

The invention relates to radiation-sensitive and acid-cleavable compounds 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. The mixture contains

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

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

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.

5 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
10 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.

15 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
20 developer. Such materials are in general distinguished by an enhanced sensitivity to actinic radiation.

25 Numerous mixtures are known which contain, as the essential components, a polymeric binder soluble in aqueous alkaline solutions, a solubility-inhibiting compound and a compound which, on irradiation, generates the acid required for cleavage. The binder is in most cases a novolak resin. Many of these mixtures have a high sensitivity to actinic radiation. They are designated as chemically amplified, photocatalytic 3-component systems.

30 Of these mixtures, especially those have gained a certain commercial importance whose acid-cleavable component contains one or more acetal units. These mixtures have, however, certain disadvantages. Thus, they possess only a limited stability on the substrate materials to which

they have to be applied, which leads to an unsatisfactory, non-reproducible reproduction of the image original. This can be improved only by introducing additional protective layers, for example according to DE-A 3,621,376 (= US-A 4,840,867). The causes of the deterioration in the image reproduction are not known in detail and have been only inadequately investigated. For example, the process window, i.e. the processing latitude, for the exposure of these mixtures is very narrow and frequently not unambiguously reproducible. In particular, the quality of the image reproduction greatly depends on the time difference between exposure and development, the so-called delay time. 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.

It is also known from the papers by C.C. Petropoulos [J. Polym. Sci., Polym. Chem. Ed., 15, 1637 (1977)] that aromatic acetals which carry a nitro group in the vicinal position, are photodecomposable by high-energy UV radiation without acid catalysis, and can be used in positive-working radiation-sensitive recording materials. The photosensitivity of these compounds is likewise inadequate for applications in practice, since their photoreaction cannot be chemically amplified.

In DE-A 3,721,741 (= US-A 4,883,740), radiation-sensitive mixtures are described which contain a polymeric binder insoluble in water and soluble in aqueous alkaline solutions, and an organic compound which contains at least one acid-cleavable grouping and a grouping which

generates a strong acid under the action of radiation. The radiation-sensitive groups described are exclusively onium salt groups, in particular sulfonium salt groups.

5 The use of onium salts, such as diazonium, phosphonium, sulfonium and iodonium salts, of non-nucleophilic acids such as HSbF_6 , HAsF_6 or HPF_6 as photolytic acid generators involves disadvantages which drastically restrict their possible uses in various fields of application. Thus, for example, many of the onium salts are toxic. Their
10 solubility is inadequate in many solvents, which is why only a few solvents are suitable for preparing a coating solution. Furthermore, when the onium salts are used, undesired foreign atoms are sometimes introduced which can cause interference with the process, especially in
15 microlithography. Moreover, the onium salts form Brönstedt acids, which have a very severe corrosive action, in the photolysis. These acids attack sensitive substrates, so that the use of such mixtures leads to unsatisfactory results. Halogen compounds such as tri-
20 chloromethyltriazine derivatives or trichloromethyl-oxadiazole derivatives also form hydrohalic acids which have a severely corrosive action.

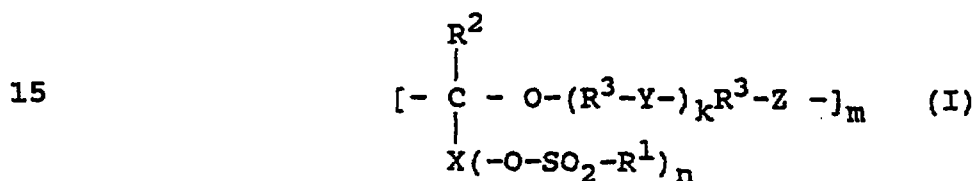
In more recent papers by F.M. Houlihan et al., SPIE 920, 67 (1988), it was shown by reference to positive-working
25 systems that, in addition to the abovementioned acid generators, nitrobenzyl tosylates, which on exposure generate sulfonic acids having a low migration tendency, can also be used in certain acid-unstable resist formulations. It can be deduced from these results that such
30 compounds can also be used for photo-curable systems. The sensitivities thus achieved, especially to UV radiation from 350 to 450 nm, and the thermal stability of the photoresists proved, however, to be inadequate.

35 Because of the inadequacies and disadvantages listed, there is therefore a demand for further radiation-sensitive mixtures which do not have the disadvantages

described above and possess a reactivity suitable in practice.

It was therefore the object of the invention to propose photolytically acid-generating and acid-cleavable compounds, and a radiation-sensitive mixture based thereon, where the photolytically acid-generating compound should be as stable as possible on all known substrates and gives an acid as the photolysis product, which does not have a corrosive action. Furthermore, the invention should provide a radiation-sensitive mixture which, in particular, avoids a segregation of the photoactive compound and of the solubility-differentiating compound.

