

The present invention relates to novel hydroxy-polyimides and to high-temperature-resistant, positive-working photoresist mixtures prepared therefrom that are developable with aqueous alkali.

5 Positive resist mixtures and the use thereof are known. They are in general prepared from alkali-soluble, phenol-formaldehyde novolaks and light- or radiation-sensitive 1,2-quinonediazides. Examples of such positive resists are described in US-A-3,666,473; 4,115,128 and
10 4,173,470.

 Conventional positive novolak resists have limited temperature dimensional stability and therefore are not well suited for modern high temperature processes and applications. Heat resistant, negative resists are
15 known in the art and disclosed in US-A-3,957,512; 4,045,223; 4,088,489, US-B-30,186 (reissue) and DE-A-34 11 659. US-A-4,093,461; 4,339,521 and 4,395,482 describe heat resistant positive resists. The advantages of positive resists over negative resists are also known
20 in the art, which include higher resolution and exposure time stability in the presence of oxygen.

 The relief structure produced by exposing and developing the photoresist layer is suitable for various purposes, for example as an exposure mask or a pattern
25 such as is employed in the manufacture of miniaturised integrated electronic components or the manufacture of a printing plate.

 The properties of a resist composition which are important in commercial practice include for example the
30 solubility of the resist in the application solvent, the photospeed of the resist, development contrast, environmentally acceptable developer solubility, resist resolution, resist adhesion, dimensional stability at elevated temperatures and abrasion resistance.

35 Photospeed is important for a resist, particular in applications where a number of exposures are needed, for example in generating multiple patterns by a repeated process, or where light of reduced intensity is employed,

for example in projection exposure. Control of the photospeed is extremely important in order to produce high resolution relief patterns in microcircuitry; too high a photospeed can for example result in narrowing the processing conditions.

Resist resolution refers to the capability of a resist system to reproduce the smallest equally spaced line pairs and intervening spaces of a mask which is utilised during exposure with a high degree of image edge acuity in the developed exposed spaces. In many industrial applications, particularly in the manufacture of miniaturised electronic components, a resist must possess a high degree of resolution (of the order of about 1 μm).

The ability of a resist to reproduce very small dimensions is extremely important in the production of large scale integrated circuits on silicon chips and similar components.

Various attempts have been made in the prior art to produce high temperature positive resists possessing the above-described desired properties. For example, US-A-4,093,461 discloses a heat resistant, positive resist composition comprising a naphthoquinonediazide and the polycondensation product of an aromatic dianhydride (pyromellitic anhydride) and an aromatic diamine (4,4'-diaminodiphenyl ether). The properties of the positive resist of the patent are discussed in US-A-4,395,482 (column 1, lines 46-64). There it is pointed out that the positive resist composition of US-A-4,093,461 has limited storage life, insufficient stability to alkaline etching solutions and relatively small differences in solubility between the exposed and unexposed portion of the resist.

To date, the use of imageable polyimide resist systems has been limited by too slow a photospeed, excessive volume contraction and shelf life problems. The exceptional dielectric and high temperature resistance properties of polyimides made them particularly useful in the semiconductor industry. They can be used, for

example, as dielectric layers, alpha particle barriers in memory devices, ion implantation masks and passivation layers. The goal of numerous development programs has been the development of a simple, reliable and cost-effective radiation-sensitive polyimide system that could be processed using the common photolithographic processes. This was the goal of the work of R. Rubner, H. Ahne, E. Kuhn and G. Kolodziej in Phot. Sci. & Eng. 23(5), 303-309, (1979), and H. Ahne, H. Krüger, E. Pammer and R. Rubner: "Polyimide Synthesis, Characterization and Application", ed. K.L. Mittal, vol. 2, 905-918, Plenum Press (1984). The basic systems described in these publications consist of polyamidedicarboxylic acid polymers bearing photoreactive side groups. To date, however, materials based on this chemistry have been plagued by poor shelf life, extraordinarily low photospeed and excessive post-development/post-cure structure contraction. Although materials based on this chemistry have yielded high resolution structures, they required exposures of 10 minutes or longer. Shelf life was also poor, particularly in highly concentrated solutions required for thick film applications and contraction of original structures upon cure was as much as 60%.

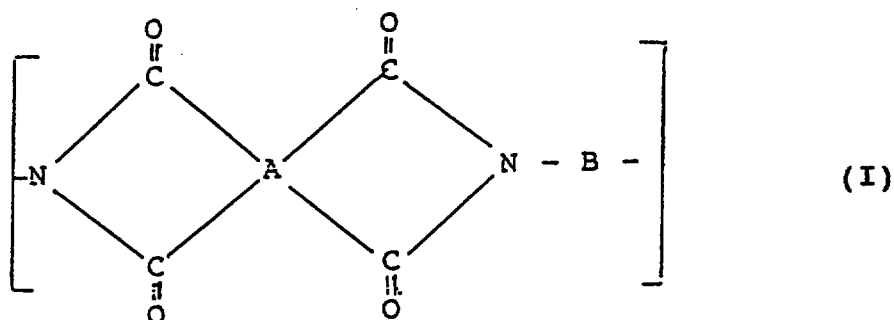
Aromatic polyimides with free hydroxyl groups, prepared by reacting pyromellitic dianhydride with either 3,3'-diamino-4,4'-dihydroxybiphenyl, 2,2-bis(3-amino-4-hydroxyphenyl)propane or bis(3-amino-4-hydroxyphenyl)-methane, are described in Chemical Abstracts, volume 68, No. 18, 6720, No. 69434r.

A radiation-sensitive mixture which in addition to an organic chromophoric azide contains a polyimide from aromatic tetracarboxylic acids and aromatic diamines is disclosed in EP-A-0 092 524. The polyimide is characterised by a minimum content of aliphatic groups and/or bridge groups, but it may also have free hydroxyl groups, since the aromatic diamines mentioned as starting materials include 5,5'-oxybis(2-aminophenol) and 5,5'-sulphonylbis(2-aminophenol). Said EP-A contains no

further mention of hydroxyl-containing polyimides.

It was the object of the invention to provide novel polyimides suitable for use as protective and planarising layers in photoresist technology and also as binders for alkali-developable photoresist mixtures having a long shelf life, which on processing exhibit minimal volume contraction, high resolution and photo-speed.

