

The invention relates to novel bis-1,2-naphthoquinone-2-diazide-sulfonic acid amides of secondary diamines, to their use in a light-sensitive mixture and to radiation-sensitive copying material.

5 A large number of derivatives, above all aromatic esters, of 1,2-naphthoquinone-2-diazide-sulfonic acids are already known, which can be used as light-sensitive components in positive-working copying materials. In the book by Jaromir Kosar: "Light-Sensitive Systems", John
10 Wiley + Sons/New York, 1965, pages 343 to 351, a number of light-sensitive naphthoquinone-diazides are described.

US-A 3,046,110 discloses esters and amides composed of a) 1,2-naphthoquinone-2-diazide-4- or -5-sulfonyl chloride and b) an aromatic hydrocarbon which is simultaneously
15 substituted by hydroxy and amino groups or by a plurality of amino groups, or by an aliphatic or aliphatic-aromatic diamine. The compounds are used as light-sensitive coating in the preparation of printing plates.

The continuing miniaturization in the manufacture of
20 electronic components requires the production of increasingly smaller structures. An important step in the manufacture of such components is the imagewise exposure and subsequent development of light-sensitive films which are applied to the material which is to be structured.

25 The wavelength of the light used for exposure is a factor which limits the resolution capacity of light-sensitive structures, and structures having smaller dimensions can be produced with light of shorter wavelength. The conventionally used materials, however, show good light
30 sensitivity only in the visible or near UV range (365 - 450 nm), whereas they have only inadequate light sensitivity in the shorter-wavelength range (300 - 350 nm). The hitherto used naphthoquinone-diazide derivatives have unsuitable absorption properties in the
35 so-called mid-UV (300 - 350 nm), i.e. the materials are

only slightly bleached, if at all, by exposure at above all 313 nm.

The effect of substituents in naphthoquinone-diazides on the absorption in this range has already been investigated (Grant Willson et al., Design of a positive resist for projection lithography in the mid-UV; Sixth International Technical Conference on Photopolymers, November 1982, Ellenville/USA), it being found that naphthoquinone-diazide-4- and -5-alkylsulfonates have favorable absorption properties in the range from 300 to 350 nm.

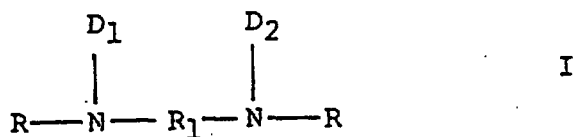
The mercury vapor lamps conventionally used in exposure apparatus have, in the wavelength range from 300 to 350 nm, two emission lines at 313 and 334 nm, so that exposure of suitable materials in this wavelength range is possible.

The disadvantage of inadequate light sensitivity on exposure in the mid-UV has already been recognized, and attempts to overcome it were made in EP-A 0,085,761, corresponding to U.S. Patent 4,397,937, by the use of bis-1,2-naphthoquinone-2-diazide-sulfonic acid esters of aliphatic diols. However, only a very limited number of tricyclic diols have so far been mentioned and, in addition, their preparation is possible only with the use of 4-dimethylamino-pyridine as a very expensive catalyst. The latter also applies to the aliphatic esters of naphthoquinone-diazide-sulfonic acids, which are mentioned in EP-A 0,147,596 and the preparation of which is possible only with the use of 4-dimethylaminopyridine or 4-(1-pyrrolidino)-pyridine.

The instability of arylsulfonic acid alkyl esters, which are used as alkylating agents, for example for the preparation of ethers (compare Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Volume IX, pages 674 et seq., 4th edition 1955; G. Thieme Verlag, Stuttgart), is generally known in the literature.

It is the object of the invention to provide novel, stable 1,2-naphthoquinone-2-diazide-sulfonic acid derivatives which, as photo-active components, impart a higher light sensitivity than that of hitherto known mixtures to light-sensitive mixtures on exposure in the mid-UV range (300 - 350 nm), these mixtures having a light sensitivity, which is at least comparable to that of the mixtures used at present or is even better, on exposure in the visible or near UV range. Furthermore, these derivatives should also be easy to prepare industrially.

The present invention relates to bis-1,2-naphthoquinone-2-diazide-sulfonic acid amides of secondary diamines, of the formula I



in which

R is a straight-chain or branched, unsubstituted or hydroxyl-substituted alkyl, cycloalkyl or aralkyl radical which has 1 - 14 carbon atoms and the carbon chain of which can be interrupted by ether oxygen atoms,

R₁ is an alkylene radical which has 2 - 12 carbon atoms and the carbon chain of which is interrupted by ether oxygen atoms, or is an arylene-dialkyl radical having 8 - 18 carbon atoms, it being possible in the case of polynuclear compounds for the aromatic members to be linked by a single bond, by -O-, -S-, -SO₂-, -CO-, -CR₂R₃-, N[C₁₋₃-alkyl]CO- or C₂₋₅-alkyl which can be interrupted by ether oxygen atoms, and

