

Description

The invention relates to polyamides having hexafluoroisopropylidene groups (groups of formula $\text{CF}_3\text{-C}(\text{CF}_3)_2$), to positive-working light-sensitive, highly temperature-resistant mixtures containing these polyamides and essentially consisting of an o-quinone-diazide and the polyamide having hexafluoroisopropylidene groups, as a binder.

Positive-working light-sensitive mixtures and their use have been described in US-A 3,666,473, 4,115,128 and 4,173,470. The binders used in these mixtures are in general alkali-soluble phenol/formaldehyde novolak resins in conjunction with light-sensitive or radiation-sensitive o-quinone or naphthoquinone-diazide compounds.

Conventional positive-working light-sensitive, novolak-based mixtures show only a limited dimensional stability under the action of elevated temperatures and are therefore not really suitable for modern high-temperature processes and applications. Heat-resistant negative-working photoresists are known and have been described, for example in US-A 3,957,512, 4,045,223 and 4,088,489 and in DE-A 3,411,659 (= US-A 4,622,285). Heat-resistant positive-working photoresists are also known, for example from US-A 4,093,461, 4,339,521 and 4,395,482. The advantages which positive-working resists show over negative-working resists include, inter alia, a higher image resolution capacity and a longer exposure stability in the presence of oxygen.

The following properties are important for the commercial utilisation of a photoresist: solubility of the resist in the particular solvent used, light sensitivity, development contrast, image resolution, adhesion of the resist to the carrier, dimensional stability at elevated temperatures and peel resistance.

Good light sensitivity is important for a photo-resist, especially if it is used for applications where a plurality of exposures are required, for example in producing multiple images by a repeat process, or in cases where light of attenuated intensity is used, for example in the projection illumination technique where the light passes through a number of lens systems and monochromatic filters. An increased light sensitivity is therefore very particularly important for a resist mixture which is used in processes where multiple exposures have to be carried out in order to produce a mask or a series of wiring diagrams on a carrier. Precise monitoring of the light sensitivity is of extreme importance for the production of relief images of high resolution in microelectronics, since the processing conditions might be restricted by unduly high light sensitivity.

The resolution of the resist is understood as the capability of a resist system to reproduce the smallest pairs of lines arranged at equal mutual distances and the respective interspaces of a mask used for the exposure, with a high degree of edge steepness of the image in the fully developed exposed interspaces. For many technical applications, especially for the production of semiconductor components in microelectronics, a photoresist must have a high degree of resolution if it is to reproduce very small line widths and interspace widths (of the order of magnitude of 1 μm).

The capability of a resist of reproducing very small dimensions of the order of magnitude of 1 μm and less is of very great importance in the production of LSI circuits on silicon chips and similar components. The wiring density on such a chip can be increased only by increasing the resolution capacity of the resist, if a photolithographic process is used.

In the past, various attempts have already been made to obtain high temperature-resistant photo-resists which have the desired properties described. For example, US-A 4,093,461 has disclosed a heat-resistant

positive-working photoresist which contains an o-quinone-
or o-naphthoquinone-diazide as the light-sensitive
compound and the polycondensation product of an aromatic
dianhydride and an aromatic diamine as the binder. The
5 properties of this resist are described in US-A 4,395,482
in column 1, lines 46 to 64. It is pointed out there
that the positive-working photoresist mixture described
in US-A 4,093,461 has only a limited storage stability
and an inadequate resistance to caustic alkalis and that
10 the solubility differences between the exposed and
unexposed resist areas are relatively small.

In addition, positive-working photoresist
mixtures are described in US-A 4,395,482 and in US-A
4,339,521, which contain oligomeric and/or polymeric
15 polyoxazole precursors in the form of polycondensation
products of aromatic and/or heterocyclic dihydroxydiamino
compounds with dicarboxylic acid chlorides or esters. In
detail, a poly-(benzidine-isophthalamide) is mentioned in
the cited specifications. The said positive-working
20 photoresist mixtures are said to have good storage stability,
heat resistance, processability and suitability for
use in microelectronics, i.e. for producing finely
structured images. They also have some disadvantages,
however, such as low solubility in the conventional
25 solvents and an unduly low light sensitivity.

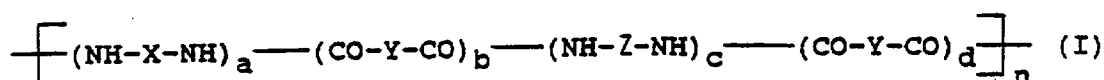
In addition, the benzidine described in Example
1 of US-A 4,395,482 is carcinogenic and difficult to
prepare. Moreover, it was found that the poly-(benzidine-
isophthalamide) according to US-A 4,395,482 arises as a
30 gel during its preparation and must be filtered off from
the reaction solvent before it is isolated. It is
regarded as a further disadvantage that even the light-
sensitive mixture which contains the poly-(benzidine-
isophthalamide) gels on prolonged standing and therefore
35 cannot have the optimum transparency.

High temperature-resistant polyamides having
hexafluoroisopropylidene groups in the main polymer chain
have also been disclosed in US-A 3,328,352. However, the
hexafluoroisopropylidene groups are in this case linked

to the carboxamido groups via para-phenylene bridges. These fluorine-containing, aromatic polycarboxamides are, however, used for fibres and films.

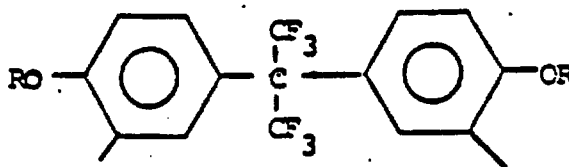
It was therefore the object to propose a polyamide for a high temperature-resistant, positive-working mixture of high light sensitivity, that is readily soluble in organic solvents, adheres well to the carrier material, allows high image resolution and can be stored for a long period in both the dry and liquid forms. Moreover, the light-sensitive mixture according to the invention should show the advantages of higher transparency and lower toxicity.

The object is achieved by providing a polyamide which is suitable as a binder for positive-working light-sensitive mixtures and is characterised in that it is of the general formula I



in which

X is a divalent group of the formula



in which the R radicals can be identical or different and are hydrogen or an optionally substituted aliphatic or aromatic radical having up to 9 carbon atoms,

Y and Z are identical or different and are an optionally substituted aliphatic, aromatic or cycloaliphatic radical having up to 60 carbon atoms, or mixtures thereof,

a represents a mole fraction of 0.10 to 0.50,
 b represents a mole fraction of 0.25 to 0.50,
 c represents a mole fraction of 0.0 to 0.40 and
 d represents a mole fraction of 0.0 to 0.25, each relative to the total molecular weight of X + Y

+ Z, with $a+b+c+d=1$, and
n is an integer from 2 to 500.

At least 40 mol % of the R radicals and possibly at least 60 mol % consist of hydrogen.

5 The polyamide is prepared by polycondensation of,
for example, hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-
propane with a dibasic acid chloride or mixtures of
dibasic acid chlorides. Some of the hexafluoro-2,2-bis-
10 (3-amino-4-hydroxyphenyl)-propane can be replaced by
another diamino comonomer, which may contain fewer
hydroxyl groups, in order to reduce the solubility of the
polymer in the aqueous-alkaline developer and to increase
the solubility of the polymer in solvents. Another
possibility of reducing the solubility of the polyamide
15 in the developer or of increasing its solvent solubility
is to neutralise the solubilisation effect, which is
caused by the hydroxyl groups in the polymer already
prepared, by converting the hydroxyl groups into less
developer-soluble groups, for example by acylating a part
20 of the hydroxyl groups of the polymer already formed. The
light sensitivity of the photoresist can therefore be
regulated by the use of comonomers free of hydroxyl
groups or by neutralisation of the hydroxyl groups after
the polycondensation.

25 The invention also relates to a positive-working
light-sensitive and high temperature-resistant mixture,
characterised in that the mixture contains the polyamide
according to the invention, described above, as the
binder and an o-quinone- and/or o-naphthaquinone-diazide
30 as the light-sensitive compound.

 It has been found, surprisingly, that the
solubility of the polymer according to the invention in
solvents and the light sensitivity of the light-sensitive
mixture according to the invention can be regulated by
35 using, in the preparation of the polyamide, a mixture of
dibasic acid chlorides and/or a mixture of hexafluoro-
2,2-bis-(3-amino-4-hydroxyphenyl)-propane and a further
diamine. Dibasic acid chlorides particularly suitable for
these purposes are isophthaloyl chloride and hexafluoro-

2,2-bis-(4-chlorocarbonylphenyl)-propane. The polycondensation of isophthaloyl chloride with hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane surprisingly produces a polyamide which gives a high light-sensitive resist when used in a positive-working light-sensitive mixture. Preferably, the isophthaloyl chloride is used as a mixture with a further dibasic acid chloride and polycondensed together with hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane.

The mixtures of dibasic acids [sic] here preferably contain 30 to 70 mol % of isophthaloyl chloride and 70 to 30 mol % of terephthaloyl chloride or hexafluoro-2,2-bis-(4-chlorocarbonylphenyl)-propane. The proportion of isophthaloyl chloride is preferably about 50 mol %. The mol % data always relate to the total content of the mixture of dibasic acid chloride.

