

Polymeric compounds and radiation-sensitive mixture containing them

5 The invention relates to new water-insoluble polymeric compounds which are soluble in aqueous alkaline solutions and which are suitable for use as binders for radiation-sensitive mixtures, in particular for the preparation of photoresist stencils and printing plates.

10 The polymers according to the invention are suitable in particular for positive working radiation- or light-sensitive mixtures based on 1,2-naphthoquinonediazides or on combinations of photolytically activable acid donors with acid-cleavable compounds; however, they are also suitable for use as binders for negative working radiation-sensitive mixtures.

15 Positive working light-sensitive mixtures, i.e. mixtures whose copying layer becomes soluble in the irradiated areas, of the constituents mentioned are known.

20 These mixtures contain as alkali-soluble binders in the vast majority of cases phenol-formaldehyde condensation products, in particular novolaks. Further possible alkali-soluble binders mentioned are copolymers of maleic anhydride and styrene, of vinyl acetate and crotonic acid, of alkyl methacrylate, butadiene and methacrylic acid (DE-A-3,107,526) and polymers of vinylphenol (DE-A-3,309,222). These polymers are evidently not preferred. Practically all known commercial products therefore contain novolaks. Novolaks used as binders have disadvantages for certain purposes.

30 The condensation of phenols or cresols with formaldehyde under acid conditions leads, owing to the polyfunctionality of the phenols used, not only to linear but also to highly branched and cyclic products which exert a strong influence on the copying properties. The correlation of

these properties with synthesis parameters is frequently very difficult or even impossible. This problem area is exhaustively discussed by T.R. Pampalone in Solid State Technology, June 1984, page 115 et seq. According to
5 said discussion, novolaks have only limited variability and adaptability to practical requirements in their material properties.

For use as binders in dry resist coatings, novolaks are too brittle owing to their low molecular weight, so that
10 the layer frequently breaks in the course of processing, for example in the course of exposure in contact with a mask or in the course of lamination as a dry resist to a base material surface. This property is particularly noticeable in the case of the higher layer thicknesses
15 preferred for dry resist materials.

Combined with o-quinonediazides, novolaks are used in positive printing plates. To increase the print run, the printing plates are baked, after exposure and development, at temperatures of about 200-250°C for a few
20 minutes. In the course of this bake, low molecular weight constituents of the novolak can escape from the layer and deposit on the bared aluminum surface, which on printing leads to toning, i.e. to undesirable ink acceptance in nonimage areas.

This poor thermal stability of novolaks is also responsible for image distortions in the preparation of integrated circuits by the dry etch method. In this method, temperatures can be above 150°C, and hence
25 distinctly higher than the softening point of the novolak. As a consequence, the image structures run and lead to a lower resolution.
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Polyvinylphenol is proposed in DE-C-2,322,230 as a novolak replacement in layers which contain o-quinone-diazides. Although the plasma resistance and the
35 adhesion to silicon surfaces are basically comparable to

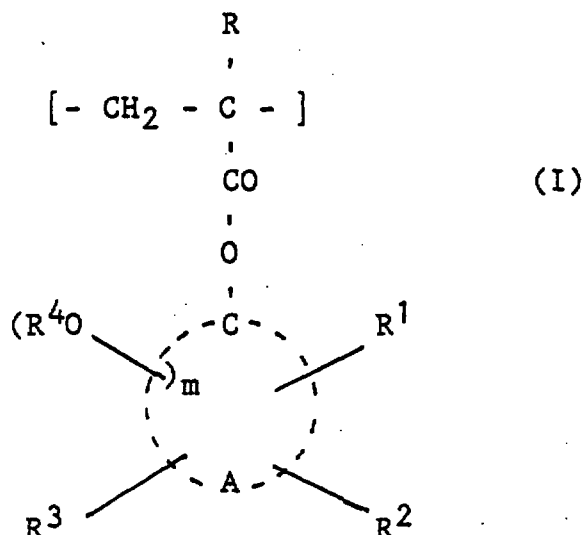
novolaks, unexposed photoresist layers based on this polymer are excessively eroded in the course of development. It is true that with increasing molecular weight, the degree of erosion decreases, but in the best cases (molecular weight = 25,000) it is still higher than in the case of novolak-based layers by a factor of approximately 100 (according to T. R. Pampalone, Solid State Technology, June 1984, page 119). A further disadvantage is the preparatively expensive synthesis and the low polymerization tendency of the monomeric vinylphenol.

JP-A-51/36,129 describes polymers based on hydroquinone monomethacrylate and dihydroxynaphthalene monomethacrylate as binders for naphthoquinonediazide layers. The synthesis of these monomers requires an expensive purification step, since the reaction of a diol with an acid chloride gives rise to the diester in a certain percentage, and this diester leads in the subsequent polymerization, even in amounts of 0.5%, to a complete cross-linking and hence insolubility of the polymer.

GB-A-1,119,667 describes this preparation phenyl esters of polyacrylic acid and copolymers thereof which, however, are insoluble in alkaline solutions.

It is therefore an object of the invention to propose alkali-soluble polymers having phenolic OH side groups, which do not form brittle layers, have good developer and plasma resistance and which are simple to prepare.