R₂ and R₃ can be identical or different and are hydrogen or substituted or unsubstituted alkyl radicals having 1 or 2 carbon atoms,

or

5 R and R₁ together are formed by a cycloalkyl radical having 4 - 16 carbon atoms, it being possible in the case of polynuclear compounds for the cycloaliphatics to be linked by a carbon chain of 1 - 6 carbon atoms,

and

10 D₁ and D₂ are identical or different and are 1,2-naphthoquinone-2-diazide-4- or -5-sulfonyl radicals.

Those compounds of the formula I are preferred in which

15 R is a straight-chain or branched, unsubstituted or hydroxyl-substituted alkyl or cycloalkyl radical which has 1 - 8, preferably 1 - 4, carbon atoms and the carbon chain of which can be interrupted by ether oxygen atoms, or an aralkyl radical having 7 - 14 carbon atoms,

20 R₁ is an alkylene radical which has 2 - 10 carbon atoms and the carbon chain of which is interrupted by 1 or 2 ether oxygen atoms, or is an arylenedialkyl radical having 8 - 14 carbon atoms, it being possible in the case of polynuclear compounds for the aromatic members to be linked by a single bond, by -O-, -S-, -SO₂-,
25 -CO-, -CR₂R₃-, N[C₁₋₃-alkyl]CO- or C₂₋₅-alkyl which can be interrupted by ether oxygen atoms, and

30 R₂ and R₃ can be identical or different and are hydrogen or unsubstituted or substituted alkyl radicals (for example substituted by one or more fluorine atoms) having 1 or 2 carbon atoms,

or

R and R₁ together can be formed by a cycloalkyl radical having 4 - 16 carbon atoms, it being possible in the case of polynuclear compounds for the cycloaliphatics to be linked by a carbon chain of 1 - 6 carbon atoms,

and

D₁ and D₂ are identical or different and are 1,2-naphthoquinone-2-diazide-4- or -5-sulfonyl radicals.

10 The present invention also relates to the use of the bis-1,2-naphthoquinone-2-diazide-sulfonic acid amides according to the invention as radiation-sensitive components in a radiation-sensitive mixture and to radiation-sensitive copying material prepared from them.

15 The naphthoquinone-diazide compounds according to the invention are used as the radiation-sensitive component in radiation-sensitive mixtures, 4- or 5-sulfonyl derivatives being used individually as the radiation-sensitive component or as a mixture or as mixed 4,5-sulfonyl derivatives. The use of a mixture of 4- and 5-sulfonyl derivatives is particularly preferred. Such mixtures or also the 4/5 mixed sulfonamides show an advantageous and uniform high absorption in the mid-UV range (300 - 350 nm), in which the two Hg emission lines
25 at 313 nm and 334 nm are located.

The compounds according to the invention are prepared by known processes by reacting secondary diamines with reactive naphthoquinone-diazide-sulfonic acid derivatives, say the acid chloride. Because of the higher
30 reactivity of the amines as compared with the alcohols, the preparation can be made less expensive, because the use of expensive catalysts is avoided. Preferred processes are the reactions in inert solvents, such as ketones or chlorinated hydrocarbons, in the presence of

inorganic or organic bases, such as sodium carbonate or tertiary amines such as triethylamine. However, the naphthoquinone-diazide-sulfonic acid amides according to the invention can also be prepared under the conditions of phase transfer catalysis, for example in a system of methylene chloride/aqueous solution of sodium carbonate or tetraalkylammonium hydroxide with a suitable catalyst such as tetrabutylammonium bromide.

General instructions for the preparation of the naphthoquinone-diazide-sulfonic acid amides according to the invention are given below:

0.1 mol of secondary diamine is added dropwise with stirring to 0.2 mol of 1,2-naphthoquinone-2-diazide-sulfonic acid chloride and 0.22 mol of sodium carbonate or triethylamine in 400 ml of acetone, the temperature being kept below 25°C by cooling. After the end of the dropwise addition, stirring is continued for 1 hour

and

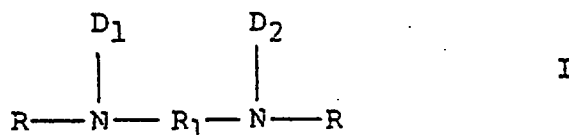
a) if the naphthoquinone-diazide-sulfonic acid amide has already precipitated, the latter is filtered off with suction, washed with cold acetone and then with water, and the filter residue is dried under reduced pressure or in a circulating-air drying oven at a moderately elevated temperature,

or

b) if the bis-naphthoquinone-diazide-sulfonic acid amide is completely soluble in the reaction mixture, the batch is freed from inorganic constituents by filtration with suction. The filtrate is stirred into ten times the quantity of 4% aqueous hydrochloric acid, and the precipitated bis-sulfonic acid amide is filtered off, washed with water until free of acid and dried as under a).

