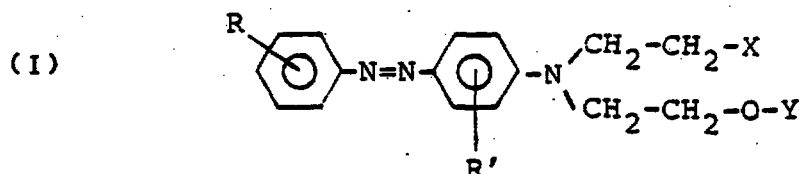


Description

The invention relates to new compounds of the general formula I



5 in which

R and R' independently of one another are hydrogen, alkyl with up to 4 C atoms or halogen, X is hydrogen or O-Y and

Y is alkyl or acyl with in each case up to 4 C atoms
10 or optionally substituted aryl with up to 10 C atoms, and their use as radiation-absorbing substances in negatively operating photoresist compositions.

Negative photoresists are at present used to a great extent in the production of electric circuits and
15 electronic components. In particular, the structuring of the conductor or semiconductor substrates by photographic techniques in the production of highly and very highly integrated semiconductor circuits is effected with the aid of photoresists.

20 The customary negative photoresist compositions of today contain, as a solution in an organic solvent, cyclised rubber, as the essential component, and a photo-sensitive bisazido compound which acts as a photo-cross-linking agent.

25 According to customary procedures, the substrate surfaces are coated with the photoresist composition by known methods and the solvent is removed by predrying at temperatures of about 100°C. The photoresist coating is then exposed to, in general, ultraviolet radiation
30 imagewise through a negative mask, whereupon crosslinking of the polymer material is caused, in accordance with the image pattern, in the areas of the coating exposed to the radiation by the radiation-sensitive bisazido compound.

The non-exposed parts of the coating are removed by treatment with a solvent, which serves as a developer, the insoluble areas of the image crosslinked by radiation remaining on the substrate surface as a relief structure.

5 The high degree of miniaturisation, which is still progressing further, of electronic components produced with the aid of photoresist techniques demands an extremely high quality of the photoresist compositions used, especially in respect of the resolving power to be
10 achieved and of the adhesion of the resist coating to the substrate.

 However, negative photoresists according to the state of the art do not adequately fulfil these quality requirements. Thus, for example, when such photoresists
15 are used on substrates which have a surface of high reflecting power, which is as a rule the case with semiconductor materials and metals, such as, for example, silicon, aluminium, copper, chromium and the like - the resolving power of the photoresists during irradiation
20 is considerably reduced by reflection phenomena occurring on the surface of the substrate. As a result of irregular scattering of the incident light on the substrate surface, the scattered light penetrates into areas of the resist coating which, according to the image pattern of
25 the negative mask, should not be exposed to radiation. The crosslinking of the polymer material which is also triggered off in these areas results, after development, in relief structures with an increased line width and reduced edge sharpness. Due to these effects, fine and
30 very fine structures such as are to be produced in microelectronics can be obtained only with a limited fidelity of reproduction.

 Attempts to solve the problem described are known.

35 Thus, for example, Japanese Auslegeschrift No. 37562/76 proposes the addition of radiation-absorbing dyestuffs, in particular 4-N,N-diethylaminoazobenzene, to photoresist compositions based on cyclised rubber and

photosensitive bisazido compounds to reduce these adverse effects.

However, the compounds mentioned here as radiation absorbers have the disadvantage that they have a great tendency to sublime at temperatures up to 100°C, such as are required during predrying to achieve good adhesion of the resist coating to the substrate. The concentration of these substances in the photoresist coating is thereby reduced to such a degree that a high, reproducible resolution cannot be achieved under these conditions.

The same applies to the compounds of U.S. Patent Specification 4,287,289.

U.S. Patent Specification 4,268,603 describes negative photoresist compositions based on cyclised rubber and bisazido compounds to which a mixture of radiation-absorbing substances which emit fluorescence is added to avoid the adverse effects described. Aminoazobenzene derivatives, inter alia the compound 4-N-ethyl-N-(2-hydroxyethyl)-aminoazobenzene, are mentioned here as radiation absorbers. These photoresists of relatively complicated composition are said to ensure high fidelity of reproduction of the resist image.

It has been found, however, that the radiation absorbers used are not sufficiently soluble in the photoresist formulations in order to be present in the resist coating in an adequately effective concentration. It has furthermore been found that some of the dissolved dyestuff crystallises out as solid substance in the coating during coating of the substrates and subsequent drying.

Such resist materials accordingly still have disadvantages in respect of current requirements.

