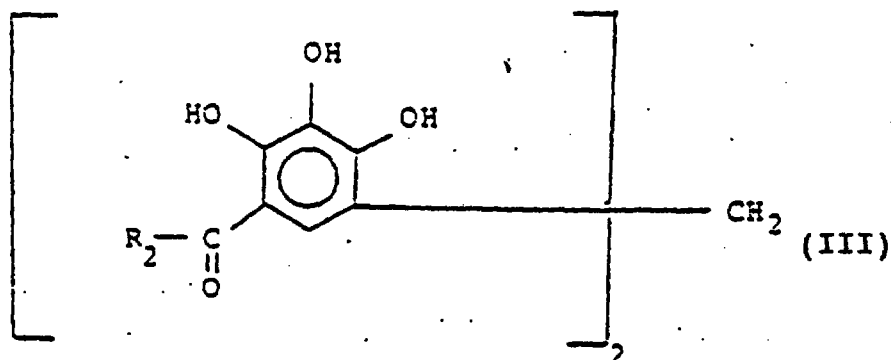
R₁ is hydrogen or



and

R_c is hydrogen or an OH group, at least two R_c 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 R₂ 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,
1,4-dihydroxybenzene,
1,2,3-trihydroxybenzene,
1,2,4-trihydroxybenzene,
5 1,3,5-trihydroxybenzene;
Dihydroxybenzophenones, such as, for example,
2,2'-dihydroxybenzophenone,
2,3'-dihydroxybenzophenone,
2,4-dihydroxybenzophenone,
10 2,4'-dihydroxybenzophenone,
2,5-dihydroxybenzophenone,
3,3'-dihydroxybenzophenone,
4,4'-dihydroxybenzophenone;
Trihydroxybenzophenones, such as, for example,
15 2,2',6-trihydroxybenzophenone,
2,3,4-trihydroxybenzophenone,
2,4,4'-trihydroxybenzophenone,
2,4,6-trihydroxybenzophenone,
2,4,5-trihydroxybenzophenone;
20 Tetrahydroxybenzophenones, such as, for example,
2,2',3,4-tetrahydroxybenzophenone,
2,2',4,4'-tetrahydroxybenzophenone,
2,2',4,6'-tetrahydroxybenzophenone,
2,2',5,6'-tetrahydroxybenzophenone,
25 2,3',4,4'-tetrahydroxybenzophenone,
2,3',4,6-tetrahydroxybenzophenone,
2,4,4',6-tetrahydroxybenzophenone,
3,3',4,4'-tetrahydroxybenzophenone;
Pentahydroxybenzophenones;
30 Hexahydroxybenzophenones;
Dihydroxy- and trihydroxyphenyl alkyl ketones, such as,
for example,
2,4-dihydroxyphenyl alkyl ketones,
2,5-dihydroxyphenyl alkyl ketones,
35 3,4-dihydroxyphenyl alkyl ketones,
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
optionally branched preferably being used, such as, for
example, methyl, ethyl, butyl, n-hexyl, heptyl, decyl,
5 dodecyl;
Dihydroxyphenyl arylalkyl ketones;
Trihydroxyphenyl arylalkyl ketones;
Dihydroxydiphenyls;
Trihydroxydiphenyls, such as, for example,
10 2,2',4-trihydroxydiphenyl;
Tetrahydroxydiphenyls, such as, for example,
2,2',4,4'-tetrahydroxydiphenyl;
Dihydroxydiphenyl ethers;
Dihydroxydibenzyl ethers;
15 Dihydroxydiphenylalkanes, preferably having lower
alkylene chains, such as, for example, methylene,
ethylene, propylene;
Dihydroxybenzoic acid;
Trihydroxybenzoic acids;
20 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,
n-butyl 2,4-, 2,5-, 3,4- and 3,5-dihydroxybenzoate,
2,4,4-trimethylpentyl 2,4-dihydroxybenzoate;
25 Phenyl dihydroxy- and trihydroxybenzoates;
Dihydroxy-, trihydroxy- and tetrahydroxydiphenyl
sulphides, such as, for example, 4,4'-dihydroxydiphenyl
sulphide;
Dihydroxydiphenyl sulphones;
30 Dihydroxy- and trihydroxyphenyl naphthyl ketones, such
as, for example,
2,3,4-trihydroxyphenyl 1-naphthyl ketone;
and similar compounds.