The invention proposes a polymer, which is insoluble in water, but soluble in aqueous alkali and which contains repeat units of the general formula I



in which

R is a hydrogen or halogen atom, a cyanide group or an alkyl group of 1-4 carbon atoms,

R¹, R² and R³ are identical or different and denote hydrogen or halogen atoms, alkyl, alkoxy or alkoxycarbonyl groups,

R⁴ is a hydrogen atom or a divalent organic group which is intermolecularly or intramolecularly linked to a further unit of the formula I, on average at least one R⁴ of each polymer unit of the formula I being hydrogen,

A denotes the atoms required for completing a mononuclear or dinuclear carbocyclic or heterocyclic aromatic ring system and

m is 2 or 3.

The invention further proposes a radiation-sensitive mixture which contains as essential constituents

A) a water-insoluble polymeric binder which is soluble in aqueous alkaline solutions and has phenolic hydroxyl side groups and

B) 1) a 1,2-quinonediazide or

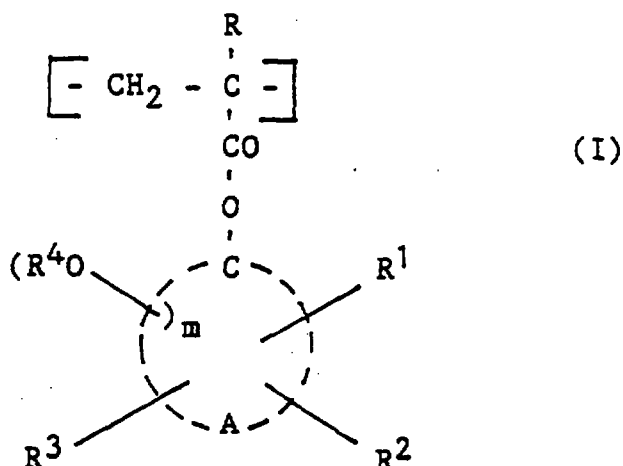
2) a combination of

a) a compound which forms a strong acid under the

action of actinic radiation and

- b) a compound which has at least one acid-cleavable C-O-C bond and the solubility of which in a developer is increased by the action of acid.

5 In the mixture according to the invention, the binder is a polymer which is insoluble in water, but soluble in aqueous alkali with repeat units of the general formula I



in which

R is a hydrogen or halogen atom, cyanide group of an alkyl group of 1-4 carbon atoms,

10 R¹, R² and R³ are identical or different and denote hydrogen or halogen atoms, alkyl, alkoxy or alkoxy carbonyl groups,

15 R⁴ is a hydrogen atom or a divalent organic group which is intermolecularly or intramolecularly linked to a further unit of the formula I, on average at least one R⁴ of each polymer unit of the formula I being hydrogen,

20 A denotes the atoms required for completing a mononuclear or dinuclear carbocyclic or heterocyclic aromatic ring system and

m is 2 or 3.

The polymer according to the invention can be a

homopolymer or a copolymer which, in addition to units of the formula I, contains other units derived from copolymerizable ethylenically unsaturated monomers. The comonomers are in general monovinyl compounds. They can also contain crosslinkable groups which can be cross-linked catalytically or thermally. The crosslinking can be effected for curing the image stencil after developing, preferably by heating.

When in the formula I R is an alkyl group, it generally contains 1 to 6, preferably 1 or 2, carbon atoms. Particular preference is given to compounds with R = H or methyl.

Of the substituents R^1 , R^2 and R^3 , preferably at least one is a hydrogen atom, particularly preferably at least two thereof are hydrogen atoms. When these symbols denote alkyl or alkoxy groups, these have preferably 1 to 6, in particular 1 to 3, carbon atoms.

In general, alkyl groups are here to be understood as meaning branched and unbranched, saturated and unsaturated groups with cyclic and open chains which can be substituted by halogen atoms or hydroxyl groups or contain ether or keto groups. Preference is given to unbranched hydrocarbon radicals having 1 to 3 carbon atoms.

When the aromatic ring system A is heterocyclic, it can be for example a pyridine, pyrimidine, pyrazine, quinoxaline, isoquinoline, quinoxaline, indole or thiophene system. Suitable aromatic ring systems are benzene, naphthalene and biphenyl; particular preference is given to a benzene ring. m is preferably 2.

The position of the OR^4 groups is not subject to any restrictions; it depends on the preparative accessibility.

The position of the radicals R^1 , R^2 and R^3 depends on the position of the OR^4 groups.

When R^4 is a divalent group, it is present in the polymer in such an amount as not to impair the solubility of the product. In general, no more than 20 mol-%, preferably no more than 10 mol-%, of the units of the formula I contain a group R^4O in which R^4 is different from H. R^4 can in this case be an aromatic or aliphatic group which preferably contains 2 to 15 carbon atoms, and for example has been formed by reacting a diepoxide or diisocyanate with OH groups. The preferred reactants are diisocyanates. Examples of suitable diisocyanates are tolylene, hexamethylene, 2,2,4-trimethylhexamethylene, lysine, isophorone and diphenylmethane diisocyanates.