The light sensitivity of the photoresists can be regulated, for example, in the range from 10 to 300 mJ/cm². This is also accomplished by a corresponding composition of the polyamide. Surprisingly, it has been found that the hexafluoroisopropylidene group leads to an increased light sensitivity and solvent solubility of the polymer, if it functions as the linking member in the diamine component of the polyamide, while it leads to a lower light sensitivity and increased solvent solubility if it is used in the dibasic acid chloride.

A material coated with the light-sensitive mixture according to the invention and exposed can be developed in aqueous-alkaline photoresist developers to give finely structured relief images which are suitable for use in fields of microelectronics and in the printing trade, and the light sensitivity of the photoresist can be adjusted to the particular requirements. The photoresist is distinguished by good heat resistance up to temperatures of 250 to 350°C, increased light sensitivity, higher solubility in conventional solvents for coating solutions and an above-average adhesion capacity.

The present invention also relates to a process for further increasing the heat resistance of the finely

structured images produced by thermal hardening of the developed photoresist, during which the polyamide is converted to a polybenzoxazole which is resistant to temperatures up to 550°C.

Owing to their excellent solubility in conventional solvents and to their good adhesion properties and heat resistance, the polyamides according to the invention are also outstandingly suitable for producing heat-resistant protective coatings.

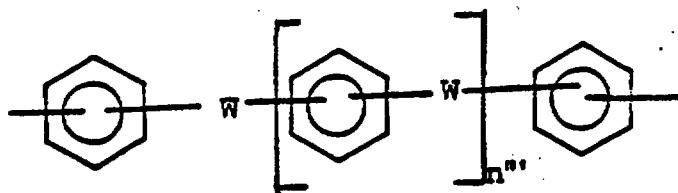
Particularly preferred polyamides of the formula I are those in which

a represents a mole fraction of 0.25 to 0.5,

R is hydrogen, methyl, ethyl or phenyl,

n is an integer from 20 to 300, especially from 5 to 200,

Y and Z can be identical or different and are methylene, difluoromethylene, polydifluoromethylene having 2 to 12 carbon atoms, an optionally substituted polymethylene having 2 to 12 carbon atoms, cyclohexylene, cyclohexenylene, piperazinylene, arylene, biarylene, naphthylene or a polyarylene according to formula II

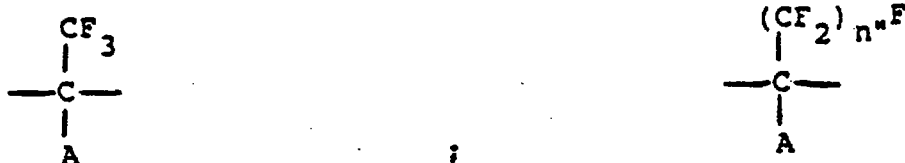
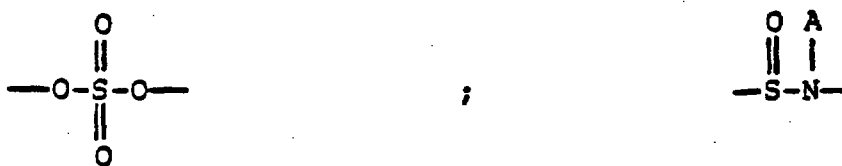
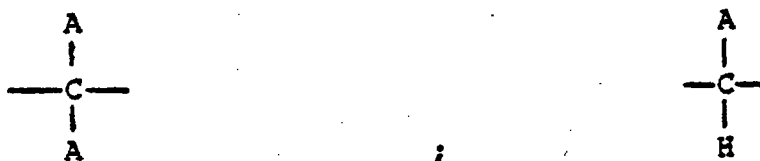


(II)

wherein

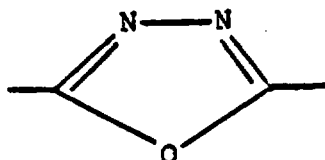
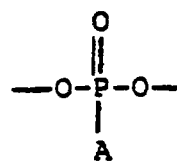
W the group forming the linking member, can in each case be one of the following groups: a single C-C bond; a methylene group; a polymethylene group having 2 to 12 carbon atoms; a difluoromethylene group; a polydifluoromethylene group having 2 to 12 carbon atoms, a hexafluoroisopropylidene group; an isopropylidene group; an oxy group or thio group; a sulphinyl group; a sulphonyl group;

a sulphonyldioxy group; a sulphonamido group; a carbonyl group or one of the following groups:

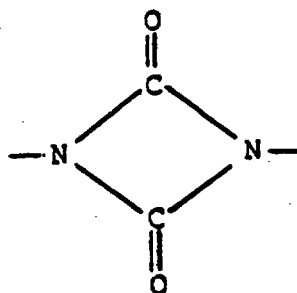
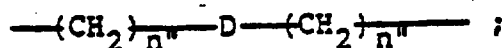
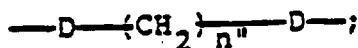




;



;



a cyclohexylene group; a cyclohexenylene group; a naphthylene group, or mixtures thereof.

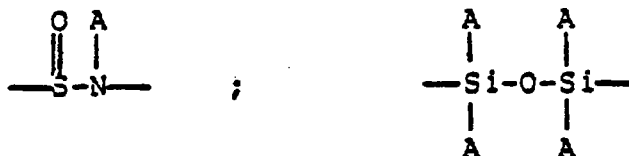
A can in each case be a substituted or unsubstituted alkyl group having 1 to 8 carbon atoms; a substituted or unsubstituted phenyl group or a substituted or unsubstituted naphthyl group.

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D can in each case be one of the following groups: an oxy group; a thio group; a carbonyl group; an oxycarbonyl group; a sulphonamido group; a sulphinyl group; a sulphonyl group; a sulphonyl-dioxy group; a benzene-dicarbonyl group; or one

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of the following groups:

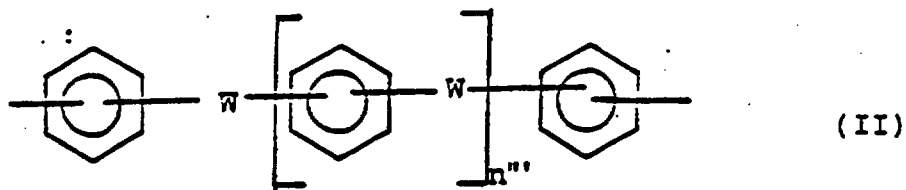


n' is an integer from 1 to 25 and

n'' is an integer from 1 to 12.

"Aromatic" and "cycloaliphatic" also represent in the present case aromatic and heterocyclic compounds in which one or more of the carbon atoms are replaced by oxygen, sulphur or nitrogen atoms.

The description "polyarylene" defines a divalent group of the general formula II



in which the "W" in each case represents one of the linking member groups described above.

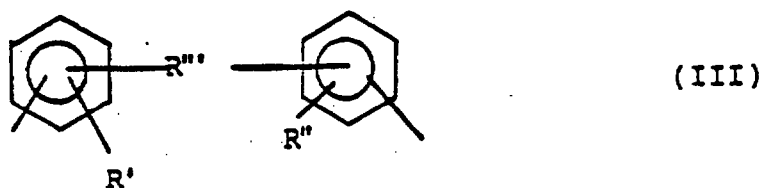
n'' designates one of the numbers 0, 1, 2 or 3, but it is to be noted that W is not a C-C bond if n'' = 0.

The hydrogen atoms of the divalent groups of type Y can be substituted by chlorine, bromine, fluorine and alkyl groups having 1 to 6 carbon atoms, perfluoroalkyl groups having 1 to 6 carbon atoms, substituted or unsubstituted aryl groups having 6 to 12 carbon atoms, alkyl- or aryl-carboxylic acid esters having 2 to 9 carbon atoms, alkoxy groups having 1 to 6 carbon atoms, aryloxy groups having 6 to 10 carbon atoms, acylamino groups having 1 to 6 carbon atoms, substituted or unsubstituted alkylaryl groups having 7 to 12 carbon atoms and substituted or unsubstituted arylalkyl groups

having 7 to 12 carbon atoms.

The hydrogen atoms of the divalent groups of type Z can also be replaced. Suitable examples thereof are hydroxyl, chlorine, bromine, fluorine and alkyl groups having 1 to 6 carbon atoms, perfluoroalkyl groups having 1 to 6 carbon atoms, substituted or unsubstituted aryl groups having 6 to 12 carbon atoms, alkyl- or aryl-carboxylic acid esters having 2 to 9 carbon atoms, alkoxy groups having 1 to 6 carbon atoms, aryloxy groups having 6 to 10 carbon atoms, acylamino groups having 1 to 6 carbon atoms, substituted or unsubstituted alkylaryl groups having 7 to 12 carbon atoms and substituted or unsubstituted arylalkyl groups having 7 to 12 carbon atoms.

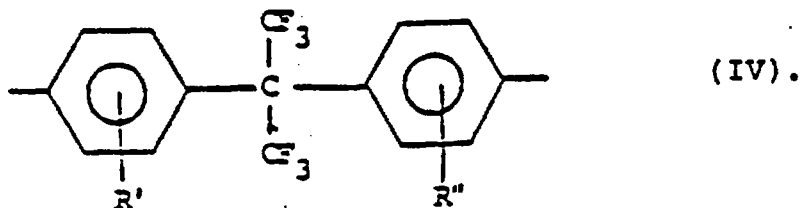
At least 70 mol % of the groups of type Z are preferably to be assigned to the aromatic divalent groups, especially the groups of the formula III



in which R' and R'' independently of one another can each be a hydrogen atom, a hydroxyl group, a lower alkyl group having 1 to 6 carbon atoms, a lower alkoxy group having 1 to 6 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, a chlorine, fluorine or nitro group or an aromatic or aliphatic carboxylic acid ester having up to 10 carbon atoms, but it is to be noted that R' and R'' must not simultaneously be hydroxyl groups if R''' is a hexafluoroisopropylidene group, and in which R''' is in each case a C-C bond, a methylene group, a polymethylene group having 2 to 16 carbon atoms, an isopropylidene group, a difluoromethylene group, a polydifluoromethylene group having 2 to 12 carbon atoms, a sulphonyl group, a sulphinyl group, a sulphur atom, an oxygen atom, a carbonyl or oxycarbonyl group, a hexafluoroisopropylidene group, a benzenecarbonyl group or a benzenedioxycarbonyl

group.