35 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,
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-butyl-
diphenyl 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).

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

Dihydroxynaphthalenes, such as, for example,

1,2-dihydroxynaphthalene,

1,4-dihydroxynaphthalene,

1,5-dihydroxynaphthalene,

1,6-dihydroxynaphthalene,

1,7-dihydroxynaphthalene,

1,8-dihydroxynaphthalene,

2,3-dihydroxynaphthalene,

2,6-dihydroxynaphthalene,

2,7-dihydroxynaphthalene;

Dihydroxydinaphthylmethanes, such as, for example,

2,2'-dihydroxydinaphthylmethane etc.

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,

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-naphthoquinone-5-sulphonyl chlorides, correspond to the

formula IV



(IV)

in which

5

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

10

R_3 is a substituted or unsubstituted alkyl or aryl group; in this connection, the alkyl groups preferably have 1 to 20 carbon atoms, are straight-chain or branched-chain and optionally have halogen atoms, in particular bromine or chlorine, or lower alkoxy groups containing 1 to 4 carbon atoms as substituents; the aryl groups preferably have 6 to 10 carbon atoms, are preferably mononuclear and optionally have lower alkyl or alkoxy groups containing 1 to 4 carbon atoms or halogen atoms, preferably bromine or chlorine, as substituents; phenyl groups are preferred; very particularly preferred are alkyl groups, in particular lower alkyl groups containing 1 to 6 carbon atoms.

15

20

The organic acid halides of the above formula include, for example,

25

Alkylsulphonyl halides, such as, for example
methanesulphonyl chloride,
ethanesulphonyl chloride,
propanesulphonyl chloride,
n-butane sulphonyl chloride,
30 dodecanesulphonyl chloride;

30

Arylsulphonyl chlorides, such as, for example,
benzene sulphonyl chloride,
naphthalenesulphonyl chlorides;

35

Acyl halides, such as, for example,
acetyl chloride,
butanoyl chloride,

valeroyl chloride,
benzoyl chloride
Benzoyl bromide
naphthoyl chloride.

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

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

15 Alkali-soluble novolaks which can be used for the 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.

20 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
25 glycol ethers such as, for example, ethylene glycol 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,
30 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
35 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.

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.

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 possible the application in a smooth and uniformly thick layer to the layer support.

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.

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 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, 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:

5 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
10 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,
15 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
20 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
25 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
30 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
35 a known manner to actinic radiation, in particular UV radiation, through suitable masks, negatives, stencils, etc.

 The imagewise exposed recording materials are

immersed in an aqueous-alkaline developer solution, the solution preferably being intensely agitated by blowing nitrogen through it.

5 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
10 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
15 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
20 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
25 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
30 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-4-sulphonyl chloride and the organic acid halide with a phenolic compound of the type I to III containing more
35 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.

Solvents suitable for carrying out the reaction

are, for example, acetone, 1,4-dioxane, tetrahydrofuran, methylene chloride, pyridine, etc.

5 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

10 A 2,3,4-trihydroxybenzophenone tri(1,2-naphthoquinone-diazide-sulphonate) modified with 10 mol% of methanesulphonyl chloride is prepared. For this purpose, 23.0 g of 2,3,4-trihydroxybenzophenone and 72.6 g of 1,2-naphthoquinone diazide-4-sulphonyl chloride (diazo compound) are mixed together in 350 ml of acetone. 3.6 g of methanesulphonyl chloride are added. Then 36.4 g of triethylamine are slowly added dropwise, the internal temperature being kept at 30°C. The reaction mixture is then cooled to a temperature below 15°C, treated with active carbon and kieselguhr, filtered, washed with 350 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 85.9 g, corresponding to 97.5% of theory.

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

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.

30 A number of condensation products in which the molar ratios of diazocompound to organic acid halide are varied in accordance with Tables 1 and 2 are prepared in accordance with the example described above.