There was thus the object of discovering new radiation-absorbing substances which effectively suppress the undesirable scattering effects which occur in photoresist coatings, especially on highly reflecting substrates. These substances should be sufficiently soluble

in negative photoresist formulations and should not volatilise out of the resist coating by evaporation or sublimation under the conditions of predrying at temperatures of about 100°C. to increase the adhesion.

5 Furthermore, negatively operating photoresist compositions which contain these radiation-absorbing substances and which fulfil the extremely high quality requirement in respect of resolving power, edge sharpness and adhesion are to be provided.

10 This object has been achieved by providing the abovementioned new compounds of the general formula I.

In British Patent Specification 422,843 the production of azo dyestuffs of the present substitution type is described, but without naming the compounds selected
15 for the present application and without making reference to specific properties which are important for use in photoresists.

Surprisingly, it has been found that, because of their good solubility, their low volatility and their
20 absorption properties, these compounds are outstandingly suitable as radiation-absorbing additives for negatively operating photoresist compositions.

The invention thus relates to compounds of the general formula I.

25 The invention furthermore relates to the use of compounds of the general formula I as radiation-absorbing substances in negatively operating photoresist compositions.

The invention furthermore relates to negatively
30 operating photoresist compositions which are based on cyclised rubber and photosensitive bisazido compounds and contain the compounds of the general formula I as radiation-absorbing substances.

The radicals R and R' on the aromatic rings are
35 as a rule hydrogen, but can also each be halogen, in particular chlorine and bromine, or alkyl with up to 4 C atoms, such as methyl, ethyl, n- and i-propyl and n-, i- and t-butyl, and can occupy any of the ring positions

which are still free.

As regards the radicals X and Y in the substituents on the amino nitrogen, X represents hydrogen or the grouping O-Y. Y represents one of the alkyl groups listed above with up to 4 C atoms or represents an acyl group, also with up to 4 C atoms, such as, for example, acetyl, propionyl or butyryl, or represents aryl or substituted aryl with up to 10 C atoms. The latter can be, for example: phenyl, alkyl-substituted phenyl, such as tolyl, or naphthyl. Compounds in which R and R' are hydrogen, X is hydrogen or O-Y and O-Y is ethoxy, acetoxy or phenoxy are preferably used as radiation absorbers in negative photoresists.

The following compounds are particularly preferred:

4-N-ethyl-N-(2-phenoxyethyl)-aminoazobenzene
4-N,N-bis(2-ethoxyethyl)-aminoazobenzene and
4-N,N-bis(2-acetoxyethyl)-aminoazobenzene.

The compounds of the formula I are prepared in a simple manner by known methods, by diazotisation of aniline and reaction of the diazonium compound with correspondingly N-substituted aniline derivatives. The N-substituted aniline derivatives are either commercially available or can easily be prepared by N-substitution of aniline.

All the compounds according to the general formula I absorb radiation in the wavelength range from 350 to 450 nm and have absorption maxima, in particular, in the range from 400 to 420 nm. On the basis of these absorption properties, these substances are particularly suitable as absorbing additives for negative photoresists in order to suppress scattering effects in resist coatings on highly reflecting substrates during structuring with ultraviolet light of this wavelength range.

Negative photoresist compositions are to be understood as those which contain, as the essential component, cyclised rubber and, as photocrosslinking agents, photosensitive bisazido compounds, dissolved in an

organic solvent, such as, for example, xylene. Appropriate components are adequately known and are usually employed in photoresists according to the state of the art. The class of substance described by the term
5 cyclised rubber includes polymer materials, such as cyclised polyisoprene, cyclised isobutylene, cyclised polybutadiene and the like. Polymer materials based on cyclised polyisoprene are preferred.

The photosensitive substances used as photo-
10 crosslinking agents are aromatic bisazido compounds such as are described, for example, in U.S. Patent Specifications 2,852,379 and 2,940,853 and in German Patent Application 32 34 301. The compound 2,6-bis-[(4-azido-phenyl)methylene]-4-methylcyclohexanone has achieved by
15 far the greatest industrial importance and is therefore particularly preferred.

The compounds of the formula I are more than sufficiently soluble in the resist compositions containing the main components above to be present in the resist
20 coating in an adequately effective concentration. In contrast to radiation absorbers according to the prior art, these compounds do not crystallise out during coating of the substrates or during drying.

The particular advantage of the radiation
25 absorbers according to the invention is that they hardly volatilise at all out of the resist coating by evaporation or sublimation under the conditions of predrying at temperatures of about 100°C. Even at temperatures of 120°C and during drying times of more than 2 hours, the
30 concentration of the compounds according to the invention in the coating remains remarkably constant.