According to the invention, compounds of the formula I



are proposed, in which

- R^1 is an alkyl, halogenoalkyl or aryl radical,
- R^2 is a hydrogen atom, an alkyl, alkenyl or aryl radical or the group $(\text{R}^1-\text{SO}_2-\text{O}-)_n\text{X}-$,
- R^3 is a cycloalkylenedialkyl, cycloalkenylenedialkyl, arylenedialkyl or heteroarylenedialkyl group, or an alkylene, alkenylene, alkynylene, cycloalkylene or arylene group,
- X is an alkyl, cycloalkyl or aryl group substituted by 1 to 3 sulfonyloxy groups $\text{R}^1-\text{SO}_2-\text{O}-$,
- Y is O, S, CO, CO-O, SO_2 , SO_2-O , NR^4 , CO-NH, O-CO-NR⁵, NH-CO-NR⁵ or NR⁵-CO-O,
- Z is O, CO-NR⁶, O-CO-NR⁶ or NH-CO-NR⁶,
- R^4 is an acyl radical,
- R^5 is a hydrogen atom or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl radical,
- R^6 is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl radical,

k is an integer from 0 to 4,
m is an integer greater than 1 and
n is an integer from 1 to 3,

5 where R^3 and Y in recurring groupings (R^3 -Y-) can have identical or different definitions.

Those compounds of the formula I are preferred in which
10 R^1 is an alkyl radical having 1 to 6 carbon atoms, which may be halogenated, in particular fluorinated, or an aryl radical having 6 to 12 carbon atoms, in particular a mononuclear aryl radical. The aryl radical can carry 1 to 3 substituents, in particular halogen atoms, nitro groups, cyano groups or alkyl or alkoxy groups having 1 to 3 carbon atoms.

15 R^2 is preferably a hydrogen atom, an alkyl radical having 1 to 6 and especially 1 to 3 carbon atoms, an alkenyl radical having 2 to 6 and especially 2 to 4 carbon atoms or an aryl radical having 6 to 12 carbon atoms, which may be substituted by halogen atoms, alkyl radicals having 1 to 3 carbon atoms, alkanesulfonyloxy radicals having 1 to 20 5 carbon atoms or alkoxy radicals having 1 to 3 carbon atoms, or a radical of the formula $(R^1-SO_2O)_nX$, and particularly preferably a hydrogen atom.

25 R^3 preferably is a cycloalkenylenedialkyl, cycloalkylenedialkyl, arylenedialkyl or heteroarylenedialkyl group having 6 to 20 and especially 6 to 15 carbon atoms, an alkylene group having 1 to 8 carbon atoms, an alkenylene or alkynylene group having 2 to 10 and especially 2 to 6 carbon atoms, a cycloalkylene group having 4 to 12 carbon atoms or an arylene group having 6 to 10 carbon atoms, in 30 particular a mononuclear arylene group having 6 to 8 carbon atoms.

X is preferably an alkyl group having 2 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms or an aryl group having 6 to 12 carbon atoms, in particular 35 a mononuclear aryl group having 6 to 10 carbon atoms,

aryl groups being particularly preferred. These groups are in each case substituted by 1 to 3 sulfonyloxy groups R^1-SO_2-O- .

5 Y preferably is O, S, NR^4 , SO_2 , $O-CO-NR^5$, $CO-O$, $NH-CO-NR^5$ or NR^5-CO-O .

In the cases where k is greater than 1, the groups R^3 and Y can have the same or a different definition in each recurring unit.

10 R^4 preferably is an alkanoyl radical having 2 to 6 carbon atoms or an aroyl radical having 7 to 10 carbon atoms. It can also be the radical of a different acid, for example a sulfonyl or phosphonyl radical. Aroyl radicals are particularly preferred.

15 R^5 preferably is a hydrogen atom, an alkyl radical having 1 to 8 and especially 1 to 5 carbon atoms, an alkenyl or alkynyl radical having 2 to 6 carbon atoms or an aryl radical having 6 to 10 and especially 6 to 8 carbon atoms.

20 R^6 preferably is an alkyl radical having 1 to 8 and especially 1 to 5 carbon atoms, an alkenyl or alkynyl radical having 2 to 6 carbon atoms or an aryl radical having 6 to 10 and especially 6 to 8 carbon atoms.

m preferably is an integer greater than 3.

25 Those compounds of the formula I are particularly preferred in which R^1 is a methyl, ethyl, trifluoromethyl or 1,1,2,3,3,3-hexafluoropropyl radical or a phenyl radical which may be substituted by 1 to 3 alkyl or alkoxy groups having 1 to 3 carbon atoms, 1 to 3 halogen atoms, 1 or 2 nitro, cyano or trifluoromethyl groups or
30 appropriate combinations.

The method of preparing such compounds is known per se.

5 This can be carried out, for example, analogously to the synthesis instructions given in DE-A 2,610,842, where the appropriate sulfonic acid ester derivative must be prepared in a preceding stage. The synthesis of typical and preferred representatives of these classes of compounds is described below by reference to individual examples.

Preparation Example 1

10 1st stage: 80.6 g (0.66 mol) of 4-hydroxybenzaldehyde were dissolved in 200 ml of tetrahydrofuran, 138 ml of triethylamine were added and the mixture was cooled to -5°C. 125.8 g (0.66 mol) of p-toluenesulfonic acid chloride, dissolved in 330 ml of tetrahydrofuran and precooled to -5°C, were added dropwise to the above
15 mixture at -8 to -5°C. Stirring was continued for 1 hour at room temperature. The solution was poured into 1,000 ml of distilled water, and the mixture was adjusted to pH 2 with concentrated hydrochloric acid. The oil which had precipitated was taken up in ether, and the aqueous
20 phase was extracted with ether. The combined organic phases were washed with water and dried. After concentrating, a residue remained which was recrystallized from cyclohexane/methylene chloride. This gave 120 g (66.1%) of 4-(toluene-4-sulfonyloxy)-
25 benzaldehyde (white solid having a melting point of 70 to 72°C).