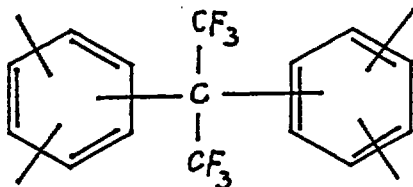
The invention provides a polyimide with recurring units of the general formula I



where

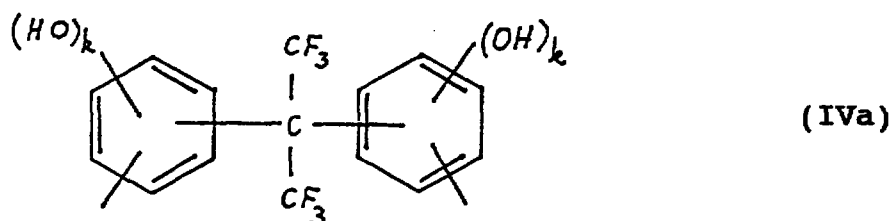
A is the radical of a compound having at least one aromatic six ring, each of the four carbonyl groups being attached to a different aromatic carbon atom of A and each pair of carbonyl groups being situated on adjacent carbon atoms, and

B is the radical of a compound having at least one aromatic six ring and at least one hydroxyl group, with the proviso that either the radical A conforms to the formula IIIa



(IIIa)

or the radical B to the formula IVa



where k is an integer from 0 to 3, or that the radical A
conforms to the formula IIIa and the radical B to the
5 formula IVa.

The invention further provides a photoresist
mixture containing as essential constituents a light-
sensitive compound and a polyimide.

The photoresist mixture of the invention is
10 characterised in that the polyimide is a compound of the
foregoing formula I.

The light-sensitive mixtures of the invention can
be used for preparing high temperature resistant relief
structures possessing excellent resolution and adhesion.

15 The polyimides of the invention can also be used
for preparing high temperature resistant protective
coatings.

The hydroxypolyimides of the invention are in
general prepared by solution condensation of, for
20 example, 2,2-bis(3-amino-4-hydroxyphenyl)perfluoropropane
with a dianhydride of a tetracarboxylic acid. A portion
of the 2,2-bis(3-amino-4-hydroxyphenyl)perfluoropropane
may be replaced with another diamine comonomer containing
no phenolic hydroxyl groups to increase the solubility of
25 the polymer in the aqueous alkaline solutions in the
coating solvent. The solubility of the polyimide in the
developer can also be reduced or its solubility in the
solvent increased by reacting, for example acylating,
some of the hydroxyl groups in the polymer.

It has also been found that the solubility of the polyimide in solvents and its developability in alkaline media can be controlled by the selection of the aminophenol and dianhydride.

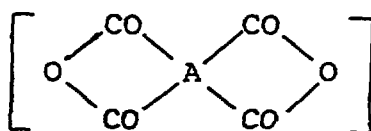
5 Examples of preferred dianhydrides are 2,2-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F-dianhydride), 3,3',4,4'-benzophenonetetracarboxylic-dianhydride (BTDA) and bis(dicarboxyphenyl) ether dianhydride.

10 The photospeed of the resists of the invention can be controlled for example to values between about 10 mJ/cm² and about 300 mJ/cm². This result is achieved by controlling the polyimide component's composition.

15 The positive resists of this invention after exposure in the conventional manner can be developed in an aqueous alkaline developer to provide fine relief structures suitable for use in microelectronics and for producing printing plates. These resists have high thermal stability (250 - 350°C), improved photospeed, improved solubility in the commonly used coating solvents and excellent adhesion. The resists of the invention have superior shelf storage stability over existing resists based on polyamidedicarboxylic acids as polyimide pre-cursors. The resist mixtures can be stored without gel formation for an extended period of time at room temperature without affecting the photospeed or viscosity.

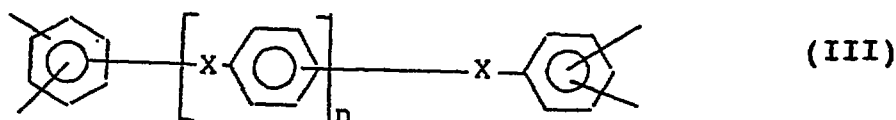
20 Aside from their use in high temperature resistant positive resists the polyimides of the invention can also be used for producing high heat resistant protective coatings.

30 The polyimides of the invention are prepared by condensation of at least one hydroxyl-substituted aromatic diamine H₂N-B-NH₂ with at least one aromatic dianhydride:



The groupings A and B in the above-indicated formula I may be substituted by alkyl, alkoxy, aryl, aryloxy or other inert radicals.

The four-valent grouping A preferably consists of substituted or unsubstituted benzene, naphthalene or polyphenyl nuclei having up to four, in particular two, phenyl rings and mixtures thereof. It has in particular the formula III



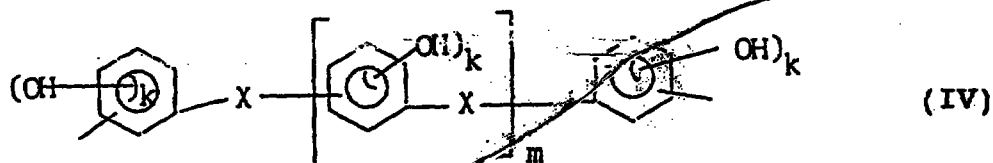
where

X is a single bond, O, CO, SO₂, an alkylene group or a fluorinated alkylene group having 1 to 6 carbon atoms, and

n is 0, 1 or 2.

Examples of the group X are C(CH₃)₂, C(CF₃)₂ and CH₂CCF₃; hexafluoropropylidene, carbonyl and ether groups are preferred.

The grouping B preferably consists of benzene or polyphenyl nuclei having up to six, in particular two, benzene rings and mixtures thereof. Particular preference is given to groupings B of the formula IV



where

X is a single bond, O, CO, SO₂, an alkylene group or a fluorinated alkylene group having 1 to 6 carbon

atoms,

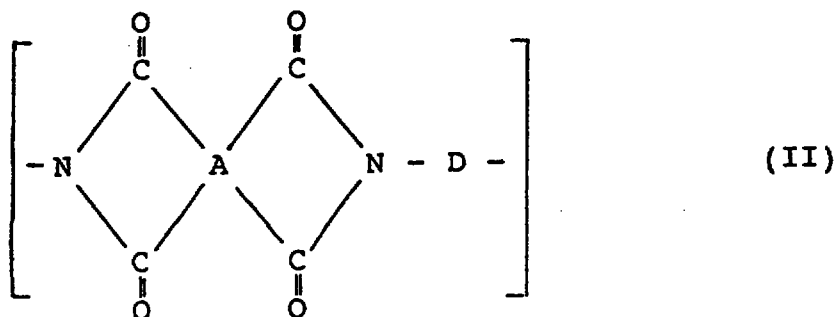
is from 0 to 4, and

is a number independently selected from 0 to 3 for each benzene ring,

the radical B containing in total at least one OH group.

X is particularly preferably a hexafluoropropylidene group.

