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Acid-cleavable compounds, positive-working radiation-sensitive mixture containing these, and radiation-sensitive recording material produced with this mixture

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The invention relates to novel acid-cleavable N,O-acetals and to a radiation-sensitive mixture which is positive-working, i.e. which becomes soluble as a result of irradiation, and which contains these compounds. Generally, the mixture contains

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- (a) a binder which is insoluble in water and soluble or at least swellable in aqueous alkaline solutions,
- (b) a compound which generates a strong acid under the action of actinic radiation, and
- (c) a compound which has at least one acid-cleavable C-O-C bond and is convertible by cleavage into products having an enhanced solubility in aqueous alkaline solutions.

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The invention also relates to a radiation-sensitive recording material which has been produced with this mixture and which is suitable for producing photoresists, electronic components, printing plates or for chemical milling.

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To produce microelectronic circuits, several lithographic techniques are currently being used. Using g-line lithography (436 nm), which is usually applied to conventional diazonaphthoquinone/novolak formulations, resist images with a resolution of down to 0.8 μm can be produced.

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Images of even finer structures (down to 0.5 μm) on a resist layer can be obtained by means of i-line lithography (365 nm). More recent modifications of i-line lithography, such as, for example, phase-shifting mask

technology, allow a further reduction in the size of the structures, of which images are to be formed, right down to about 0.35 μm or less. An even higher resolution can be achieved with UV2 photoresists. In this case, two irradiation techniques are used: UV2 wide band exposure (240 to 260 nm) or exposure with KrF-excimer lasers which emit at 248 nm.

The continuing reduction in the size of the structures, for example in chip manufacture down into the range of less than 1 μm , requires modified lithographic techniques. To form images of such fine structures, radiation of a short wavelength is used, such as high-energy UV light, electron beams and X-rays. The radiation-sensitive mixture must be adapted to the short-wave radiation. A compilation of the requirements to be met by the radiation-sensitive mixture is given in the article by C.G. Willson "Organic Resist Materials - Theory and Chemistry" [Introduction to Microlithography, Theory, Materials, and Processing, editors L.F. Thompson, C.G. Willson, M.J. Bowden, ACS Symp. Ser., 219, 87 (1983), American Chemical Society, Washington]. There was therefore an increased demand for radiation-sensitive mixtures which can be used in the more recent technologies, such as mid-UV or deep-UV lithography [exposure, for example, with excimer lasers at wavelengths of 305 nm (XeF), 248 nm (KrF), 193 nm (ArF)], electron beam lithography or X-ray lithography, and which, furthermore, are preferably sensitive in a wide spectral range and correspondingly can also be used in conventional UV lithography.

Positive-working radiation-sensitive mixtures for producing radiation-sensitive recording materials are known. Mixtures which contain o-quinone-diazide derivatives in binders soluble in aqueous alkaline media, for example novolaks or polyhydroxystyrenes, are commercially available. However, the sensitivity of these materials to actinic radiation, and especially high-energy short-wave



radiation, such as light from a KrF-excimer laser having a wavelength of 248 nm or electron beams, is inadequate.

5 Positive-working radiation-sensitive mixtures are also known in which an acid is generated by the action of actinic radiation on a photoinitiator contained in this mixture and this acid then, in a subsequent reaction, renders an acid-cleavable compound likewise contained in the mixture soluble in the irradiated areas under the action of an appropriate, preferably aqueous alkaline developer. Such materials are in general distinguished by an enhanced sensitivity to actinic radiation.

15 Numerous mixtures of acid-cleavable, solubility-inhibiting compounds are known, which always contain a small quantity of a photolytic acid generator, whose acidic photolysis product initiates the cleavage. These mixtures, some of which have high sensitivities to actinic radiation, are designated as chemically amplified, photocatalytic 3-component systems since they contain, as essential constituents, a polymeric binder soluble in aqueous alkaline solutions, in most cases a novolak resin, a photoactive compound and a solubility inhibitor.

25 Amongst these mixtures, especially those have gained a certain commercial importance which contain either monomeric or oligomeric acetal units as the acid-cleavable components. These mixtures have, however, certain disadvantages since they possess only a limited stability on the substrate materials to which they have to be applied, and lead to unsatisfactory, not reproducible images of the original, and this can be improved only by introducing additional protective layers, for example according to DE-A 3,621,376 (= US-A 4,840,867). Furthermore, it can be observed generally that the process window, i.e. the processing latitude, for the exposure of these mixtures is very narrow and frequently



not unambiguously reproducible, which in turn manifests itself in unsatisfactory reproductions of originals. In particular, the quality of the image reproduction greatly depends on the time difference between exposure and development, the so-called delay time. The reasons for the deterioration in image reproduction are not known in detail or have been investigated only inadequately. In principle, it must be assumed that diffusion processes which cause this behavior are not easily controllable. In addition, however, it may be presumed that, during drying of the mixture on a substrate material, partial vaporization of the photoinitiator or of the acid-unstable compound or segregation of the individual mixture constituents takes place, which is observed with particular frequency in the case of acid-unstable compounds having a low solubility in the usual coating solvents.

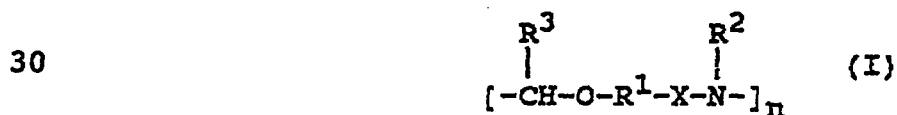
The decisive disadvantage of the known compounds containing acetal groups is, however, the fact that the solubility differentiation, resulting from their cleavage, between exposed and unexposed image areas is in general inadequate. The cause of this probably is that either the acetal derivative used as solution inhibitor has an insufficient inhibiting property and, in imagewise differentiation, in addition to the exposed image areas those areas are also severely attacked and removed which were not exposed, or that the exposed areas do not have a solubility sufficient to permit an imagewise differentiation during development. The problem can be summarized by saying that it is not possible using the known compounds to provide a material which causes a sufficiently large solubility difference between exposed and unexposed areas. Whereas this effect is in general still acceptable in the case of the novolak resins used according to the state of the art, it is observed, when other polymers are used, that the known acetal derivatives virtually no longer show any inhibiting action and thus no longer permit an image differentiation as required in practice.



There is therefore a demand for radiation-sensitive mixtures which do not show the disadvantages described above, possess a reactivity suitable in practice and, in particular, permit good imagewise differentiation in combination with the most diverse matrix polymers.

It was the object of the invention to propose novel acid-cleavable compounds and a radiation-sensitive mixture, which contains these compounds, of the generic type described at the outset. The novel acid-cleavable compounds c) should have a sufficient reactivity on the one hand and a stability meeting the needs of practice on the other hand. Furthermore, they should form homogeneous mixtures with the most diverse matrix polymers and, in the unirradiated form, should act as an efficient solution inhibitor, while their cleavage products should assist the developability of the exposed areas in aqueous alkaline developers. The mixture containing the acid-cleavable compounds should also be as stable as possible both in solution and on the substrates used in practice, and allow a differentiation between exposed and unexposed areas, which permits the highest possible resolutions with virtually perpendicular flanks. Furthermore, a radiation-sensitive mixture was to be provided which, especially, largely avoids segregation of the compound (b) and of the solubility-differentiating compound (c) and thus likewise allows an enhanced differentiation between image areas and non-image areas.

According to the invention, acid-cleavable compounds of the formula I



are proposed, in which

R^1 is an alkylene, cycloalkylene, alkenylene,

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- alkynylene or arylenebisalkyl group, wherein one or more aliphatic CH_2 group(s) can have been replaced by oxygen or sulfur atoms,
- 5 R^2 is an alkyl, alkenyl, alkynyl, cycloalkyl, alkoxyalkyl, aryl, aralkyl or aryloxyalkyl radical,
- R^3 is an alkyl or aryl radical,
- X is one of the groups $-\text{CO}-$, $-\text{O}-\text{CO}-$ or $-\text{NH}-\text{CO}-$ and
- n is an integer greater than 1.

Those compounds of the formula I are preferred in which

- 10 R^1 is an alkylene, alkenylene or alkynylene group having 2 to 18 carbon atoms, in which 1 to 3 CH_2 groups can have been replaced by oxygen or sulfur atoms, a cycloalkylene group having 4 to 18 carbon atoms, an aralkylene group having 7 to 18 carbon atoms or an arylenebisalkyl group having 8 to 18 carbon atoms,
- 15 R^2 is an alkyl radical having 1 to 12 carbon atoms, an alkenyl or alkynyl radical having 2 to 12 carbon atoms, an alkoxyalkyl radical having 3 to 12 carbon atoms, a cycloalkyl radical having 4 to 12 carbon atoms, an aryl radical having 6 to 12 carbon atoms, an aralkyl radical having 7 to 12 carbon atoms or an aryloxyalkyl radical having 8 to 12 carbon atoms, and
- 20 R^3 is an alkyl radical having 1 to 12 carbon atoms, an alkenyl or alkynyl radical having 2 to 12 carbon atoms, an alkoxyalkyl radical having 3 to 12 carbon atoms, a cycloalkyl radical having 4 to 12 carbon atoms, an aryl radical having 6 to 12 carbon atoms, an aralkyl radical having 7 to 12 carbon atoms or an aryloxyalkyl radical having 8 to 12 carbon atoms, and
- 25 n is an integer greater than 3.

Those compounds of the formula I are particularly preferred in which

- 30 R^1 is an unbranched or branched alkylene, cycloalkylene, cycloalkylenedialkyl, alkenylene or alkynylene group having up to 8 carbon atoms, wherein a carbon atom may have been replaced by an oxygen or sulfur atom, or an arylenedialkyl group having 8 to 12 carbon atoms,
- 35 R^2 is an alkyl, alkenyl, alkynyl, cycloalkyl or alkoxyalkyl radical having up to 6 carbon atoms or an



- aryl, arylalkyl or aryloxyalkyl radical having 7 to 12 carbon atoms,
- 5 R^3 is an alkyl radical having 1 to 6 carbon atoms, an unsubstituted or substituted mononuclear or polynuclear aryl radical having 6 to 12 carbon atoms, and
- n is an integer between 3 and 50.

Those compounds of the formula I are very particularly preferred in which

- 10 R^1 is an unbranched or branched alkylene group having 2 to 4 carbon atoms,
- R^2 is an alkyl, alkenyl, alkynyl or cycloalkyl radical having up to 6 carbon atoms and
- 15 R^3 is an alkyl radical having 1 to 6 carbon atoms or an unsubstituted or substituted six-membered aryl radical.

In detail, amongst the particularly preferred compounds, the radical R^3 can, for example, have the following meanings:

- 20 methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-hexyl, phenyl, 4-acetylamino-phenyl, 4-acetoxyphenyl, 3- and 4-benzyloxy-phenyl, 3-benzyloxy-4- and 4-benzyloxy-3-methoxyphenyl, biphenyl-4-yl, 3,5-bis-trifluoromethyl-phenyl, 2-, 3- and 4-fluorophenyl, 2-, 3- and 4-chloro-phenyl, 2-, 3- and 4-bromophenyl, 4-iodophenyl, 2-, 3- and 4-cyanophenyl, 2-, 3- and 4-methyl-, -ethyl-, -propyl-, -isopropyl-, -butyl-, -isobutyl-, -t-butyl-, -pentyl-, -hexyl-, -cyclohexyl-, -nonyl- and -dodecyl-phenyl, 2-, 3- and 4-methoxy-, -ethoxy-, -isopropoxy-, 30 -butoxy-, -pentyloxy-, -octyloxy- and -decyloxyphenyl, 2,3-, 2,4-, 2,6-, 3,4- and 3,5-difluoro-, -dichloro- and -dibromophenyl, 3-(3,4-dichlorophenoxy)-phenyl, 3-(3,5-dichlorophenoxy)-phenyl, 3-bromo-4-fluorophenyl, 5-bromo-2,4-dimethoxyphenyl, 2-chloro-6-fluorophenyl, 35 2-chloro-5-, 2-chloro-6-, 4-chloro-3- and 5-chloro-



2-nitrophenyl, 3-(4-chlorophenoxy)-phenyl, 3,4-bis-
benzyloxyphenyl, 2,3-, 2,4-, 2,5-, 3,4- and
3,5-dimethoxy-, -diethoxy-, -dibutoxy- and -dihexyloxy-
phenyl, 2,4-dimethoxy-3-methylphenyl, 2-ethoxy-
5-methoxyphenyl, 3-chloro-4-methylphenyl, 2,4- and
2,5-dimethylphenyl, 2-(2-methoxyethyl)-,
2-(2-ethoxyethyl)- and 2-(2-butoxyethyl)-phenyl,
3-(2-methoxyethyl)-, 3-(2-ethoxyethyl)- and 3-(2-butoxy-
ethyl)-phenyl, 4-(2-methoxyethyl)-, 4-(2-ethoxyethyl)-
and 4-(2-butoxyethyl)-phenyl, 2,6-dinitrophenyl, 2,4,6-
trimethylphenyl, 3,4,5-trimethoxy- and -triethoxy-phenyl,
2,3- and 3,4-methylenedioxyphenyl, 2- and 3-thienyl,
2-fluorenyl, 9-anthryl, 5-bromo-2-thienyl, 3-methyl-
2-thienyl, 5-methyl-2-thienyl, 5-nitrofuryl, 10-chloro-
9-anthryl and ferrocenyl.