With particular preference, Z is of the formula
IV



5 Preferably, at least 70 mol % of each Y and Z consist of aromatic divalent groups or mixtures thereof.

In particular, Y and/or Z are a phenylene group, a hexafluoro-2,2-bis-(phenyl)-propane group or a mixture of these groups. With particular preference, Y and/or Z are a mixture of m-phenylene groups, p-phenylene groups and hexafluoro-2,2-bis-(p-phenyl)-propane groups, the
10 proportion of m-phenylene groups being 20 to 100 mol % preferably 30 to 70 mol % and especially 40 to 60 mol %. The following mixtures are used with particular preference as a divalent group of type Y:

- 15 1. an equimolar mixture of m-phenylene and p-phenylene;
2. an equimolar mixture of m-phenylene and hexafluoro-2,2-bis-(phenyl)-propane;
3. a mixture of 50 mol % of m-phenylene, 25 mol % of p-phenylene and 25 mol % of hexafluoro-2,2-bis-(p-phenyl)-propane;
- 20 4. an equimolar mixture of m-phenylene, p-phenylene and hexafluoro-2,2-bis-(p-phenyl)-propane.

The mol % data each relate to the total mole fraction of the groups of type Y in the polymer.

25 Since the polycondensation reaction of the polyamides according to the invention is governed by statistical aspects, the general formula (I) of course only represents the schematic average molecular structure of the polyamides according to the invention, so that the
30 divalent group of type Z can neither be a methylene group nor a difluoromethylene group.

The polyamides according to the invention are prepared by condensation of equimolar quantities of hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane and a chloride of a dibasic acid, preferably a mixture of corresponding acid chlorides. If desired, up to 80 mol %, preferably up to 50 mol % and especially up to 30 mol % of the hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane monomer can be replaced by a further diamino comonomer which may contain fewer hydroxyl groups. The light sensitivity of the positive-working light-sensitive mixtures can be regulated in this way. Examples of comonomers suitable for this purpose are m-phenylenediamine, p-phenylenediamine, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 1,3-bis-(aminophenoxy)-benzene (m-APB), 1,4-bis-(aminophenoxy)-benzene (p-APB), benzidine, 3,3'-dimethoxybenzidine, 3,3'-dimethylbenzidine, 3,3'-dihydroxybenzidine, 3,3'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, 3,3'-diaminodiphenyl sulphone, 4,4'-diaminodiphenyl sulphone, 4,4'-diaminodiphenyl sulphide, 3,3'-dihydroxy-4,4'-diaminodiphenyl sulphone, bis-(3-hydroxy-4-aminophenyl)-methane, 3,3'-dihydroxy-4,4'-diaminobenzophenone, α,α -bis-(aminophenyl)-p-diisopropylbenzene, 1,3-bis[4-(4-aminophenoxy)- α,α -bistrifluoromethyl]-benzene, 2,2-bis[4-(4-aminophenoxy)-phenyl]-hexafluoropropane, Hexafluoro-2,2-bis-(3-amino-4-methylhexafluoro-2,2-bis-(4-aminophenyl)-propane [sic], hexafluoro-2,2-bis-(3-aminophenyl)-propane, 1,2-bis-(3-aminopropoxy)-ethane, m-xylylenediamine, p-xylylenediamine, bis-(4-aminocyclohexyl)-methane, hexamethylenediamine, octamethylenediamine, decamethylenediamine, dodecamethylenediamine, 1,4-cyclohexanediamine, bis-(3-aminopropyl) sulphide, N-methyl-bis-(3-aminopropyl)-amine, 4,4'-bis-(p-aminophenoxy)-diphenyl sulphide, 4,4'-bis-(3''-aminophenoxy)-diphenyl sulphide, 4,4'-(3''-aminophenoxy)-(4'-aminophenoxy)-diphenyl sulphide, 4,4'-(3''-aminophenoxy)-diphenyl sulphone, 4,4'-bis-(3''-amino)-phenyl sulphone, 2,2-bis-[4'-p-(aminophenoxy)phenyl]-propane,

2,2-bis-[3'-p-aminophenoxy)-phenyl]-propane, 1,1-bis-[4'-(p-aminophenoxy)-phenyl]-ethylbenzene and mixtures of two or more of the said compounds.

5 It is also possible to modify the polyamide after it has been polycondensed, for example by acylation of some of its hydroxyl groups, the acylating agent used being an aliphatic or aromatic carboxylic acid derivative having up to 10 carbon atoms, such as, for example, acetic anhydride, propionic anhydride, benzoic acid
10 chloride or a diketene.

The preparation of the diamino compounds and of the chlorides of dibasic acids, which can be used as monomers in the preparation of the polyamides according to the invention, is carried out by known processes, which are described, for example, in "Synthesis of
15 Polymer Intermediates Containing the Hexafluorisopropylidene Group", by K.S. Lau, A.L. Landis, W.J. Kelleghan and C.D. Beard, in J. Polym. Sci., Vol. 20, pages 2381-2391 (1982).

20 The preparation of the polyamides according to the invention is carried out by known polymerisation processes, which are described, for example, in "Preparation of Fully Aromatic Polybenzoxazoles" by T. Kubota and R. Nakanishiu, in Polymer Letters, Vol. 2,
25 pages 655 - 659 (1964), wherein a typical process for condensing a diamine with an acid chloride is presented.

The preparation of the polyamides according to the invention starts with hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane or an analogously reacting
30 derivative, for example hexafluoro-2,2-bis-(3-amino-4-methoxyphenyl)-propane in which the hydroxyl group has been replaced by an alkoxy group or an aryloxy group having up to 10 carbon atoms, for example by ethoxy, propoxy, butoxy or phenoxy group. The proportion of this
35 diamine in the total diamine constituents of the polymer is about 20 to 100 mol %, especially 70 to 100 mol % and preferably about 50 mol %.

The acid chlorides typically used for the preparation of the polyamides according to the invention

include the acid chlorides of isophthalic acid, of terephthalic acid, of 4,4'-hexafluoroisopropylidenedibenzoic acid, of 1,4-cyclohexanedicarboxylic acid, of pentanedicarboxylic acid, of hexanedicarboxylic acid, of phthalic acid, of 2,4-furandicarboxylic acid, of 1,4-phenylene-diethanecarboxylic acid, of 4,4'-biphenyldicarboxylic acid, of 1,1-bis-(4-carboxyphenyl)-1-phenyl-2,2,2-trifluoroethane, of 4,4'-dicarboxydiphenyl ether, of bis-(4-carboxyphenyl)-methylphosphane oxide, of 4,4'-dicarboxytetraphenylsilane, of bis-(4-carboxyphenyl) sulphone, of 5-tert.butylisophthalic acid, of 5-bromo-isophthalic acid, of 5-fluoro-isophthalic acid, of 5-chloro-isophthalic acid, of 2,2-bis(p-carboxyphenyl)-propane, of 4,4'-(p-phenylenedioxy)-dibenzoic acid, of 2,6-naphthalenedicarboxylic acid and mixtures of these compounds.

The polyamides according to the invention are used in positive-working light-sensitive mixtures. The mixtures essentially contain one of the polyamides according to the invention and a light-sensitive compound. These components are, if appropriate, dissolved in a suitable solvent and applied to the particular desired carrier material. The preparation of the photoresists is known and is carried out by one of the usual processes.

In this connection, the use of o-quinone-diazides is known to those skilled in the art, as described in "Light Sensitive Systems" by J. Kosar, John Wiley & Sons, New York, 1965, Chapter 7.4. These light-sensitive compounds belong to the group of substituted light-sensitive naphthoquinone diazides, such as are conventionally used in positive-working light-sensitive mixtures. Such compounds are known, for example, from US-A 2,797,213, US-A 3,106,465, US-A 3,148,983, US-A 3,130,047, US-A 3,201,329, US-A 3,785,825 and US-A 3,802,885. Suitable light-sensitive compounds are, for example, also 1,2-naphthoquinone-diazide-5-sulphonyl chloride and 1,2-naphthoquinone-diazide-4-sulphonyl chloride condensed with phenolic compounds such as hydroxybenzophenones.

Additives such as, for example, colorants, dyes, flow agents, plasticisers, adhesion promoters, development accelerators, further solvents and surfactants, for example, nonionic surfactants, can also be added to the solution of polyamide, light-sensitive compound and solvent before the solution is applied to a layer carrier.

Examples of dyes which can be used as additives for the light-sensitive mixtures according to 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. 44 045) and neutral red (C.I. 50 040). These dyes are added in a quantity from 1 to 10% by weight, relative to the total weight of polyamide and light-sensitive compound. The dye additions reduce the back-scattering of light by the carrier and thus contribute to improved resolution.