35 As a comparison, 2,3,4-trihydroxybenzophenone is condensed with 1,2-naphthoquinone-diazide-4-sulphonyl chloride in a molar ratio of 1:3.

Solution stability

Light-sensitive mixtures are prepared by the

method already described. The mixtures containing the various light-sensitive compounds are dissolved in a filtered solution composed of 24% Novolak resin and 76% propylene glycol methyl ether acetate (PGMEA). The resist mixtures are so adjusted that the absorptivity of the light-sensitive compound is 1.0 l/g.cm at a wavelength of 377 nm. If, for example, a sample of 30 mg of 2,3,4-trihydroxybenzophenone tri(1,2-naphthoquinone-diazide-4-sulphonate) in one litre of acetone has an absorbtivity of 0.731 at 377 nm, the photoresist mixture has the following composition:

4.1%	light-sensitive compound
23.0%	Novolak resin
72.9%	PGMEA

The photoresist test solutions are first filtered off through an Ertel filter number 8 and then through a Fluoropore filter (manufactured by Millipore Corporation) having filter apertures of 0.2 to 0.5 μ m diameter. The test solutions are stored in a drying oven at a constant temperature of 50°C for 5 days with light excluded. Whether a visible precipitate has settled is then checked. If so, the solution concerned has not passed the stability test. The test results for a number of modified and unmodified photoresist mixtures are summarised in Table 1 below.

Table 1

Light-sensitive compound	Modification (mol%)	Solution stability
5	A none B none C none D 2.5% methanesulphonyl chloride	failed failed failed passed
10	E 2.5% methanesulphonyl chloride F 5% methanesulphonyl chloride G 5% methanesulphonyl chloride	passed passed passed
15	H 10% methanesulphonyl chloride I 10% methanesulphonyl chloride	passed passed
20	J 10% methanesulphonyl chloride K 20% methanesulphonyl chloride	passed passed
25	L 20% methanesulphonyl chloride M 10% ethanesulphonyl chloride N 10% benzenesulphonyl chloride	passed passed passed
30	O 10% valerylchloride P 10% dichlorobenzoyl chloride	passed passed

(1) The light-sensitive compounds of the samples were prepared by reacting 2,3,4-trihydroxyben3ophenone with a stoichiometric quantity of a mixture of diazocompound and organic acid halide. The figures in this column specify the respective quantity of

organic acid halide in the mixtures. In the experiments in which no modification took place, 2,3,4-trihydroxybenzophenone was condensed with the diazocompound alone.

From the table it can be seen that the modified light-sensitive compounds yield mixtures with better solution stability than the unmodified light-sensitive compounds.

The possibility of preparing a solution of a particular light-sensitive compound may be adversely affected by the choice of solvent system. It happens that a light-sensitive compound is only 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 ... (lacuna), a precipitation is to be observed with these compounds ... (lacuna) virtually all cases before three months have elapsed. The individual results of the three-month storage test are shown below in Table 2.

Table 2

Light-sensitive compound	Modification ⁽¹⁾ (mol%)	S o l u t i o n stability ⁽²⁾ (shelf life)
B	none	failed
U	none	failed
V	none	failed
F	5% methanesulphonyl chloride	passed
G	5% methanesulphonyl chloride	passed
H	10% methanesulphonyl chloride	passed
I	10% methanesulphonyl chloride	passed

Light-sensitive compound	Modification (mol%) ⁽¹⁾	S o l u t i o n stability ⁽²⁾ (shelf life)
--------------------------	------------------------------------	---

5	J	10% methanesulphonyl chloride	passed
	K	20% methanesulphonyl chloride	passed
10	L	20% methanesulphonyl (lacuna)	passed

(1) see Table 1.

(2) The samples were examined after three months. "Failed" means that a precipitation occurred visibly, and "passed" means that no precipitation was detectable.

The data shows that the modified light-sensitive compounds exhibit a far lower tendency to precipitation than the unmodified light-sensitive compound containing the diazocompound alone. Consequently, the photoresistant mixtures prepared with the light-sensitive compounds according to the invention have an increased shelf life.