These radicals are preferred particularly for the reason
that the starting compounds on which they are based are
commercially available. They can also be selected under
aspects other than optical, i.e. care should be taken
that the absorption of the prepared N,O-acetal according
to the invention in the wavelength range of the radiation
used is kept as low as possible. Further starting com-
pounds are accessible in a simple manner.

The preparation of the compounds according to the inven-
tion of the formula I can be carried out by methods known
per se via a multi-stage synthesis. This requires the
provision of suitable alcohols which contain amide,
urethane or urea groups and whose preparation is
described below. These are reacted in a subsequent step
with suitable monomeric acetals or acetal precursors, for
example according to EP-A 0,312,751. The synthesis is
illustrated below by reference to some examples according
to the invention. P.b.w. means parts by weight.

Preparation Example 1

1st stage: 59.1 p.b.w. of n-propylamine were added to
88.1 p.b.w. of ethylene carbonate. The mixture warming up



was stirred for 5 hours at 70°C and distilled in vacuo. Colorless oil which distils over at 102 to 105°C/0.06 mm Hg (2-hydroxyethyl N-propyl-carbamate).

5 2nd stage: 15.2 p.b.w. of benzaldehyde dimethylacetal, prepared by acetalization of benzaldehyde and methanol, were heated under reflux with 29.4 p.b.w. of the urethane-alcohol described in 200 p.b.w. of toluene in the presence of 0.2 p.b.w. of p-toluenesulfonic acid. From time to time, the toluene/methanol mixture formed
10 was distilled off until, after about 6 hours, the top temperature remained constant at 110°C for a prolonged period. The mixture was cooled down and washed with dilute sodium hydroxide solution and then with water until neutral. After drying, the toluene was distilled
15 off in a rotary evaporator and the remaining residue was condensed in a high vacuum (0.01 mm Hg) at 200°C. This gave an oligomeric compound of the formula I in which R₁ is an ethylene group, X is the group -O-CO-, R₂ is an n-propyl group and R₃ is a phenyl group (Compound 1).

20 Preparation Example 2

Compound 1 was also obtained by the following route:
15.2 p.b.w. of benzaldehyde dimethylacetal were mixed with 14.7 p.b.w. of the urethane-alcohol described above and, after addition of 0.2 p.b.w. of p-toluenesulfonic
25 acid, slowly heated to 160°C. The methanol formed was distilled off. After about 2 hours, a vacuum (0.01 mm Hg) was applied, and the mixture was heated to 200°C. The mixture was exposed for a further 2 hours to these conditions. A highly viscous oil remained whose pro-
30 perties were virtually identical to those of Compound 1.

Preparation Example 3

Compound 1 was also obtainable by the following route:

15.2 p.b.w. of benzaldehyde dimethylacetal, prepared by acetalization of benzaldehyde with methanol, were heated
35 under reflux with 29.4 p.b.w. of the urethane-alcohol



described in Example 1 in 200 p.b.w. of toluene in the presence of 0.2 p.b.w. of p-toluenesulfonic acid. From time to time, the toluene/methanol mixture formed was distilled off until, after about 6 hours, the top temperature remained constant at 110°C for a prolonged period. The mixture was cooled down and washed with dilute sodium hydroxide solution and then with water until neutral. After concentrating the solvent, an oily residue remained which was reprecipitated from hot diisopropyl ether. On cooling, white crystals having a melting point of 54.5°C crystallized out of the solution. With stirring, 19.1 p.b.w. of these crystals were slowly heated to 160°C with 7.6 p.b.w. of benzaldehyde dimethylacetal and 0.2 p.b.w. of p-toluenesulfonic acid. The methanol formed was distilled off. After about 2 hours, a vacuum (0.01 mm Hg) was applied, and the mixture was heated to 200°C. The mixture was exposed to these conditions for a further 2 hours. A highly viscous oil remained whose properties were virtually identical to those of Compound 1.

Preparation Example 4

1st stage: 101.2 p.b.w. of n-hexylamine were added to 88.1 p.b.w. of ethylene carbonate. The mixture warming up was stirred for 5 hours at 70°C and distilled in vacuo. Colorless oil which distills over at 117 to 119°C/0.05 mm Hg (2-hydroxyethyl N-hexyl-carbamate).

2nd stage: 19.6 p.b.w. of piperonal dimethylacetal were heated under reflux with 38.0 p.b.w. of the urethane-alcohol described above in 200 p.b.w. of toluene in the presence of 0.2 p.b.w. of p-toluenesulfonic acid. From time to time, the toluene/methanol mixture formed was distilled off until, after about 6 hours, the top temperature remained constant at 110°C for a prolonged period. The mixture was cooled down and washed with dilute sodium hydroxide solution and then with water until neutral. After drying, the toluene was distilled off in a rotary evaporator and the remaining residue was



condensed in a high vacuum (0.01 mm Hg) at 200°C. This gave an oligomeric compound of the formula I in which R₁ is an ethylene group, X is the group -O-CO-, R₂ is the n-hexyl group and R₃ is the 4-piperonyl group (Compound 2).

Preparation Example 5

1st stage: 73.1 p.b.w. of i-butylamine were added to 88.06 p.b.w. of ethylene carbonate. The mixture warming up was stirred for 5 hours at 70°C and distilled in vacuo. Colorless oil which distils over at 101 to 104°C/0.06 mm Hg (2-hydroxyethyl N-isobutyl-carbamate).

2nd stage: 18.6 p.b.w. of 4-chlorobenzaldehyde dimethyl-acetal were heated under reflux with 32.2 p.b.w. of the urethane-alcohol described above in 200 p.b.w. of toluene in the presence of 0.2 p.b.w. of p-toluenesulfonic acid. The toluene/methanol mixture formed was distilled off at intervals until, after about 6 hours, the top temperature remained constant at 110°C over a prolonged period. The mixture was cooled down and washed with dilute sodium hydroxide solution and then with water until neutral. After drying, the toluene was evaporated off and the remaining residue was condensed in a high vacuum (0.01 mm Hg) at 200°C. This gave an oligomeric compound of the formula I in which R₁ is an ethylene group, X is the group -O-CO-, R₂ an i-butyl group and R₃ is a 4-chlorophenyl group (Compound 3).

Preparation Example 6

1st stage: 21.3 p.b.w. of propyl isocyanate and 25 p.b.w. of diethyl ether were added dropwise at room temperature to 20.6 p.b.w. of aminopropanol in 250 p.b.w. of diethyl ether and 25 p.b.w. of isopropanol. The product which had precipitated was filtered off with suction. (N-(3-Hydroxypropyl)-N'-propyl-urea, white powder, melting point 76°C).



2nd stage: 15.2 p.b.w. of benzaldehyde dimethylacetal were heated under reflux with 32.2 p.b.w. of the urea-alcohol described above in 200 p.b.w. of toluene in the presence of 0.2 p.b.w. of p-toluenesulfonic acid. From time to time, the toluene/methanol mixture formed was distilled off until, after about 6 hours, the top temperature remained constant at 110°C for a prolonged period. The mixture was cooled down and washed with dilute sodium hydroxide solution and with water until neutral. After drying, the toluene was evaporated off and the remaining residue was condensed in a high vacuum (0.01 mm Hg) at 220°C. This gave an oligomeric compound of the formula I in which R₁ is a propylene group, X is the group -NH-CO-, R₂ is an n-propyl group and R₃ is a phenyl group (Compound 4).

Preparation Example 7

1st stage: 139.1 p.b.w. of butyl isocyanate were added dropwise to a mixture of 200 p.b.w. of ethylene glycol and 0.5 p.b.w. of diazabicyclo[2,2,2]octane in 200 p.b.w. of tetrahydrofuran. The mixture warming up was stirred for 5 hours at 70°C and distilled in vacuo. Colorless oil which distils over at 110 to 112°C/0.03 mm Hg (2-hydroxyethyl N-butyl-carbamate).

2nd stage: 19.6 p.b.w. of piperonal dimethylacetal were heated under reflux with 32.2 p.b.w. of the urethane-alcohol described above in 200 p.b.w. of toluene in the presence of 0.2 p.b.w. of p-toluenesulfonic acid. At intervals, the toluene/methanol mixture formed was distilled off until, after about 6 hours, the top temperature remained constant at 110°C for a prolonged period. The mixture was cooled down and washed with dilute sodium hydroxide solution and then with water until neutral. After drying, the toluene was distilled off and the remaining residue was condensed in a high vacuum (0.01 mm Hg) at 200°C. This gave an oligomeric compound of the formula I in which R₁ is an ethylene group, X is a group -O-CO-, R₂ is an n-butyl group and R₃



is a [1,3]benzodioxol-5-yl group (Compound 5).

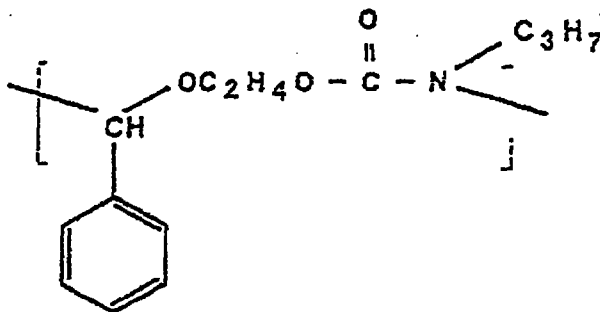
Preparation Example 8

5 1st stage: 73.1 p.b.w. of isobutylamine were added to 88.06 p.b.w. of ethylene carbonate. The mixture warming up was stirred for 5 hours at 70°C and distilled in vacuum. Colorless oil which distils over at 101 to 104°C/0.06 mm Hg.

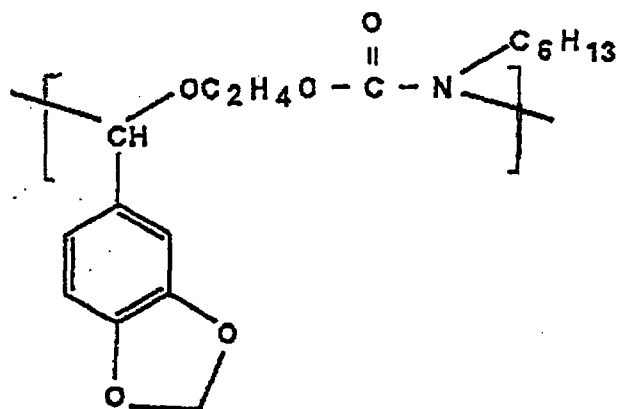
10 2nd stage: 25.8 p.b.w. of 4-benzyloxy-benzaldehyde dimethylacetal were heated under reflux with 32.2 p.b.w. of the urethane-alcohol described above in 200 p.b.w. of toluene in the presence of 0.2 p.b.w. of p-toluene-sulfonic acid. At intervals, the toluene/methanol mixture formed was distilled off until, after about 6 hours, the top temperature remained constant at 110°C for a prolonged period. The mixture was cooled down and washed with dilute sodium hydroxide solution and then with water until neutral. After drying, the toluene was evaporated off and the remaining residue was condensed in a high vacuum (0.01 mm Hg) at 200°C. This gave an oligomeric compound of the formula I in which R₁ is an ethylene group, X is the group -O-CO-, R₂ is a butyl group and R₃ is a 4-benzyloxyphenyl group (Compound 6).

25 Further compounds were prepared in a corresponding manner by known methods; a listing of particularly preferred compounds for the preparation of radiation-sensitive mixtures is given in the attached formula drawings.