Flow agents can be used in a quantity of up to 5% by weight, relative to the total weight of polyamide and light-sensitive compound.

Examples of suitable adhesion promoters are β -(3,4-epoxycyclohexyl)-ethyltrimethoxysilane, p-methyldisilanemethyl methacrylate, vinyltrichlorosilane and γ -aminopropyltriethoxysilane in a proportion of up to 4% by weight, relative to the total weight of polyamide and light-sensitive compound.

Examples of development accelerators which can be added are picric acid, nicotinic acid or nitrocinammic acid in a proportion of up to 20% by weight, relative to the total weight of polyamide and light-sensitive compound. These accelerators lead to the solubility of the photoresist layer increasing in both the exposed and unexposed areas. They are used in those applications where the development speed is particularly important, even if a certain degree of contrast is sacrificed; in fact, while the exposed areas of the photoresist layer are more rapidly dissolved by the developer as a result of the addition of accelerators, the development accelerators simultaneously also effect a greater loss of

photoresist layer from the unexposed areas.

Suitable solvents in the preparation of the photoresist mixtures according to the invention are all commercially available solvents typical for this purpose.

5 The proportion of solvent in the total photoresist solution can amount to up to 95% by weight. The solubility of the known polyamides in N-methylpyrrolidone and dimethylacetamide is limited, whereas the polyamides according to the invention are very readily soluble in
10 these solvents and in other commercially available solvents. In addition to N-methylpyrrolidone and dimethylacetamide, suitable solvents also include, for example, propylene glycol methyl ether, methyl ethyl ketone, cyclohexanone, butyrolactone and mixtures
15 thereof. Preferably, N-methylpyrrolidone and propylene glycol methyl ether are used.

The finished photoresist solution can be applied to a carrier by one of the methods conventional in photoresist technology, such as dipping, spraying and
20 whirler-coating. In the case of whirler-coating, for example, the percentage content of solids in the resist solution can be adjusted such that a coating of the desired thickness results, depending on the whirler-coating device used in the individual case and on the
25 time span for the whirler-coating step. Examples of suitable carrier materials are: silicon, aluminium or polymeric resins, silica, doped silica, silicon nitride, tantalum, copper, polycrystalline silicon (polysilicon), ceramics and aluminium/copper alloys.

30 The photoresist solutions prepared by the process described are particularly suitable for application to silicon wafers which carry a layer of thermally grown silica, such as are used in the production of micro-processors and other semiconductor components used in
35 microelectronics. Likewise, an aluminium wafer with an alumina layer can also be used. The carrier can also consist of various polymeric resins, especially of transparent polymers such as, for example, polyesters.

Suitable developer solutions used for the

light-sensitive mixtures according to the invention are aqueous solutions of inorganic alkaline compounds, such as sodium silicate, potassium silicate, sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium phosphate, sodium monohydrogen phosphate, ammonium phosphate, ammonium monohydrogen phosphate, sodium metasilicate, sodium bicarbonate, ammonia and the like, and the concentration of these compounds can be 0.1 to 10% by weight, preferably 0.5 to 5% by weight. Examples of suitable developer solutions are precisely described, inter alia, in US-A 3,110,596, US-A 3,173,788 and US-A 3,586,504.

In an individual case, the alkaline developer solutions can also contain certain organic solvents such as alcohols (for example methanol, ethanol, benzyl alcohol and the like) and wetting agents, (for example sodium alkyl naphthalenesulphonate, sodium lauryl sulphate and the like).

After the photoresist solution has been applied to the layer carrier, the carrier is subjected to predrying at about 80 to 105°C, preferably at temperatures of around 90°C. This heat treatment is continued until the solvent or solvent mixture has evaporated substantially completely and only a thin layer of photoresist mixture of a thickness of about 1 μ m remains on the layer carrier.

The coated carrier is then exposed imagewise in the known manner by means of actinic radiation through suitable masks, negatives, stencils and the like.

Next, the layer carrier coated with the photoresist mixture and exposed is dipped into an aqueous-alkaline developer solution. The solution is preferably agitated vigorously, which can be effected, for example, by blowing nitrogen through.

The carriers remain in the developer bath until the photoresist layer has been entirely or at least almost entirely detached in the exposed areas.

After the coated wafer has been taken out of the developer solution, a thermal aftertreatment or baking

treatment can be carried out in order to increase the adhesion and the chemical resistance of the layer to etching solutions and other substances.

5 The adhesion of the light-sensitive layer according to the invention to carrier materials such as, for example, silicon wafers, aluminium plates, glass, polyester films and the like is excellent. No adhesion-promoting layer therefore needs to be applied to the carrier for processing the mixtures. The heat treatment
10 after development can be carried out in an oven at temperatures below the softening point of the layer. The temperatures are between 80 and 375°C, preferably between 225 and 350°C. The duration of this heat treatment varies between 30 minutes and 2 hours. The glass transition
15 temperature (T_g) of the polyamide is usually 250 to 300°C before the heat treatment and about 300 to 350°C, especially 305 to 325°C, after the heat treatment and conversion of the polyamide into a polyoxazole.

20 After the hardening, the developed material can also be treated with a buffered solution based on hydrofluoric acid or with an alkaline etching solution. The photoresist mixtures according to the invention are equally resistant to alkaline and acidic etching solutions and represent an effective protection of the
25 unexposed, i.e. resist-covered surfaces of the carrier. The developed and hardened photoresist material shows relief images of excellent resolution and sharpness, and has outstanding heat resistance.

30 Although the invention was described above only with respect to a wet etching process, the relief images produced according to the invention are also suitable for powder-etching processes. The photoresist structures obtained are outstandingly suitable as insulating layers in semiconductor production or as masks for vapour-
35 coating processes, ion implantation processes and the like. Moreover, the photoresists according to the invention can be used for producing printing plates, test foils for planographic printing, image transfer foils for planographic printing and for similar purposes. The

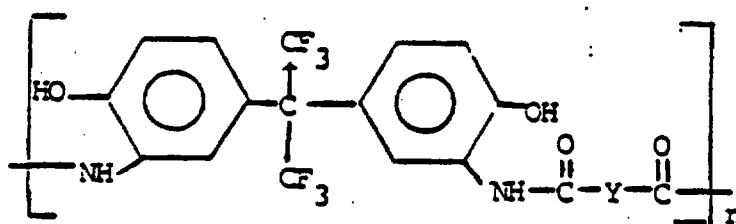
production of printing plates from positive-working photoresists is known and described, for example, in US-A 3,493,371.

5 The photoresists according to the invention can also be used as protective coatings in numerous other fields well known to those skilled in the art. Moreover, due to their good solubility, the polyamides according to the invention are equally suitable for high temperature-resistant protective coatings as for the photoresist mixtures. A typical coating mixture for a protective coating contains, for example, 5 to 30% by weight of the polyamide according to the invention in solution for application to a carrier material. Yet further constituents, such as antioxidants, UV stabilisers, adhesion promoters, colorants, flame retarders, fillers and further auxiliaries in a total quantity of up to 20% by weight can also be added to the coating solution. The solvent is removed at an elevated temperature, in general in the range from 90 to 150°C and, if desired, a reduced pressure can also be applied to facilitate this process step. Subsequently, the material coated with the polyamide is heated for a period of about half an hour up to six hours to a temperature of 200 to 350°C, whereby the polyamide is converted into a highly temperature-resistant polyoxazole.

15 In the examples which follow, the processes for preparing and using mixtures according to the invention are explained in detail. However, these examples are not intended to restrict the scope of the invention in any way, and they should not be interpreted in such a way that they indicate conditions, parameters or other values which are to be exclusively applied to the execution of the invention in practice. In the examples, the term "layer denudation in the dark" was shortened to "denudation".

35 Example 1

By means of a polycondensation in solution, a polyamide of the following general formula was prepared:



In the formula, Y represents an equimolar mixture (50:50 mole parts) of isophthaloyl and terephthaloyl groups, and n is a number of around 200.

5 An equimolar mixture of 5.5 mmol (= 1.1165 mg) of isophthaloyl chloride and 5.5 mmol (= 1.1165 mg) of terephthaloyl chloride was added dropwise at a temperature of -10 to -15°C in the course of 30 minutes with vigorous stirring to a solution of 0.01 mol (= 3.66 mg) of hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane
10 in 16.5 ml of dimethylacetamide and 3 ml of pyridine. The mixture was stirred for a further 24 hours at room temperature, and the solution obtained was then poured into ice-water to precipitate the polymer. The precipitated polyamide was filtered off, washed with water and
15 dried overnight in vacuo at 90°C.

The polymer was obtained in an almost quantitative yield and had a logarithmic viscosity number of 0.40 dl g⁻¹, measured in 0.5% dimethylacetamide at 25°C.

Example 2

20 To prepare a photoresist solution, 10 p.b.w. (parts by weight) of the polymeric precursor, described in Example 1, for a polybenzoxazole, 5 parts by weight of a light-sensitive compound (a mixed tris-ester of trihydroxybenzophenone) and 0.08 parts by weight of a red
25 dye were dissolved in 12 parts by weight of methyl ethyl ketone and 8.0 parts by weight of propylene glycol methyl ether. The solution was filtered and then applied to an anodically oxidised aluminium plate by roller application. After a drying time of 3 minutes at 90°C, a 2 to
30 3 µm thick resist layer was obtained on the carrier

material.