30 2nd stage: 7.2 g (0.026 mol) of 4-(toluene-4-sulfonyloxy)-benzaldehyde were heated under reflux together with 2.4 g (0.026 mol) of butane-1,4diol, 4.25 g (0.0286 mol) of triethyl orthoformate and 100 mg of p-toluenesulfonic acid in 150 ml of toluene. After about 2 hours, a part of the distillate was taken off until the top temperature corresponded to the boiling point of pure toluene. This procedure was repeated until the top
35 temperature no longer fell below the boiling point of pure toluene. After a further 2 hours, the distillation was assisted for about 45 minutes by applying a vacuum of

4 mm Hg, and all volatile constituents were distilled off. The cooled-down residue was taken up in methylene chloride, washed twice with 2% sodium hydroxide solution and deionized water each time, and the organic phase was
5 dried. After removal of the solvent, 9.1 g of a yellow oil remained which proved to be the desired Compound 1 on the basis of its NMR spectrum.

Preparation Example 2

1st stage: 80.6 g (0.66 mol) of 3-hydroxybenzaldehyde
10 were dissolved in 200 ml of tetrahydrofuran, 138 ml of triethylamine were added and the mixture was cooled to -5°C. 125.8 g (0.66 mol) of p-toluenesulfonic acid chloride, dissolved in 330 ml of tetrahydrofuran and
15 precooled to -5°C, were added dropwise to the above mixture at -8 to -5°C. Stirring was continued for 1 hour at room temperature. The solution was poured into 1,000 ml of distilled water, and the mixture was adjusted to
20 pH 2 with concentrated hydrochloric acid. The oil which had precipitated was taken up in ether, and the aqueous phase was extracted with ether. The combined organic
phases were washed with water and dried. After concentrating, an oil remained which was recrystallized from cyclohexane. This gave 115 g (63.7%) of 3-(toluene-
4-sulfonyloxy)-benzaldehyde (white solid having a melting
25 point of 65 to 67°C).

2nd stage: 7.2 g (0.026 mol) of 3-(toluene-4-sulfonyloxy)-benzaldehyde were heated in an oil bath to 130°C together with 4.15 g (0.026 mol) of butyne-1,4-diol, 4.25 g (0.0286 mol) of triethyl orthoformate and
30 100 mg of p-toluenesulfonic acid in 150 ml of toluene. After about 2 hours, a part of the distillate was taken off until the top temperature corresponded to the boiling point of pure toluene. This procedure was repeated until
35 the top temperature no longer fell below the boiling point of pure toluene. After a further 2 hours, the distillation was assisted for about 45 minutes by applying a vacuum of 4 mm Hg, and all volatile

constituents were distilled off. The cooled-down residue was taken up in methylene chloride, washed twice with 2% sodium hydroxide solution and deionized water each time, and the organic phase was dried. After removal of the solvent, 9.8 g of a dark, amber-colored melt remained which proved to be the Compound 2.

Preparation Example 3

1st stage: 8.29 g (0.06 mol) of 3,4-dihydroxybenzaldehyde were dissolved in 40 ml of tetrahydrofuran, 18.5 ml of triethylamine were added, and the mixture cooled to -5°C. 22.9 g (0.12 mol) of p-toluenesulfonic acid chloride, dissolved in 80 ml of tetrahydrofuran and pre-cooled to -5°C, were added dropwise thereto at -8 to -5°C. Stirring was continued for 2 hours at room temperature. The solution was poured into 1,000 ml of distilled water, and the mixture was adjusted to pH 2 with concentrated hydrochloric acid. The oil which had precipitated solidified after prolonged stirring, to give a brown crystal paste. The crude product was filtered off with suction and dried. It was recrystallized from cyclohexane/methylene chloride with addition of active charcoal. This gave 15.9 g (59.4%) of 3,4-bis-(toluene-4-sulfonyloxy)-benzaldehyde (white solid having a melting point of 95 to 97°C).

2nd stage: 11.6 g (0.026 mol) of 3,4-bis-(toluene-4-sulfonyloxy)-benzaldehyde were heated in an oil bath at 130°C together with 3.75 g (0.026 mol) of triethylene glycol, 4.25 g (0.0286 mol) of triethyl orthoformate and 100 mg of p-toluenesulfonic acid in 150 ml of toluene. After about 2 hours, a part of the distillate was taken off until the top temperature corresponded to the boiling point of pure toluene. This procedure was repeated until the top temperature no longer fell below the boiling point of pure toluene. After a further 2 hours, the distillation was assisted for about 45 minutes by applying a vacuum of 4 mm Hg, and all volatile constituents were distilled off. The cooled-down residue was taken up

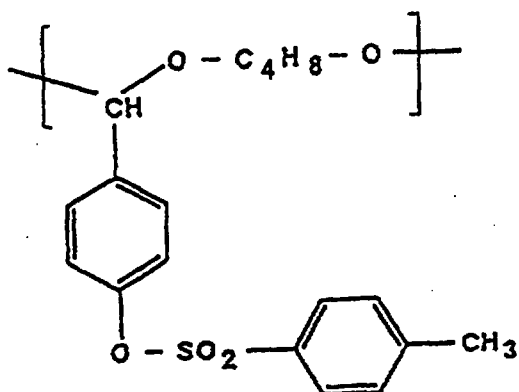
in methylene chloride, washed twice with 2% sodium hydroxide solution and deionized water each time, and the organic phase was dried. After removal of the solvent, 13.8 g of a dark, honey-like liquid remained, which proved to be Compound 3.