Examples of units of the formula I which are suitable according to the invention are those of monoacrylates or monomethacrylates of pyrogallol, of phloroglucin, of hydroxyhydroquinone, or ethyl 3,4,5-trihydroxybenzoate, of 2,3,4-trihydroxytoluene, of 3,3',4,4'-tetrahydroxybiphenyl or of a trihydroxyquinoline. The esters of trihydroxybenzenes, in particular of pyrogallol, are particularly preferred.

The preparation of preferred monomers which form units of the formula I is effected by converting, in trihydroxyaromatics which contain at least two hydroxyl groups in adjacent positions, these hydroxyl groups first, for example by reacting with phosgene, into the cyclic carbonates, then converting the third hydroxyl group into the ester of an acrylic acid of the formula $CH_2=C(R)-COOH$, and finally hydrolyzing the carbonate back again. Further monomers are prepared in analogy to known processes or to the process mentioned.

The homopolymerization of these monomers or their copolymerization with other monomers can be carried out by conventional methods, for example in the presence of a

polymerization initiator such as azobisisobutyronitrile in organic solvents such as butanone or ethanol at elevated temperatures within 1 to 20 hours. In addition, however, it is also possible to effect a suspension, emulsion or mass polymerization which can be initiated by radiation, heat or ionic initiators.

The polymers of units of the formula I can be homopolymers which contain only structural units of the formula I or copolymers of monomers conforming to the formula I and one or more other vinyl monomers, including, where appropriate, those having phenolic groups.

It is also possible to copolymerize different monomers conforming to the formula I, for example pyrogallol acrylate and pyrogallol methacrylate, with one another, and also, where appropriate, with other vinyl monomers.

The molecular weight of the homopolymers and copolymers can be varied within wide limits; preference is given to polymers with $M_n = 1000 - 200,000$, in particular those with $M_n = 5000 - 100,000$. The hydroxyl number is in general within the range from 100 to about 450, preferably between 200 and 350.

The choice of suitable homopolymers and copolymers depends in the individual case on the intended purpose and on the nature of the other components in the radiation- or light-sensitive mixture.

For instance, the hydrophilic character of the binder of a light-sensitive mixture is of importance for the light sensitivity, developing time and developer resistance. The hydrophilic character must therefore be adapted to the particular light-sensitive system. Systems with o-quinonediazides require a more hydrophilic binder than systems with acid-cleavable orthoester or acetal groupings.

The application properties of a light-sensitive mixture are further governed by its softening temperature, which is essentially determined by that of the binder. In the case of printing plates or in the case of microresists for the manufacture of integrated circuits, a high softening temperature is required in order to avoid the disadvantages mentioned at the start, such as toning or image distortion. By contrast, the use as a dry resist requires a system having lower softening points in order to make possible dry layer transfer by means of pressure and heat.

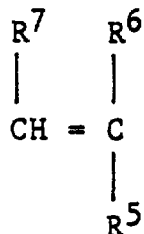
The mixture according to the invention makes it possible to vary the properties mentioned in a controlled manner and to tailor them to the particular requirements.

This can be done for example by

- varying the radicals R, R¹, R², R³ and R⁴
- varying the number of phenolic groups
- varying the mixing ratio of the units of the formula I
- varying the mixing ratio and the nature of additional comonomers.

The examples given below illustrate these possibilities.

Preferred comonomers for the compounds which polymerize to give units of the formula I are compounds of the general formula



in which

R⁵ is a hydrogen or halogen atom or an alkyl group,
R⁶ is an alkyl, alkoxy, alkyloxycarbonyl, acyl,

acyloxy, aryl, formyl, cyanide, carboxyl, hydroxyl or aminocarbonyl group and

R^7 is a hydrogen atom or a carboxyl group which can be bonded to R^6 , when the latter is a carboxyl group, to form an acid anhydride.

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When R^5 or R^6 are alkyl groups, they generally have 1 - 4 carbon atoms; suitable representatives of R^6 are: alkoxy groups having 1 - 8 carbon atoms, alkyloxycarbonyl groups having 2 - 13 carbon atoms, acyl groups having 2 - 9 carbon atoms and acyloxy groups having 2 - 5 carbon atoms. The aminocarbonyl groups can be unsubstituted or be substituted by one or two alkyl groups having 1 - 8 carbon atoms. The alkyl groups have the abovementioned meaning.

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Examples of such compounds are styrene, α -chlorostyrene, α -methylstyrene, 2-, 3- or 4-chloromethylstyrene, 4-bromostyrene, methyl vinyl ether, ethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, acrylonitrile, acrolein, butadiene, acrylic acid, methacrylic acid, the methyl, ethyl, propyl, butyl, pentyl, hexyl, decyl, dodecyl, 2-ethylhexyl, phenyl, benzyl, biphenyl and naphthyl esters of these acids, methacrylamide, acrylamide, vinyl acetate, vinyl isobutyl ketone and maleic anhydride.

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The level of units of the formula I in the copolymer depends on the other components of the mixture and on the intended use. In general, polymers used in the mixture according to the invention contain 20 to 100 mol-%, preferably 40 to 100 mol-%, of units of the formula I.