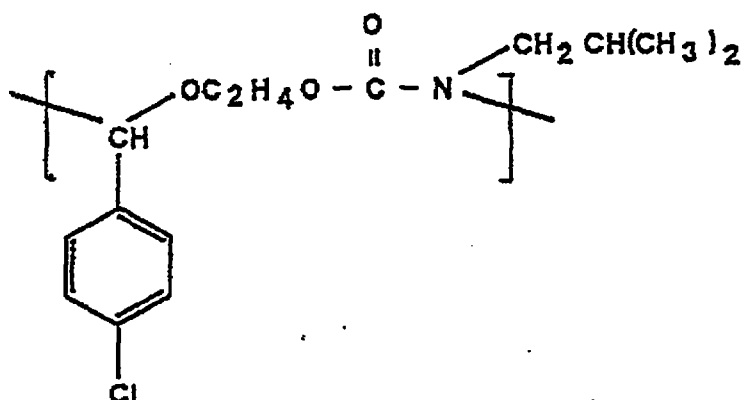
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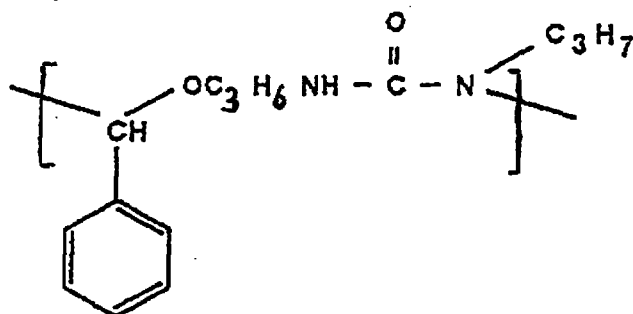
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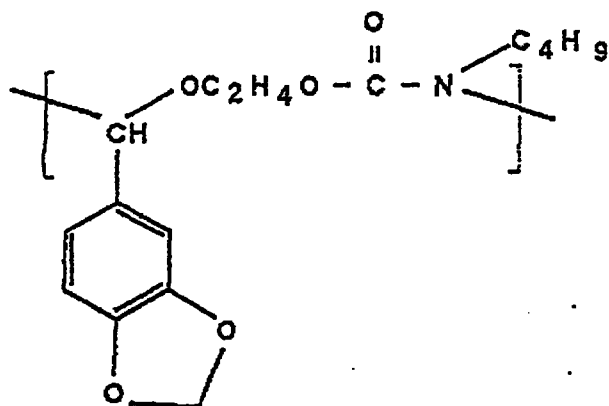
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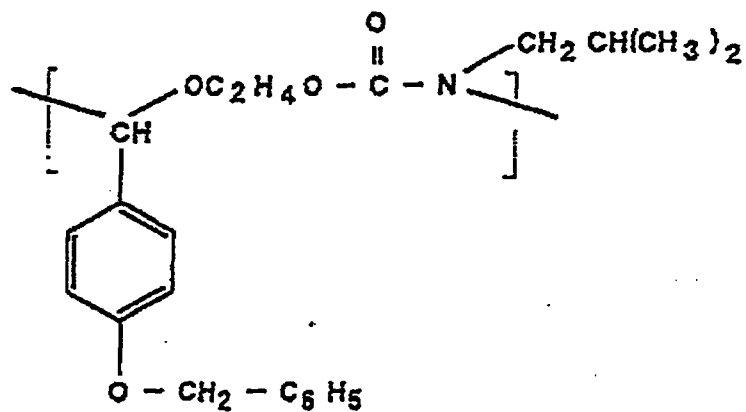
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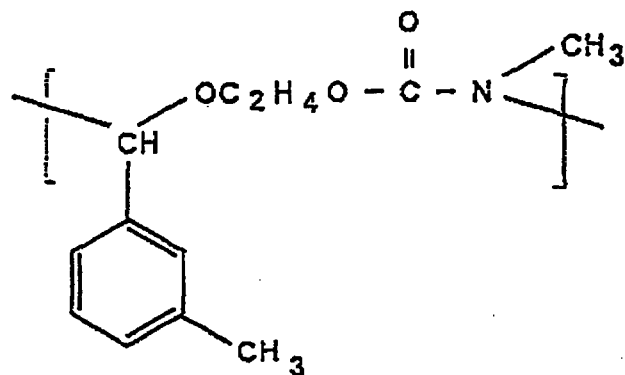
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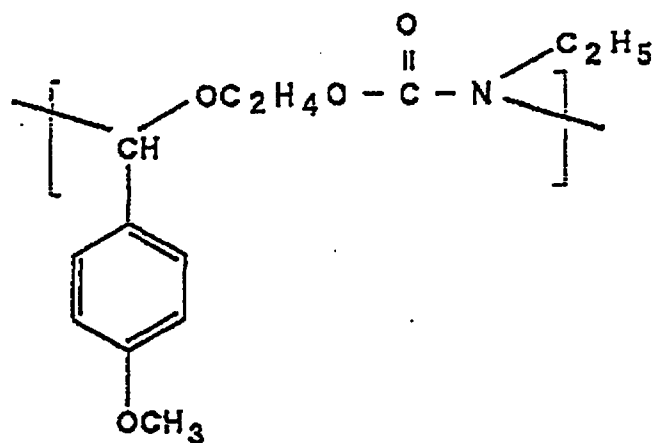
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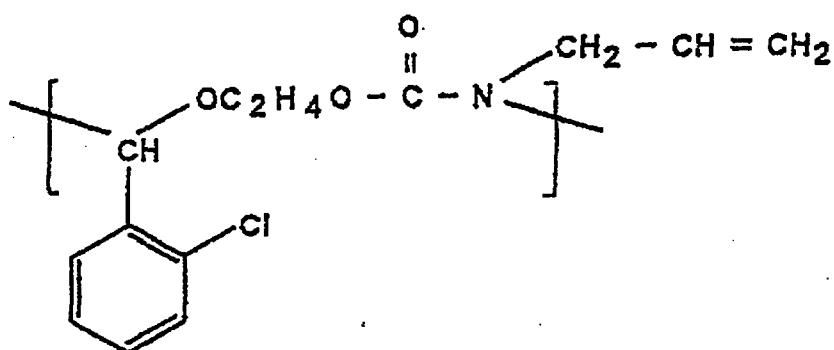
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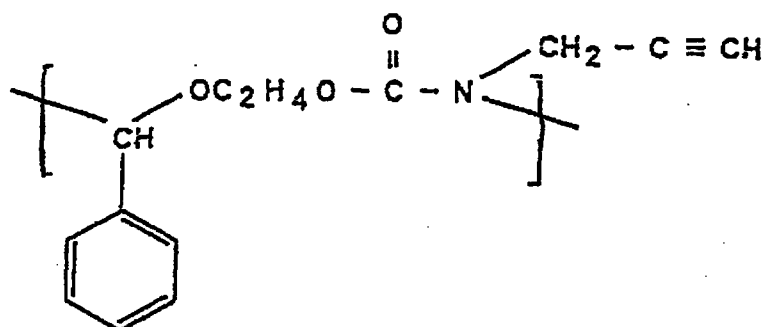
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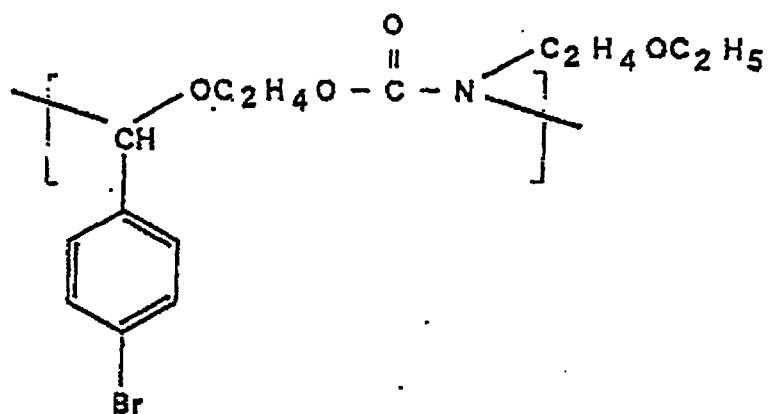
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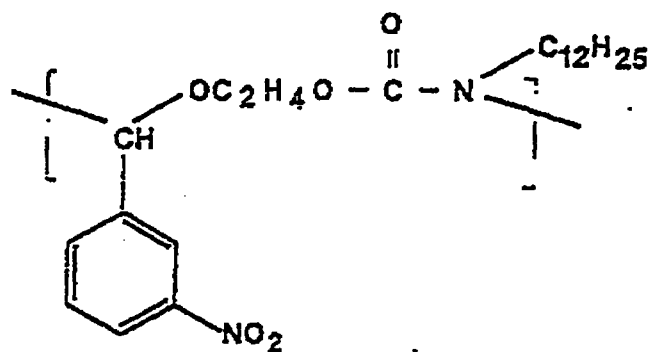
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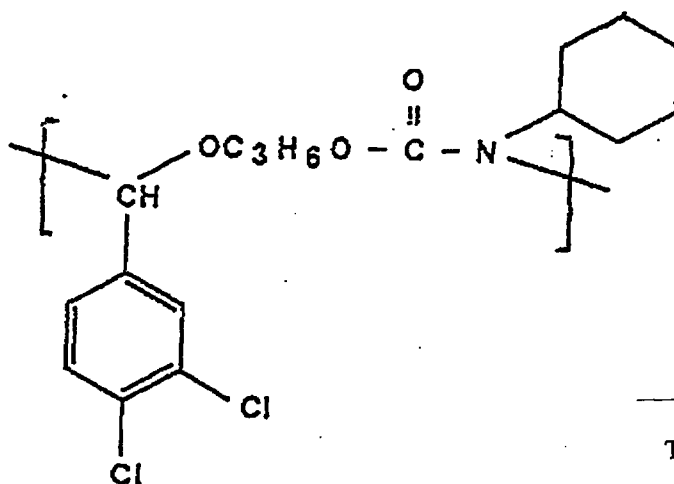
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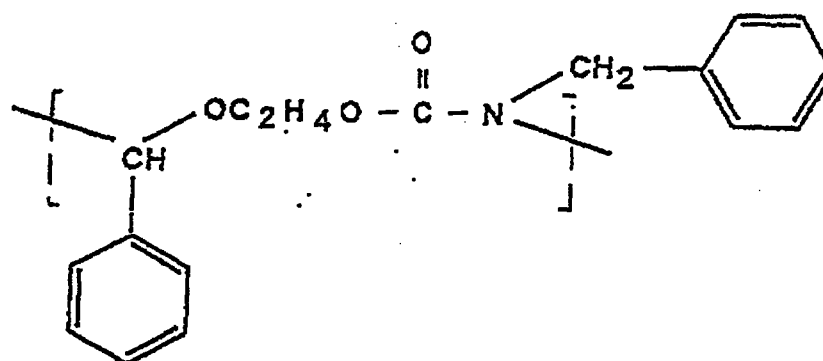
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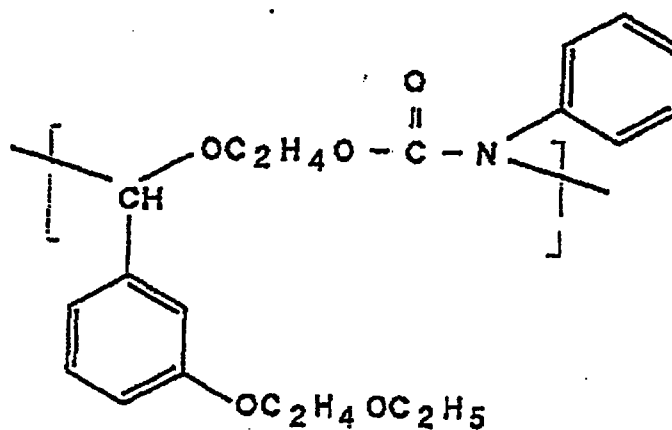
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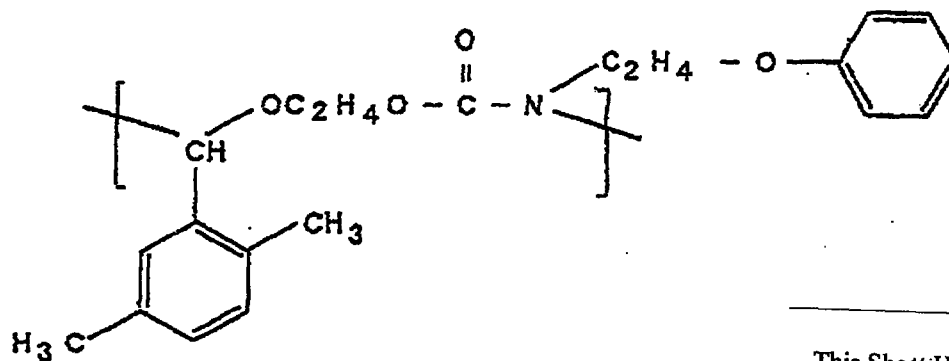
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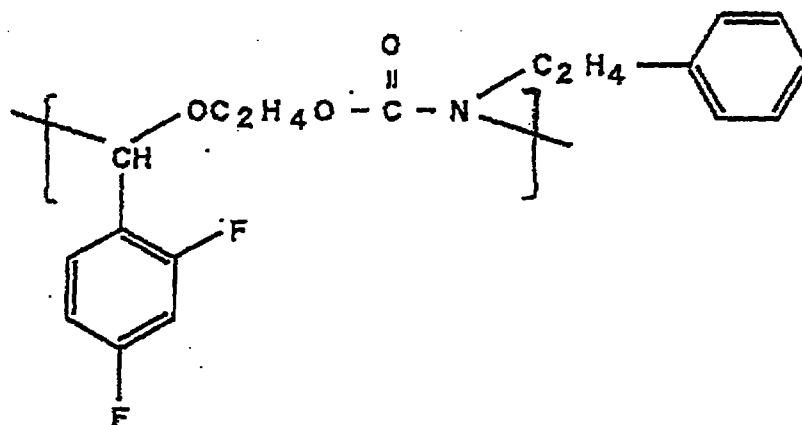
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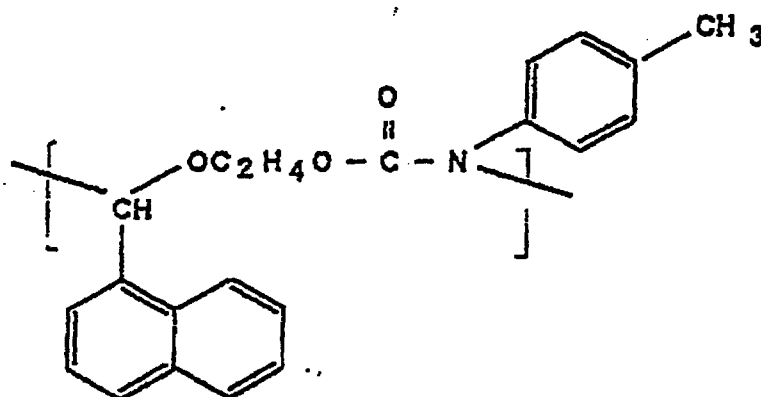
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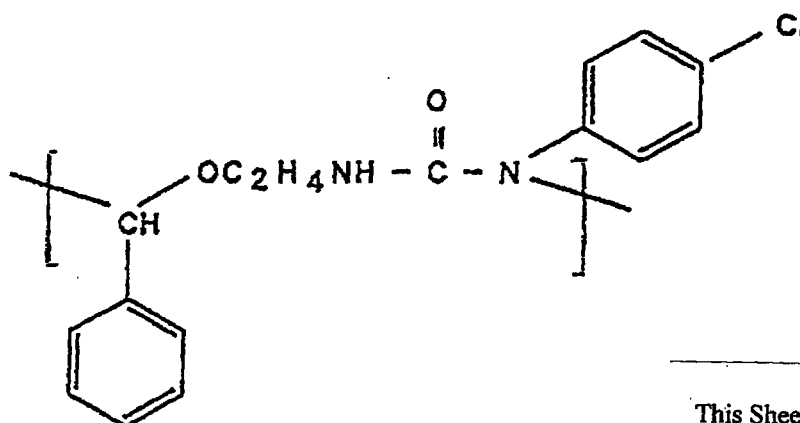
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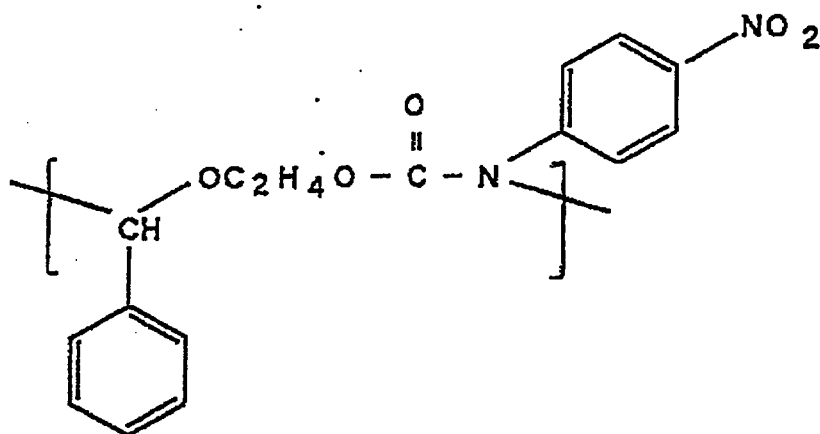
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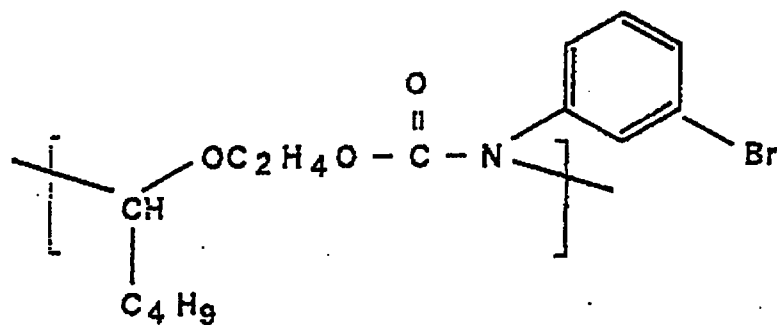
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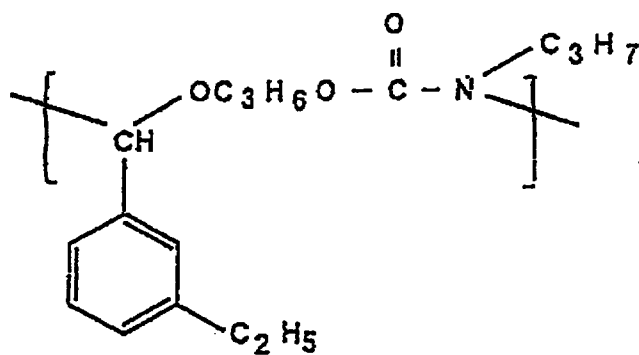
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Compound No. 21:



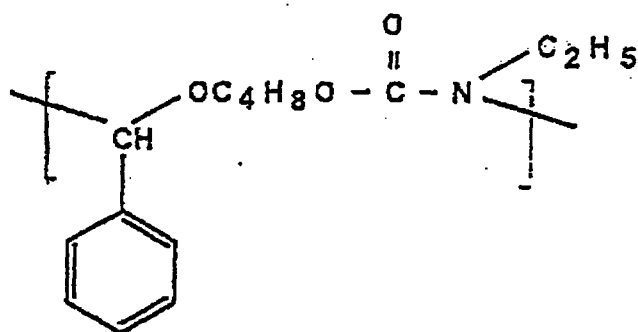
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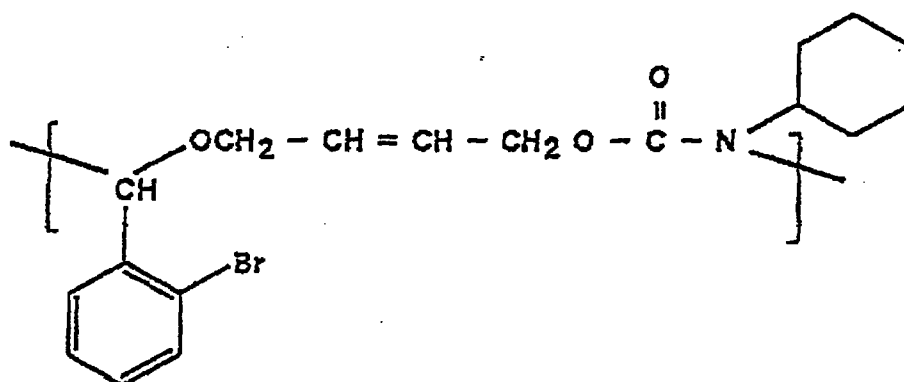
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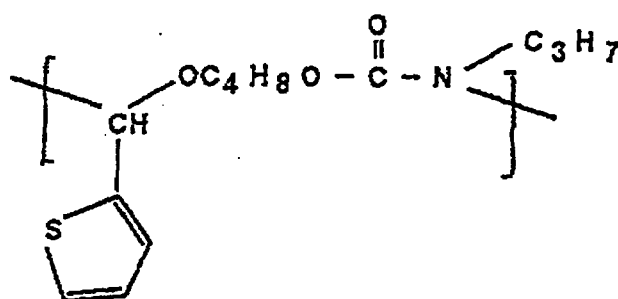
Compound No. 23:



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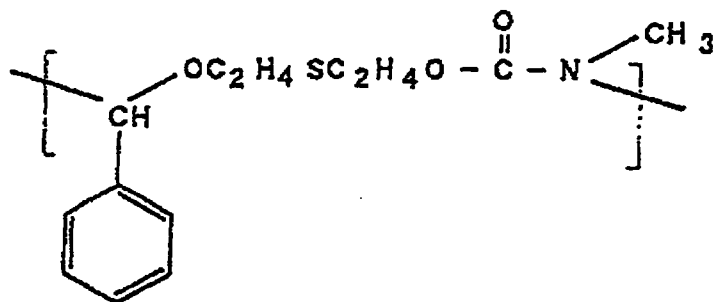
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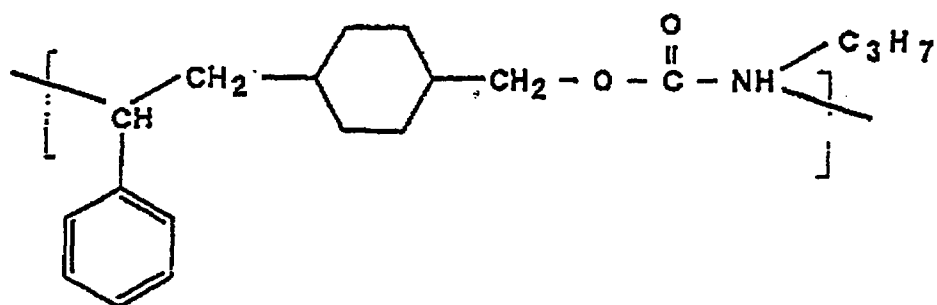
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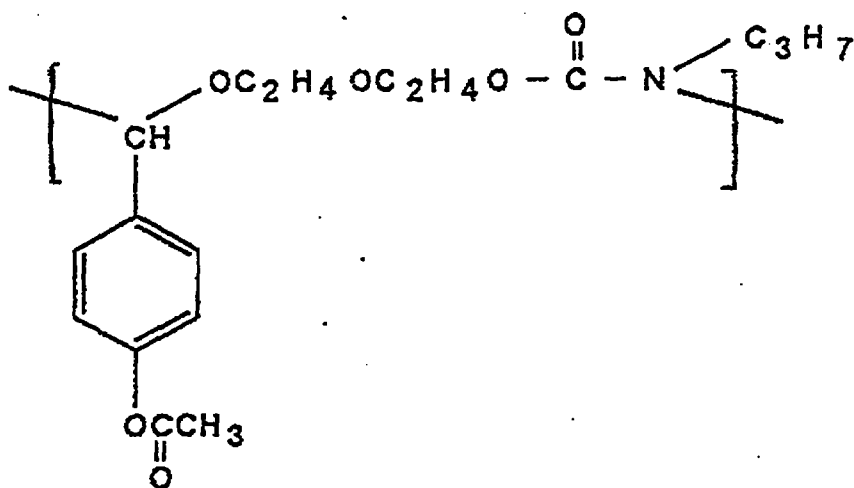
Compound No. 26:



Compound No. 27:



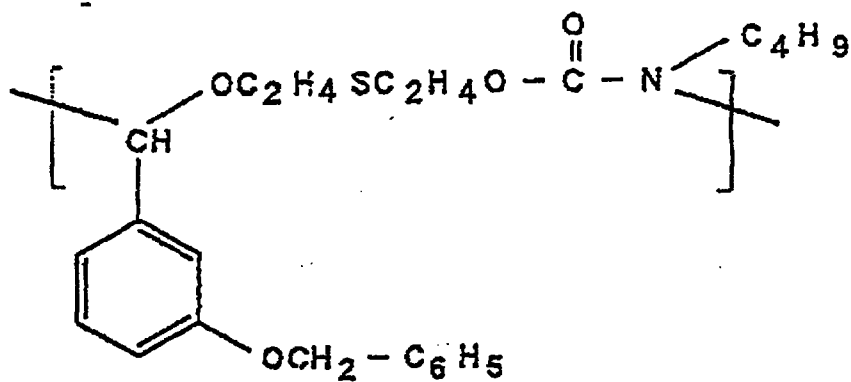
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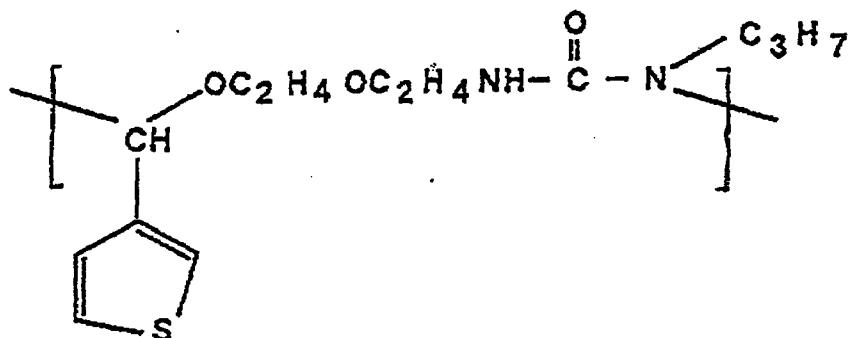
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Compound No. 29:



Compound No. 30:



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Further compounds of the formula I which have similarly favorable properties are summarized in the table below:

	No.	X	R ¹	R ²	R ³
5	31	O-CO	C ₂ H ₄	C ₃ H ₇	C ₂ H ₅
	32	CO	C ₃ H ₆	C ₃ H ₇	C ₄ H ₉
	33	O-CO	C ₂ H ₄	C ₃ H ₇	C ₄ H ₉
	34	O-CO	C ₃ H ₆	C ₃ H ₇	C ₄ H ₉
	35	NH-CO	C ₃ H ₆	C ₄ H ₉	C ₄ H ₉
10	36	NH-CO	CH(CH ₃)CH ₂	C ₃ H ₇	C ₄ H ₉
	37	O-CO	C ₂ H ₄	C ₃ H ₆ Cl	C ₄ H ₉
	38	NH-CO	C ₃ H ₆	C ₃ H ₇	4-Bromophenyl
	39	O-CO	C ₂ H ₄	C ₃ H ₇	4-Methoxyphenyl
	40	CO	C ₃ H ₆	C ₃ H ₇	4-Tolyl
15	41	O-CO	C ₄ H ₈	C ₄ H ₉	2-Naphthyl
	42	NH-CO	C ₃ H ₆	C ₃ H ₇	4-Nitrophenyl
	43	NH-CO	C ₂ H ₄	C ₃ H ₇	3-Methoxyphenyl
	44	O-CO	C ₃ H ₆	C ₃ H ₇	3,4-Dichlorophenyl
	45	O-CO	C ₂ H ₄	C ₃ H ₇	2,6-Dichlorophenyl
20	46	O-CO	CH(CH ₃)CH ₂	C ₃ H ₇	2,4-Difluorophenyl
	47	O-CO	C ₃ H ₆	C ₃ H ₇	2,3,5-Trichlorophenyl
	48	O-CO	C ₂ H ₄	C ₃ H ₇	Ferrocenyl

According to the invention, a radiation-sensitive mixture is also proposed which contains, as essential constituents,

- (a) a binder which is insoluble in water and soluble or at least swellable in aqueous alkaline solutions,
- (b) a compound which generates a strong acid under the action of actinic radiation, and
- (c) a compound which has at least one acid-cleavable C-O-C bond and whose acid cleavage products are more readily soluble in aqueous alkaline solutions than the compound itself.



In the mixture according to the invention, the acid-cleavable compound (c) is an oligomeric N,O-acetal of the formula I described above.

5 The radiation-sensitive mixture according to the invention is distinguished by a high sensitivity over a wide spectral range. It shows a high thermal stability and makes it possible accurately to reproduce even superfine structures of an original. This is due to the property of the mixture containing the compounds according to the
10 invention of allowing an unusually high differentiation of the solubility between image areas and non-image areas to be achieved.

15 The content of acid-cleavable material (c) in the radiation-sensitive mixture according to the invention should be 1 to 60% by weight, preferably 5 to 50% by weight, each relative to the total weight of the mixture.

20 Photolytic acid donors b) are added to the acid-cleavable compounds c) contained in the radiation-sensitive mixture according to the invention, for which purpose onium salts, such as diazonium, phosphonium, sulfonium and
25 iodonium salts of non-nucleophilic acids, for example of HSbF_6 , HAsF_6 or HPF_6 [J.V. Crivello, Polym. Eng. Sci., 23, 953 (1983)], halogen compounds (EP-A 0,232,972, DE-A 1,572,089, DE-A 1,817,540, DE-A 1,949,010, US-A 3,912,606 and DE-A 2,317,846), especially trichloro-
30 methyltriazine derivatives (US-A 3,515,552, US-A 3,536,489, US-A 3,779,778, DE-A 2,718,259, DE-A 3,337,024, DE-A 3,333,450, DE-A 2,306,248, DE-A 2,243,621 and DE-A 1,298,414) or trichloromethyloxadiazole derivatives (DE-A 3,021,590, DE-A 3,021,599, DE-A 2,851,472, DE-A 2,949,396, DE-A 3,333,450 and EP-A 0,135,348), o-quinonediazidesulfochlorides or organometal/organohalogen combinations are suitable. Although very good results are obtainable with such
35 compounds, these are altogether not preferred since acids having a highly corrosive action are generated in such



radiation-sensitive mixtures. Rather, those photolytic acid donors are preferred which generate sulfonic acids on exposure. Examples of such compounds which may be mentioned are the α -carbonyl- α -sulfonyldiazomethanes, or α,α -bis-sulfonyldiazomethanes described in DE-A 3,930,087 and 3,930,086, nitrobenzyl sulfonates (F.M. Houlihan et al., J. Photopolym. Sci. Techn., 3, 259, 1990; T. Yamaoka et al., J. Photopolym. Sci. Techn., 3, 275, 1990), pyrogallol sulfonates [T. Ueno et al., Chemical Amplification Positive Resist Systems Using Novel Sulfonates as Acid Generators, in "Polymers for Microelectronics - Science and Technology", edited by Y. Tabata et al., Kodansha-Weinheim-New York, 1989, pages 66-67] or iminosulfonates (M Shirai et al., J. Photopolym. Sci. Techn., 3, 301, 1990). The α -pyridones containing N-sulfonyloxy groups mentioned in the applications P 41 12 967.9, P 41 12 966.0 and P 41 12 965.2 filed concomitantly are particularly preferred.

In general, 0.2 to 25% by weight of the photolytic acid donors are added to the mixture. Proportions of 0.5 to 15% by weight are preferred, and 1 to 10% by weight is particularly preferred. These quantities can be fixed precisely only in a concrete formulation and differ from type to type. The photolytic acid donors have absorption maxima in the region between 200 and 500 nm. Consequently, the spectral sensitivity of the mixtures according to the invention was thereby fixed, and they can be selected in such a way that sensitivities appropriate to practice can be obtained in the range of the technically important radiation sources, for example g-line (436 nm), i-line (365 nm) or UV2 (248 nm). The acid-cleavable compounds (c) which can be used according to the invention can then be selected in such a way that they have virtually no characteristic absorption in these ranges. By means of steps known to those skilled in the art, for example by spectral sensitization, the sensitivity range of the acid-donating compounds (b) can be further widened, so that even radiation sources in the



visible region or in the short-wave region of X-ray radiation can be used. Finally, other radiation sources, such as electron beams or ion beams, can also be used for the imagewise differentiation of the mixture according to the invention, especially if highly active acid donors are used, such as are described, for example, in EP-A 0,318,649.

If desired, other acid-cleavable compounds can be added to the mixtures according to the invention; in this case, above all the following compound classes have proven suitable:

- (1) those having at least one orthocarboxylic acid ester group and/or carboxylic acid amide-acetal group, the compounds also having a polymeric character and it being possible for the said groupings to occur as linking elements in the main chain or as substituents in side chains (DE-A 2,610,842 and 2,928,636),
- (2) oligomeric or polymeric compounds with recurring acetal and/or ketal groupings in the main chain (DE-A 2,306,248 and 2,718,254),
- (3) compounds having at least one enol ether grouping or N-acyliminocarbonate grouping (EP-A 0,006,626 and 0,006,627),
- (4) cyclic acetals or ketals of β -ketoesters or β -keto-amides (EP-A 0,202,196),
- (5) compounds having silyl ether groupings (DE-A 3,544,165 and 3,601,264),
- (6) compounds having silyl enol ether groupings (DE-A 3,730,785 and 3,730,783),
- (7) monoacetals and monoketals, whose aldehyde or keto component respectively has a solubility of between 0.1 and 100 g/l in the developer (DE-A 3,730,787),
- (8) ethers based on tertiary alcohols (US-A 4,603,101) and
- (9) carboxylic acid esters and carbonates of tertiary alcohols, allylic alcohols or benzylic alcohols [US-A 4,491,628 and J.M. Fréchet et al., J. Imaging



Sci. 30, 59-64 (1986)].

Mixtures of the said acid-cleavable compounds can also be used. Amongst these, however, acid-cleavable compounds can preferably be used which have to be classified under one of the abovementioned types (1) to (9) and, amongst these, especially those which have an acid-cleavable C-O-C bond. Amongst these, those compounds are particularly preferred which belong to the types (1), (2), (7) and (9). Under type (2), especially the polymeric acetals should be singled out, and, of the acid-cleavable compounds of type (7), especially those whose aldehyde or ketone component has a boiling point above 150°C, preferably above 200°C. Overall, however, such mixtures are not preferred.

The compound (c) or the combination of compounds (c) is present in a concentration from 1 to 60% by weight.

The radiation-sensitive mixture according to the invention also contains at least one polymeric binder which is insoluble in water but soluble or at least swellable in aqueous alkaline solutions. The binder is distinguished in particular by being well compatible with the other constituents of the radiation-sensitive mixture according to the invention and having the lowest possible characteristic absorption, i.e. high transparency, especially in the wavelength range from 190 to 550 nm. Binders based on novolak condensation resins, which are as a rule used in combination with naphthoquinonediazides as the photoactive components, do not meet this requirement. Although novolak condensation resins show, after image-wise exposure, an increase in the solubility in aqueous alkaline developers in the exposed areas, their characteristic absorption is undesirably high in the region of the short wavelength desired for the irradiation.

For the conventional applications, i.e. with light sources in the near UV region, binders based on novolak



condensation resins are particularly suitable, which have as a rule been used in combination with naphthoquinone-diazides as the photoactive components. Such phenol/formaldehyde condensates have been described many times and can, as a phenolic component, contain phenol, the three position-isomeric cresols or other alkylphenols, for example xlenols, as components. Apart from formaldehyde, other aldehydes can also be utilized for preparing the polymer. However, the polymers containing hydroxy groups, described below, can also be used for irradiations with near UV light, and these can be admixed to the novolak polymers described above in a proportion of up to 50%, preferably up to 20%.

For applications in the UV2 range, however, novolak condensation resins can be used as a mixture with other resins of higher transparency, suitable as binders. The mixing ratios here depend predominantly on the nature of the binder to be mixed with the novolak resin. Especially important factors are the degree of characteristic absorption of the binder in the said wavelength range, and also the miscibility with the other constituents of the radiation-sensitive mixture. In general, however, the binder of the radiation-sensitive mixture according to the invention can contain up to 50% by weight, especially up to 20% by weight, of a novolak condensation resin.

Suitable binders are homopolymers or copolymers of p-hydroxystyrene and alkyl derivatives thereof, for example of 3-methyl-4-hydroxystyrene, of 3,5-dimethyl-4-hydroxystyrene or 2,3-dimethyl-4-hydroxystyrene, and homopolymers or copolymers of other vinylphenols, for example of 2- or 3-hydroxystyrene or of 4-methyl-3-hydroxystyrene, or the esters or amides of methacrylic acid with phenols, for example pyrocatechol, resorcinol, hydroquinone, pyrogallol or aminophenols and the corresponding amides with aromatic amines. Polymerizable compounds such as styrene, methyl methacrylate, methyl acrylate or the like can be used as comonomers.