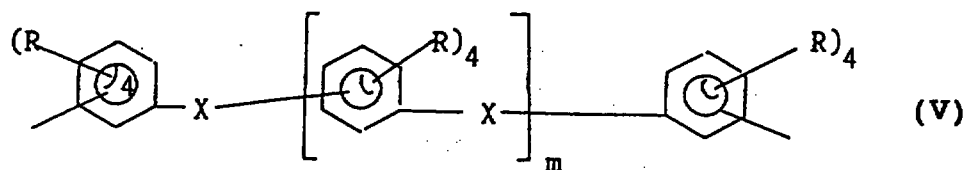
A portion of the aromatic, hydroxyl-substituted groupings may be replaced with aromatic groupings D containing no hydroxyl substituents to give a copolyimide containing units of the above-indicated formula I and units of the general formula II:



where D is a hydroxyl-devoid aromatic radical that has at least one aromatic six ring and A is as defined above. D consists of aromatic, divalent nuclei or mixtures thereof containing no hydroxyl substituents. The polyimide contains up to 80, preferably 50, in particular up to 30, mol% of units of the formula II, based on the sum total of units I and II.

In addition the copolyimides of the invention may be further modified by the addition of aliphatic and alicyclic groups ~~analogous to the polyimides herein~~. The aliphatic and/or alicyclic component may be hydroxyl-substituted when present as the diamino component. The amount of aliphatic and alicyclic groups should not exceed 50 mol%, preferably ~~not~~ in excess of 30 mol%, of the copolyimide.

The grouping D is preferably a divalent group conforming to the formula V



where

X is a single bond O, CO, SO₂, an alkylene group or a fluorinated alkylene group having 1 to 6 carbon atoms,

R is in each case independently selected from hydrogen, halogen, alkyl or alkoxy having 1 to 6 carbon atoms and acyl having 2 to 10 carbon atoms, and

m is from 0 to 4.

In the formula V m is preferably 0 and X is preferably a hexafluoropropylidene group.

Illustrative of the aromatic dianhydrides suitable for use in the preparation of the polyimides of the invention are pyromellitic dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 2,2',3,3'-biphenyltetracarboxylic dianhydride, 2,2-bis-(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, bis(3,4-dicarboxyphenyl) sulphone dianhydride, 3,4,9,10-perylenetetracarboxylic dianhydride, bis-(3,4-dicarboxyphenyl) ether dianhydride, 2,2-bis-(2,3-dicarboxyphenyl)propane dianhydride, 1,1-bis-(2,3-dicarboxyphenyl)ethane dianhydride, bis-(3,4-dicarboxyphenyl)methane dianhydride, bis-(2,3-dicarboxyphenyl) sulphone dianhydride and benzo-phenonetetracarboxylic dianhydride. The methods for preparing these aromatic dianhydrides are known, see for example US-A-3,310,573; 3,408,411; 3,553,282 and 4,030,948.

Examples of hydroxyl-substituted aromatic diamines of the formula NH₂-B-NH₂ are

3,3'-dihydroxybenzidine, 3,4'-diamino-3',4'-dihydroxybiphenyl, 3,3'-dihydroxy-4,4'-diaminodiphenyl oxide, 3,3'-dihydroxy-4,4'-diaminodiphenyl sulphone, 2,2-bis-(3-amino-4-hydroxyphenyl)propane, bis(3-hydroxy-4-aminophenyl)methane, 2,4-diaminophenol, 3,3'-dihydroxy-4,4'-diaminobenzophenone, 1,1-bis(3-hydroxy-4-aminophenyl)ethane, 1,3-bis(3-hydroxy-4-aminophenyl)propane, 2,2-bis(3-hydroxy-4-aminophenyl)propane and 2,2-bis-(3-amino-4-hydroxyphenyl)hexafluoropropane.

10 Their preparation is known; see for example J. Polymer Sci., vol. 20, 2381-2391 (1982).

A portion of the hydroxyl-substituted aromatic diamines may as mentioned earlier be replaced with a diamine of the formula $\text{NH}_2\text{-D-NH}_2$ wherein D is as previously defined.

15 Examples of aromatic diamines of the formula $\text{NH}_2\text{-D-NH}_2$ are m-phenylenediamine, p-phenylenediamine, 4,4'-diaminodiphenyl ether, 3,3'-diaminophenyl ether, 3,4'-diaminodiphenyl ether, 1,3-bis(aminophenoxy)benzene, 20 1,4-bis(aminophenoxy)benzene, benzidine, 3,3'-dimethoxybenzidine, 3,3'-dimethylbenzidine, 3,3'-diethylbenzidine, 3,3'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, 3,3'-diaminodiphenyl sulphone, 4,4'-diaminodiphenyl sulphone, 4,4'-diaminodiphenyl sulphide, 2,2'-bis(4-aminophenyl)perfluoropropane, α,α -bis(aminophenyl)-p-diisopropylbenzene, 1,3-bis(4-aminophenoxy)benzene, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, 2,2-bis(3-aminophenyl)-hexafluoropropane, m-xylylenediamine, p-xylylenediamine, 30 4,4'-bis(p-aminophenoxy)diphenyl sulphide, 4,4'-bis(3-aminophenoxy)diphenyl sulphide, 4,4'-bis(p-aminophenoxy)diphenyl sulphone, 4,4'-bis(3-aminophenyl) sulphone, 2,2-bis(4-aminophenoxyphenyl)propane and mixtures thereof.

35 Examples of aliphatic and alicyclic diamines suitable for preparing copolyimides are 1,2-bis(3-aminopropoxy)ethane, bis(4-aminocyclohexyl)methane, hexamethylenediamine, octamethylenediamine,

1,4-cyclohexanediamine, decamethylenediamine, dodecamethylenediamine, bis(3-aminopropyl) sulphide, 3-hydroxyhexamethylenediamine, 1,3-diamino-2-hydroxypropane, 2,6-diaminocyclohexanol.

5 Examples of aliphatic and alicyclic dianhydrides suitable for preparing copolyimides of the invention are ethylenetetracarboxylic dianhydride, 1,2,3,4-butanetetracarboxylic dianhydride, 1,2,3,4-cyclopentanetetracarboxylic dianhydride and 2,3,5,6-cyclohexanetetracarboxylic dianhydride.

10 Of the polyimides, particularly preferred ones are those that have been obtained from 2,2-bis(3-amino-4-hydroxyphenyl)perfluoropropane and 2,2-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride.

15 Further examples of preferred polyimides are those prepared from the same diamine and one of the following dianhydrides: bis(3,4-dicarboxyphenyl) ether dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhy-

20 dride. Preferred diamine comonomers are for example 2,2-bis(3-aminophenyl)hexafluoropropane and 2,2-bis-(4-aminophenyl)hexafluoropropane.