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To prepare the mixtures according to the invention, the binder described is combined with radiation-sensitive compounds or mixtures whose solubility in aqueous alkali is increased on exposure to light or high-energy radiation. They include in particular o-quinonediazides and combinations of photolytic acid donors with

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acid-cleavable compounds.

5 The o-quinonediazides (1,2-quinonediazides) used are preferably naphto-1,2-quinone-2-diazide-4- or -5-sulfonic esters or amides. Of these, the esters, in particular those of the 5-sulfonic acids, are particularly preferred. Suitable compounds of this type are known and described for example in DE-C-938,233, DE-A-2,131,377, DE-A-2,547,905 and DE-A-2,828,017.

10 The amount of o-quinonediazide compounds is in general 3 to 50, preferably 7 to 35, % by weight, based on the nonvolatile portions of the mixture. The amount of binder is in general 30 to 90, preferably 55 to 85, % by weight, based on the same basis.

15 Further suitable constituents are in the known way for example plasticizers, dyes, indicators, pigments, sensitizers and flow control agents.

Even materials based on acid-cleavable compounds can be used highly successfully in the mixture according to the invention.

20 Representatives of acid-cleavable compounds are primarily:

- 25 (i) those with at least one orthocarboxylic acid ester and/or carboxylic acid amide acetal grouping, it being possible for the compounds also to have polymeric character and for the groupings mentioned to appear as linking elements in the main chain or as lateral substituents,
- (ii) oligomer or polymer compounds having recurring acetal and/or ketal groupings in the main chain and
- 30 (iii) compounds having at least one enolic ether or N-acyliminocarbonate grouping.

Acid-cleavable compounds of type (i) as components of

radiation-sensitive mixtures are described in detail in EP-A-0,022,571; mixtures which contain compounds of type (ii) are described in DE-C-2,306,248 and DE-C-2,718,254; compounds of type (iii) are described in EP-A-0,006,626 and EP-A-0,006,627.

The nature and the amount of binder and of cleavable compound can vary according to the intended use; preference is given to binder contents between 30 and 90% by weight, in particular 55 to 85% by weight. The amount of cleavable compound can be varied between 5 and 70% by weight, preference being given to the range from 5 to 40% by weight.

Additionally it is also possible to include many other oligomers and polymers for example phenolic resins of the novalak type or vinyl polymers such as polyvinyl acetals, polymethacrylates, polyacrylates, polyvinyl ethers and polyvinylpyrrolidones, which can themselves have been modified by comonomers.

The most favorable amount of these additives depends on the application requirements and on the effect on the developing conditions and is in general not more than 40% of the polymer of units of the formula I. For specific requirements such as flexibility, adhesion, gloss, etc. the light-sensitive layer can additionally contain, in small amounts, substances such as polyglycols, cellulose ether, for example ethyl cellulose, wetting agents, flow control agents, dyes and finely divided pigments.

Suitable radiation-sensitive components which on irradiation preferably form or eliminate strong acids are a large number of known compounds and mixtures, such as diazonium, phosphonium, sulfonium and iodonium salts, halogen compounds, o-quinonediazidesulfochlorides and organometal-organohalogen combinations.

The diazonium, phosphonium, sulfonium and iodonium

compounds mentioned are generally used in the form of their salts which are soluble in organic solvents, usually as deposition product with complex acids such as hydroborofluoric acid, hexafluorophosphoric, hexafluoro-antimonic and hexafluoroarsenic acid.

In principle, the halogen-containing radiation-sensitive compounds which form halohydric acid used can be any organic halogen compound also known as a photochemical free radical initiator, for example those having more than one halogen atom on a carbon atom or on an aromatic ring. Examples are described in US-A-3,515,552, US-A-3,536,489, US-A-3,779,778, DE-C-2,610,842, DE-A-2,243,621, DE-A-2,718,259 and DE-A-3,337,024. Of these compounds, preference is given to the s-triazine derivatives with 2 halogenomethyl groups, in particular trichloromethyl groups and an aromatic or unsaturated substituent in the triazine nucleus which are described in DE-A-2,718,259 and DE-A-3,337,024. The action of these halogen-containing compounds can also be spectrally influenced and enhanced by known sensitizers.

Examples of suitable initiators are: 4-(di-n-propyl-amino)-benzenediazonium tetrafluoroborate, 4-p-tolyl-mercapto-2,5-diethoxybenzenediazonium hexafluorophosphate and tetrafluoroborate, diphenylamine-4-diazonium sulfate, 4-methyl-6-trichloromethyl-2-pyrone, 4-(3,4,5-trimethoxystyryl)-6-trichloromethyl-2-pyrone, 4-(4-methoxystyryl)-6-(3,3,3-trichloropropenyl)-2-pyrone, 2-trichloromethylbenzimidazole, 2-tribromomethylquinoline, 2,4-dimethyl-1-tribromoacetylbenzene, 3-nitro-1-tribromoacetylbenzene, 4-dibromoacetylbenzoic acid, 1,4-bis-dibromomethylbenzene, tris-dibromomethyl-s-triazine, 2-(6-methoxynaphth-2-yl)-, 2-(naphth-1-yl)-, 2-(naphth-2-yl)-, 2-(4-ethoxyethylnaphth-1-yl)-, 2-benzopyran-3-yl)-, 2-(4-methoxyanthrac-1-yl)-, 2-(4-styrylphenyl)-, 2-(phenanthr-9-yl)-4,6-bis-trichloromethyl-s-triazine and the compounds listed in the examples.