Example 2

Resist solutions are formulated with the light-sensitive mixtures according to the invention and are adjusted so that the absorptivity of the light-sensitive compound is 0.76 ± 0.025 l/g · cm at a wavelength of 377 nm. The light-sensitive compound to be tested in each case is dissolved in a filtered stock solution composed of 24% novolak resin and 76% propylene glycol methyl ether acetate. The resist solutions are then filtered through an Ertel filter No. 8.

The photoresist mixtures are then spun onto silicon wafers which give 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 composed of KOH and boric acid and containing metal ions, which developer was diluted with deionised water in the ratio 1:3. With this developer concentration, the dark erosion or degree of erosion of the unexposed resist layer parts by the developer can in general be kept at 0.005 to 0.015 μm per minute. The remaining layer thickness is then measured and in this way the layer loss occurring for a particular energy dose is determined.

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

The results obtained on testing the light sensitivity, the contrast and the dark erosion of several photoresist mixtures containing the light-sensitive compounds according to the invention are shown in summarised form in Table 4 [sic] and are compared with photoresist mixtures which contain the unmodified light-sensitive compounds. Statistical comparison values are obtained by examining three photoresist samples which contain an unmodified 2,3,4-trihydroxybenzophenone-1,2-naphthochinondiazide-4-sulphonic acid triester (prepared with diazocompound alone). Each sample is subjected to a light-sensitivity and contrast measurement three times so that a total of 9 sets of data are obtained. The range of variation of the light sensitivity (mJ/cm^2) from the mean light sensitivity is ± 10 per cent. The absolute difference between the maximum and minimum light-sensitivity value is 20 per cent, referred to the lower

value. The range of variation of the individual contrast values from the mean value is also ± 10 per cent; the absolute difference between the maximum and minimum measured value is in this case 24 per cent, again referred to the lower value.

5

The test results shown in Table 3 show that the photoresist mixtures prepared according to the invention are also not inferior to the analogous unmodified mixtures in relation to their copying properties.

Table 3

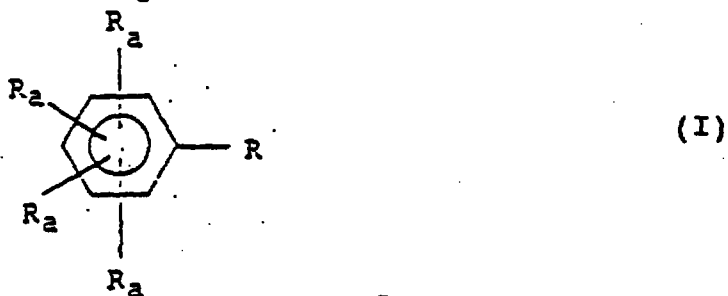
Light-sensitive compound No.	Modification (mol %)	Absorptivities (1/g·cm at 377nm)	Dark erosion ($\mu\text{m}/\text{min}$)	Light-sensitivity ⁽¹⁾ (% higher(-) [sic] or lower (+) than comp. value)	Image Contrast ⁽²⁾ (% higher (+) or lower (-) than comparison value)
D	2.5 % methanesulphonyl chloride	0.762	0.007	+4	0
F	5% methanesulphonyl chloride	0.759	0.011	+22	+15
G	5% methanesulphonyl chloride	0.782	0.009	+13	+16
H	10% methanesulphonyl chloride	0.758	0.006	-3	+3
I	10% methanesulphonyl chloride	0.752	0.003	+8	-3
J	10% methanesulphonyl chloride	0.778	0.001	+6	-2
K	20% methanesulphonyl chloride	0.775	0.005	+43	+23
L	20% methanesulphonyl chloride	0.770	0.006	+54	+18
M	10% ethanesulphonyl chloride	0.756	0.011	+16	+12
N	10% benzenesulphonyl chloride	0.775	0.007	+39	+6
O	10% valeryl chloride	0.770	0.010	+29	-17
P	10% dichlorobenzoyl chloride	0.767	0.008	+38	-15

(1) The typical light sensitivity of standards [sic] 2,3,4-trihydroxybenzophenone tri(1,2-naphthochinondiazide-4-sulphonate) with a broad-band exposure (350-450 nm) is 18.9 mJ/cm², measured at 405 nm, with a narrow-band exposure (365 nm) is 20.6 mJ/cm², measured at 365 nm.