A photomask with a line pattern was placed upon the resist layer in such a way that the layer and the photomask were in close mutual contact. The exposure to UV light was carried out by means of a mercury vapour lamp of 200 W rating for 60 seconds. The intensity of the UV light at a wavelength of 365 nm on the layer surface was 5 mW/cm². After the exposure, the layer was developed with a mixture of an alkaline developer (AZ developer, Hoechst Celanese Corp.) and water (1:5). The developed plate was washed with water. The image obtained showed a fine, uniform relief pattern, in which line widths down to 3 μm were reproduced. The plate was then subjected to a heat treatment at 250°C for one hour.

Even after a heat treatment for 6 hours at 250°C, the image still showed sharp edges and unchanged good resolution. No even hairline cracks as a consequence of the development and heat treatment were detectable. Only a slight layer loss was measured after the heat treatment.

Example 3

To prepare a photoresist solution, 10 parts by weight of a polymeric precursor, prepared according to Example 1, for a polybenzoxazole, a polycondensation product of hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane, and 5 parts by weight of a light-sensitive compound (a mixed tris-ester of trihydroxybenzophenone) and 0.08 part by weight of a red dye (Disperse Red 179) were dissolved in 12 parts by weight of methyl ethyl ketone and 8.0 parts by weight of propylene glycol methyl ether. The solution was filtered and then applied to an anodically oxidised aluminium plate by roller application. After a drying time of 3 minutes at 90°C, a 2 to 3 μm thick resist layer was obtained on the carrier material.

For exposure, a photomask with a line pattern was placed upon the resist layer in such a way that the layer and the photomask were in close mutual contact. The

exposure to UV light was carried out by means of a mercury vapour lamp of 200 W rating for 60 seconds. The intensity of the UV light of a wavelength of 365 nm on the layer surface was 5 mW/cm².

5 After the exposure, the layer was developed with a mixture of an alkaline developer (AZ developer, Hoechst Celanese Corp.) and water (1:5). The developed plate was washed with water. The image obtained showed a fine, uniform relief pattern, in which line widths down to 3 μ m were reproduced. The plate was then subjected to a heat treatment at 250°C for 1 hour.

10 Even after a heat treatment for 6 hours at 250°C, the image still showed sharp edges and unchanged good resolution. Not even hairline cracks as a consequence of the development and heat treatment were detectable.

Example 4

By means of this example, the acetylation of the hydroxyl groups of the polyamide according to the invention (condensation product of hexafluoro-2,2-bis-(3-aminohydroxyphenyl)-propane and an equimolar mixture of isophthaloyl chloride and terephthaloyl chloride) is illustrated.

20 4.96 mg (=0.01 mol) of the polyamide copolymer were dissolved in 25 ml of dimethylacetamide in a 100 ml three-necked flask fitted with a stirrer, reflux condenser and thermometer, heated to 100°C with stirring and 0.2 mg of acetic anhydride were added. The reaction mixture was kept at 100°C for 7 hours and then poured into ice-water. A white, solid, fibrous polymer was obtained which was washed with water and dried overnight at 100°C in a vacuum cabinet. About 20% of the hydroxyl groups of the polymer had been esterified.

30 The following Table 1 demonstrates the good solubility of the polyamides used, according to the invention. The polymer A, which was prepared according to Example 1, is a condensation product of hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane and an equimolar mixture of isophthaloyl chloride and terephthaloyl

chloride. The polymer B, which was prepared by the process according to Example 1 of US-A 4,395,482, is a condensation product of 3,3'-dihydroxybenzidine and isophthaloyl chloride.

5

Table 1

Solvent	Solubility (% by weight)	
	Polymer A	Polymer B
10 N-Methylpyrrolidone	30	<20*
Dimethylacetamide	30	<20*
15 Propylene glycol methyl ether	30	insoluble
Methyl ethyl ketone	20	insoluble
Cyclohexanone	20	insoluble
20 Butyrolactone	20	insoluble

* incompletely dissolved, gel formation

25 The comparative examples which follow were carried out in order to demonstrate the superiority of the positive-working photoresist mixtures according to the invention, especially of photoresist mixtures which contain the polyamides according to the invention, over known mixtures.

30 For this purpose, photoresist mixtures were first prepared, in which the polyamides according to the invention (polymeric precursors for polyoxazoles) were used which had been obtained essentially by the process described in Example 1 of the present application. In addition, photoresist mixtures were prepared which
35 contained a poly-(benzidine-isophthalamide) according to Example 1 of US-A 4,339,521.

By means of the method described below, the light sensitivity of the mixture was then determined. The duration of the particular heat treatment, the

whirler-coating speed and other parameters of the individual experiments are also given below:

5 Silicon wafers were whirler-coated with the photoresist mixtures at a constant speed (in the range from 500 to 1,500 rpm). The wafers were dried for 30 to 45 minutes at 90°C, in order to remove the solvent. The original thickness of the applied, dry photoresist layers was determined by a Rudolph thickness-measuring instrument. The light sensitivity was measured by preparing a contrast curve as described in "C. G. Willson, Introduction to Microlithography, Chapter 3, page 105, American Chemical Society, Washington, D.C. 1983". In this method, the layer thickness loss after a development time of one minute is plotted against the logarithm (ln) of the UV exposure dose. The layer thickness was measured by means of laser interferometry by the method described. The photoresist was developed at a temperature of 25.0°C ± 0.5°C with a solution, diluted with deionised water, of an aqueous-alkaline developer. The particular light sensitivity value (mJ/cm²) is obtained by extrapolation of the curve to the total layer thickness loss.

The following light-sensitive compounds were used. In the examples, they are labelled in brief by a), b) or c).

- 25 a) Bis-1,2-naphthoquinone-diazide sulphonate of trihydroxybenzophenone;
- b) Bis-1,2-naphthoquinone-diazide-5-sulphonate of trihydroxyoctanophenone;
- 30 c) Bis-1,2-naphthoquinone diazide-5-sulphonate of 2,2-bis-(4-hydroxyphenyl)-propane (light-sensitive compound from Example 1 of US-A 4,339,521).

Example 5

35 To prepare a photoresist solution, 15 parts by weight of the polyamide from Example 1 and 15 parts by weight of the light-sensitive compound b) were dissolved in 70 parts by weight of a solvent mixture of equal parts of propylene glycol methyl ether and N-methylpyrrolidone.

5 A wafer was whirler-coated with this solution, dried and exposed by means of a 200 W mercury vapour lamp to light of a wavelength of 365 nm, as already described. The developer concentration was 1 part of AZ developer: 2 parts of water. The resist obtained was evaluated in the manner described. The following results were obtained:

Light sensitivity: 76.4 mJ/cm²
Denudation: 0.007 μm/minute

10 The described characteristic curve of the resist was within the normal range; the adhesion of the resist to the wafer was excellent.

Example 6

15 A photoresist solution was prepared from 16 parts by weight of the polyamide from Example 1, 8 parts by weight of the light-sensitive compound b) and 76 parts by weight of an equimolar mixture of N-Methylpyrrolidone and propylene glycol methyl ether. The procedure followed was as in Example 5, and the development was carried out in a mixture of AZ developer in water in a ratio of 1:8.

20 The following results were obtained:

Light sensitivity: 74.8 mJ/cm²
Denudation: 0.019 μm/minute

25 The characteristic curve of the resist was within the normal range; the adhesion of the resist to the wafer was excellent.

Example 7

30 A polyamide was prepared in accordance with the instructions of Example 1, with the exception that 30 mol % of hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane were replaced by the same molar quantity of hexafluoro-2,2-bis-(3-amino-4-methyl)-propane [sic]. The resulting polyamide was used in the photoresist formulation of Example 5. Development was carried out with a mixture of

AZ developer in water in the ratio of 1:6, the procedure otherwise being as in Example 5.

The following results were obtained:

5 Light sensitivity: 65 mJ/cm²
Denudation: 0.016 μm/minute

The characteristic curve of the resist was within the normal range; the adhesion of the resist to the wafer was excellent.

Example 8

10 Using the polyamide from Example 7, a photoresist mixture was prepared and evaluated by the method already described. For this purpose, 20 parts by weight of the polyamide from Example 7 and 10 parts by weight of the light-sensitive compound b) were dissolved in 70 parts by weight of a mixture consisting of equal molar parts of propylene glycol methyl ether and N-methylpyrrolidone. 15 The developer used was a mixture of 1 part by weight of AZ developer and 2 parts by weight of water.

The following results were obtained:

20 Light sensitivity: 81 mJ/cm²
Denudation: 0.007 μm/minute

Example 9

25 Using the polyamides from Example 4, a photoresist mixture was prepared and evaluated by the method described in Example 5. For this purpose, 13 parts by weight of acylated polyamide from Example 4 and 13 parts by weight of the light-sensitive compound b) were dissolved in 74 parts by weight of a solvent mixture consisting of equal parts of propylene glycol methyl ether and N-methylpyrrolidone. The developer used was a 30 mixture of 1 part by weight of AZ developer and 2 parts by weight of water.

The following results were obtained:

Light sensitivity: 77.6 mJ/cm²
Denudation: 0.011 μm/minute

5 The characteristic curve was within the normal range; the adhesion of the resist to the wafer was excellent.

Example 10

10 A polyamide was prepared by the method described in Example 1, but 30 mol % of the diamino monomer used therein were replaced by dianisidine as the comonomer and terephthaloyl chloride was used as the acid chloride.