Preparation Example 4

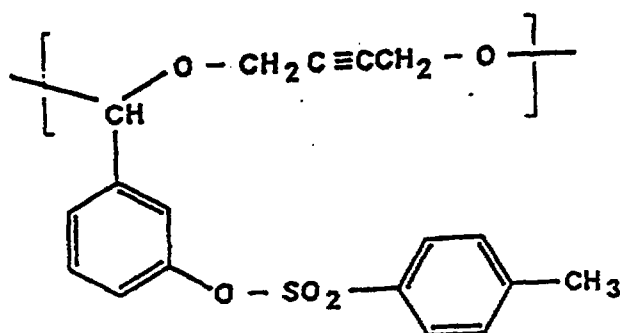
7.2 g (0.026 mol) of 4-(toluene-4-sulfonyloxy)-benzaldehyde (see Preparation Example 1, 1st stage) were heated under reflux in 150 ml of toluene together with 5.2 g (0.035 mol) of triethyl orthoformate and 8.82 g (0.06 mol) of a urethane alcohol prepared by reacting 1 mol of ethylene carbonate with 1 mol of n-propylamine, and 100 mg of p-toluenesulfonic acid. After about 2 hours, a part of the distillate was taken off until the top temperature corresponded to the boiling point of pure toluene. This procedure was repeated until the top temperature no longer fell below the boiling point of pure toluene. After a further 2 hours, the distillation was assisted for about 45 minutes by applying a vacuum of 4 mm Hg, and all volatile constituents were distilled off. The cooled-down residue was taken up in methylene chloride, washed twice with 2% sodium hydroxide solution and deionized water each time, and the organic phase was dried. After removal of the solvent, 10.8 g of a light-colored, viscous liquid remained which was subjected to a vacuum treatment at 180°C/0.01 mm Hg. In this treatment, a colorless liquid was stripped off. The remaining highly viscous residue proved to be Compound 4.

Further examples of compounds according to the invention are listed in the attached formulae 5 to 49.