 It is also possible to use mixtures of the diamine and dianhydride monomers to produce copolyimides

25 having superior properties. Particularly preferred polyimides are those containing at least 50 mol%, in particular at least 70 mol%, of units of 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane.

 The polyimide can also be modified after poly-

30 merisation, for example by acylating a portion of the hydroxyl groups in the polymer with an acylating agent having up to 10 carbon atoms, e.g. acetic anhydride, propionic anhydride, benzoyl chloride or diketene.

 The polyimides of the invention are prepared by

35 known polymerisation techniques, typically by the high-temperature solution condensation method using p-toluene-sulphonic acid as catalyst (see for example EP-A-0 163 518).

The polyimides of this invention are useful in the preparation of positive-working photoresist mixtures. These resist mixtures contain a polyimide as heretofore described and a radiation- or light-sensitive compound.

5 The use of radiation-sensitive compounds, for example o-quinonediazides, is known, for example from "Light-Sensitive Systems" by J. Kosar, John Wiley & Sons, New York, 1965, chapter 7.4. The radiation-sensitive compounds used can be substituted naphthoquinonediazides
10 which are conventionally used in the art in positive resist formulations. Such radiation-sensitive compounds are described for example in US-A-2,797,213; 3,106,465; 3,148,983; 3,130,047; 3,201,329; 3,785,825 and 3,802,885. Useful ones include the condensation products of
15 1,2-naphthoquinone-2-diazide-5- or -4-sulphonyl chloride with phenols, e.g. hydroxybenzophenones.

In general, any radiation-sensitive compounds or composition may be used with the hydroxypolyimides of the invention provided that: 1) the compound or composition
20 has a developer solubility inhibiting effect on the polyimide and 2) the compound or composition upon exposure to actinic radiation is directly or indirectly converted into molecules possessing enhanced solubility, tackiness or volatility. Such radiation-sensitive compositions are disclosed in US-A-4,247,611 and 4,619,998.
25

Radiation-sensitive compositions such as those disclosed in the above-referenced patents comprise a radiation-sensitive compound which upon exposure to radiation generates an acid and a second compound containing at least one acid-cleavable group.
30

Examples of acid-cleavable compounds are:

- A. compounds containing at least one orthocarboxylic acid ester and/or carboxylic acid amide acetal group, which compounds also have a polymeric character and may contain the abovementioned groups as
35 connecting members in the main chain or as side groups; and

B. polymeric compounds with recurrent acetal and/or ketal groups in which preferably both α -carbon atoms of the alcohols required forming the groups are aliphatic.

5 Acid-cleavable compounds of type A are described in detail as components of radiation-sensitive mixtures in US-A-4,101,323 and 4,247,611, while compositions containing compounds of type B are the subject of US-A-4,189,323.

10 Suitable acid-cleavable compounds also include for example the aryl-alkyl acetals and amins disclosed in DE-C-23 06 248. Other compounds of this type are enolic ethers and acyliminocarbonates, as disclosed in EP-A-0 006 626 and 0 006 627.

15 A large number of known compounds and mixtures may be used as radiation-sensitive constituents forming or splitting off acids on irradiation, for example diazonium salts, phosphonium salts, sulphonium salts and iodonium salts or halogen compounds, quinonediazide-
20 sulphonyl chlorides and organometal/organohalogen combinations. Suitable diazonium salts are the compounds with a useful absorption range between 300 and 600 nm. Generally these diazonium, phosphonium, sulphonium and iodonium compounds are used in the form of salts soluble
25 in organic solvents, normally as the separation products with complex acids, for example hydrofluoboric acid, hexafluorophosphoric acid, hexafluoroantimonic acid or hexafluoroarsenic acid. Alternatively, derivatives of positive-working o-quinonediazides can be used. Of this
30 group of compounds, 1,2-naphthoquinonediazide-4-sulphonyl chloride is preferred, since on exposure it forms three acid functions which bring about a relatively high degree of intensification during splitting of the polyacetals and polyketals.

35 In principle, the halogen-containing radiation-sensitive compounds used as capable of forming a hydrohalic acid can be any organic halogen compound known as a free radical initiator, for example an organic halogen

compound which contains more than one halogen atom bonded to a carbon atom or to an aromatic ring. Examples of such compounds are disclosed in US-A-3,515,552; 3,536,489; 3,779,778 and 3,395,475. In addition, certain substituted
5 trichloromethylpyrones such as described in US-A-4,101,323 and the 2-aryl-4,6-bistrichloromethyl-s-triazines disclosed in US-A-4,189,323 may be used as acid generating components.

Examples of suitable acid forming compounds are
10 4-(di-n-propylamino)benzenediazonium tetrafluoroborate, 4-p-tolylmercapto-2,5-diethoxybenzenediazonium hexafluorophosphate, 4-p-tolylmercapto-2,5-diethoxybenzenediazonium tetrafluoroborate, diphenylamine-4-diazonium sulphate, 4-methyl-6-trichloromethyl-2-pyrone,
15 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,
20 1,4-bisdibromomethylbenzene, trisdibromomethyl-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)- and 2-(phenanthr-9-yl)-4,6-bistrichloromethyl-s-triazine.

25 Additives such as pigments, dyes, anti-striation agents, plasticisers, adhesion promoters, speed enhancers, solvents and nonionic surfactants may be added to the solution of polyimide, radiation-sensitive compound and solvent before the solution is coated onto a
30 substrate.

Examples of dyes which can be added to the photoresist compositions of the invention are Methyl Violet 2B (C.I.42 535), Crystal Violet (C.I.42 555), Malachite Green (C.I. 42 000), Victoria Blue B (C.I.
35 44 045) and Neutral Red (C.I. 50 040). These dyes are added in proportions of 1-10% by weight, based on the combined weight of polyimide and light-sensitive compound. The dye additives help provide increased

resolution by inhibiting back scattering of light off the substrate.

Anti-striation agents may be used up to a 5% by weight level, based on the combined weight of polyimide and radiation-sensitive compound.

Suitable adhesion promoters are for example β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, vinyltrichlorosilane and γ -aminopropyltriethoxysilane, which can be used in a proportion of up to 4% by weight, based on the combined weight of polyimide and radiation-sensitive compound.

Development accelerants that may be used include for example picric acid, nicotinic acid or nitrocinnamic acid at a weight level of up to 20% by weight, based on the combined weight of polyimide and radiation-sensitive compound. These accelerants tend to increase the solubility of the resist coating in both the exposed and the unexposed areas, and thus they are used in applications where speed of development is the overriding consideration even though some degree of contrast may be sacrificed; i.e. while the exposed areas of the resist coating will be dissolved more quickly by the developer, the development accelerants will equally cause a larger loss of resist coating from the unexposed areas.