The properties of the photoresist mixture were evaluated by the method described in Example 5.

15 The photoresist mixture contained 15 parts by weight of the polyamide copolymer, 15 parts by weight of the light-sensitive compound b) and 70 parts by weight of the solvent mixture of equal parts of N-methylpyrrolidone and propylene glycol methyl ether. The developer concentration was 1 part by weight of AZ developer to 2 parts by weight of water.

20 Light sensitivity: 199.5 mJ/cm²
Denudation: 0.013 μm/minute

Example 11

25 A polyamide was prepared according to Example 1, with the exception that 20 mol % of the diamino monomer of Example 1 were replaced by an equimolar proportion of hexafluoro-2,2-bis-(3-amino-4-methyphenyl)-propane and terephthaloyl chloride was used as the dibasic acid chloride.

30 15 parts by weight of the resulting polyamide and 15 parts by weight of the light-sensitive compound a) were dissolved in 70 parts by weight of N-methylpyrrolidone. The wafers coated with this solution were prepared and tested in accordance with the preceding examples. The developer solution used was a mixture of 1 part by weight
35 of AZ developer and 2 parts by weight of water.

The following results were obtained:

Light sensitivity:	237.9 mJ/cm ²
Denudation:	0.008 μm/minute

Example 12 (Comparison Example)

5 Corresponding to Example 5, a solution was prepared from 8.5 parts by weight of poly-(dihydroxybenzidineisophthalamide), prepared according to the instructions in Example 1 of US-A 4,339,521, and 8.5 parts by weight of the light-sensitive compound b) in 83 parts by weight of N-methylpyrrolidone.

10 A wafer was whirler-coated with this solution at a speed of 500 rpm and further processed in accordance with the instructions of the present example. The developer used was a solution of 1 part by weight of AZ developer and 5 parts by weight of water.

The following results were obtained:

Light sensitivity:	589 mJ/cm ²
Denudation:	0.015 μm/minute

Example 13 (Comparison Example)

20 Example 12 was repeated, with the exception that the solution now contains 6.8 parts by weight of poly-(dihydroxybenzidine-isophthalamide) and 6.8 parts by weight of the light-sensitive compound c) in 84.4 parts by weight of N-methylpyrrolidone. The developer used was undiluted AZ developer.

The following results were obtained:

Light sensitivity:	364 mJ/cm ²
Denudation:	0.007 μm/...[sic]

30 The following Table 2 once more summarises the results of the present examples.

Table 2

Example	Light sensitivity (mJ/cm ²)	
5	5	76.4
	6	74.8
	7	65.0
	8	81.0
	9	77.6
10	10	199.5
	11	237.9
	12	589
	13	364

Invention

State of the art

15 The following additional examples were carried out in order to demonstrate the advantageous properties of the polyamides according to the invention in the field of lithography. In these examples, the polyamide/light-sensitive compound ratio was varied. The following
20 general procedure was adhered to in these examples.

 The polyamide in the light-sensitive compounds was dissolved in a solvent and applied by the "roller-coat" process to an anodised aluminium carrier. The solvent was removed by drying the layer at 90°C, and a
25 light-sensitive layer of a thickness of 2-3 μm remained.

 For determining the light sensitivity, the light-sensitive layer was covered with a GATF photomask which contained a 21-step half-tone wedge with density steps of 0.15 each. The procedures can be taken from GATF
30 Research Bulletin 215.

 The light-sensitive recording material was exposed to UV light through the GATF photomask and exposed [sic] to an aqueous-alkaline developer. The values found for exposure time, light sensitivity, developer concentration, developing time and the
35 polyamide/light-sensitive compound ratio are summarised in the following examples and in Table 3.

The polyamides mentioned in the examples were prepared according to the instructions in Example 1.

Example 14

5 The polycondensation product of hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane and terephthaloyl chloride was prepared.

Example 15

10 The polycondensation product of hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane and isophthaloyl chloride was prepared.

Example 16

The polycondensation product of hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane and hexafluoro-2,2-bis-(4-chlorocarbonylphenyl)-propane was prepared.

15 Example 17

A polycondensation product of hexafluoro-2,2-bis-(3-amino-4-hydroxyphenyl)-propane and an equimolar mixture of hexafluoro-2,2-bis-(4-chlorocarbonylphenyl)-propane and isophthaloyl chloride was prepared.

20 Using the polyamides described in Examples 1, 14, 15, 16 and 17, light-sensitive mixtures were prepared, each with the light-sensitive compound a), in a solvent mixture of 60% by weight of methyl ethyl ketone and 40% by weight of propylene glycol methyl ether.

25 After exposure to UV light of a wavelength of 365 nm for 90 seconds, the layers were developed with an AZ developer dissolved in one part of water. The solids content (polyamide and light-sensitive compound) was 10% by weight in each example.

Table 3

	Polyamide	Polyamide/light-sensitive compound ratio	Wedge steps	Light-sensitivity
5	Example 1	1:1	7	good
		6:1	21	fast
	Example 14	1:1	4	slow
		6:1	21	fast
10	Example 15	1:1	21	fast
		6:1	21	fast
	Example 16	1:1	2	slow
		6:1	6	good
	Example 17	1:1	7	good
15		6:1	21	fast

20 The values listed above show that the light sensitivity can be controlled by varying the polyamide/light-sensitive compound ratio. The light sensitivity based on the light-sensitive mixture according to Example 16 is extremely high, but the light-sensitive mixture according to Example 18 shows the best resolution and the best adhesion of the layer to the carrier.

Example 18

25 The polyamide of Example 16 was used in a light-sensitive mixture in which a mixture of 10% by weight of methyl ethyl ketone and 90% by weight of propylene glycol methyl ether was used as the solvent. Corresponding to the instructions in Examples 14 to 17, the wedge steps were determined as a function of various polyamide/light-sensitive compound ratios.

30 The following results were obtained:

Polyamide/light-sensitive
compound ratio

Wedge step

5	1:1	3
	2:1	5
	3:1	6
	4:1	6
	5:1	7
	6:1	7

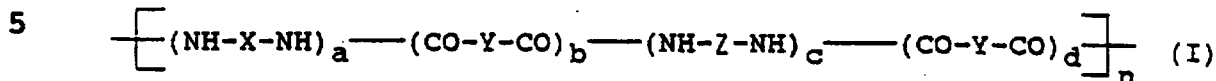
10

The adhesion of the light-sensitive layer to the aluminium carrier was very good, which implies that this polyamide would probably also represent a good protective layer in other cases not in the photoresists field.



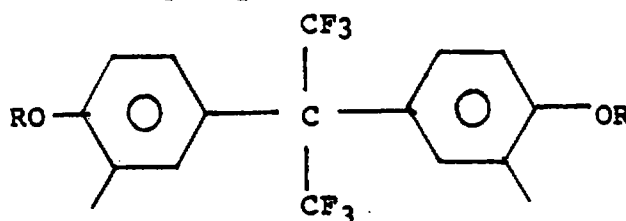
Patent claims

1. Polyamide, suitable as a binder for positive-working light-sensitive mixtures, characterised in that it is of the general formula I



in which

X is a divalent group of the formula



10 in which the R radicals can be identical or different and are hydrogen or an optionally substituted aliphatic or aromatic radical having up to 9 carbon atoms,

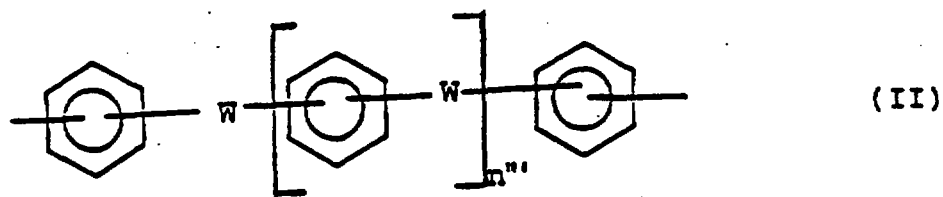
15 Y and Z are identical or different and are an optionally substituted aliphatic, aromatic or cycloaliphatic radical having up to 60 carbon atoms, or mixtures thereof,

a represents a mole fraction of 0.10 to 0.50,
b represents a mole fraction of 0.25 to 0.50,
c represents a mole fraction of 0.0 to 0.40 and
20 d represents a mole fraction of 0.0 to 0.25, each relative to the total molecular weight of X + Y + Z, with a+b+c+d=1, and

n is an integer from 2 to 500.