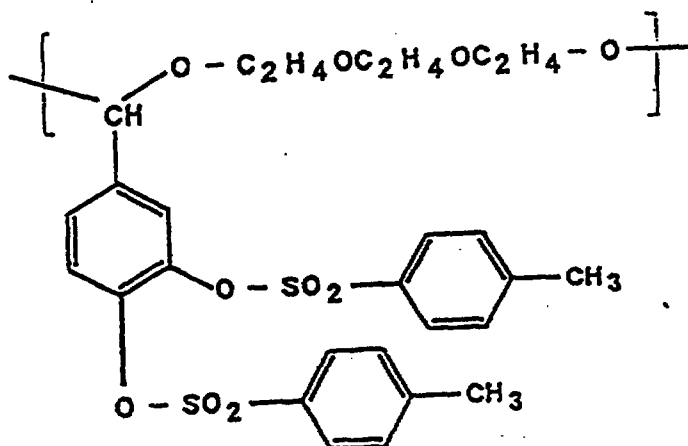
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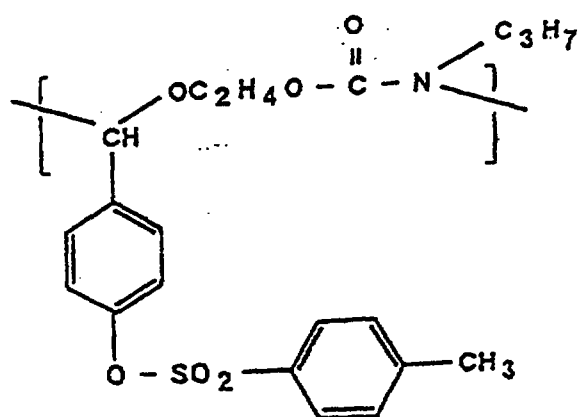
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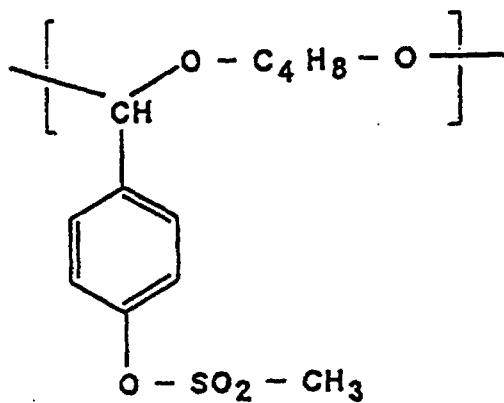
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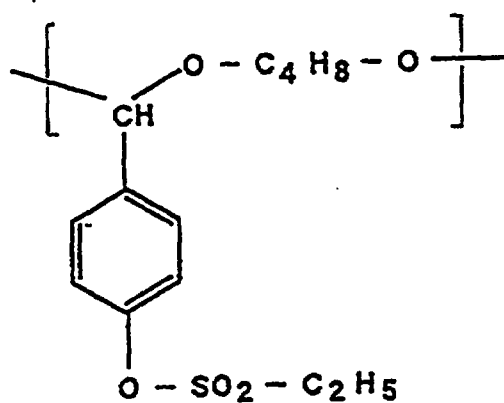
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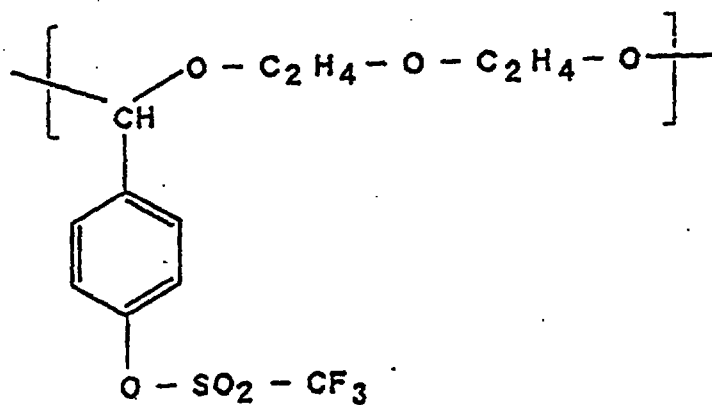
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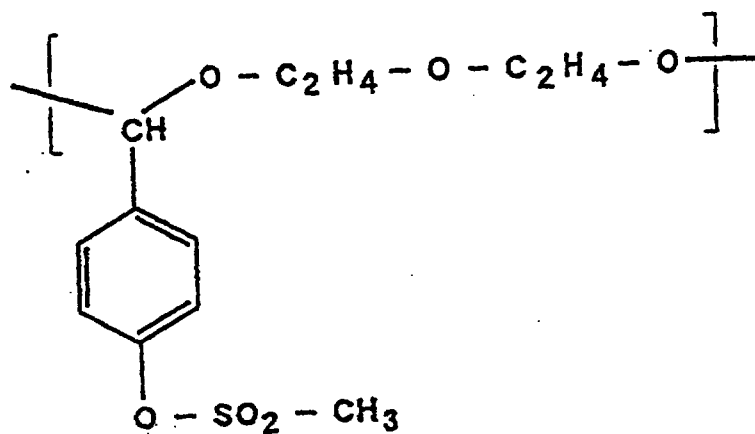
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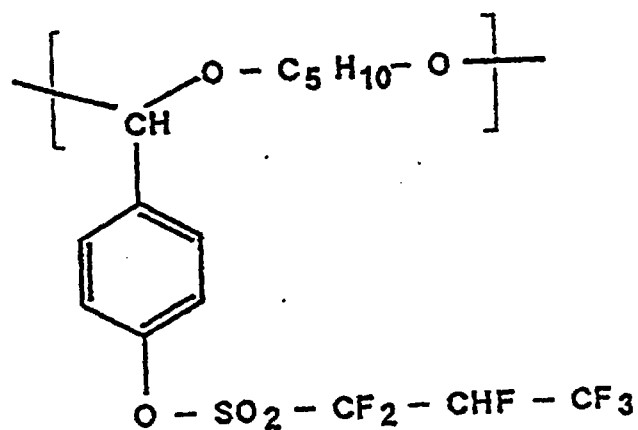