5 The amount of initiator can likewise vary very widely according to its chemical nature and the composition of the mixture. Favorable results are obtained with about 0.1 to 10% by weight, based on the total solids, preference being given to 0.2 to 5%. In particular in the case of copying layers over 10 μ m thickness it is advisable to use relatively less acid donor.

10 Finally, the light-sensitive mixture can also have added to it soluble or even finely divided dispersible dyes and, depending on the intended use, even UV absorbers. Suitable dyes are the triphenylmethane dyes, in particular in the form of their carbinol bases. The most favorable mixing ratios of the components can easily be determined in the individual case by means of preliminary
15 experiments.

Suitable base materials for the light-sensitive mixtures are all materials customarily used in the art in copying processes. Examples which may be mentioned are plastic films, insulating boards with copper layer, mechanically
20 or electrochemically roughened and optionally anodized aluminum, screen printing stencil supports, wood, ceramics, glass and silicon whose surface can have been chemically converted for example into silicon nitride or silicon dioxide.

25 Preferred base materials for thick layers over 10 μ m are plastic films which then serve as temporary base materials for transfer layers. For this purpose and for color films preference is given to polyester films, for example polyethylene terephthalate. Polyolefin films such as
30 polypropylene, however, are likewise suitable. The base materials used for layer thicknesses below about 10 μ m are usually metals. In the case of offset printing plates it is possible to use: mechanically or chemically roughened and optionally anodized aluminum which can in
35 addition also have been chemically pretreated, for example with polyvinylphosphonic acid, silicates or

phosphates.

5 Finally, coating can be effected directly or by layer transfer from temporary base materials onto circuit board materials which comprise insulating boards with a copper layer on one or both sides, onto glass or ceramic materials which may have been given a tackifying pre-treatment, and onto silicon disks. It is also possible to coat wood, textiles and surfaces of many materials which are advantageously imaged by projection and resistant to the action of alkaline developers.

10 For the drying after coating, it is possible to adopt the customary equipment and conditions, temperatures around 100°C and briefly up to 120°C being withstood without loss of radiation sensitivity.

15 Exposure can be effected with the customary light sources such as fluorescent lamps, xenon pulsed lamps, metal halide doped mercury vapor high pressure lamps and carbon arc lamps.

20 For the purposes of this description, irradiation is the action of actinic electromagnetic radiation in the wavelength region below about 500 nm. All the radiation sources which emit in this wavelength region are suitable in principle.

25 It is advantageous to use laser irradiators, in particular automatic processing systems, which contain an argon ion laser as the source of radiation.

30 Irradiation can also be effected with electron beams. In this case it is also possible to use compounds which in the customary sense do not form light-sensitive acid as initiators of the solubilizing reaction, for example halogenated aromatic compounds or halogenated polymeric hydrocarbons. X- or ion rays can likewise be used for image generation.

The imagewise exposed or irradiated layer can be removed in the known way with the developers known for commercially available naphthoquinonediazide layers and photoresists, and the new materials can be adapted in their copying behavior with advantage to the known auxiliaries such as developers and programmed spray development apparatus. The aqueous developer solutions can contain for example alkali metal phosphates, silicates or hydroxides and also wetting agents as well as, if desired, minor amounts of organic solvents. In certain cases even solvent-water mixtures are usable as developer. The choice of the most favorable developer can be determined by experiments on the particular layer used. If necessary, the development can also be aided mechanically.

In the case of use as printing plates, the developed plates can be briefly heated to elevated temperatures to increase the durability in printing and the resistance to washing-out agents, correcting agents and UV-curable printing inks, as known for diazo layers from GB-A-1,154,749.

The invention also proposes a process for preparing relief images by imagewise irradiating a radiation-sensitive recording material composed of a base material and recording layer which comprises the radiation-sensitive mixture defined at the beginning to actinic radiation in such an amount that the solubility of the layer in an aqueous alkaline developer solution increases and the irradiated parts of the layer are removed by means of an aqueous alkaline developer solution, wherein the recording layer contains as binder a polymer of units of the general formula I.

The invention makes it possible to obtain positive layers whose properties are adjustable in a controlled manner according to the application requirements. Through suitable choice of the binders according to the invention it is possible for example to obtain positive layers for

use in a thin layer, which have excellent adhesion to the substrate and outstanding temperature, etch and abrasion stability.

5 On the other hand, the binders proposed here can also be used to obtain positive layers for uses in higher layer thicknesses of about 15 μm to 100 μm or more, for example as dry resist. These dry films have a high light sensitivity and an excellent flexibility and can be satisfactorily processed from the roll.