Mixtures having an increased plasma resistance are obtained when silicon-containing vinyl monomers, for example vinyltrimethylsilane or allyltrimethylsilane, are used for the preparation of copolymers of the above type.

5 The transparency of these binders is generally higher in the region of interest, so that improved structuring is possible.

Equally well, homopolymers or copolymers of maleimide can also be used. These binders too show a high transparency

10 in the wavelength range described. Here again, the comonomers preferably used are styrene, substituted styrenes, vinylphenols, propenylphenols, vinyl ethers, vinyl esters, vinylsilyl compounds or (meth)acrylates.

Finally, copolymers of styrene can, furthermore, also be

15 used with comonomers which effect an increase in solubility in aqueous alkaline solutions. These include, for example, maleic anhydride, maleic acid half-esters or the like.

The said binders can also advantageously be mixed with

20 one another if this does not impair the film-forming properties and the optical quality of the radiation-sensitive mixture.

The quantity of binder is in general 40 to 95% by weight, especially 40 to 90% by weight, preferably 50 to 85% by

25 weight, relative to the total weight of the radiation-sensitive mixture.

The extinction of the binder or of the combination of binders (a) in the wavelength range of the sensitivity of compound (b) should be less than $0.5 \mu\text{m}^{-1}$.

If appropriate, dyes, pigments, plasticizers, wetting

30 agents and flow agents, and also polyglycols and cellulose ethers, for example ethylcellulose, can also be added to the radiation-sensitive mixtures according to



the invention to improve special requirements, such as flexibility, adhesion and gloss.

When a substrate is to be coated, the radiation-sensitive mixture according to the invention is expediently dissolved in a solvent or in a combination of solvents. Ethylene glycol, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol monoethyl ether or propylene glycol monoalkyl ethers, especially propylene glycol methyl ether, aliphatic esters (for example ethyl acetate, hydroxyethyl acetate, alkoxyethyl acetate, n-butyl acetate, propylene glycol alkyl ether-acetate, especially propylene glycol methyl ether-acetate or amyl acetate), ethers (for example dioxane), ketones (for example methyl ethyl ketone, methyl isobutyl ketone, cyclopentanone and cyclohexanone), dimethylformamide, dimethylacetamide, hexamethylphosphoramide, N-methylpyrrolidone, butyrolactone, tetrahydrofuran and mixtures thereof are particularly suitable for this purpose. Glycol ethers, aliphatic esters and ketones are particularly preferred.

Ultimately, the choice of the solvents depends on the coating process used, on the desired layer thickness and on the drying conditions. The solvents must also be chemically neutral, i.e. they must not react irreversibly with the other layer components.

The solution prepared with the said solvents has as a rule a solids content from 5 to 60% by weight, preferably up to 50% by weight.

Finally, the invention also relates to a radiation-sensitive recording material which is composed essentially of a substrate and, located thereon, a radiation-sensitive layer of the radiation-sensitive mixture according to the invention.

Possible substrates are all those materials of which



capacitors, semiconductors, multi-layer printed circuits or integrated circuits are composed or from which these can be produced. Silicon substrates which can also be thermally oxidized and/or coated with aluminum, and also
5 doped, merit special mention. In addition, all other substrates usual in semiconductor technology are possible, such as silicon nitride, gallium arsenide and indium phosphide. Moreover, the substrates known from liquid crystal display manufacture are possible, such as,
10 for example, glass and indium-tin oxide and also metal plates and foils - for example of aluminum, copper and zinc, bimetal foils and trimetal foils, and also electrically non-conductive foils on which metals have been vapor-deposited, and paper. These substrates can have
15 been thermally pretreated, superficially roughened, incipiently etched or, to improve desired properties, for example to enhance the hydrophilic character, pretreated with chemicals.

To impart better cohesion and/or better adhesion of the
20 radiation-sensitive layer to the substrate surface, the layer can contain an adhesion promoter. In the case of silicon or silica substrates, adhesion promoters of the aminosilane type such as, for example, 3-aminopropyltriethoxysilane or hexamethyldisilazane, can be used for
25 this purpose.

Suitable supports for the production of photomechanical recording layers, such as printing forms for letterpress printing, planographic printing, screen printing and flexographic printing, are in particular aluminum plates,
30 which may have been anodically oxidized, grained and/or silicated beforehand, and also zinc and steel plates which may be chromium-plated, and also plastic films and paper.

The recording material according to the invention is
35 exposed imagewise to actinic radiation. Within the scope of this description, actinic radiation is to be

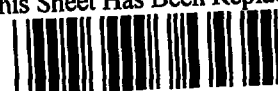


understood as any radiation having an energy at least corresponding to that of short-wave visible light. Suitable radiation sources are especially metal halide lamps, carbon arc lamps, xenon lamps and mercury vapor lamps.

5 Likewise, exposure can be carried out with high-energy radiation such as laser radiation, electron beams or X-rays. However, lamps which can emit light of a wavelength from 190 to 260 nm, i.e. especially xenon lamps and mercury vapor lamps, are particularly preferred. Further-
10 more, laser light sources can also be used, for example excimer lasers, especially KrF or ArF lasers, which emit at 248 and 193 nm respectively. The radiation sources must show adequate emission in the said wavelength ranges.

15 The thickness of the light-sensitive layer depends on the intended use. In general it is between 0.1 and 100 μm , preferably 1 and 10 μm .

The invention also relates to a process for producing a radiation-sensitive recording material. The radiation-
20 sensitive mixture can be applied to the substrate by spraying, flow-coating, rolling, whirler-coating and dip-coating. The solvent is then removed by evaporation, so that the radiation-sensitive layer remains on the surface of the substrate. The removal of the solvent can be
25 promoted by heating the layer to temperatures of up to 150°C. The mixture can, however, also be first applied in the abovementioned way to a temporary support, from which it is transferred under pressure and at an elevated temperature to the final support material. The materials
30 used as temporary support can in principle be all those which are also suitable as support materials. Subsequently, the layer is irradiated imagewise. The layer is then treated with a developer solution which dissolves and removes the irradiated areas of the layer,
35 so that an image of the original used in the imagewise irradiation remains on the substrate surface.



Suitable developers are especially aqueous solutions which contain silicates, metasilicates, hydroxides, hydrogen phosphates and dihydrogen phosphates, carbonates or hydrogen carbonates of alkali metal ions, alkaline earth metal ions and/or ammonium ions, and also ammonia and the like. Metal ion-free developers are described in US-A 4,729,941, EP-A 0,062,733, US-A 4,628,023, US-A 4,141,733, EP-A 0,097,282 and EP-A 0,023,758. The content of these substances in the developer solution is in general 0.1 to 15% by weight, preferably 0.5 to 5% by weight, relative to the weight of the developer solution. Preferably, metal ion-free developers are used. Small quantities of a wetting agent can have been added to the developers, in order to facilitate the detachment of the soluble areas of the layer.

The developed layer structures can be post-hardened. This is effected in general by heating on a hotplate up to a temperature below the flow temperature and subsequent exposure of the whole area to the UV light from a xenon-mercury vapor lamp (range from 200 to 250 nm). As a result of the post-hardening, the image structures are crosslinked, so that in general they have a flow resistance up to temperatures of more than 200°C. The post-hardening can also be effected without a temperature increase solely by irradiation with high-energy UV light.

The radiation-sensitive mixture according to the invention is used in the production of integrated circuits or of individual electronic components by lithographic processes. The developed resist layer here serves as a mask for the subsequent process steps. Examples of such steps are etching of the layer support, the implantation of ions in the layer support or the precipitation of metals or other materials on the layer support.

Examples 1 to 17 which follow illustrate the suitability of the mixture according to the invention for recording materials in microlithography, using radiation of very



diverse energy. The superiority of the mixtures according to the invention over the state of the art is demonstrated by reference to the comparison examples 18 to 21. Examples 22 to 24 document the applicability of the mixture in printed circuits and planographic printing plates.

In the examples, the quantities are as a rule stated as parts by weight (p.b.w.). Unless otherwise stated, percentage figures and quantitative ratios are to be understood as being in weight units.

Example 1

A coating solution was prepared from

7.5 p.b.w. of a cresol/formaldehyde novolak having a softening range from 105 to 120°C,
2.0 p.b.w. of Compound 1 and
0.6 p.b.w. of α,α -bis(4-tert.-butyl-benzenesulfonyl)-diazomethane in
42 p.b.w. of propylene glycol monomethyl ether-acetate.

The solution was filtered through a filter of 0.2 μ m pore diameter and whirler-coated at 3,200 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying for 1 minute at 100°C on the hotplate, a layer thickness of 1.1 μ m was obtained.

The recording material was exposed imagewise under an original to the radiation of a xenon-mercury vapor lamp at 365 nm with an energy of 80 mJ/cm². To complete the cleavage of the solution inhibitor, the material was heated for 1 minute to 60°C.

The recording material was developed using the developer of the following composition:

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5.3 p.b.w. of sodium metasilicate $\times 9 \text{ H}_2\text{O}$,
3.4 p.b.w. of trisodium phosphate $\times 12 \text{ H}_2\text{O}$,
0.3 p.b.w. of sodium dihydrogen phosphate and
191 p.b.w. of deionized water.

5 After a developing time of 60 seconds, this gave a
defect-free image of the mask with steep resist flanks,
structures of $< 0.55 \mu\text{m}$ also being resolved in true
detail. An examination of the flanks of the resist
profiles by means of scanning electron microscopy proved
10 that these were aligned virtually perpendicular to the
substrate surface. The contrast was 3.8.

The contrast of a positive resist, γ_p , is defined as

$$\gamma_p = 1 / (\log D_p - \log D_p^0) = [\log(D_p/D_p^0)]^{-1}$$

where D_p^0 is the irradiation dosage at which the developer
15 starts to attack the exposed film, and D_p is the resist
space point (= resist sensitivity). An accurate des-
cription of this parameter has been given in the article
by L.F. Thompson and M.J. Bowden "Resist Processing"
(Introduction to Microlithography, Theory, Materials and
20 Processing, edited by C.G. Willson, L.F. Thompson and
M.J. Bowden, ACS Symp. Ser., 219, 164 et seq. (1983),
American Chemical Society, Washington).

Example 2

A coating solution was prepared from

25 7.5 p.b.w. of a styrene/p-hydroxystyrene copolymer
(molar ratio 20:80) having a mean molecular
weight of 32,000,
2.0 p.b.w. of Compound 2 and
0.5 p.b.w. of α, α -bis-(4-tert.-butyl-benzenesulfonyl)-
30 diazomethane in
42 p.b.w. of propylene glycol monomethyl ether-
acetate.



5 The solution was filtered through a filter of 0.2 μm pore diameter and whirler-coated at 3,000 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying for 1 minute at 100°C on the hotplate, a layer thickness of 1.12 μm was obtained.

10 The recording material was exposed imagewise under an original to the radiation of a xenon-mercury vapor lamp at 260 nm with an energy of 92 mJ/cm² and then heated for 1 minute at 65°C. It was then processed using an aqueous developer which contained 2.38% of tetramethylammonium hydroxide. After 60 seconds, this gave a defect-free image of the mask with high flank stability. A contrast value of 5.6 was determined, and here again structures of < 0.55 μm were resolved in true detail.

15 Example 3

A coating solution was prepared from

7.5 p.b.w. of a poly(pyrocatechol monomethacrylate)
having a softening range from 125 to 135°C,
2.0 p.b.w. of Compound 3 and
20 0.4 p.b.w. of 2-(4-ethoxy-naphthalen-1-yl)-4,6-bis-
trichloromethyl-1,3,5-triazine in
42 p.b.w. of propylene glycol monomethyl ether-
acetate.

25 The solution was filtered through a filter of 0.2 μm pore diameter and whirler-coated at 3,200 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying for 1 minute at 100°C on the hotplate, a layer thickness of 1.1 μm was obtained.

30 A wafer coated in this way was irradiated under an original with light of a wavelength of 405 nm and an energy of 100 mJ/cm². The material was then heated for 1 minute at 60°C. After development, an image true to the original was obtained.



Example 4

5 The experiment of Example 3 was repeated, but light of a wavelength of 436 nm was used. To obtain a sharp-edged image of the original, it was necessary to use an exposure energy of 135 mJ/cm².