Typical commercial solvents employed in the art may be used in preparing the resist compositions of this invention. The amount of solvent used in the preparation of the resist solution may range up to 95% by weight of the solution. The known polyimides have only limited solubility in N-methylpyrrolidone and dimethylacetamide, whereas the polyimides of the present invention have enhanced solubility in those solvents and additional solvents acceptable for commercial use. Suitable solvents are for example N-methylpyrrolidone, dimethylacetamide, propylene glycol monomethyl ether, methyl ethyl ketone, cyclohexanone, butyrolactone and mixtures thereof. The preferred solvents are N-methylpyrrolidone and propylene glycol methyl ether.

The resist solution can be applied to a substrate by any conventional method used in the resist art, for example by dipping, spraying or spincoating. If spincoating is employed, the solids content of the resist solution can for example be adjusted to a certain value in order to obtain a coating of the desired thickness for a given spincoating apparatus and spincoating time. Suitable substrates include for example silicon, aluminium, polymers, silicon dioxide, doped silicon dioxide, silicon nitride, tantalum, copper, polysilicon, ceramics and aluminium-copper alloys.

The resist compositions of the invention are particularly suitable for application to silicon wafers coated with thermally grown silicon dioxide, as are utilised in the production of microprocessors and other miniaturised integrated circuit components. It is similarly possible to use an aluminium/aluminium oxide substrate or else a substrate composed of various polymers, in particular of transparent polymers, for example polyesters.

Preferred developers for the radiation-sensitive compositions of this invention are aqueous solutions of inorganic alkaline compounds, for example aqueous solutions of sodium silicate, potassium silicate, sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium phosphate, sodium monohydrogenphosphate, ammonium phosphate, ammonium monohydrogenphosphate, sodium metasilicate, sodium bicarbonate, ammonia, etc., with the suitable concentration of these compounds being between 0.1 and 10% by weight, preferably between 0.5 and 5% by weight. Examples of such developers are described in US-A-3,110,596; 3,173,788 and 3,586,504.

An alkaline solution of this type can also contain certain organic solvents, such as alcohols (e.g. methanol, ethanol, benzyl alcohol, etc.), and a surfactant (e.g. sodium alkyl naphthalenesulphonate, sodium laurylsulphate, etc.), depending on the requirements.

After the solution of the resist composition has been applied to the substrate, the substrate is heated to about 80-105°C, for example to about 90°C, until substantially all the solvent has been expelled and only a thin coating of the photoresist mixture about 1 μ m in thickness remains behind on the substrate. The coated substrate can then be structured with actinic light in any desired pattern produced per use of suitable masks, negatives, stencils, etc.

The exposed resist-coated substrates are then immersed in a developer, which is preferably agitated, for example by blowing in nitrogen.

The substrates are allowed to remain in the developer until the entire or essentially the entire resist coating has been dissolved away from the exposed areas.

After removal of the coated wafers from the developer, a post-development heat treatment may be employed to increase the adhesion of the coating and its chemical resistance to etching solutions and other substances. The resist compositions of the invention have excellent adhesion to substrates such as silicon wafers, aluminium plates, glass, polyesters films, etc. No adhesion promoter is necessary for processing the resists.

After curing, the developed substrate may be treated with a buffered hydrofluoric acid or alkaline etching solution. The resist compositions of the invention are resistant to acid and alkaline etching solutions and provide effective protection for the unexposed (resist-coated) areas of the substrate. The developed and cured photoresist gives relief structures of excellent resolution and high thermal stability.

Although the above description relates to a wet-etching process, the relief patterns of the invention can be used not only in wet- but also in dry-etching processes. The resulting structures are particularly good insulating layers for microcircuitry applications, and as

5 masks for vapour deposition processes and ion implantation processes. The resists of the invention can similarly be used in the production of printing plates, lithographic proofing applications, lithographic transfer foils and other similar applications. The production of printing plates using positive-working light-sensitive mixtures is known for example from US-A-3,493,371.

10 The mixtures can also be used as normal protective coatings for many applications. For instance, owing to their high solubility the polyimides of the invention are particularly suitable for example for high temperature protective coatings per se as well as for resist applications. In a typical coating process, a coating mixture which contains about 5-30% by weight of the
15 polyimide of the invention in solution is applied to a substrate. The coating mixture may additionally contain antioxidants, UV stabilisers, adhesion promoters, dyes, pigments, flame retardants, fillers and other auxiliaries at up to 20% by weight. The solvent is driven off at a
20 temperature of in general 90-150°C with or without the use of reduced pressure to facilitate removal of the solvent. The polyimide-coated substrate can then be further heat treated to harden the coating.

25 In the examples which follow the processes for preparing and using the mixtures of the invention are more particularly described. In the examples the term dark film erosion rate has been abbreviated to erosion rate.

Example 1

30 This example describes the preparation of a hydroxypolyimide having recurring structural units of the formula I where A = 2,2-diphenylperfluoropropane-3',3",4',4"-tetrayl and B = 2,2-bis(4-hydroxyphenyl)-perfluoropropane-3',3"-diyl.

35 A 500 ml four necked flask equipped with a thermometer, a condenser, a water trap, a mechanical stirrer and a nitrogen inlet tube was charged with 7.32 g (0.02 mol) of 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoro-

propane (6F-aminophenol) under a nitrogen atmosphere together with 128 ml of monochlorobenzene (MCB) (80%) and 32 ml of N-methylpyrrolidone (NMP) (20%). The mixture was stirred until a clear solution was obtained, at which point 8.88 g (0.02 mol) of 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride were added. The contents of the flask were heated to 90°C, admixed with 0.04 g of paratoluenesulphonic acid (PTSA) and then heated to the reflux temperature (about 142°C). In the first hour about 100 ml of the water-chlorobenzene azeotrope were collected in the water trap. 100 ml of fresh chlorobenzene were then added to the flask and the contents were refluxed at 142-145°C for 10 hours.

100 ml of NMP were then added and the monochlorobenzene was distilled off at 160-165°C. The reaction mixture was cooled down and slowly precipitated in an ice-water-methanol mixture. The result was a white precipitate, which was thoroughly washed with hot water. The polymer was dried overnight at 125°C in a vacuum drying cabinet.

The polymer had an inherent viscosity of 0.50 dl/g in dimethylacetamide at 25°C and was soluble in common organic solvents such as N-methylpyrrolidone, dimethylacetamide, tetrahydrofuran, diethylene glycol monomethyl ether, propylene glycol monomethyl ether (PGME) and ethylene glycol monomethyl ether. The glass transition temperature (T_g) of the polymer as determined by differential thermoanalysis (DTA) was 306°C.