The predrying operation at these temperatures is therefore of particular importance, because it imparts to the resist coating an increased adhesion to the sub-
35 strate. This is indispensable in the current production processes for highly miniaturised electronic circuits.

The photoresist compositions according to the invention can contain these new radiation-absorbing

substances in an amount of 0.1 to 7, preferably 0.5 to 4, per cent by weight, based on the amount of cyclised rubber.

In this concentration range, they very effectively prevent virtually any light scattering in the resist coating during irradiation of substrates coated with the photoresist materials according to the invention.

Photoresist relief structures of the highest quality in respect of resolving power, edge sharpness and adhesion can thus be obtained, even on highly reflecting substrates, by the present invention.

Example 1:

Preparation of 4-N-ethyl-N-(2-phenoxyethyl)-aminoazobenzene (substance 1).

5.2 g of aniline are diazotised with 4.1 g of sodium nitrite in sulfuric acid-aqueous solution in the customary manner; the resulting diazonium salt solution is diluted with 50 ml of ethanol. This solution is added dropwise to a solution of 13.9 g of N-ethyl-N-(2-phenoxyethyl)-aniline hydrochloride in 50 ml of 50% ethanol at 5 - 10°C. The pH value of the reaction mixture is then brought to 4 with 2 N sodium hydroxide solution, and a further 50 ml of ethanol are added.

The mixture is stirred at 0 - 5°C, the pH value falling to about 3. The mixture is brought to pH 4 again by renewed addition of 2 N sodium hydroxide solution, and the product precipitated is filtered off with suction, washed with water and dried. After recrystallisation from isopropanol or purification by chromatography, dark yellow crystals of m.p. 85 - 86°C are obtained.

The following compounds are prepared analogously: 4-N,N-bis(2-ethoxyethyl)-aminoazobenzene (substance 2) 4-N,N-bis(2-acetoxyethyl)-aminoazobenzene (substance 3).

Example 2:

Determination of the tendency towards sublimation.

In each case 10 g of cyclised polyisoprene are dissolved in 90 g of xylene and in each case 0.3 g of substance 1, 2, 3 or 4-N,N-diethylaminoazobenzene

(comparison substance 4) are added. Quartz discs are each coated with the solutions thus obtained.

No comparable resist formulation can be produced with 4-N-ethyl-N-(2-hydroxyethyl)-aminoazobenzene (comparison substance 5), since about 0.1 g of undissolved substance remains after filtration of the resist solution.

The extinction values in the particular absorption maxima (408 - 412 nm), measured after various drying times at elevated temperatures and in per cent in comparison with the starting value, serve as a measure of the tendency of the absorber substances contained in the resist coating to sublime.

Drying conditions	Extinction of the resist coating, containing substance			
	1	2	3	4
80°C, 30 minutes	100 %	100 %	100 %	95 %
80°C, 150 minutes	100 %	100 %	100 %	75 %
100°C, 30 minutes	100 %	100 %	98 %	90 %
100°C, 150 minutes	100 %	95 %	90 %	60 %
120°C, 30 minutes	100 %	95 %	95 %	81 %
120°C, 150 minutes	100 %	85 %	78 %	50 %

Example 3:

Production of negative relief images.

Silicone wafers which have first been provided with a 0.2 μ m thick aluminium coating on the surface are each coated with a photosensitive composition of in each case 10 g of cyclised polyisoprene, 90 g of xylene, 0.4 g of 2,6-bis-[(4-azidophenyl)methylene]-4-methylcyclohexanone and

- A) 0.3 g of substance 1,
- B) 0.3 g of substance 2,
- C) 0.3 g of substance 3,
- D) 0.3 g of comparison substance 4 or
- E) 0.3 g of comparison substance 5⁺.

⁺ After filtration of the resist solution, about 0.1 g

of undissolved substance remains in solid deposits in the coating; cannot be used.

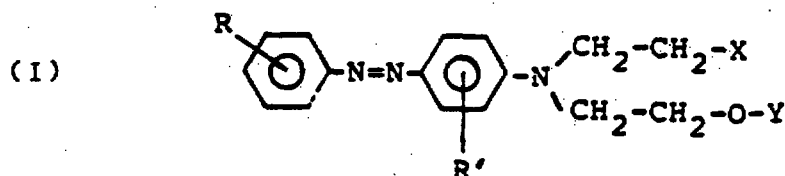
After drying (20 minutes, 100°C), the resulting photosensitive coatings (coating thickness 1 μm) are exposed imagewise through a resolution test mask of chromium. Development is effected by treatment with a commercially available developer solution for 50 seconds.