Example 5

A coating solution was prepared from

10 7.5 p.b.w. of a styrene/maleimide copolymer (molar ratio 1:1) having a softening range from 165 to 180°C,
2.0 p.b.w. of Compound 3 and
0.6 p.b.w. of benzenesulfonyl-(4-chlorobenzoyl)-diazomethane in
15 42 p.b.w. of propylene glycol monomethyl ether-acetate.

20 The solution was filtered through a filter of 0.2 µm pore diameter and whirler-coated at 3,700 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying for 1 minute at 100°C, a layer thickness of 0.98 µm was obtained.

The recording material was exposed imagewise under an original to the radiation of a xenon-mercury vapor lamp at 260 nm with an energy of 120 mJ/cm². The material was then heated for 2 minutes at 65°C.

25 The recording material was developed using a 0.02 N aqueous solution of tetramethylammonium hydroxide, the exposed areas being detached without residue within 60 seconds. A defect-free image of the mask with steep resist flanks was obtained. The loss in the dark was
30 < 20 nm; even structures of < 0.6 µm were resolved in true detail.

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Example 6

A coating solution was prepared from

7.5 p.b.w. of the copolymer from Example 5,
2.0 p.b.w. of Compound 4 and
5 0.4 p.b.w. of 4-(2-[2]furyl-vinyl)-6-trichloromethyl-
2-pyrone in
42 p.b.w. of propylene glycol monomethyl ether-
acetate.

10 The solution was filtered through a filter of 0.2 μm pore
diameter and whirler-coated at 3,500 rpm onto a wafer
treated with an adhesion promoter (hexamethyldisilazane).
After drying for 1 minute at 100°C, a layer thickness of
1.00 μm was obtained.

15 The recording material was exposed imagewise under an
original to radiation from a xenon-mercury vapor lamp at
260 nm with an energy of 112 mJ/cm² and then heated for 1
minute at 60°C.

20 The recording material was developed using a 0.02 N
aqueous solution of tetramethylammonium hydroxide, the
exposed areas being detached without residue within
60 seconds and an image of the original true to detail
being obtained. The measured contrast was about 8; the
edge steepness of the image was correspondingly
excellent.

25 Example 7

A coating solution was prepared from

7.5 p.b.w. of the copolymer described in Example 2,
2.0 p.b.w. of Compound 11 and
30 0.3 p.b.w. of triphenylsulfonium trifluoromethanesul-
fonate in
42 p.b.w. of propylene glycol monomethyl ether-
acetate.



5 The solution was filtered through a filter of 0.2 μm pore diameter and whirler-coated at 3,500 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying for 1 minute at 100°C, a layer thickness of 1.04 μm was obtained.

The recording material was exposed imagewise under an original to radiation from a xenon-mercury vapor lamp at 260 nm with an energy of 112 mJ/cm². It was then heated for 1 minute at 60°C.

10 The recording material was developed using a 0.27 N aqueous solution of tetramethylammonium hydroxide, the exposed areas being detached without residue within 60 seconds and an image of the original true to detail being obtained. Lines and gaps down to 0.5 μm were reproduced true to the mask.

Example 8

20 The recording material from Example 7 was irradiated with synchrotron radiation (BESSY, Berlin, 754 MeV) through a gold-on-silicon mask at a dosage of 120 mJ/cm². The experimental arrangement is to be found in A. Heuberger, Microelectr. Eng., 3, 535 (1985). The exposed material was left to lie for 30 minutes at room temperature. After development using the developer described in Example 7 and a developing time of 120 seconds, a defect-free image of the mask down to structures of < 0.4 μm was obtained. 25 The contrast was determined to be > 8; the resist flanks were virtually perpendicular to the planar substrate surface.

Example 9

30 A coating solution was prepared from

7.5 p.b.w. of a formaldehyde/m-kresol/p-kresol novolak
having a softening point from 100 to 110°C,
2.0 p.b.w. of Compound 14 and
0.3 p.b.w. of 2-(4-methoxystyryl)-4,6-bis-trichloro-



methy1-1,3,5-triazine in
42 p.b.w. of propylene glycol monomethyl ether-
acetate.

5 The solution was filtered through a filter of 0.2 μm pore
diameter and whirler-coated at 3,200 rpm onto a wafer
treated with an adhesion promoter (hexamethyldisilazane).
After drying for 1 minute at 100°C, a layer thickness of
1.05 μm was obtained.

10 The recording material was exposed imagewise under an
original to radiation of a wavelength of 365 nm with an
energy of 95 mJ/cm² and then heated for 1 minute at 65°C.

The recording material was developed using a developer of
the following composition:

15 5.5 p.b.w. of sodium metasilicate $\times$ 9 H₂O,
3.4 p.b.w. of trisodium phosphate $\times$ 12 H₂O, and
0.4 p.b.w. of anhydrous monosodium phosphate in
90.7 p.b.w. of deionized water,

20 the exposed areas being detached without residue within
60 seconds and an image of the original true to detail
being obtained. Lines and gaps down to 0.5 μm were
reproduced true to the mask.

Example 10

A coating solution was prepared from

25 6.0 p.b.w. of a homopolymer of 3-methyl-4-hydroxysty-
rene having a softening point from 155 to
160°C and a molecular weight of 22,000,
3.5 p.b.w. of Compound 1 and
0.1 p.b.w. of 1,2,3-tris-methanesulfonyloxybenzene in
42 p.b.w. of propylene glycol monomethyl ether-
30 acetate.

The solution was filtered through a filter of 0.2 μm pore



diameter and whirler-coated at 3,000 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying for 1 minute at 100°C, a layer thickness of 1.05 μm was obtained.

- 5 The recording material was exposed imagewise under an original to radiation of a wavelength of 248 nm with an energy of 25 mJ/cm². The recording material was then heated for 1 minute at 60°C.

- 10 The recording material was developed using an aqueous developer which contained 2.38% of tetramethylammonium hydroxide. Even after a few seconds, it was possible to obtain an image true to the original, in which even details of < 0.5 μm were resolved. The contrast was determined to be 4.5.

15 Example 10a

- 5 wafers were coated as described in Example 10 but, in place of the quantity of Compound 1 indicated therein, 0.3, 0.6, 0.9, 1.2 and 1.5 p.b.w. were used. The samples were processed as described in Example 10. The results are shown in the tables after Comparison Example 21.

Example 11

- 25 The mixture described in Example 10 was applied, exposed and finally heated as described therein. The development was carried out using the developer described therein, to which 10% of isopropanol had been added. Details down to 0.3 μm were reproduced true to the original. The profiles of even the smallest fractures were virtually vertical.

Example 12

A coating solution was prepared from

- 30 6.0 p.b.w. of the homopolymer indicated in Example 10,
3.5 p.b.w. of Compound 1 and
0.2 p.b.w. of 4-methyl-6-(4-methoxystyryl)-N-methane-sulfonyloxy- α -pyridone in



42 p.b.w. of propylene glycol monomethyl ether-acetate.

5 The solution was filtered through a filter of 0.2 μm pore diameter and whirler-coated at 3,100 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying for 1 minute at 100°C, a layer thickness of 1.05 μm was obtained.

10 The recording material was exposed imagewise under an original to the radiation of a KrF-excimer laser at 248 nm with an energy of 65 mJ/cm². The recording material was then heated for 1 minute at 60°C.

15 The recording material was developed using an aqueous developer which contained 2.38% of tetramethylammonium hydroxide. Even after a few seconds, it was possible to obtain an image true to the original, in which even details of less than 0.5 μm were resolved.

Example 13

20 The material described in Example 12 was irradiated with light of a wavelength of 240 to 260 nm and further processed as described therein. In order to obtain a true image of the original down to 0.6 μm , a dosage of 45 mJ/cm² was necessary.

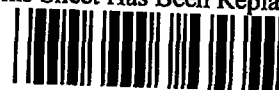
Example 14

25 The material described in Example 12 was irradiated with light of a wavelength of 365 nm and further processed as described therein. In order to obtain a true image of the original down to 0.6 μm , a dosage of 85 mJ/cm² was necessary.

Example 15

30 The material described in Example 12 was irradiated with light of a wavelength of 405 nm and further processed as described therein. In order to obtain a true image of the original down to 0.65 μm , a dosage of 97 mJ/cm² was





necessary.

Example 16

5 The material described in Example 12 was irradiated with light of a wavelength of 436 nm and further processed as described therein. In order to obtain a true image of the original down to 0.65 μm , a dosage of 122 mJ/cm² was necessary.

Example 17 and Comparison Examples 18 to 21

10 In each case five coating solutions of the five basic formulations identified below were prepared, the solution inhibitor being employed in a quantity of 5% by weight, 10% by weight, 15% by weight, 20% by weight and 25% by weight, relative to the quantity of the polymer used (= 0.3 p.b.w., 0.6 p.b.w., 0.9 p.b.w., 1.2 p.b.w., 15 1.5 p.b.w.):

Example 17

6.0 p.b.w. of the homopolymer indicated in Example 10,
x p.b.w. of Compound 1 and
0.2 p.b.w. of 2-(4-methoxystyryl)-4,6-bis-trichloro-
20 methyl-1,3,5-triazine in
42 p.b.w. of propylene glycol monomethyl ether-
acetate.

Comparison Example 18

25 6.0 p.b.w. of the homopolymer indicated in Example 10,
x p.b.w. of a monomeric acetal prepared from 1 mol of benzaldehyde and 2 mol of phenoxyethanol and
0.2 p.b.w. of 2-(4-methoxystyryl)-4,6-bis-trichloro-
methyl-1,3,5-triazine in
42 p.b.w. of propylene glycol monomethyl ether-
30 acetate.

Comparison Example 19

6.0 p.b.w. of the homopolymer indicated in Example 10,
x p.b.w. of an oligomeric acetal prepared from 1 mol
of benzaldehyde and 1 mol of diethylene

glycol and
0.2 p.b.w. of 2-(4-methoxystyryl)-4,6-bis-trichloro-
methyl-1,3,5-triazine in
42 p.b.w. of propylene glycol monomethyl ether-
5 acetate.

Comparison Example 20

6.0 p.b.w. of the homopolymer indicated in Example 10,
x p.b.w. of an oligomeric acetal from 1 mol of
benzaldehyde and 1 mol of butyne-1,4-diol
10 and
0.2 p.b.w. of 2-(4-methoxystyryl)-4,6-bis-trichloro-
methyl-1,3,5-triazine in
42 p.b.w. of propylene glycol monomethyl ether-
acetate.

15 Comparison Example 21

6.0 p.b.w. of the homopolymer indicated in Example 10,
x p.b.w. of a monomeric acetal prepared from 1 mol of
benzaldehyde with 2 mol of 1,4-bis-hydroxy-
methyl-cyclohexane and
20 0.2 p.b.w. of 2-(4-methoxystyryl)-4,6-bis-trichloro-
methyl-1,3,5-triazine in
42 p.b.w. of propylene glycol monomethyl ether-
acetate.

25 The solutions were filtered through a filter of 0.2 μ m
pore diameter and each whirler-coated onto two wafers
treated with an adhesion promoter (hexamethyldisilazane),
the conditions being selected such that a layer thickness
of $1.00 \pm 0.05 \mu$ m was obtained after drying at 100°C.

30 The wafers were then dipped for 1 minute at 21°C into an
aqueous developer containing 0.27 mol/l of tetramethyl-
ammonium hydroxide, and the layer loss was determined by
means of a layer thickness-measuring instrument. The pure
polymer had a loss rate of 327 nm/minute in this
35 developer. The following values were obtained for the
rates of loss in the dark from the various mixtures



(nm/minute):

Example No.	Concentration of solution inhibitor				
	5%	10%	15%	20%	25%
10	103	39	6	8	6
17	92	45	10	10	8
18	370	225	157	143	182
19	340	309	299	266	287
20	192	152	96	107	163
21	197	145	114	97	65

It can be seen from this result that the oligomeric N,O-acetals according to the invention show a significantly improved inhibiting effect for polyhydroxystyrene polymers. Similar results could also be obtained with other phenolic polymers.

The remaining wafers were then irradiated by a KrF excimer laser at a dosage of 100 mJ/cm², heated for 1 minute at 60°C, and the loss in bright light was determined (nm/minute):

Example No.	Concentration of solution inhibitor				
	5%	10%	15%	20%	25%
10	450	600	780	900	977
17	412	450	617	822	897
18	470	521	640	842	912
19	320	350	345	375	360
20	400	510	590	690	820
21	420	478	534	590	700

This shows that the mixtures containing the N,O-acetals according to the invention have a very good



dissolution-promoting action after exposure. The ratio of the loss rates between exposed and unexposed layer areas is in their case by far the greatest of all the examples, i.e. they allow a very good differentiation between image areas and non-image areas.