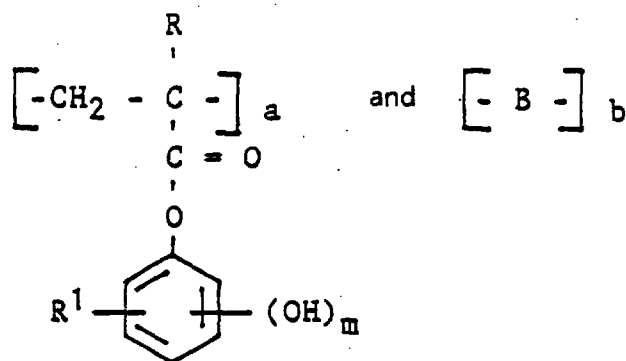
10 General method for preparing the polymers

In a four-necked flask with stirrer, reflux condenser, internal thermometer and dripping funnel, 40 pbv of ethanol are heated to the boil in the absence of oxygen. In the course of 3 hours at gentle reflux, a mixture of
15 40 pbw of the monomer(s), dissolved in 60 pbw of ethanol, and 0.4 pbw of azobisisobutyronitrile is added dropwise. This is followed by 12 hours of reaction, and after cooling down and possible dilution with ethanol, the solution is then added dropwise to about 10,000 pbv of
20 water with vigorous stirring. The precipitated, colorless polymer is filtered off with suction, washed and dried at 50°C in vacuo for 48 hours.

Table 1 summarizes the polymers prepared in this way.

Table 1

Polymers prepared from units of the types



No. of polymer	R	m	Position OH	R ¹	Position R ¹	B	a : b (mol-%)
1	H	2	2,3	H	-	-	-
2	CH ₃	2	2,3	H	-	-	-
3	H	2	2,3	COOC ₂ H ₅	5	-	-
4	CH ₃	2	2,3	COOC ₂ H ₅	5	-	-
5	H	2	2,3	H	-	MMA	30 : 70
6	H	2	2,3	H	-	"	40 : 60
7	H	2	2,3	H	-	"	50 : 50
8	CH ₃	2	2,3	H	-	EHMA	60 : 40
9	CH ₃	2	2,3	H	-	"	65 : 35
10	CH ₃	2	2,3	H	-	"	70 : 30
11	CH ₃	2	2,3	H	-	"	85 : 15
12	CH ₃	2	2,3	H	-	BMA	50 : 50
13	CH ₃	2	2,3	H	-	"	80 : 20
14	CH ₃	2	2,3	H	-	"	90 : 10
15	CH ₃	2	2,3	COOC ₂ H ₅	5	HMA	60 : 40

Table 1 (continued)

No. of polymer	R	m	Position OH	R ¹	Position R ¹	B	a : b (mol-%)
16	CH ₃	2	3,4	H	-	HMA	60 : 40
17	CH ₃	2	3,4	H	-	"	70 : 30
18	CH ₃	2	3,4	H	-	BMA	80 : 20
19	CH ₃	2	3,5	H	-	EHMA	60 : 40
20	CH ₃	2	3,5	H	-	S	70 : 30
21	CH ₃	2	2,6	H	-	-	-
22	CH ₃	2	2,6	H	-	HMA	75 : 25
23	CH ₃	3	3,4,5	H	-	BuMa	60 : 40
24	CH ₃	3	3,4,5	H	-	BMA	65 : 35
25	CH ₃	3	3,4,6	H	-	HMA	70 : 30
26	CH ₃	3	3,4,6	H	-	-	-

BMA Biphenyl 4-methacrylate
BuMa n-Butyl methacrylate
EHMA 2-Ethylhexyl methacrylate
HMA n-Hexylmethacrylate
MMA Methyl methacrylate
S Styrene

The polymers described in Table 1 can be processed in a mixture with light-sensitive systems into reproduction layers. The examples below show the many possible uses of these binders in the mixtures according to the invention.

Percentages and weights are unless otherwise stated by weight. Parts by weight (pbw) relate to parts by volume (pbv) as the g relates to the ml.

The following coating solutions are prepared for various

application possibilities:

Coating solution A:

	8	pbw of binder,
5	1	" of esterification product of 1 mol of 2,3,4-trihydroxybenzophenone and 3 mol of naphtho-1,2-quinone-2-diazide-5-sulfonyl chloride and
	0.01	" crystal violet base in
	80	" 1-methoxy-2-propanol and
	20	" butyl acetate.

10 Coating solution B:

	40	pbw of binder,
	10	" of polyacetal of triethylene glycol and butyraldehyde,
15	0.5	" of 2-(4-ethoxynaphth-1-yl)-4,6-bis-trichloromethyl-s-triazine and
	0.05	" of crystal violet base in
	110	" butanone.