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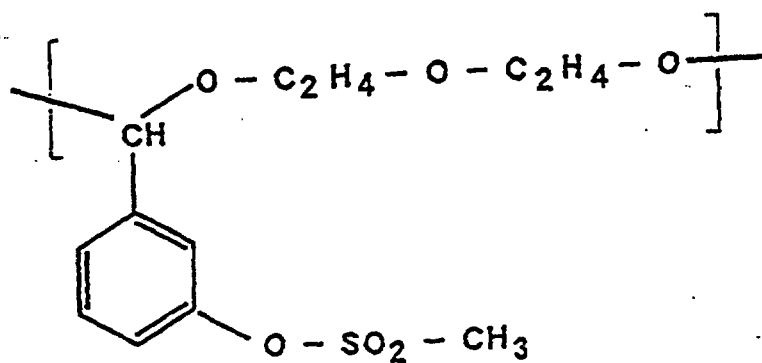
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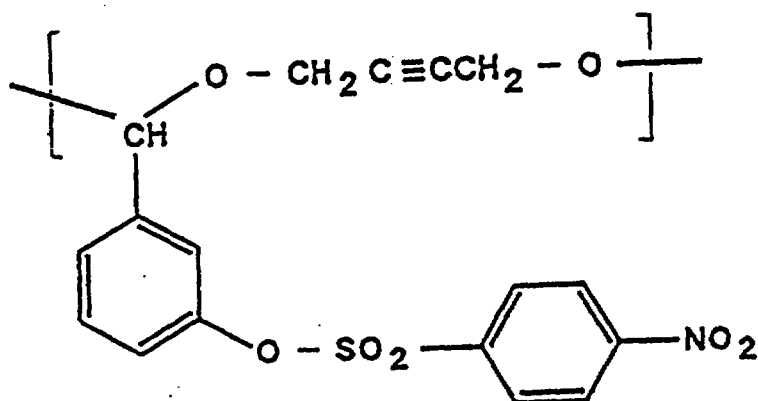
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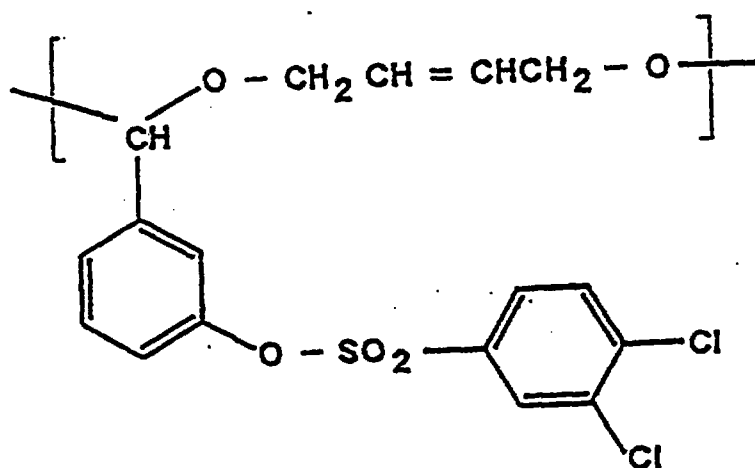
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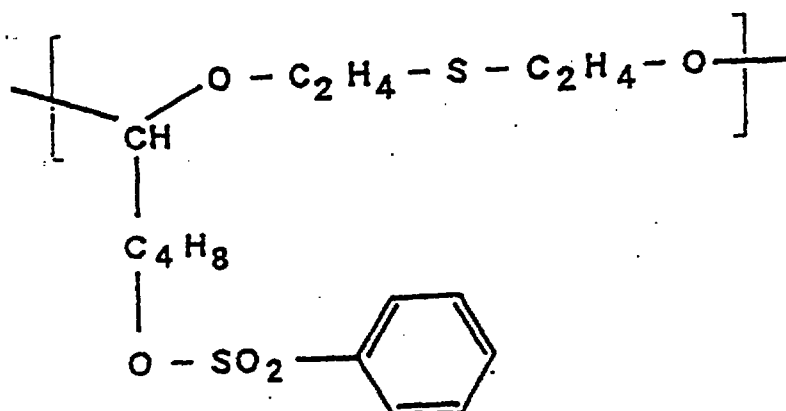
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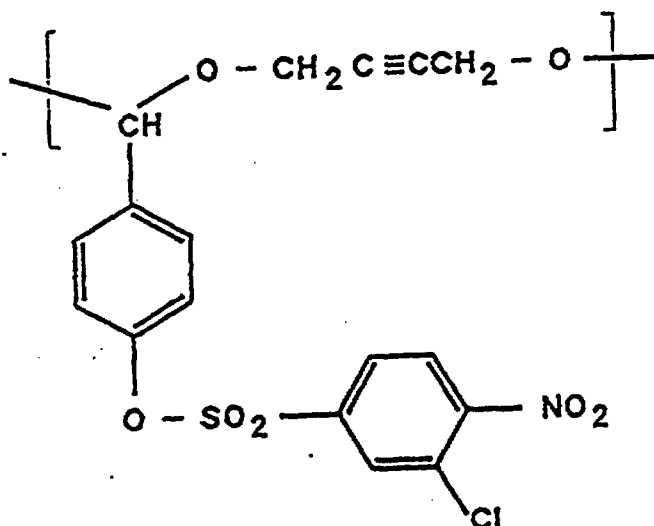
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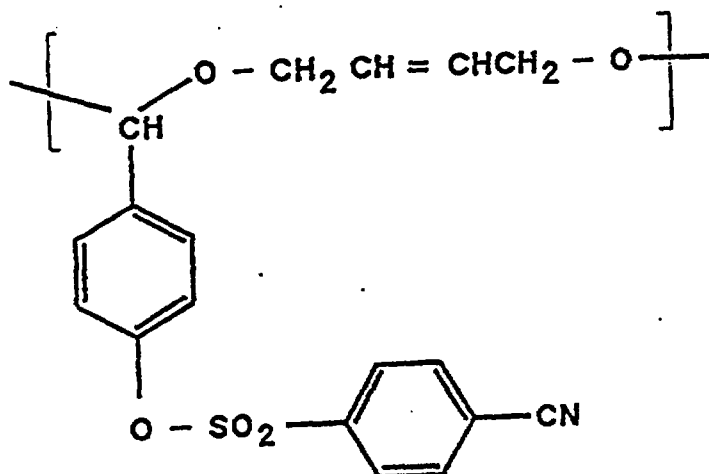
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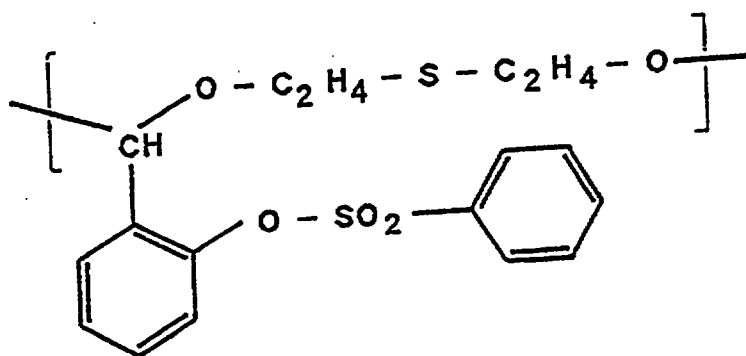