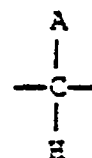
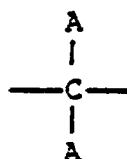
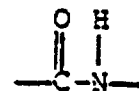
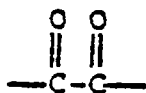
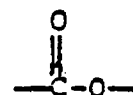
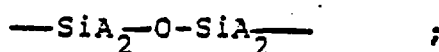
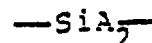
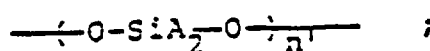
25 2. Polyamide according to Claim 1, characterised in that

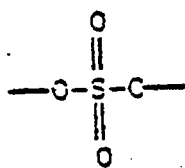
30 Y and Z can be identical or different and are methylene, difluoromethylene, polydifluoromethylene having 2 to 12 carbon atoms, an optionally substituted polymethylene having 2 to 12 carbon atoms, cyclohexylene, cyclohexenylene, piperazinylenes, arylene, biarylene, naphthylene or a polyarylene according to formula II



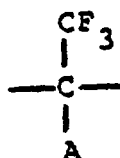
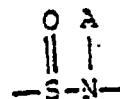
wherein

W the group forming the linking member, can in each case be one of the following groups: a single C-C bond; a methylene group; a polymethylene group having 2 to 12 carbon atoms, a difluoromethylene group; a polydifluoromethylene group having 2 to 12 carbon atoms, a hexafluoroisopropylidene group; an isopropylidene group; an oxy group or thio group; a sulphinyl group; a sulphonyl group; a sulphonyldioxy group; a sulphonamido group; a carbonyl group or one of the following groups:

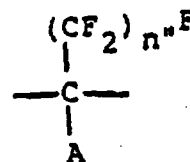




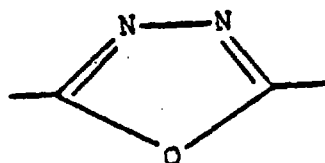
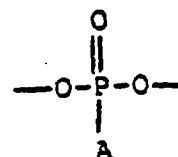
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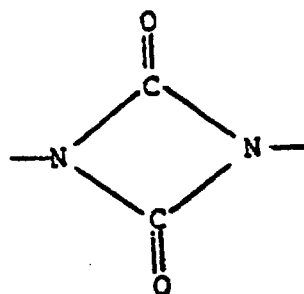
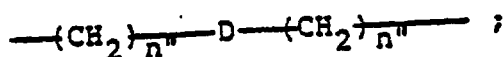
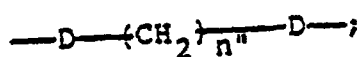
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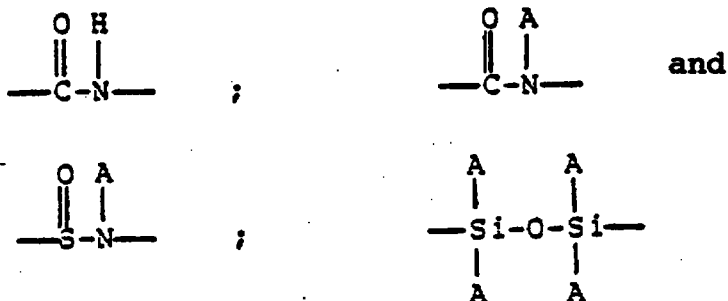




a cyclohexylene group; a cyclohexenylene group; a naphthylene group, or mixtures thereof.

A can in each case be a substituted or unsubstituted alkyl group having 1 to 8 carbon atoms; a substituted or unsubstituted phenyl group or a substituted or unsubstituted naphthyl group.

D can in each case be one of the following groups: an oxy group; a thio group; a carbonyl group; an oxycarbonyl group; a sulphonamido group; a sulphinyl group; a sulphonyl group; a sulphonyldioxy group; a benzenedicarbonyl group; or one of the following groups:



n' is an integer from 1 to 25,

n" is an integer from 1 to 12 and

n''' is an integer from 0 to 3, with the proviso that W is not a C-C single bond if n''' = 0.

3. Polyamide according to Claims 1 or 2, characterised in that a corresponds to a mole fraction of 0.25 to 0.5.

4. Polyamide according to one or more of Claims 1 to 3, characterised in that Y and/or Z consist in each case of at least 70 mol % of aromatic divalent groups or mixtures thereof.

5. Polyamide according to one or more of Claims 1 to 4, characterised in that Y and/or Z are a mixture of m-phenylene groups, p-phenylene groups or hexafluoro-2,2-bis-(p-phenyl)-propane groups.

6. Positive-working light-sensitive mixture, essentially consisting of an o-quinone-diazide and a binder soluble in an aqueous-alkaline solution, characterised in that the polyamide according to one or more of Claims 1 to 5 is present as the binder.



7. Light-sensitive mixture according to Claim 6, characterised in that it additionally contains a solvent.

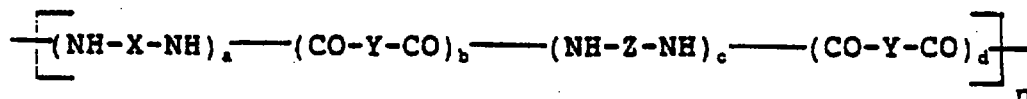
5 8. Light-sensitive mixture according to Claims 6 or 7, characterised in that the o-quinone-diazide is a (mixed) ester of a phenol compound having at least two hydroxyl groups.

10 9. Light-sensitive recording material, essentially consisting of a carrier and a light-sensitive layer, characterised in that the light-sensitive layer is a layer according to one or more of Claims 6 to 8.

10. Light-sensitive recording material according to Claim 9, characterised in that, after imagewise exposure and subsequent development, it is heat-treated at temperatures of around 250°C.

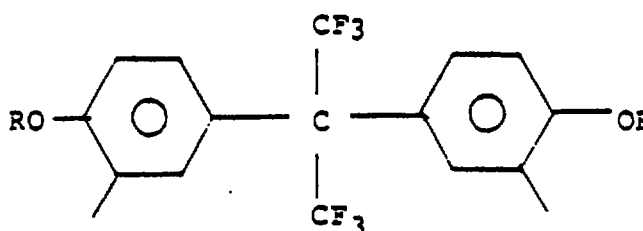
**As printed
Claims**

1. Polyamide, suitable as a binder for positive-working light-sensitive mixtures, characterised in that it is of the general formula I



in which

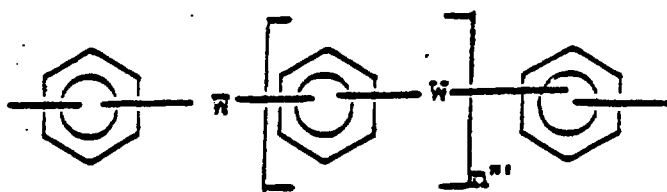
X is a divalent group of the formula



- in which the R can be identical or different and are hydrogen or an optionally substituted aliphatic or aromatic radical having up to 9 carbon atoms,
Y and Z are identical or different and are an optionally substituted aliphatic, aromatic or cycloaliphatic radical having up to 60 carbon atoms, or mixtures thereof,
a represents a mole fraction of 0.10 to 0.50,
b represents a mole fraction of 0.25 to 0.50,
c represents a mole fraction of 0.0 to 0.40 and
d represents a mole fraction of 0.0 to 0.25, each relative to the total molecular weight of X + Y + Z, with a + b + c + d = 1, and
n is an integer from 2 to 500.

2. Polyamide according to Claim 1, characterised in that

Y and Z can be identical or different and are methylene, difluoromethylene, polydifluoromethylene having 2 to 12 carbon atoms, an optionally substituted polymethylene having 2 to 12 carbon atoms, cyclohexylene, cyclohexenylenes, piperazinylenes, arylene, biarylene, naphthylene or a polyarylene according to formula II

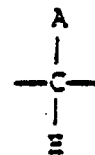
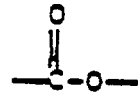
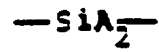
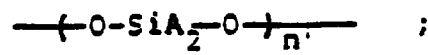


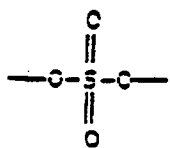
wherein

W, the group forming the linking member, can in each case be one of the following groups: a single C-C bond; a methylene group; a polymethylene group having 2 to 12 carbon atoms; a difluoromethylene group; a polydifluoromethylene group having 2 to 12 carbon atoms; a hexafluoroisopropylidene group; an isopropylidene group; an oxy group or thio group; a sulphinyl group; a sulphonyl group; a sulphonyldioxy group; a sulphonamido group; a carbonyl group or one of the following groups:

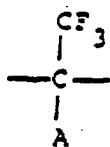


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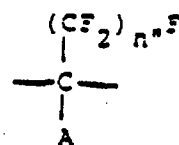




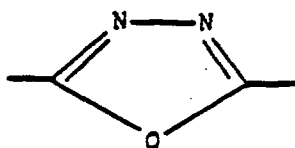
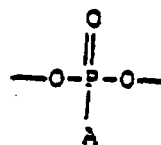
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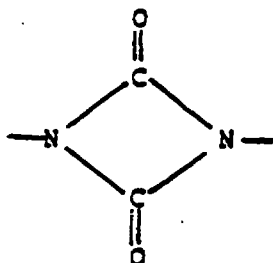
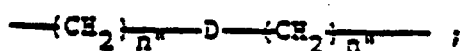
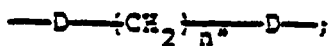
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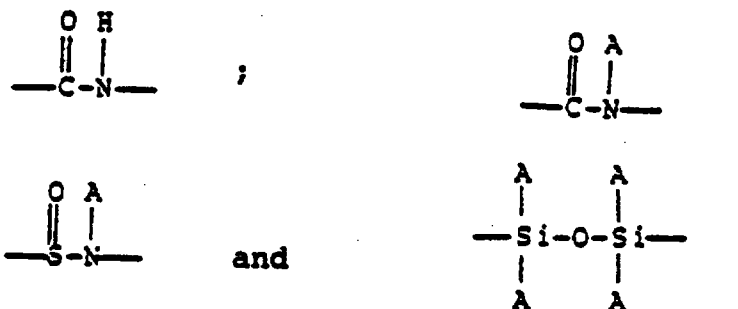
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- a cyclohexylene group; a cyclohexenylene group; a naphthylene group, or mixtures thereof,
- A can in each case be a substituted or unsubstituted alkyl group having 1 to 8 carbon atoms; a substituted or unsubstituted phenyl group or a substituted or unsubstituted naphthyl group;
- D can in each case be one of the following groups: an oxy group; a thio group; a carbonyl group; an oxycarbonyl group; a sulphonamido group; a sulphinyl group; a sulphonyl group; a



sulphonyl dioxy group; a benzene dicarbonyl group; or one of the following groups:



n' is an integer from 1 to 25,

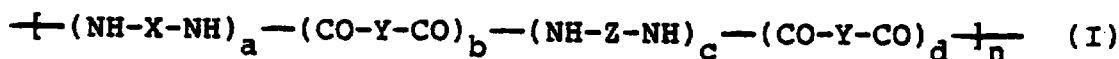
n'' is an integer from 1 to 12 and

n''' is an integer from 0 to 3, with the proviso that W is not a C-C single bond if $n''' = 0$.