	Photosensitive composition	Resolving power	Adhesion
10	A	1.8 μm	good
	B	2.1 μm	good
	C	2.0 μm	good
	D	2.6 μm	moderate (drying at 85°C)
15	E	. /. ++	good

Patent Claims

for the Contracting States CH, DE, FR, GB, IT, LI, NL, SE

1. Compounds of the general formula I



in which

R and R' independently of one another are hydrogen, alkyl with up to 4 C atoms or halogen,

X is hydrogen or O-Y and

Y is alkyl or acyl with in each case up to 4 C atoms or optionally substituted aryl with up to 10 C atoms.

2. Use of compounds of the general formula I according to Claim 1 as radiation-absorbing substances in negative-working photoresist compositions.

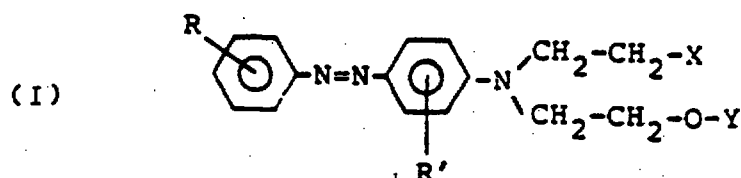
3. Negative-working photoresist compositions based on cyclised rubber and photosensitive bisazido compounds, characterised in that they contain compounds of the general formula I according to Claim 1 as radiation-absorbing substances.

4. Photoresist compositions according to Claim 3, characterised in that they contain the compounds of the formula I according to claim 1 in an amount of 0.1 - 7% by eight, preferably 0.5 - 4% by weight, based on the amount of cyclised rubber.

Patent Claims

for the Contracting State AT

1. Use of compounds of the general formula I



in which

R and R' independently of one another are hydrogen, alkyl with up to 4 C atoms or halogen,



38

X is hydrogen or O-Y and

Y is alkyl or acyl with in each case up to 4 C atoms or optionally substituted aryl with up to 10 C atoms, as radiation-absorbing substances in negative-working photoresist compositions.

2. Negative-working photoresist compositions based on cyclised rubber and photosensitive bisazido compounds, characterised in that they contain compounds of the general formula I according to Claim 1 as radiation-absorbing substances.

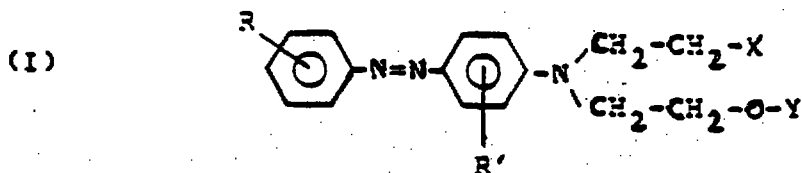
3. Photoresist compositions according to Claim 2, characterised in that they contain the compounds of the formula I according to claim 1 in an amount of 0.1 - 7% by eight, preferably 0.5 - 4% by weight, based on the amount of cyclised rubber.



(39)

Claims (as printed)

for the Contracting States CH, DE, FR, GB, IT, LI, NL, SE

1. Compounds of the general formula I

in which

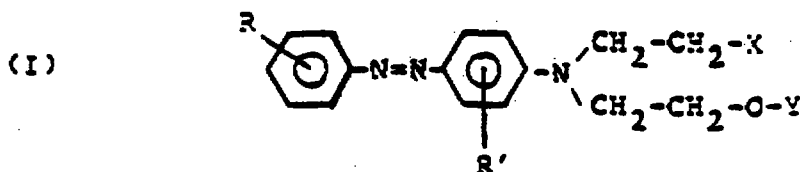
R and R' independently of one another denote hydrogen, alkyl with up to 4 C atoms or halogen,

X denotes hydrogen or O-Y and

Y denotes alkyl or acyl with in each case up to 4 C atoms or optionally substituted aryl with up to 10 C atoms.