The 1,2-naphthoquinone-2-diazide-sulfonamides are thus obtained in good to very good and frequently almost quantitative yields. The compounds according to the invention prepared in this way are obtained in such a
 5 purity that further purification is unnecessary before use in a radiation-sensitive mixture. The purity is frequently so good that the values determined experimentally by combustion analysis correspond to the calculated values. In some cases, however, recrystallization or reprecipitation in suitable solvents or
 10 solvent mixtures is advantageous.

The invention also relates to a radiation-sensitive mixture containing a polymeric resinous binder which is insoluble in water and soluble or swellable in aqueous-
 15 alkaline solution, and a 1,2-naphthoquinone-2-diazide-sulfonic acid derivative, which, as the 1,2-naphthoquinone-2-diazide-sulfonic acid derivative, comprises at least one compound of the said formula I



in which

- 20 R is a straight-chain or branched, unsubstituted or hydroxyl-substituted alkyl, cycloalkyl or aralkyl radical which has 1 - 14 carbon atoms and the carbon chain of which can be interrupted by ether oxygen atoms,
- 25 R₁ is an alkylene radical which has 2 - 12 carbon atoms and the carbon chain of which is interrupted by ether oxygen atoms, or is an arylenedi-alkyl radical having 8 - 18 carbon atoms, it
 30 being possible in the case of polynuclear compounds for the aromatic members to be linked by a single bond, by -O-, -S-, -SO₂-, -CO-, -CR₂R₃-, N[C₁₋₃-alkyl]CO- or C₂₋₅-alkyl which can be interrupted by ether oxygen atoms, and

R_2 and R_3 can be identical or different and are hydrogen or substituted or unsubstituted alkyl radicals having 1 or 2 carbon atoms,

or

5 R and R_1 together are formed by a cycloalkyl radical having 4 - 16 carbon atoms, it being possible in the case of polynuclear compounds for the cycloaliphatics to be linked by a carbon chain of 1 - 6 carbon atoms,

10 and

D_1 and D_2 are identical or different and are 1,2-naphthoquinone-2-diazide-4- or -5-sulfonyl radicals.

Mixtures are preferred in which

15 R is a straight-chain or branched, unsubstituted or hydroxyl-substituted alkyl or cycloalkyl radical which has 1 - 8, preferably 1 - 4 carbon atoms and the carbon chain of which can be interrupted by ether oxygen atoms, or an aralkyl radical
20 having 7 - 14 carbon atoms,

R_1 is an alkylene radical which has 2 - 10 carbon atoms and the carbon chain of which is interrupted by 1 or 2 ether oxygen atoms, or is an arylenedialkyl radical having 8 - 14 carbon
25 atoms, it being possible in the case of polynuclear compounds for the aromatic members to be linked by a single bond, by -O-, -S-, -SO₂-, CO-, -CR₂R₃-, N[C₁₋₃-alkyl]CO- or C₂₋₅-alkyl which can be interrupted by ether oxygen atoms, and

30 R_2 and R_3 can be identical or different and are hydrogen or unsubstituted or substituted alkyl radicals

(for example substituted by one or more fluorine atoms) having 1 or 2 carbon atoms,

or

5 R and R₁ together can be formed by a cycloalkyl radical having 1 - 16 carbon atoms, it being possible in the case of polynuclear compounds for the cycloaliphatics to be linked by a carbon chain of 1 - 6 carbon atoms,

and

10 D₁ and D₂ are identical or different and are 1,2-naphthoquinone-2-diazide-4- or -5-sulfonyl radicals.

15 The radiation-sensitive mixtures according to the invention are distinguished by a high light sensitivity in practice, which is generally superior to the conventional systems in the visible or near UV range and is markedly better than that of the hitherto known systems in the mid-UV range. The radiation-sensitive mixtures formulated with the naphthoquinone-diazide compounds according to
20 the invention also show good sensitivities to high-energy radiation, for example electron beams or X-rays, and give good lithographic results. Moreover, very good contrasts values are achieved with the radiation-sensitive layers.

25 High light sensitivity of the mixture is an essential factor in the production of microelectronic circuits or components, above all in the so-called "in-line" processing of wafers, where the throughput of the wafers is determined by the most time-consuming process step. A critical point here is the exposure time, i.e. the
30 throughput in the exposure apparatus. Above all in the case of monochromatic irradiation or exposure with shorter-wavelength actinic light, this usually led to unsatisfactory cycle times in the past and hence to

inadequate throughput of wafers, which finally entailed an unacceptable, slow production rate.

5 The concentration of the naphthoquinone-diazide-sulfonic acid amides according to the invention in the radiation-sensitive mixture can fluctuate within relatively wide limits. In general, the proportion is about 4% to 40%, preferably between 6% and 25%, relative to the weight of the solids content of the mixture.