3. Polyamide according to Claim 1 or 2, characterised in that a corresponds to a mol fraction of 0.25 to 0.5.
4. Polyamide according to one or more of Claims 1 to 3, characterised in that Y and/or Z consist in each case of at least 70 mol % of aromatic divalent groups or mixtures thereof.
5. Polyamide according to one or more of Claims 1 to 4, characterised in that Y and/or Z are a mixture of m-phenylene groups, p-phenylene groups or hexafluoro-2,2-bis-(p-phenyl)-propene groups.
6. Positive-working light-sensitive mixture, essentially consisting of an o-quinone-diazide and a binder soluble in an aqueous-alkaline solution, characterised in that the polyamide according to one or more of Claims 1 to 5 is present as the binder.
7. Light-sensitive mixture according to Claim 6, characterised in that it additionally contains a solvent.
8. Light-sensitive mixture according to Claim 6 or 7, characterised in that the o-quinone-diazide is a (mixed) ester of a phenol compound having at least two hydroxyl groups.
9. Light-sensitive recording material, essentially consisting of a support and a light-sensitive layer, characterised in that the light-sensitive layer is a layer according to one or more of Claims 6 to 8.
10. Light-sensitive recording material according to Claim 9, characterised in that, after imagewise exposure and subsequent development, it is heat-treated at temperatures of around 250° C.

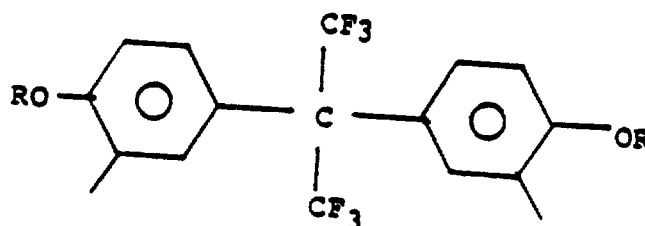
**As printed
Revendications**

1. Polyamide, approprié en tant que liant pour compositions photosensibles travaillant en positif, caractérisé en ce qu'il correspond à la formule générale I



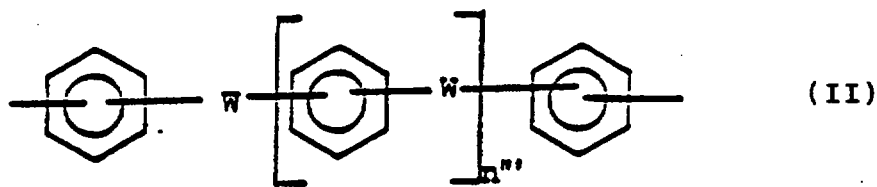
dans laquelle

X représente un groupe bivalent de formule



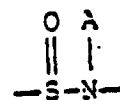
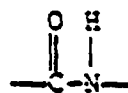
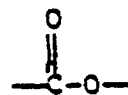
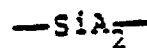
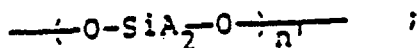
- dans laquelle les radicaux R peuvent être identiques ou différents et représentent un atome d'hydrogène ou un radical aliphatique ou aromatique éventuellement substitué, ayant jusqu'à 9 atomes de carbone,
- Y et Z sont identiques ou différents et représentent un radical aliphatique, aromatique ou cycloaliphatique éventuellement substitué, ayant jusqu'à 60 atomes de carbone, ainsi que des mélanges de ceux-ci,
- a représente de 0,10 à 0,50 partie en mole,
 - b représente de 0,25 à 0,50 partie en mole,
 - c représente de 0,0 à 0,40 partie en moles et
 - d représente de 0,0 à 0,25 partie en mole, dans chaque cas par rapport à la masse moléculaire totale de X + Y + Z, a + b + c + d étant égal à 1, et
 - n représente un nombre entier allant de 2 à 500.

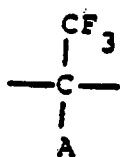
2. Polyamide selon la revendication 1, caractérisé en ce que
- Y, Z peuvent être identiques ou différents et représentent le groupe méthylène, difluorométhylène, un groupe polydifluorométhylène ayant de 2 à 12 atomes de carbone, un polyméthylène éventuellement substitué ayant de 2 à 12 atomes de carbone, un groupe cyclohexylène, cyclohexénylène, pipérazinylène, arylène, biarylène, naphtylène ou un groupe polyarylène de formule II



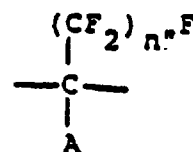
- W, groupe formant le chaînon de liaison, pouvant être respectivement un des groupes suivants: une simple liaison C-C, un groupe méthylène, un groupe polyméthylène ayant de 2 à 12 atomes de carbone, un groupe difluorométhylène, un groupe polydifluorométhylène ayant de 2 à 12 atomes de carbone, un groupe hexafluoroisopropylidène, un groupe isopropylidène, un groupe oxy ou thio, un groupe sulfinyle, un groupe sulfonyle, un groupe sulfonyldioxy, un groupe sulfonamido, un groupe carbonyle ou l'un des groupes suivants:

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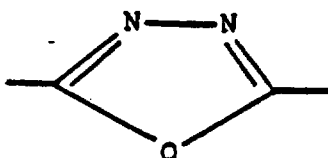
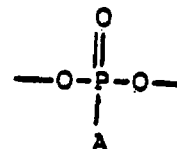




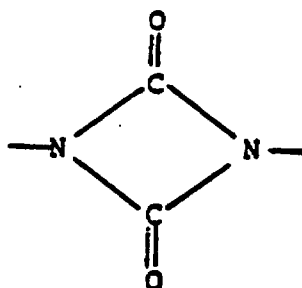
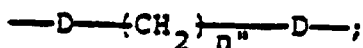
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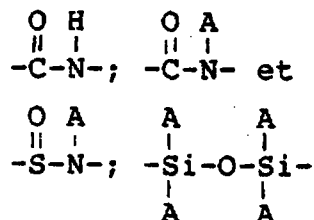
un groupe cyclohexylène, un groupe cyclohexénylène, un groupe naphtylène, ainsi que des mélanges de ceux-ci,

A pouvant représenter dans chaque cas un groupe alkyle substitué ou non substitué ayant de 1 à 8 atomes de carbone, un groupe phényle substitué ou non substitué ou un groupe naphtyle substitué ou non substitué,

D pouvant représenter dans chaque cas l'un des groupes suivants: un groupe oxy, un groupe



thio, un groupe carbonyle, un groupe oxycarbonyle, un groupe sulfonamido, un groupe sulfinyle, un groupe sulfonyle, un groupe sulfonyldioxy, un groupe benzènedicarbonyle, ou l'un des groupes suivants:



- n' représente un nombre entier allant de 1 à 25,
n'' représente un nombre entier allant de 1 à 12 et
n''' représente un nombre entier allant de 0 à 3, étant entendu que W ne représente pas une simple liaison C-C lorsque n''' = 0.

3. Polyamide selon la revendication 1 ou 2, caractérisé en ce que a correspond à 0,25-0,5 partie en mole.
4. Polyamide selon une ou plusieurs des revendications 1 à 3, caractérisé en ce que Y et/ou Z consistent chacun, à raison d'au moins 70 % en moles, en des groupes aromatiques divalents ou des mélanges de ceux-ci.
5. Polyamide selon une ou plusieurs des revendications 1 à 4, caractérisé en ce que Y et/ou Z représente(nt) un mélange de groupes m-phénylène, p-phénylène ou hexafluoro2,2-bis(p-phényl)-propane.
6. Composition photosensible travaillant en positif, essentiellement constituée d'un o-quinonediazide et d'un liant soluble dans une solution aqueuse-alcaline, caractérisée en ce qu'un polyamide selon une ou plusieurs des revendications 1 à 5 est contenu en tant que liant.
7. Composition photosensible selon la revendication 6, caractérisée en ce qu'elle contient en outre un solvant.
8. Composition photosensible selon la revendication 6 ou 7, caractérisée en ce que le o-quinonediazide est un ester (mixte) d'un composé phénolique comportant au moins deux groupes hydroxy.
9. Matériau de reproduction photosensible, essentiellement constitué d'un support et d'une couche photosensible, caractérisé en ce qu'une composition selon une ou plusieurs des revendications 6 à 8 est contenue en tant que couche photosensible.
10. Matériau de reproduction photosensible selon la revendication 9, caractérisé en ce qu'après insolation selon une image et développement subséquent, il est traité thermiquement à des températures d'environ 250°C.