(2) The typical image contrast values of the standard 2,3,4-trihydroxybenzophenone tri(1,2-naphthoquinone-diazide-4-sulphonate) with a broad-band exposure (350-450 nm) is 3.09, measured at 405 nm with a narrow-band exposure (365 nm) is 2.43, measured at 365 nm.

Patent claims

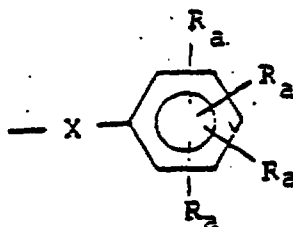
1. Light-sensitive mixture, containing a binder, which is insoluble in aqueous systems and soluble or at least swellable in aqueous-alkaline and organic solvents, and also a light-sensitive compound, characterised in that the light-sensitive compound is a condensation product of a phenolic compound of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



in which

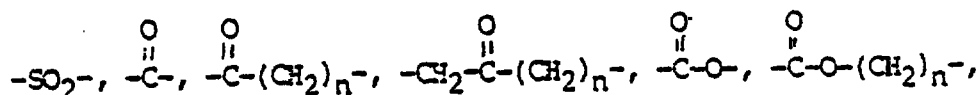
10

R is hydrogen, $-X-R_b$ or

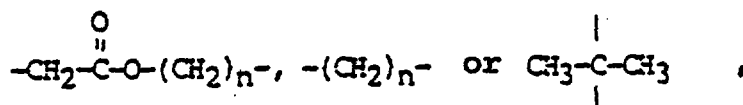


R_a is hydrogen, an OH group, halogen or a lower alkyl group, at least two and at most six R_a groups being OH groups,

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



15

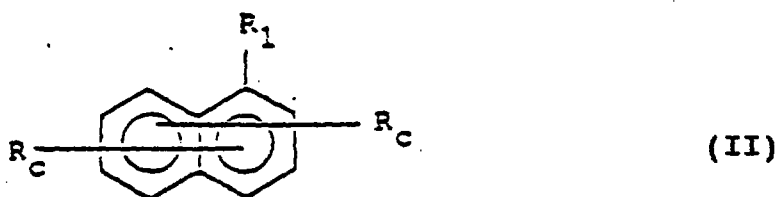


n is 1 or 2 and

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

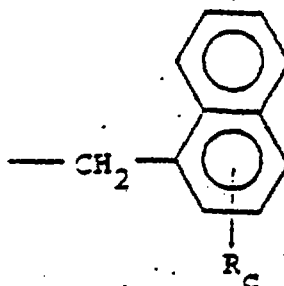
or of the formula II





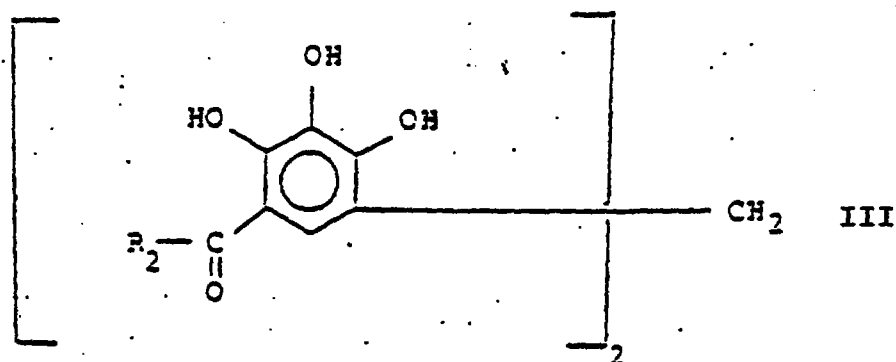
in which

R₁ 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 R₂ 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



in which

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

20

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

5 R is $-X-R_b$,
R_a is hydrogen and OH groups,

x[sic] is $-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$ and

10 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

15 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.

20 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.

25 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.

30 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.

35 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-sensi-
tive compound is present in a concentration from 1 to



85 % by weight, relative to the solid constituents of the light-sensitive mixture.