Example 22

A coating solution was prepared from

- 7.5 p.b.w. of a copolymer of 3-methyl-4-hydroxystyrene/
4-hydroxystyrene (molar ratio 2:1) having a
mean molecular weight of 18,000,
- 2.0 p.b.w. of Compound 1 (molecular weight approx. 3,000),
- 0.2 p.b.w. of α,α -bis-(4-methylbenzenesulfonyl)-diazomethane
in
- 42 p.b.w. of propylene glycol monomethyl ether-acetate.

The solution was filtered through a filter of 0.2 μm pore diameter and whirler-coated at 3,200 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying for one minute on a hot plate, a layer thickness of 1.03 μm was obtained.

The recording material was exposed imagewise under an original to the radiation of a KrF-excimer laser with an energy of 34 mJ/cm², using a PAS 5000/70 exposure apparatus (manufacturer ASM-Lithography) and then heated for 1 minute at 60 °C.

The recording material was developed using an aqueous developer which contained 2.38 % of tetramethylammonium hydroxide. After 60 seconds a flawless reproduction of the mask was obtained, structures down to 0.35 μm being resolved in true detail.

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Example 23

A coating solution was prepared from

7.5 p.b.w. of a copolymer of 3-methyl-4-hydroxystyrene/
4-hydroxystyrene (molar ratio 1:1) having a
mean molecular weight of 17,000,

2.0 p.b.w. of Compound 1 (molecular weight approx. 5,000),

0.3 p.b.w. of α,α -bis-(4-chlorobenzenesulfonyl)-diazomethane
in

42 p.b.w. of propylene glycol monomethyl ether-acetate.

The solution was filtered through a filter of 0.2 μm pore
diameter and whirler-coated at 3,500 rpm onto a wafer treated
with an adhesion promoter (hexamethyldisilazane). After
drying for one minute on a hot plate, a layer thickness of
0.98 μm was obtained.

The recording material was exposed imagewise under an
original to the radiation of a KrF-excimer laser with an
energy of 38 mJ/cm^2 , using a PAS 5000/70 exposure apparatus
(manufacturer ASM-Lithography) and then heated for 1 minute
at 60 °C.

The recording material was developed using an aqueous
developer which contained 2.38 % of tetramethylammonium
hydroxide. After 60 seconds a flawless reproduction of the
mask was obtained, in which even structures down to 0.30 μm
were resolved in true detail. The angle of structure edges
was in the range of $90^\circ \pm 3^\circ$.

Example 24

A coating solution was prepared from

4.5 p.b.w. of a homopolymer of 3-methyl-4-hydroxystyrene
having a mean molecular weight of 22,000,



3.0 p.b.w. of a homopolymer of 4-hydroxystyrene having a
mean molecular weight of 30,000 (PHS from
HOECHST CELANESE CORPORATION),

2.0 p.b.w. of Compound 1 (molecular weight approx. 5,000),

5 0.3 p.b.w. of α,α -bis-(4-bromobenzenesulfonyl)-diazomethane
in

42 p.b.w. of propylene glycol monomethyl ether-acetate.

10 The solution was filtered through a filter of 0.2 μm pore
diameter and whirler-coated at 3,500 rpm onto a wafer treated
with an adhesion promoter (hexamethyldisilazane). After
drying for one minute on a hot plate, a layer thickness of
0.94 μm was obtained.

15 The recording material was exposed imagewise under an
original to the radiation of a KrF-excimer laser with an
energy of 30 mJ/cm^2 , using a PAS 5000/70 exposure apparatus
(manufacturer ASM-Lithography) and then heated for 1 minute
at 60 °C.

20 The recording material was developed using an aqueous
developer which contained 2.38 % of tetramethylammonium
hydroxide. While the non-image areas showed an erosion of
< 20 nm/min, the erosion produced by the developer in the
exposed areas was >10,000 nm/min. After 60 seconds a
flawless reproduction of the mask was again obtained,
structures down to 0.30 μm being resolved in true detail.
25 The angle of the structure edges was in the range of 90° $\pm$
3°.

Example 25

A coating solution was prepared from

30 3.0 p.b.w. of a homopolymer of 3-methyl-4-hydroxystyrene
having a mean molecular weight of 22,000,



- 4.5 p.b.w. of a homopolymer of 4-hydroxystyrene having a mean molecular weight of 30,000 (PHS from HOECHST CELANESE CORPORATION),
2.0 p.b.w. of Compound 1 (molecular weight approx. 5,000),
5 0.3 p.b.w. of α,α -bis-(4-chlorobenzenesulfonyl)-diazomethane in
42 p.b.w. of propylene glycol monomethyl ether-acetate.

10 The solution was filtered through a filter of 0.2 μm pore diameter and whirler-coated at 3,500 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying for one minute on a hot plate, a layer thickness of 0.90 μm was obtained.

15 The recording material was exposed imagewise under an original to the radiation of a KrF-excimer laser with an energy of 30 mJ/cm^2 , using a PAS 5000/70 exposure apparatus (manufacturer ASM-Lithography) and then heated for 1 minute at 60 °C.

20 The recording material was developed using an aqueous developer which contained 2.38 % of tetramethylammonium hydroxide. While the non-image areas showed an erosion of < 20 nm/min, the erosion produced by the developer in the exposed areas was >10,000 nm/min. After 60 seconds a flawless reproduction of the mask was obtained, structures down to 0.35 μm being resolved in true detail. The angle of
25 the structure edges was in the range of $90^\circ \pm 3^\circ$.

Example 26

30 The coated wafer of Example 23 was exposed through a phase-shifting mask, using the exposure apparatus there described. Under the conditions described in this example, structures down to 0.16 μm could be reproduced true to scale and with virtually vertical resist profiles.



Example 27

The coated wafer of Example 24 was exposed through a phase-shifting mask, using the exposure apparatus there described. Under the conditions described in this example, structures down to 0.16 μm could be reproduced true to scale and with virtually vertical resist profiles.

Example 28

For producing an offset printing plate, an aluminum foil having a mechanically roughened and anodized surface was whirler-coated with a coating solution of the following composition:

7.5 p.b.w. of the novolak indicated in Example 1,
2.3 p.b.w. of Compound 1,
0.3 p.b.w. of 2-(4-methoxystyryl)-4,6-bis-trichloro-
methyl-1,3,5-triazine and
0.05p.b.w. of crystal violet base in
90 p.b.w. of propylene glycol monomethyl ether-
acetate.

After drying of the layer (dry weight about 2.5 g/cm²), it was exposed under a positive test original for 30 seconds, stored for 15 minutes at room temperature and developed using a developer of the following composition:

0.5 p.b.w. of sodium hydroxide,
0.8 p.b.w. of sodium metasilicate $\times 9 \text{ H}_2\text{O}$ and
1.0 p.b.w. of 2-n-butoxyethanol in
97.7p.b.w. of deionized water.

After rinsing with water, the plate was made ready for treating by wiping with 1% phosphoric acid. After clamping into a printing press, 55,000 perfect prints of the original were obtained.

Example 29

The solution of a positive dry resist was prepared by preparing the following composition:



- 12.5 p.b.w. of the novolak described in Example 9,
10.0 p.b.w. of Compound 7,
0.5 p.b.w. of 4-(2-[2]furyl-vinyl)-6-trichloromethyl-
2-pyrone and
5 0.1 p.b.w. of crystal violet in
25 p.b.w. of butanone.

10 A 25 μ m thick polyethylene terephthalate film was coated
with this solution to give a dry layer thickness of
16 μ m. The surface of the dry resist film was laminated
to a further polyethylene terephthalate film having lower
adhesion. After peeling off the cover film, the dry film
was laminated under pressure and heat to a brass plate.
After cooling and peeling off the support film, the plate
was exposed through an original, good image contrast
15 becoming visible. After storage for 20 minutes, the
exposed areas were spray-developed using a developer of
the composition indicated in Example 11. The plate was
then etched through to smooth flanks. The milled products
20 obtained can be yet further processed before they are
separated.

Example 30

A coating solution was prepared from

- 7.5 p.b.w. of the novolak indicated in Example 9,
2.0 p.b.w. of Compound 14,
25 0.05 p.b.w. of crystal violet base and
0.6 p.b.w. of 2-(4-methoxystyryl)-4,6-bis-trichloro-
methyl-1,3,5-triazine in
42 p.b.w. of propylene glycol monomethyl ether-
acetate.

30 The solution was whirler-coated onto an electrolytically
roughened and anodized aluminum plate, which had been
treated beforehand with an aqueous solution of polyvinyl-
phosphonic acid, and dried. The layer weight of the dried
layer was 1.5 μ m.



5 The imagewise exposure was carried out under a 5 kW metal halide lamp at a distance of 110 cm. After a waiting time of 10 minutes, the plate was developed using the developer described in Example 9, the exposed areas being detached. The printing form thus obtained was gummed and clamped into a planographic printing press, where it gave more than 125,000 prints of excellent quality.

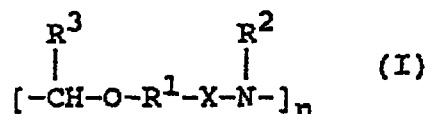
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91/K023

April 10, 1992
WL-Dr.P.-wfPatent claims

1. A compound of the formula I



5 in which

R¹ is an alkylene, cycloalkylene, alkenylene, alkynylene or arylenebisalkyl group, in which one or more aliphatic CH₂ group(s) can have been replaced by oxygen or sulfur atoms,

10 R² is an alkyl, alkenyl, alkynyl, cycloalkyl, alkoxyalkyl, aryl, aralkyl or aryloxyalkyl radical,

R³ is an alkyl or aryl radical,

X is one of the groups -CO-, -O-CO- or -NH-CO- and

15 n is an integer greater than 1.

2. A compound as claimed in claim 1, wherein R¹ is an alkylene, alkenylene or alkynylene group having 2 to 18 carbon atoms, in which 1 to 3 CH₂ groups can have been replaced by oxygen or sulfur atoms, a cyclo-
20 alkylene group having 4 to 18 carbon atoms, an aralkylene group having 7 to 18 carbon atoms or an arylenebisalkyl group having 8 to 18 carbon atoms.

3. A compound as claimed in claim 1, wherein R² is an alkyl radical having 1 to 12 carbon atoms, an alkenyl or alkynyl radical having 2 to 12 carbon atoms, an alkoxyalkyl radical having 3 to 12 carbon atoms, a cycloalkyl radical having 4 to 12 carbon atoms, an aryl radical having 6 to 12 carbon atoms, an aralkyl radical having 7 to 12 carbon atoms or an
25 aryloxyalkyl radical having 8 to 12 carbon atoms.
30

4. A compound as claimed in claim 1, wherein n is an





integer from 3 to 50.

5. A radiation-sensitive mixture which contains, as essential constituents,

(a) a binder which is insoluble in water and soluble or at least swellable in aqueous alkaline solutions,

(b) a compound which generates a strong acid under the action of actinic radiation and

(c) a compound which has at least one acid-cleavable C-O-C bond and whose acid cleavage products are more readily soluble in aqueous alkaline solutions than the compound itself,

wherein the acid-cleavable compound (c) is a compound as claimed in any of claims 1 to 4.

6. A radiation-sensitive mixture as claimed in claim 5, wherein the compound (b) is sensitive to light of a wavelength from 150 to 550 nm.

7. A radiation-sensitive mixture as claimed in claim 5, which contains the compound (c) in a concentration from 1 to 60% by weight.

8. A radiation-sensitive mixture as claimed in claim 5, wherein the binder (a) has an extinction of less than $0.5 \mu\text{m}^{-1}$ in the wavelength region of the sensitivity of compound (b).

9. A radiation-sensitive mixture as claimed in claim 8, wherein the binder is a polymer having phenolic hydroxy groups.

10. A radiation-sensitive mixture as claimed in claim 8, wherein the binder contains a mixture of various polymers having phenolic hydroxyl groups.



11. A radiation-sensitive mixture as claimed in claim 5, which contains the binder (a) in a concentration from 30 to 95 % by weight.

5 12. A radiation-sensitive mixture as claimed in claim 5, which contains the compounds (b) in a concentration from 0.2 to 25 % by weight.

13. A radiation-sensitive mixture as claimed in claim 5, wherein the compound (b) generates a sulfonic acid on photolysis.

10 14. A radiation-sensitive recording material comprising a layer support and a radiation-sensitive layer, wherein the layer is composed of a radiation-sensitive mixture as claimed in any of claims 5 to 13.

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