Example 2

This example describes the preparation of a hydroxypolyimide having recurring structural units of the formula I in which A is an oxydiphenyl-3,3',4,4'-tetrayl group and B has the same meaning as in Example 1.

A 500 ml four necked flask equipped with a thermometer, a condenser, a water trap, a mechanical stirrer and a nitrogen inlet tube was charged with 7.32 g (0.02 mol) of 6F-aminophenol under nitrogen together with 128 ml of monochlorobenzene (80%) and 32 ml of

N-methylpyrrolidone (20%). The mixture was stirred until a clear solution was obtained, at which point 6.2 g (0.02 mol) of bis(3,4-dicarboxyphenyl) ether dianhydride were added. The contents of the flask were heated to 90°C, admixed with 0.04 g of p-toluenesulphonic acid and then heated to the reflux temperature (about 142°C). In the first hour about 100 ml of water-chlorobenzene azeotrope were collected in the water trap. 100 ml of fresh chlorobenzene were then added to the flask and the contents were refluxed at 142-145°C for 10 hours.

100 ml of NMP were then added to the flask and excess monochlorobenzene was distilled off at 160-165°C. The reaction mixture was cooled down and slowly precipitated in an ice-water-methanol mixture. The result was a white precipitate, which was thoroughly washed with hot water. The polymer was dried overnight at 125°C in a vacuum drying cabinet.

The polymer had a viscosity of 0.50 dl/g in dimethylacetamide at 25°C and was soluble in common organic solvents such as N-methylpyrrolidone, dimethylacetamide, tetrahydrofuran, diethylene glycol monomethyl ether, propylene glycol monomethyl ether. The glass transition temperature (Tg) of the polymer was 251°C.

Example 3

This example describes the preparation of a hydroxypolyimide containing recurring structural units of the formula I in which A is a benzophenone-3,3',4,4'-tetrayl group and B has the same meaning as in Example 1.

A 500 ml four necked flask equipped with a thermometer, a condenser, a water trap, a mechanical stirrer and a nitrogen inlet tube was charged with 7.32 g (0.02 mol) of 6F-aminophenol under nitrogen together with 128 ml of monochlorobenzene (80%) and 32 ml of N-methylpyrrolidone (20%). The mixture was stirred until a clear solution was obtained, at which point 6.48 g (0.02 mol) of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were added. The contents of the flask were heated

to 90°C, admixed with 0.04 g of p-toluenesulphonic acid and then heated to the reflux temperature (about 142°C). In the first hour about 100 ml of the water-chlorobenzene azeotrope were collected in the water trap. 100 ml of fresh chlorobenzene were then added to the flask and the contents were refluxed for 10 hours.

100 ml of NMP were then added to the flask and excess monochlorobenzene was distilled off at 160-165°C. The reaction mixture was cooled down and slowly precipitated in an ice-water-methanol mixture. The result was a white precipitate, which was thoroughly washed with hot water. The polymer was dried overnight at 125°C in a vacuum drying cabinet.

The polymer had a viscosity of 0.51 dl/g in dimethylacetamide at 25°C and was soluble in common organic solvents such as N-methylpyrrolidone, dimethylacetamide, tetrahydrofuran, diethylene glycol monomethyl ether, propylene glycol monomethyl ether and ethylene glycol monomethyl ether.

20 Example 4

This example describes the preparation of copolyimides having recurring structural units of the formulae I and II wherein A has in both cases the same meaning as in Example 1, B likewise has the meaning indicated in Example 1, and D is a 2,2-diphenylperfluoropropane-4',4"-diyl group. The polymer contains 80 mol% of units of the formula I and 20 mol% of units of the formula II.

A 500 ml four-necked flask equipped with a thermometer, a condenser, a water trap, a mechanical stirrer and a nitrogen inlet tube was charged under nitrogen with 5.856 g (0.016 mol) of 6F-aminophenol and 1.336 g (0.004 mol) of 2,2-bis(4-aminophenyl)hexafluoropropane together with 128 ml of monochlorobenzene (MCB) (80%) and 32 ml of N-methylpyrrolidone (NMP) (20%). The mixture was stirred until a clear solution was obtained and then 8.88 g (0.01 mol) of the dianhydride specified in Example 1 were added. The contents of the flask were heated to 90°C, admixed with 0.04 g of p-toluenesulphonic

acid and then heated to the reflux temperature (about 142°C). In the first hour about 100 ml of water-chlorobenzene azeotrope were collected in the water trap. 100 ml of fresh chlorobenzene were then added to the flask and the contents were refluxed for 10 hours.

Then 100 ml of NMP were added to the flask and excess monochlorobenzene was distilled off at 160-165°C. The reaction mixture was cooled down and slowly added to an ice-water-methanol mixture. The result was a white precipitate, which was thoroughly washed with hot water. The polymer was dried overnight at 125°C in a vacuum drying cabinet.

The polymer had a viscosity of 0.65 dl/g in dimethylacetamide at 25°C and was soluble in common organic solvents.

Example 5

A photoresist solution was prepared by dissolving 10 parts by weight of the hydroxypolyimide of Example 1, 0.5 parts by weight of 2,3,4-trihydroxybenzophenone tris-1,2-naphthoquinone-2-diazide-5-sulphonic acid ester and 0.08 part by weight of red dye in 10 parts by weight of N-methylpyrrolidone and 10 parts by weight of propylene glycol monomethyl ether. The solution was filtered and then applied to an anodised aluminium plate by roller coating. Drying at 90°C for 30 minutes left a 2-3 μm thick resist layer. This layer was covered with a photo-mask having a line structure in such a way that the layer and photomask were in close contact. Then UV light was radiated thereon for 60 s by the use of a 200 W mercury vapour lamp. The intensity of the UV light at the surface of the resist layer was 5 mW/cm² at 365 nm. After the radiation, the coating was developed with a solution of 1.08% by weight of sodium metasilicate $\times 9 \text{ H}_2\text{O}$, 0.06% by weight of sodium dihydrogenphosphate, and 0.68% by weight of trisodium phosphate $\times 12 \text{ H}_2\text{O}$ in fully demineralised water. The developed plate was washed with water to obtain a fine, uniform relief pattern having a narrowest line width of 2 μm .

Example 6

A photoresist solution was prepared by dissolving 1 part by weight of the hydroxypolyimide of Example 2, 0.5 part by weight of the naphthoquinonediazide specified in Example 5 and 0.08 part by weight of red dye (Disperse Red 179) in 10 parts by weight of N-methylpyrrolidone and 10 parts by weight of propylene glycol monomethyl ether. The solution was filtered and then applied to an anodised aluminium plate by roller coating. The coated plate was dried at 90°C for 30 minutes to obtain a 2-3 μm thick resist layer. This layer was covered with a photomask. Then UV light was radiated thereon for 60 s by use of a 200 W mercury vapour lamp. The UV light intensity at the surface of the layer was 5 mW/cm^2 at 365 nm. Then the photoresist was developed with the developer specified in Example 5 and rinsed with water to obtain a relief structure having a narrowest line width of 2 μm .