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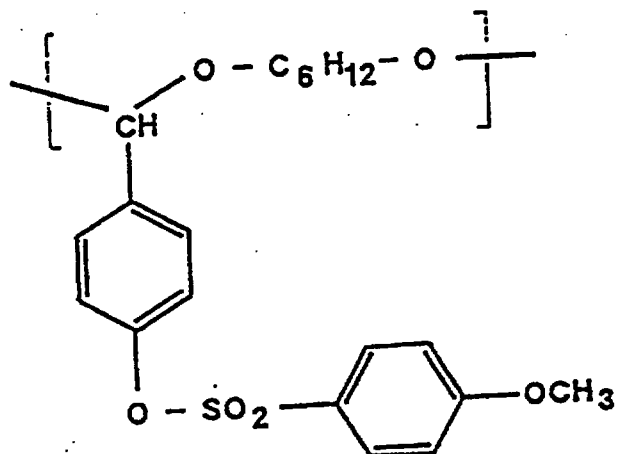
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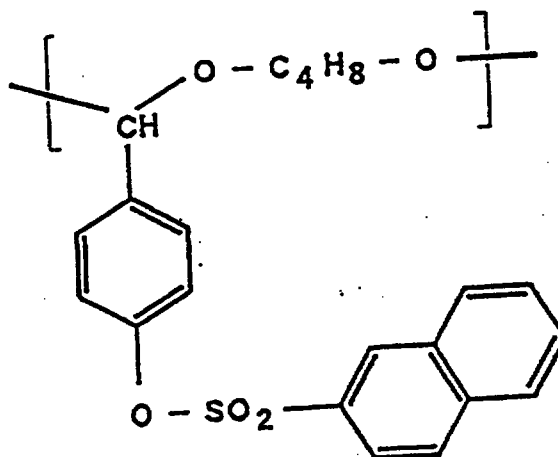
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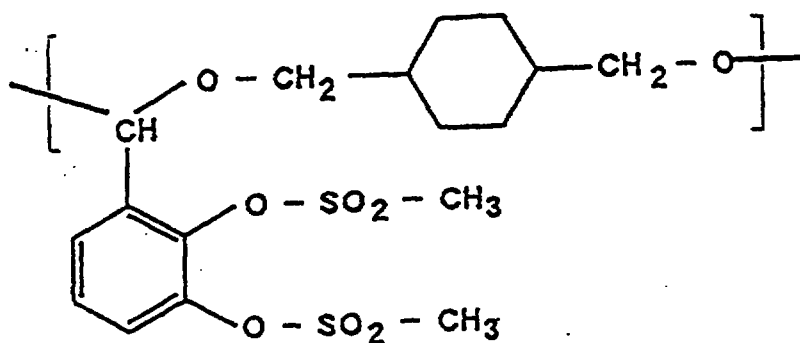
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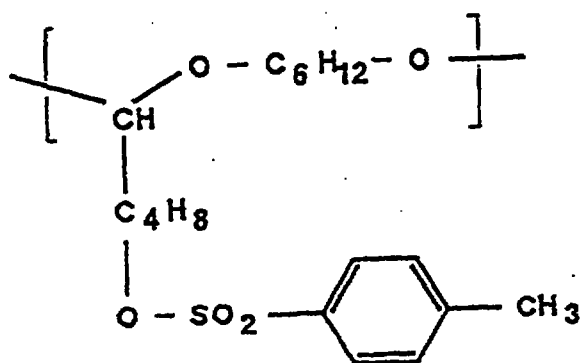
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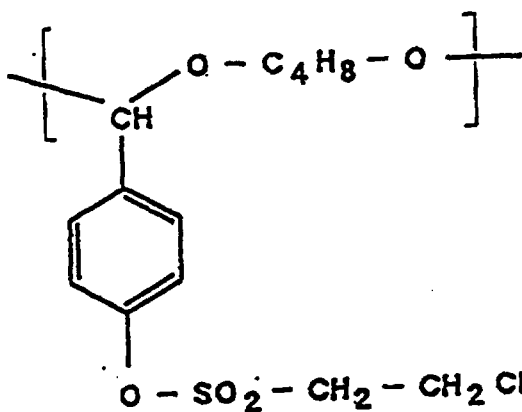
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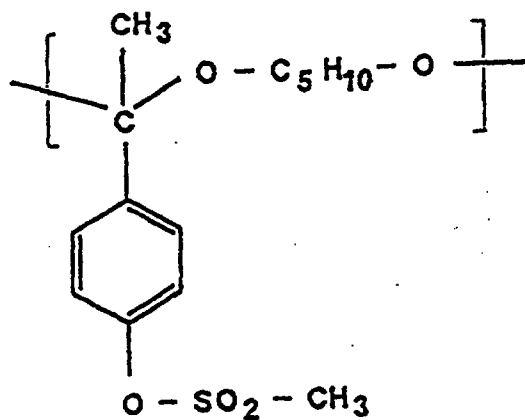