2. Use of compounds of the general formula I according to claim 1 as radiation-absorbing substances in negatively operating photoresist compositions.**3. Negatively operating photoresist compositions based on cyclised rubber and photosensitive bisazido compounds, characterised in that they contain compounds of the general formula I according to claim 1 as radiation-absorbing substances.****4. Photoresist compositions according to Claim 3, characterised in that they contain the compounds of the formula I according to claim 1 in an amount of 0.1 - 7% by weight, preferably 0.5 - 4% by weight, based on the amount of cyclised rubber.****Claims (as printed)**

for the Contracting State AT

1. Use of compounds of the general formula I

in which

R and R' independently of one another denote hydrogen, alkyl with up to 4 C atoms or halogen,

X denotes hydrogen or O-Y and

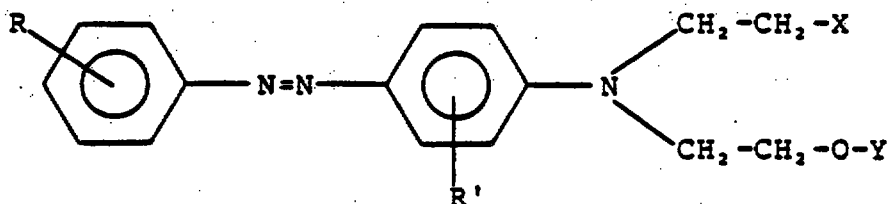
Y denotes alkyl or acyl with in each case up to 4 C atoms or optionally substituted aryl with up to 10 C atoms, according to claim 1 as radiation-absorbing substances in negatively operating photoresist compositions.

2. Negatively operating photoresist compositions based on cyclised rubber and photosensitive bisazido compounds, characterised in that they contain compounds of the general formula I according to claim 1 as radiation-absorbing substances.**3. Photoresist compositions according to Claim 2, characterised in that they contain the compounds of the formula I according to claim 1 in an amount of 0.1 - 7% by weight, preferably 0.5 - 4% by weight, based on the amount of cyclised rubber.**

H9

Revendications (as printed)

pour les Etats contractants CH, DE, FR, GB, IT, LI, NL, SE

1.- Composés de formule générale I :

dans laquelle:

R et R' représentent chacun, indépendamment l'un de l'autre, l'hydrogène, un groupe alkyle contenant jusqu'à 4 atomes de carbone ou un halogène.

X représente l'hydrogène ou le groupe O-Y et

Y représente un radical alkyle ou acyle contenant chacun jusqu'à 4 atomes de carbone ou un radical aryle éventuellement substitué contenant jusqu'à 10 atomes de carbone.

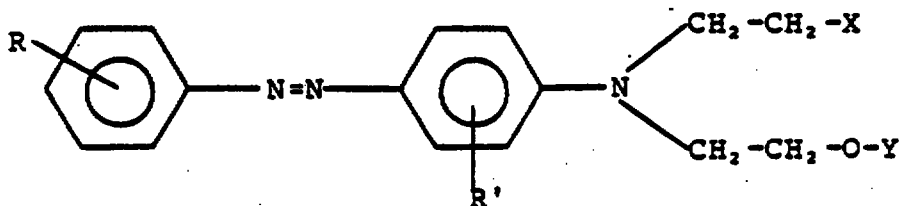
2.- Utilisation des composés de formule générale I selon la revendication 1, en tant que substances absorbant les radiations dans des compositions de photorésists opérant en négatif.

3.- Compositions de photorésists opérant en négatif, à base de caoutchouc cyclisé et de composés photosensibles du type bis-azide, caractérisées en ce qu'elles contiennent en tant que substances absorbant les radiations des composés de formule générale I selon la revendication 1.

4.- Compositions de photorésists selon la revendication 3, caractérisées en ce qu'elles contiennent les composés de formule I selon la revendication 1 en proportions de 0,1 à 7 % en poids, de préférence de 0,5 à 4 % en poids, par rapport à la quantité de caoutchouc cyclisé.

Revendications (as printed)

pour l'Etat contractant AT

1.- Utilisation de composés de formule générale I:

dans laquelle

R et R' représentent chacun, indépendamment l'un de l'autre l'hydrogène, un groupe alkyle contenant jusqu'à 4 atomes de carbone ou un halogène,

X représente l'hydrogène ou le groupe O-Y et

Y représente un radical alkyle ou acyle contenant chacun jusqu'à 4 atomes de carbone ou un radical aryle éventuellement substitué contenant jusqu'à 10 atomes de carbone.

en tant que substances absorbant les radiations dans des compositions de photorésists opérant en négatif.

2.- Compositions de photorésists opérant en négatif, à base de caoutchouc cyclisé et de composés photosensibles du type bis-azide, caractérisées en ce qu'elles contiennent des composés de formule générale I selon la revendication 1 en tant que substances absorbant les radiations.

3.- Compositions de photorésists selon la revendication 2, caractérisées en ce qu'elles contiennent les composés de formule I selon la revendication 1 en proportions de 0,1 à 7 % en poids, de préférence de 0,5 à 4 % en poids, par rapport à la quantité de caoutchouc cyclisé.