10 The light-sensitive mixtures according to the invention also contain a polymeric, water-insoluble resinous binder which dissolves in the solvents used for the mixture according to the invention and is also soluble or at least swellable in aqueous alkalis.

15 The novolak condensation resins proven in many positive copying materials based on naphthoquinone-diazides have also proved particularly useful and advantageous as an addition to the mixtures according to the invention with the novel naphthoquinone-diazide-sulfonic acid amides. The nature and quantity of the novolak resins can differ
20 depending on the application. Novolak proportions in total solids of between 60% and 96%, and particularly preferably 75 - 95%, are preferred. For special requirements such as adhesion, surface smoothness, special absorption properties etc., the light-sensitive mixture
25 can also contain small quantities of substances such as wetting agents, adhesion promoters and dyes.

Other suitable binders are polymeric binders with phenolic hydroxyl groups in side chains, such as, for example, vinylphenols or esters and amides of acrylic acid and
30 methacrylic acid with, for example, hydroquinone, pyrocatechol, resorcinol, pyrogallol or hydroxyphenylamine. In addition to the homopolymers, copolymers of the said monomers with one another or also with other polymerizable monomers such as styrene, methacrylic acid
35 methacrylate, biphenylol methacrylate or biphenylol

acrylate can also be used as binders in the mixtures according to the invention. Mixtures of the polymers with novolaks can also be used. The nature and quantity of the binders can differ depending on the application, but
5 largely corresponds to the ranges given for novolak.

For coating a suitable support for the preparation of the copying material according to the invention, the mixtures are generally dissolved in a solvent. The selection of the solvents must be matched to the intended coating
10 process, the layer thickness and the drying conditions. Suitable solvents for the mixture according to the invention are ketones, such as methyl ethyl ketone, or N-methylpyrrolidone, alcohol ethers such as ethylene glycol monoethyl ether or propylene glycol monoethyl ether,
15 alcohol ether-acetates such as ethylene glycol monoethyl ether-acetate or propylene glycol monoethyl ether-acetate, and esters such as butyl acetate. Mixtures of solvents can also be used, which can, inter alia, also contain xylene. In principle, all solvents can be used
20 which do not irreversibly react with the layer components.

The mixtures according to the invention can be used in copying materials such as photoresists for the micro-electronics industry. The preferred supports are silicon
25 wafers, which can also have been superficially oxidized. The layers which arise during the conventional micro-electronic fabrication processes such as, for example, silicon nitride, polysilicon, silicon oxide, polyimides or metals such as aluminum and also silicon implanted
30 with suitable doping materials, are likewise suitable as supports for the mixtures according to the invention. Wafers of GaAs alloys also represent suitable supports. Moreover, the mixtures according to the invention can be used in the production of printed circuit boards, the
35 supports conventional for this purpose being used. Further possible supports are aluminum plates which have undergone suitable pretreatment and are suitable for the

production of printing plates.

Coating of the supports conventional in the micro-electronics industry is carried out in the known manner by whirler-coating. However, coating-techniques such as
5 spraying, roller application, dipping, use of slot dies, blades or application by casting can also be used for these and other supports.

Conventional light sources are used for exposure, and exposure apparatus can be used with particular advantage,
10 the optical systems of which are permeable only for actinic light in the mid-UV range.

The aqueous-alkaline solutions which are used for developing and which can also contain minor amounts of wetting agent, remove those areas of the light-sensitive
15 layer which have been struck by light and thus generate a positive image of the original.

The radiation-sensitive mixtures according to the invention are preferably used in lithographic processes for the production of integrated circuits or of discrete
20 electrical components. They are used here as a masking material for various process steps such as, for example, etching of the support, implantation of ions into the support or deposition of materials on the support.

For a comparison of the light sensitivities, the photo-resist formulation, i.e. the weight ratio of radiation-sensitive component to binder, and the developer were
25 selected such that, during the developing step, the mixtures according to the invention always had approximately the same loss in the dark as the comparison resist which was developed in the developer usual for the
30 latter. The loss in the dark describes the reduction in layer thickness of a light-sensitive layer, which is caused by the in most cases slight solubility of the layer in the developer during the developing step even in

the unexposed areas. The comparison was always carried out at the same layer thicknesses. The layer thickness was adjusted by choosing a suitable solids content.

After filtration, the radiation-sensitive mixtures were
5 applied to suitable supports, such as silicon wafers, by whirler-coating. Adjustment of the speed of rotation of the coating whirler permits accurate adjustment of the layer thickness of the photoresists. The layers were dried for 30 minutes at 90°C in a circulating-air drying
10 cabinet. After the drying process, the layer thicknesses of the photoresists used for the light sensitivity comparison were 1.0 μm .