Coating solution C:

	40	pbw of binder,
20	8	" of a polymeric orthoester prepared by condensing trimethyl orthoformate with 4-oxa-6,6-bis-hydroxymethyl-octan-1-ol,
	0.5	" of 2-(4-styrylphenyl)-4,6-bis-trichloromethyl-5-triazine and
25	0.05	" of crystal violet base in
	80	" butanone and
	20	" of ethanol

Coating solution D:

	26.5	pbw of binder and
30	3.5	" of naphthoquinonediazide of coating solution A in

70 pbw of a solvent mixture of 1-methoxy-propanol-
2, butylacetate and xylene (8:1:1)

Coating solution E:

20 pbw of binder,
5 6.5 " of kresol-formaldehyde-novolak with a soften-
ing range of 105-120°C and
3.5 " of the naphthoquinonediazide of coating
solution A in
10 70 " of a solvent mixture of 1-methoxy-propanol-
2, butylacetate and xylene (8:1:1)

Coating solution F:

10 pbw of binder,
3 " of the bis-(5-butyl-5-ethyl-1,3-dioxan-2-yl)
ether of 2-butyl-2-ethylpropanediol and
15 0.25 " of 2-(acenaphth-5-yl)-4,6-bis-trichloro-
methyl-s-triazine in
90 " of butanone

Examples 1 to 16:

20 To prepare offset printing plates, binders of Table 1 are
mixed with the components specified there in accordance
with the directions concerning coating solutions A, E and
F (see Table 2).

Table 2:

Example No.	Polymer No.	Coating solution	Exposure time (s)	Developing time (s)
1	1	E	100	60
2	2	E	100	60
3	3	E	100	70
4	4	E	100	80
5	9	F	20	40
6	11	A	100	55
7	13	F	20	40
8	14	A	100	50
9	15	E	100	60
10	17	A	100	80
11	18	F	20	70
12	20	F	20	70
13	21	E	100	90
14	22	F	20	40
15	24	F	40	70
16	25	A	100	60

5 These solutions are whirler-coated onto electrolytically roughened and anodized aluminum plates which have been treated beforehand with an aqueous solution of polyvinylphosphonic acid. Through adjusting the speed of rotation of the whirler the layer thickness (dry) is brought to about 1.5 μm for all plates.

The plates are then dried at 100°C in a through circulation cabinet for 10 minutes.

10 After exposure under a 5kW metal halide lamp at a distance of 100 cm and after a delay time of 10 minutes for the layers prepared with coating solution F, the plates are developed in a solution of

5.3 pbw of sodium metasilicate x 9 H₂O
3.4 " of trisodium phosphate x 12 H₂O and
0.3 " of sodium dihydrogenphosphate
(anhydrous) in
5 91.0 " water,

the parts of copying layer which have been affected by the light being removed, leaving the nonirradiated image areas behind on the plate.

10 Table 2 shows the binders used, the coating solutions used in each case and the exposure and developing times for the individual layers.

After inking with oleophilic printing ink the printing forms thus prepared can be used to prepare 100,000 satisfactory prints in an offset printing machine.

15 Examples 17 to 25

To prepare a positive dry resist, binders of Table 1 are mixed with the other components in accordance with the directions concerning coating solutions B and C (see Table 3).

20 These solutions are in each case whirler-coated onto 26 μ m thick, biaxially oriented and heat-set polyethylene terephthalate films and then subsequently dried at 110°C in the through circulation cabinet for 10 minutes. The speed of the whirler is regulated so as to obtain a layer
25 thickness of about 25 μ m. As protection against dust and scratching, a polyethylene film, is additionally laminated on top.

As comparison, a dry resist is prepared with exclusively cresol-formaldehyde novolak as binder (Example 25).

30 The dry resists with the binders according to the invention exhibit a distinctly improved flexibility compared

with the dry resist with novolak. While the novolak-containing resist easily tears in the course of laminating or in the course of folding, these disadvantages do not arise in the case of the dry resists prepared with the new binders.

5

To prepare circuit boards, the dry resists, after the cover film has been pulled off, are laminated in a commercially available laminator onto a cleaned, preheated base which comprises an insulating board with a 35 μm thick copper layer. Removal of the base film and possible subsequent drying is followed by exposure under a master to a 5 kW metal halide lamp at a distance of 110 cm and, after a waiting time of 10 minutes, by development in the developer specified in the Examples 1 to 16.

10

15

The resist stencils obtained in this way have an excellent electroplating resistance, in particular in the case of the electroplating buildup of copper and Pb/Sn alloys.

Boards treated in this way can subsequently be subjected to renewed exposure and development. By this procedure it is possible, in a first step, to electroplate Pb/Sn land at the drilled holes, and in a second exposure and developing step the conducting path image can then be transferred to the still light-sensitive resist stencil. Etching of the bared copper with ammoniacal Cu(II) chloride solution gives a circuit board in copper technology, i.e. the Pb/Sn alloy is built up only where it is required in the subsequent soldering process.

20

25

Table 3

Example No.	Polymer No.	Coating solution	Exposure times (s)	Developing times (s)
17	7	B	20	50
18	9	C	20	40
19	10	B	20	90
20	15	B	20	45
21	19	B	10	50
22	22	C	10	50
23	23	C	10	30
24	25	B	50	30
25 (CT)	cresol- Novolak	B	30	60

(CT) Comparative Test

Examples 26 to 37:

5 To prepare microelectronic circuit elements of high integration, binders given in Table 1 are mixed with the other components in accordance with the directions concerning coating solutions D, E and F (see Table 4). After filtration through a filter having a pore diameter of 0.2 μm (millipore), the photoresist solutions are whirler-coated onto commercial silicon disks which have been provided with an 0.2 μm thick SiO_2 layer by oxidation and polished as customary. By varying the speed of rotation, the layer thicknesses are adjusted to about 0.9 μm to 1.2 μm .