5 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.

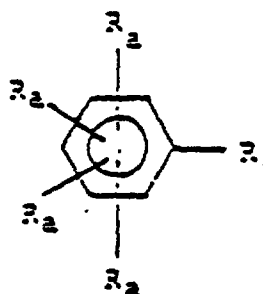
10 10. Recording material according to Claim 9, characterised in that the support is a silicon wafer coated with a thermally grown silicon dioxide layer.

15 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.



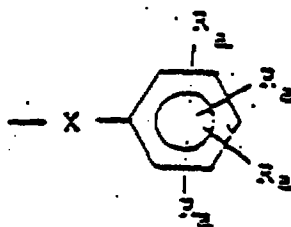
As printed
Claims

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



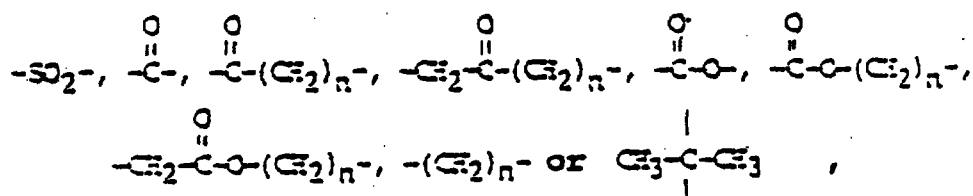
in which

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,

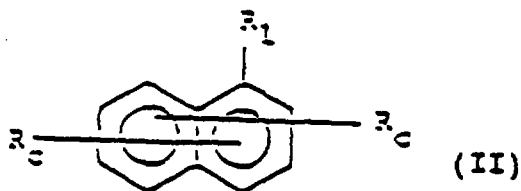
X is a C-C bond, -O-, -S-,



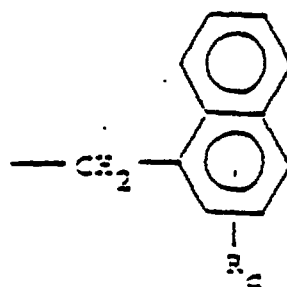
n is 1 or 2 and



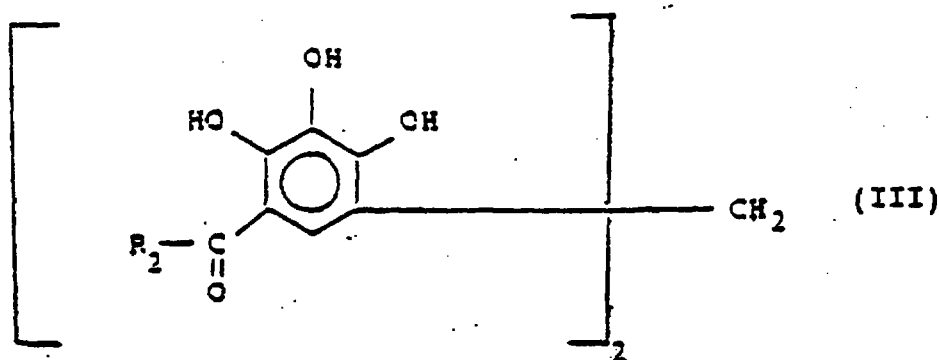
R_b is hydrogen or a substituted or unsubstituted alkyl or aryl group, or of the formula II



in which
 R_1 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-4-sulphonic acid chloride (diaz compound) and an organic acid halide of the formula IV

W- R_3 (IV)

in which

W is



or $-SO_2-V$, 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 1:1 to 39:1.
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



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.
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.