Of course, lower and higher layer thicknesses can also be produced with the mixtures according to the invention,
15 and the ratio of radiation-sensitive component to the binder and the total solids content must then be adapted according to the application, in order to obtain the best lithographic results.

The light sensitivity comparisons were carried out by
20 exposure with the conventional wavelengths (365 - 436 nm) and in the mid-UV range (300 - 350 nm). Contact exposure apparatus from Messrs. Süss GmbH & Co. was used. The exposure power was measured by an Optical Associates Model 205 UV Powermeter which was fitted with sensors
25 suitable for the exposure wavelength ranges. Hg lamps and a suitable optical system for separating out certain wavelength ranges were installed in the exposure apparatus. The photoresists were exposed at constant exposure power for different times and then developed in
30 a suitable developer, the developing times being of the same length. Suitable developers are aqueous-alkaline solutions which are free of metal ions but can also contain metal ions such as sodium and/or potassium ions. The developer solutions can be buffered, for example with
35 silicate, borate or phosphate solutions or suitable mixtures of salt solutions, and they can also contain

small amounts of surfactants.

5 The measure of light sensitivity used was the value of the exposure energy density which was necessary for dissolving away 0.5 μm of the radiation-sensitive layer during the developing step. The layer thicknesses were measured by the layer thickness measuring instruments Sloan Dektak I or Dektak II or Rudolph FTM.

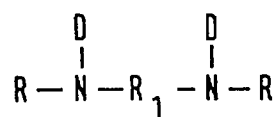
10 Under the above conditions, the radiation-sensitive mixtures according to the invention show, on exposure in the visible or near UV range, a light sensitivity which is at least comparable with the conventional photoresists and in most cases better and, on exposure in the mid-UV range, show a markedly increased light sensitivity which is about twice that of a conventional photoresist.

15 Examples of the bis-1,2-naphthoquinone-2-diazide-sulfonic acid amides according to the invention or used in the mixtures according to the invention and of the light-sensitive mixtures according to the invention are given below, but the inventive concept is not restricted to
20 these.

Examples 1 - 44

see Table I

Table 1



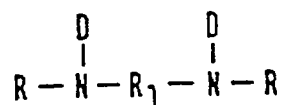
Nr.	R	R ₁	D	Analysis [%]	
				S _{calc.}	S _{found}
1	-CH ₃	-(CH ₂) ₂ -	1	11,61	11,2
2	-CH ₃	-(CH ₂) ₂ -	2	11,61	10,7
3	-CH ₃	-(CH ₂) ₆ -	1	10,54	10,6
4	-CH ₃	-(CH ₂) ₆ -	2	10,54	10,5
5	-CH ₃	-(CH ₂) ₁₀ -	1	9,65	9,5
6	-CH ₃	-(CH ₂) ₁₀ -	2	9,65	9,8
7	-CH ₃	-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -	1	10,01	9,3
8	-CH ₃	-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -	2	10,01	9,8
9	-CH ₃	-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -	3	10,01	10,0
10	-CH ₃	-CH ₂ -  -O-  -CH ₂ -	1	8,90	8,6
11	-CH ₃	-CH ₂ -  -O-  -CH ₂ -	2	8,90	8,7
12	-CH ₂ -CH ₂ -CH ₃	-(CH ₂) ₁₀ -	1	8,90	9,0
13	-CH ₂ -CH ₂ -CH ₃	-(CH ₂) ₁₀ -	2	8,90	8,9
14	-CH ₂ -CH ₂ -CH ₃	-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -	1	9,20	9,3
15	-CH ₂ -CH ₂ -CH ₃	-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -	2	9,20	8,7
16	-CH ₂ -CH ₂ -CH ₃	-CH ₂ -  -O-  -CH ₂ -	1	8,25	8,1
17	-CH ₂ -CH ₂ -CH ₃	-CH ₂ -  -O-  -CH ₂ -	2	8,25	8,4
18	-CH ₂ -CH ₂ -CH ₃	-CH ₂ -  -O-  -CH ₂ -	3	8,25	7,9
19	-CH(CH ₃) ₂	-(CH ₂) ₁₀ -	1	8,90	9,0
20	-CH(CH ₃) ₂	-(CH ₂) ₁₀ -	2	8,90	9,3
21	-CH(CH ₃) ₂	-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -	1	9,20	9,2
22	-CH(CH ₃) ₂	-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -	2	9,20	8,6

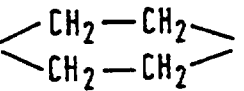
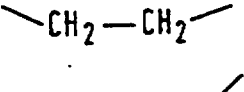
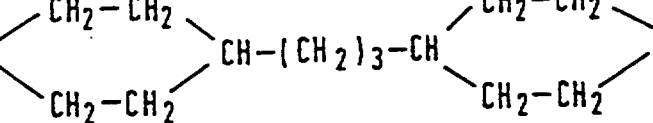
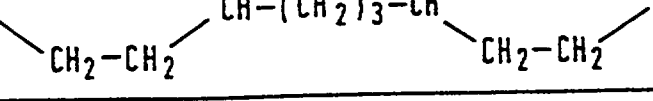
1) 1,2-naphthoquinone-2-diazide-5-sulfonyl