Example 7

A photoresist solution was prepared by dissolving 10 parts by weight of the hydroxypolyimide of Example 3, 0.5 part by weight of the naphthoquinonediazide specified in Example 5 and 0.08 part by weight of red dye in 10 parts by weight of N-methylpyrrolidine and 10 parts by weight of propylene glycol monomethyl ether. The solution was filtered and then applied to an anodised aluminium plate by roller coating. Drying at 90°C for 30 minutes left a 2-3 μm thick resist layer. This layer was covered with a photomask. Then UV light was radiated thereon for 60 s by use of a 200 W mercury vapour lamp. The UV light intensity at the surface of the layer was 5 mW/cm^2 at 365 nm. After irradiation, the coating was developed with the developer indicated in Example 5. The developed plate was rinsed with water to obtain a fine, uniform relief pattern having a narrowest line width of 2 μm .

Example 8

A photoresist solution was prepared by dissolving 10 parts by weight of the hydroxycopolyimide of Example 4, 0.5 part by weight of the naphthoquinonediazide

specified in Example 5 and 0.08 part by weight of red dye in 10 parts by weight of N-methylpyrrolidone and 10 parts by weight of propylene glycol monomethyl ether. The solution was filtered and then applied to an anodised aluminium plate by roller coating. Drying at 90°C for 30 minutes left a 2-3 μm thick resist layer. This layer was covered with a photomask having a line structure. Then UV light was radiated thereon for 60 s by use of a 200 W mercury vapour lamp. The UV light intensity at the surface of the layer was 5 mW/cm² at 365 nm. After irradiation, the coating was developed with a solution of 2.7 % by weight of sodium metasilicate $\times$ 9 H₂O, 0.15% by weight of sodium dihydrogenphosphate, and 1.7 % by weight of trisodium phosphate $\times$ 12 H₂O in fully demineralised water. The developed plate was rinsed with water to obtain a fine, uniform relief pattern having a narrowest line width of 2 μm .

The following examples were carried out to particularly characterise the superiority of the positive photoresist mixtures obtained with the hydroxypolyimides of the invention compared with photoresists based on polyamidecarboxylic acids as polyimide precursors.

Photoresist mixtures were prepared from the polyimides of the invention which have been prepared substantially in accordance with Examples 1-4.

The photosensitivity of each resist mixture was evaluated by the general procedure described hereinafter. The drying time, the spincoating speed and other experimental conditions and results for each experiment are reported below.

The photoresist solution was spincoated onto silicon wafers at a constant, predetermined spin speed between 500 and 1500 revolutions per minute (rpm). The solvent was then driven off by drying for 30-45 minutes. The thicknesses of the resist layers were measured with a Rudolf film thickness monitor. Photosensitivity was measured by generating a contrast curve as described in C.G., Willson: "Introduction to Microlithography",

chapter 3, 105, American Chemical Society, Washington, (1983). The layer thickness after developing for 1 minute was plotted against the logarithm (ln) of the UV exposure dose. The layer thickness was determined by laser interference measurements. The resist was then developed at 25 $\pm$ 5°C using an aqueous alkaline developer. Extrapolation of the plot to the total film thickness loss gives the photosensitivity (mJ/cm²).

These experiments were carried out using the following radiation-sensitive compounds, which are identified by the following abbreviations:

- a) Z-2000 = a trihydroxybenzophenone 1,2-naphthoquinone-2-diazide-5-sulphonic acid ester mixture
- b) TOOL = 1,2-naphthoquinone-2-diazide-5-sulphonic acid tris ester of trihydroxyoctanophenone

Example 9

A photoresist solution was prepared by dissolving 13 parts by weight of the polyimide of Example 1 and 13 parts by weight of Z-2000 in 74 parts by weight of a solvent mixture consisting of equal parts by weight of propylene glycol monomethyl ether and N-methylpyrrolidone. This solution was spincoated onto the wafer, dried and exposed to the light source specified in Example 5.

The developer consisted of a solution of

0.8 % by weight of sodium metasilicate $\times$ 9 H₂O,
0.04% by weight of sodium dihydrogenphosphate, and
0.5 % by weight of trisodium phosphate $\times$ 12 H₂O

in fully demineralised water. The following results were obtained:

photosensitivity:	97 mJ/cm ²
erosion rate:	15 nm/min
contrast:	1.5

Example 10

A photoresist solution was prepared by dissolving 13 parts by weight of the polyimide of Example 2 and 13 parts by weight of Z-2000 in 74 parts by weight of the solvent mixture specified in Example 9. This solution was

spincoated onto a wafer, dried and exposed to the light source specified in Example 5. The developer consisted of a solution of

5 0.6 % by weight of sodium metasilicate $\times 9 \text{ H}_2\text{O}$,
 0.03% by weight of sodium dihydrogenphosphate, and
 0.4 % by weight of trisodium phosphate $\times 12 \text{ H}_2\text{O}$
in fully demineralised water. The following results were obtained:

10 photosensitivity: 82 mJ/cm²
 erosion rate: 20 nm/min
 contrast: 1.3

Example 11

15 A photoresist solution was prepared by dissolving
 13 parts by weight of the polyimide of Example 3 and 13
 parts by weight of Z-2000 in 74 parts by weight of the
 solvent mixture specified in Example 9. This solution was
 spincoated onto the wafer, dried and exposed to the light
 source specified in Example 5. The developer consisted of
 a solution of

20 0.5 % by weight of sodium metasilicate $\times 9 \text{ H}_2\text{O}$,
 0.03% by weight of sodium dihydrogenphosphate, and
 0.3 % by weight of trisodium phosphate $\times 12 \text{ H}_2\text{O}$
in fully demineralised water. The following results were obtained:

25 photosensitivity: 96 mJ/cm²
 erosion rate: 22 nm/min
 contrast: 1.42

Example 12

30 A photoresist solution was prepared by dissolving
 13 parts by weight of the copolyimide of Example 4 and 13
 parts by weight of Z-2000 in 74 parts by weight of the
 solvent mixture specified in Example 9. This solution was
 spincoated onto the wafer, dried and exposed to the light
 source specified in Example 5. The developer consisted of
35 a solution of

 1.8% by weight of sodium metasilicate $\times 9 \text{ H}_2\text{O}$,
 0.1% by weight of sodium dihydrogenphosphate, and
 1.1% by weight of trisodium phosphate $\times 12 \text{ H}_2\text{O}$