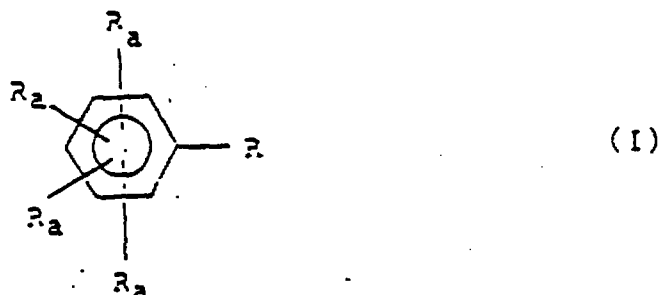
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Revendications

1. Composition photosensible contenant un liant insoluble dans des systèmes aqueux, soluble ou au moins

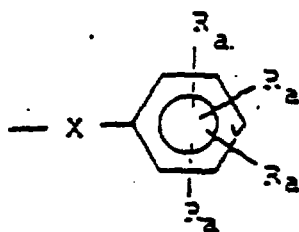


apte à gonfler dans des solvants organiques et aqueux-alcalins, ainsi qu'un composé photosensible, caractérisée en ce que le composé photosensible est un produit de condensation obtenu à partir d'un composé de type phénol de formule I



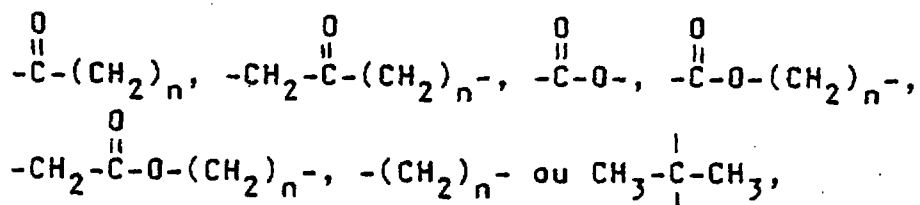
dans laquelle

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



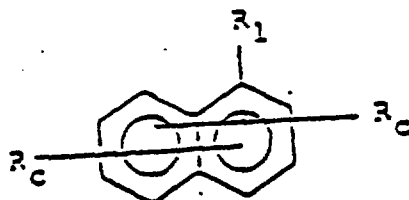
R_a représente un atome d'hydrogène ou d'halogène, le groupe OH ou un groupe alkyle inférieur, au moins deux et au maximum six groupes R_a étant des groupes OH,

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



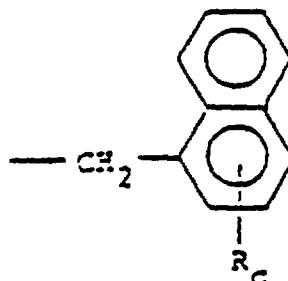
n est 1 ou 2 et

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



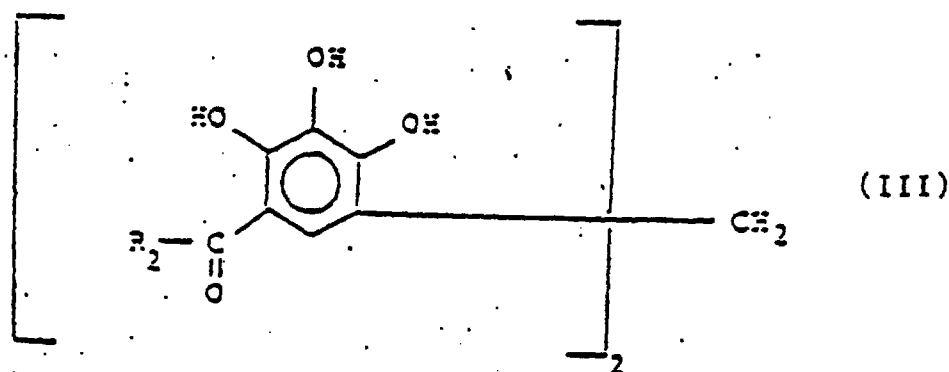
dans laquelle

R_1 représente un atome d'hydrogène ou



et

R_c représente un atome d'hydrogène ou le groupe OH, au moins deux groupes R_c étant des groupes OH;
ou de formule III



dans laquelle

R_2 représente un atome d'hydrogène ou un groupe alkyle ou aryle éventuellement substitué;
avec un mélange d'un chlorure de 1,2-naphtoquinonediazide-4-sulfonyl (composé diazo) et d'un halogénure d'acide organique de formule IV

W- R_3 (IV)

dans laquelle

W représente



ou $-SO_2-V$, V représentant un halogène, et
 R_3 représente un groupe alkyle ou aryle éventuellement substitué.

- 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 1:1 à 39:1.
- 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.