2) 1,2-naphthoquinone-2-diazide-4-sulfonyl

3) 1,2-naphthoquinone-2-diazide-4-sulfonyl and
-5-sulfonyl

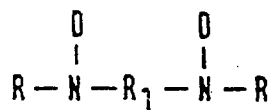
Table 1 (continuation)

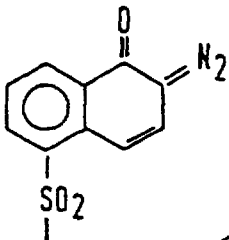
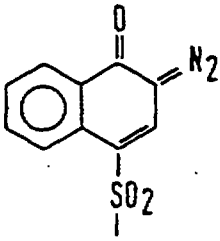


No.	R	R ₁	D	analysis [%]	
				S _{calc.}	S _{found}
23	-CH(CH ₃) ₂	-CH ₂ -  -CH ₂ -	1	9,36	9,2
24	-CH(CH ₃) ₂	-CH ₂ -  -CH ₂ -	2	9,36	9,3
25	-CH(CH ₃) ₂	-CH ₂ -  -O-  -CH ₂ -	1	8,25	8,2
26	-CH(CH ₃) ₂	-CH ₂ -  -O-  -CH ₂ -	2	8,25	8,1
27	-CH(CH ₃) ₂	-CH ₂ -  -O-  -CH ₂ -	3	8,25	8,3
28	-CH ₂ -CH(CH ₃) ₂	-(CH ₂) ₁₀ -	1	8,56	8,5
29	-CH ₂ -CH(CH ₃) ₂	-(CH ₂) ₁₀ -	2	8,56	8,3
30	-CH ₂ -CH(CH ₃) ₂	-CH ₂ -  -O-  -CH ₂ -	1	7,97	8,0
31	-CH ₂ -CH(CH ₃) ₂	-CH ₂ -  -O-  -CH ₂ -	2	7,97	7,9
32	-CH ₂ -(CH ₂) ₆ -CH ₃	-CH ₂ -  -O-  -CH ₂ -	1	6,99	6,5
33	-CH ₂ -(CH ₂) ₆ -CH ₃	-CH ₂ -  -O-  -CH ₂ -	2	6,99	6,9
34			1	11,64	11,6
35			2	11,64	11,4
36			1	9,50	9,6
37			2	9,50	9,4

- 1) 1,2-naphthoquinone-2-diazide-5-sulfonyl
- 2) 1,2-naphthoquinone-2-diazide-4-sulfonyl
- 3) 1,2-naphthoquinone-2-diazide-4-sulfonyl and
-5-sulfonyl

Table 1 (continuation)



No.	R	R ₁	D	analysis [%]	
				S _{calc.}	S _{found}
38	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array}$	$\text{CH}-(\text{CH}_2)_6-\text{CH}$	1	8,95	9,0
39			2	8,95	8,9
40	H ₃ C-O-CH ₂ -CH ₂ -	-CH ₂ -  -O-  -CH ₂ -	1	7,93	7,6
41	H ₃ C-O-CH ₂ -CH ₂ -	-CH ₂ -  -O-  -CH ₂ -	2	7,93	7,9
42	 -CH ₂ -CH ₂ -	-CH ₂ -  -O-  -CH ₂ -	1	7,12	7,1
43	 -CH ₂ -CH ₂ -	-CH ₂ -  -O-  -CH ₂ -	2	7,12	7,0
44	 -CH ₂ -CH ₂ -	-CH ₂ -  -O-  -CH ₂ -	3	7,12	6,3
1)  2) 					

- 1) 1,2-naphthoquinone-2-diazide-5-sulfonyl
 2) 1,2-naphthoquinone-2-diazide-4-sulfonyl
 3) 1,2-naphthoquinone-2-diazide-4-sulfonyl and
 -5-sulfonyl

Example 45

A silicon wafer is whirler-coated with a coating solution composed of

5 21.24 parts by weight of a cresol/formaldehyde novolak (melting range 106°C-115°C according to DIN 53181),

0.88 part by weight of compound 21,

10 0.88 part by weight of compound 24 and

77.00 parts by weight of propylene glycol monomethyl ether-acetate

15 such that a layer thickness of 1.0 μm results after drying. The layer is exposed at constant exposure power for different lengths of time and then developed in 0.530 N buffered NaOH. The energy density necessary to enable 0.5 μm of the layer to be dissolved away by the developing process is 50% lower after exposure in the mid-UV range and 25% lower after exposure at 365-436 nm than the energy density required for a conventional photoresist. A similar result is obtained when compound 21 in the above mixture is replaced by compound 5 and when compound 24 is replaced by compound 6. The said 20 conventional photoresist has, in a 31% solution, a relative decadic absorption coefficient of 0.74. Its solids fraction is composed of a cresol/formaldehyde novolak and suitable naphthoquinone-diazide derivatives. 25