15 The disks thus coated are dried at 90°C for 30 minutes. After cooling down and conditioning in the defined atmosphere of 23°C and 40 - 50% relative humidity, the wafers are exposed under a commercially available chromium mask in a contact exposure apparatus.

The exposure times are about 1 second for the layers

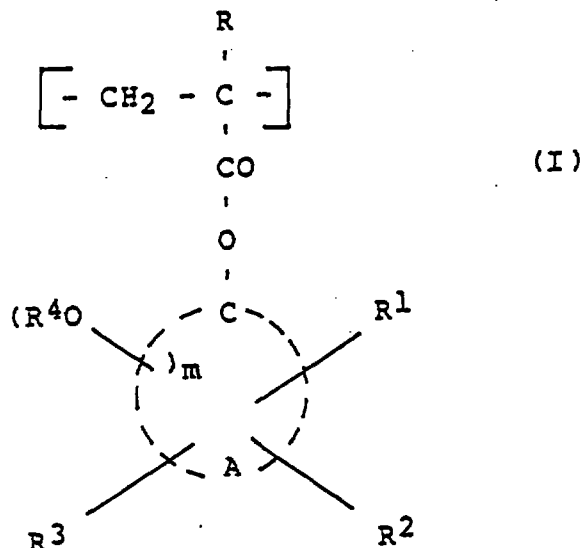
prepared with coating solutions B and C and about 3 seconds for the layers prepared with coating solutions D and E. A waiting time of 10 minutes in the case of Examples 30, 33, 34 and 36 is followed by development in the developer specified in Examples 1 to 16.

In all cases it is possible to obtain satisfactory resolution of image elements in the region of 1 μm .



Claims

1. A polymer which is insoluble in water, but soluble in aqueous alkali and which contains repeat units of the general formula I



5 in which

R is a hydrogen or halogen atom, a cyanide group or an alkyl group of 1-4 carbon atoms,

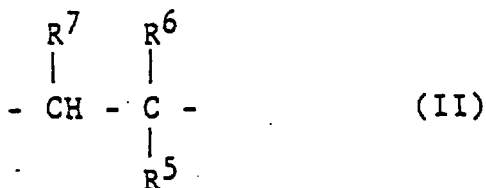
10 R¹, R² and R³ are identical or different and denote hydrogen or halogen atoms, alkyl, alkoxy or alkoxy carbonyl groups,

R⁴ is a hydrogen atom or a divalent organic group which is intermolecularly or intramolecularly linked to a further unit of the formula I, on average at least one R⁴ of each polymer unit of
15 the formula I being hydrogen,

A denotes the atoms required for completing a mononuclear or dinuclear carbocyclic or heterocyclic aromatic ring system and

m is 2 or 3.

20 2. The polymer as claimed in claim 1, which further contains repeat units of the general formula II



in which

R^5 is a hydrogen or halogen atom or an alkyl group,

R^6 is an alkyl, alkoxy, alkyloxycarbonyl, acyl, acyloxy, aryl, formyl, cyanide, carboxyl, hydroxyl or aminocarbonyl group and

R^7 denotes a hydrogen atom or a carbonyl group which can be bonded to R^6 , when the latter is a carboxyl group, to form an acid anhydride.

3. The polymer as claimed in claim 1, wherein A denotes the carbon atoms required for completing a benzene ring.

4. The polymer as claimed in claim 1, which has a molecular weight M_n of 1000 to 200,000.

5. The polymer as claimed in claim 1, wherein m is 2.

6. The polymer as claimed in claim 1, which contains 20 to 100 mol-% of units of the formula I.

7. A radiation-sensitive mixture which contains as essential constituents

A) a water-insoluble polymeric binder which is soluble in aqueous alkali and has phenolic hydroxyl side groups and

B) 1) a 1,2-quinonediazide or

2) a combination of

a) a compound which forms a strong acid under the action of actinic radiation and

b) a compound which has at least one acid-cleavable C-O-C bond and the solubility of which in a



developer is increased by the action of acid, wherein the binder is a polymer as claimed in any of claims 1 or 2.

5 8. A radiation-sensitive recording material comprising a base material and a radiation-sensitive recording layer which contains as essential constituents

A) a water-insoluble polymeric binder which is soluble in aqueous alkaline solutions and has phenolic hydroxyl side groups and

10 B) 1) a 1,2-quinonediazide or

2) a combination of

a) a compound which forms a strong acid under the action of actinic radiation and

15 b) a compound which has at least one acid-cleavable C-O-C bond and the solubility of which in a developer is increased by the action of acid,

wherein the binder is a polymer as claimed in claim 1.

20 9. A process for preparing relief images, which comprises a radiation-sensitive recording material as claimed in claim 8 to imagewise irradiation with actinic radiation of such a dose level that the solubility of the recording layer in aqueous alkali increases and the irradiated parts of the layer are washed out by means of aqueous alkali.