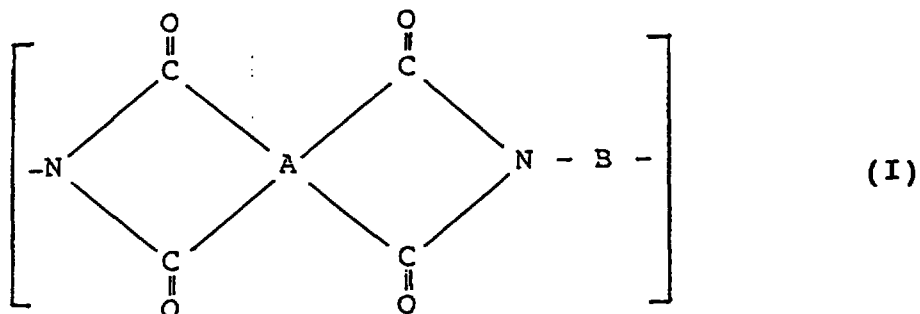
in fully demineralised water. The following results were obtained:

	photosensitivity:	242 mJ/cm ²
	erosion rate:	16 nm/min
5	contrast:	1.6



Claims

1. Polyimide having recurring units of the general formula I



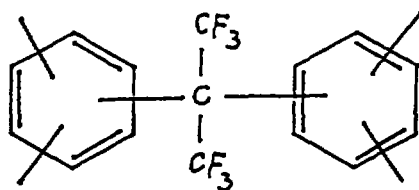
5 where

A is the radical of a compound having at least one aromatic six ring, each of the four carbonyl groups being attached to a different aromatic carbon atom of A and each pair of carbonyl groups being situated on adjacent carbon atoms, and

10

B is the radical of a compound having at least one aromatic six ring and at least one hydroxyl group, with the proviso that either the radical A conforms to the formula IIIa

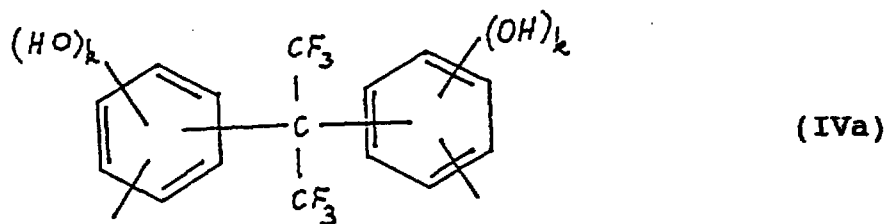
15



(IIIa)

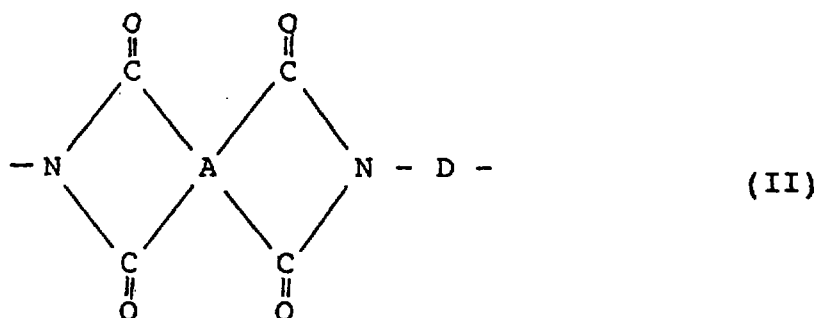


or the radical B to the formula IVa



where k is an integer from 0 to 3, or that the radical A conforms to the formula IIIa and the radical B to the formula IVa.

2. Polyimide according to Claim 1, characterised in that in addition to units of the general formula I it contains up to 80 mol% of units of the general formula II

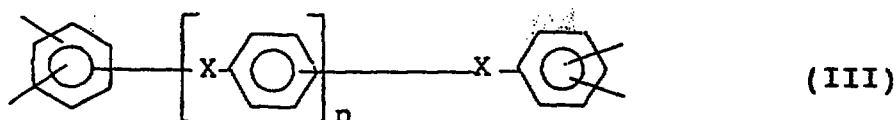


based on the sum total of units I and II, wherein D is a hydroxyl-devoid aromatic radical having at least one aromatic six ring and A is as defined in Claim 1.

3. Polyimide according to Claim 1, characterised in that A contains at least two aromatic six rings.

4. Polyimide according to Claim 1, characterised in that B contains at least two aromatic six rings.

5. Polyimide according to Claim 1, characterised in that A is a radical of the formula III

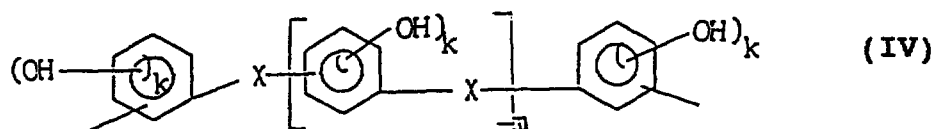


where

X is a single bond, O, CO, SO₂, an alkylene group or a fluorinated alkylene group having 1 to 6 carbon atoms, and

n is 0, 1 or 2.

6. Polyimide according to Claim 1, characterised in that B is a radical of the formula IV



10 where

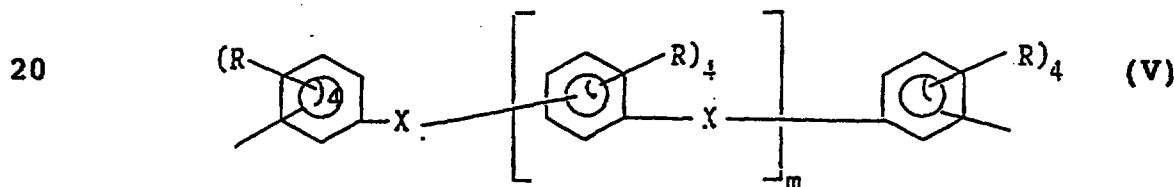
X is a single bond, O, CO, SO₂, an alkylene group or a fluorinated alkylene group having 1 to 6 carbon atoms,

m is from 0 to 4, and

15 k is a number independently selected from 0 to 3 for each benzene ring,

the radical B containing in total at least one OH group.

7. Polyimide according to Claim 2, characterised in that D is a radical of the formula V



where

X is a single bond O, CO, SO₂, an alkylene group or a fluorinated alkylene group having 1 to 6 carbon atoms,

25 R is in each case independently selected from hydrogen, halogen, alkyl or alkoxy having 1 to 6 carbon



atoms and acyl having 2 to 10 carbon atoms, and
m is from 0 to 4.

8. Photoresist mixture containing as essential constituents a light-sensitive compound and a polyimide,
5 characterised in that the polyimide is a compound according to any one of Claims 1 to 7.