Example 46

30 A silicon wafer is whirler-coated with a coating solution composed of

22.22 parts by weight of a cresol/formaldehyde novolak (melting range 122°C-132°C according to DIN 53181),

5 1.39 parts by weight of compound 17,

1.39 parts by weight of compound 25 and

75.00 parts by weight of propylene glycol mono-methyl ether-acetate

such that a layer thickness of 1.0 μm results after drying. Exposure is carried out as in Example 45; development is effected in 0.478 N buffered NaOH. The energy density necessary to enable 0.5 μm of the layer to be dissolved away by the developing process is 50% lower after exposure in the mid-UV range and 30% lower after exposure at 365-436 nm than the energy density required for a conventional photoresist (see Example 45). Similar results are obtained when the said combination of compounds 17 and 25 is replaced by corresponding mixtures of compounds 30/31, 16/17 or 25/26 or by compounds 9, 18 or 27. The solids content of the coating solutions can then vary. The normality of the developer must be adjusted to the particular mixture.

Example 47

25 A silicon wafer is whirler-coated with a coating solution composed of

18.67 parts by weight of a cresol/formaldehyde novolak (melting range 122°C-132°C according to DIN 53181),

30 2.33 parts by weight of compound 6 and

79.00 parts by weight of propylene glycol mono-
methyl ether-acetate

such that a layer thickness of 1.0 μm results after drying. Exposure is carried out as indicated in Example 45. Development is effected in 0.484 N buffered NaOH. After exposure in the mid-UV range, the energy density necessary to enable 0.5 μm of the layer to be dissolved away by the developing process is 45% lower and, after exposure at 365-436 nm, 25% lower than the energy density required for a conventional photoresist (see Example 45). Compound 6 can be replaced by compounds 5, 16, 17, 21, 22, 25 or 26, and the developer normalities must again be adjusted.

Example 48

15 A silicon wafer is whirler-coated with a coating solution composed of

13.9 parts by weight of poly-(pyrocatechol mono-
methacrylate),

2.8 parts by weight of compound 42 and

20 83.3 parts by weight of propylene glycol mono-
methyl ether-acetate

such that a layer thickness of 1.0 μm results after drying. After exposure, the layer obtained is distinguished by good solubility in 0.36 N NaOH, coupled with low solubility in the unexposed layer areas. Compound 42 can, inter alia, be replaced by compounds 5, 13, 19, 20, 23, 32 or 40 or by mixtures of naphthoquinone-4- and -5-sulfonyl derivatives such as, for example, 28/29, and the developer normalities must be adjusted.

Example 49

A coating solution composed of

7.60 parts by weight of a cresol/formaldehyde no-
volak (melting range
106°C-115°C according to
DIN 53181),

0.96 part by weight of compound 21 and

10 91.44 parts by weight of a solvent mixture composed of ethylene glycol monoethyl ether-acetate, butyl acetate and xylene in a weight ratio of 9:1:1

is applied to an electrolytically roughened and anodized
15 aluminum support such that a layer weight of 2.34 g/m²
results after drying. The coated printing plate is, after
drying, exposed under a positive halftone original, which
has 13 equal density strips from 0.15 to 1.95, for 10
seconds with a 5 kW metal halide lamp at a distance of
20 120 cm and developed with a developer composed of

5.3 parts by weight of sodium metasilicate $\cdot 9 \text{ H}_2\text{O}$.

3.4 parts by weight of trisodium phosphate $\cdot 12 \text{ H}_2\text{O}$,

0.3 part by weight of sodium dihydrogen phosphate
(anhydrous) and

25 91.0 parts by weight of water

for 1 minute, the exposed layer areas being removed. This gives a print image of steep gradation with 4 wedge steps. A similar result is obtained if, in the above formulation, compound 21 is replaced by compounds 5, 7,

10, 14, 23 or 30 or by mixtures of 14/15, 16/17 or 28/29 (in each case 0.48 part by weight of one of the two radiation-sensitive components).

Example 50

5 A solution of

3.9 parts by weight of compound 40 or 42,

10 19.5 parts by weight of a cresol/formaldehyde novolac (melting range 106°C-115°C according to DIN 53181),

6.5 parts by weight of a polyvinyl methyl ether (having a K value of 45 - 55) and

15 0.4 part by weight of the dye Sudan Blue II (C.I. Solvent Blue 35)

in

49.7 parts by weight of propylene glycol monoethyl ether-acetate,

20 10.0 parts by weight of propylene glycol monoethyl ether and

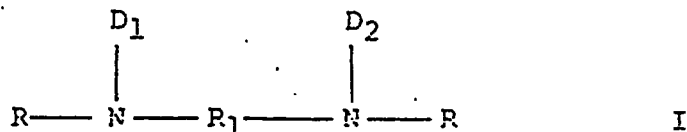
10.0 parts by weight of butyl acetate

25 gives a copying resist which is very suitable for the production of printed circuit boards. The copying resist can be applied to copper plates or other substrates suitable for the production of printed circuit boards, inter alia, by roller application.



Patent claims

1. Bis-1,2-naphthoquinone-2-diazide-sulfonic acid amides of secondary diamines, of the formula I



in which

- 5 R is a straight-chain or branched, unsubstituted or hydroxyl-substituted alkyl, cycloalkyl or aralkyl radical which has 1 - 14 carbon atoms and the carbon chain of which can be interrupted by ether oxygen atoms,
- 10 R₁ is an alkylene radical which has 2 - 12 carbon atoms and the carbon chain of which is interrupted by ether oxygen atoms, or is an arylenedialkyl radical having 8 - 18 carbon atoms, it being possible in the case of polynuclear compounds for the aromatic members to be linked by a single bond, by -O-, -S-, -SO₂-, -CO-, -CR₂R₃-, -N[C₁₋₃-alkyl]CO- or C₂₋₅-alkyl which can be interrupted by ether oxygen atoms, and
- 15
- 20 R₂ and R₃ can be identical or different and are hydrogen or unsubstituted or substituted alkyl radicals having 1 or 2 carbon atoms,
- or
- 25 R and R₁ together are formed by a cycloalkyl radical having 4 - 16 carbon atoms, it being possible in the case of polynuclear compounds for the cycloaliphatics to be linked by a carbon chain of 1 - 6 carbon atoms,

and



D_1 and D_2 are identical or different and are 1,2-naphthoquinone-2-diazide-4- or -5-sulfonyl radicals.

2. Bis-1,2-naphthoquinone-2-diazide-sulfonic acid amides of secondary diamines of the formula I, as claimed in claim 1, wherein

R is a straight-chain or branched, unsubstituted or hydroxyl-substituted alkyl or cycloalkyl radical which has 1 - 8, preferably 1 - 4, carbon atoms and the carbon chain of which can be interrupted by ether oxygen atoms, or an aralkyl radical having 7 - 14 carbon atoms,

R_1 is an alkylene radical which has 2 - 10 carbon atoms and the carbon chain of which is interrupted by 1 or 2 ether oxygen atoms, or is an arylenedialkyl radical having 8 - 14 carbon atoms, it being possible in the case of polynuclear compounds for the aromatic members to be linked by a single bond, by -O-, -S-, -SO₂-, -CO-, -CR₂R₃- -N[C₁₋₃-alkyl]CO- or C₂₋₅-alkyl which can be interrupted by ether oxygen atoms, and

R_2 and R_3 can be identical or different and are hydrogen or unsubstituted or substituted alkyl radicals having 1 or 2 carbon atoms, for example, alkyl radicals substituted by one or more fluorine atoms,

or

R and R_1 together are formed by a cycloalkyl radical having 4 - 16 carbon atoms, it being possible in the case of polynuclear compounds for the cycloaliphatics to be linked by a



carbon chain of 1 - 6 carbon atoms,

and

D₁ and D₂ are identical or different and are 1,2-naphthoquinone-2-diazide-4- or -5-sulfonyl radicals.

5

3. The use of the bis-1,2-naphthoquinone-2-diazide-sulfonic acid amides as claimed in claim 1 as radiation-sensitive components in a radiation-sensitive mixture.

10 4. The use as claimed in claim 3, wherein the radiation-sensitive component used is a 4- or 5-sulfonyl derivative individually or in a mixture or a mixed 4,5-sulfonyl derivative.

15 5. The use as claimed in claim 4, wherein the radiation-sensitive component used is a mixture of 4- and 5-sulfonyl derivatives.

20 6. A radiation-sensitive mixture, containing a polymeric resinous binder which is insoluble in water and soluble or swellable in aqueous-alkaline solution, and a 1,2-naphthoquinone-2-diazide-sulfonic acid derivative, characterised in that it comprises at least one compound as claimed in claim 1 as the 1,2-naphthoquinone-2-diazide-sulphonic acid derivative.

25 7. A mixture as claimed in claim 6, characterised in that it comprises at least one compound as claimed in claim 2 as the 1,2-naphthoquinone-2-diazide-sulphonic acid derivative.

30 8. A mixture as claimed in claim 6 or 7, wherein the content of radiation-sensitive component is 4 to



- 26 -

40%, relative to the solids content of the mixture.

9. A radiation-sensitive copying material, comprised of a layer support and a radiation-sensitive layer wherein said layer is comprised of a mixture as claimed in one or several claims 6 to 8.
- 5