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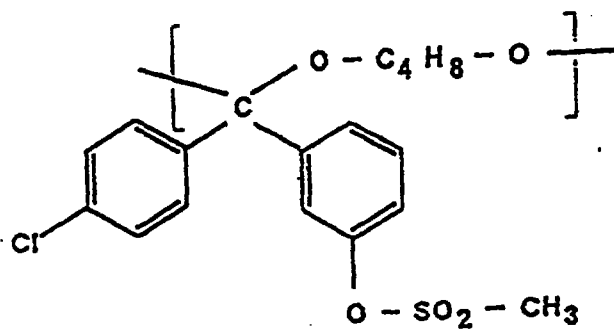
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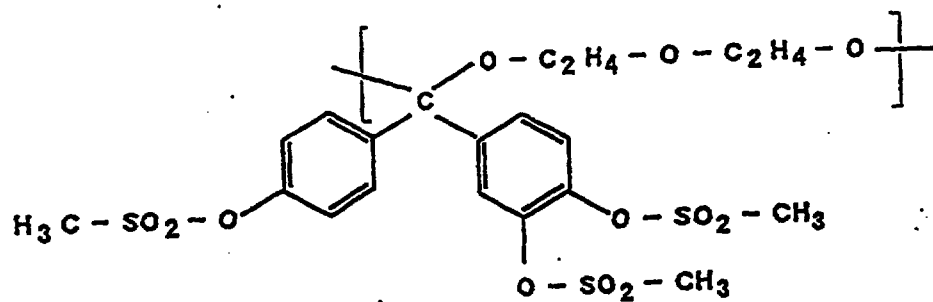
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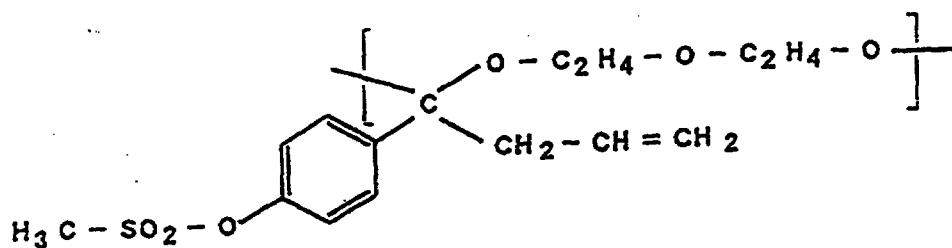
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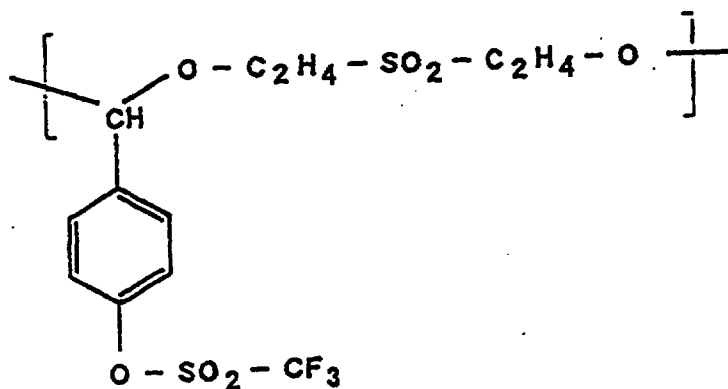
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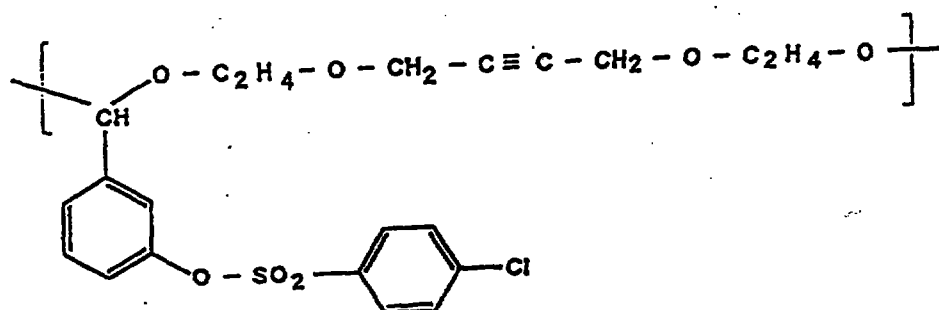
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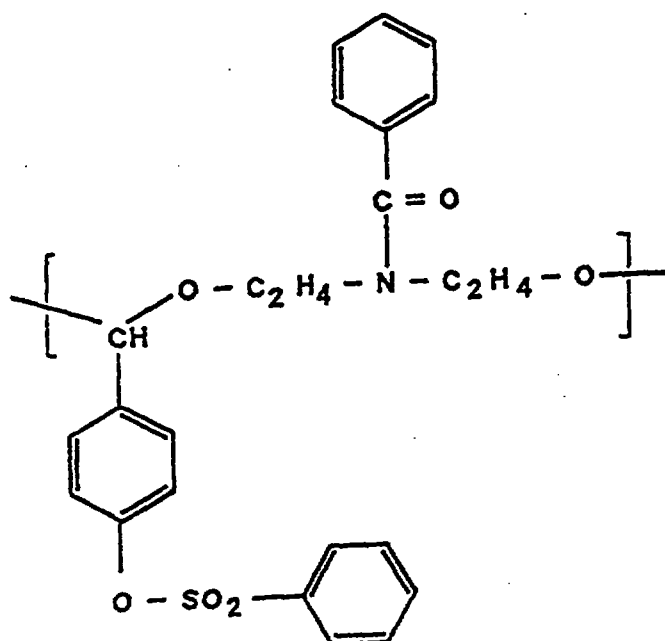
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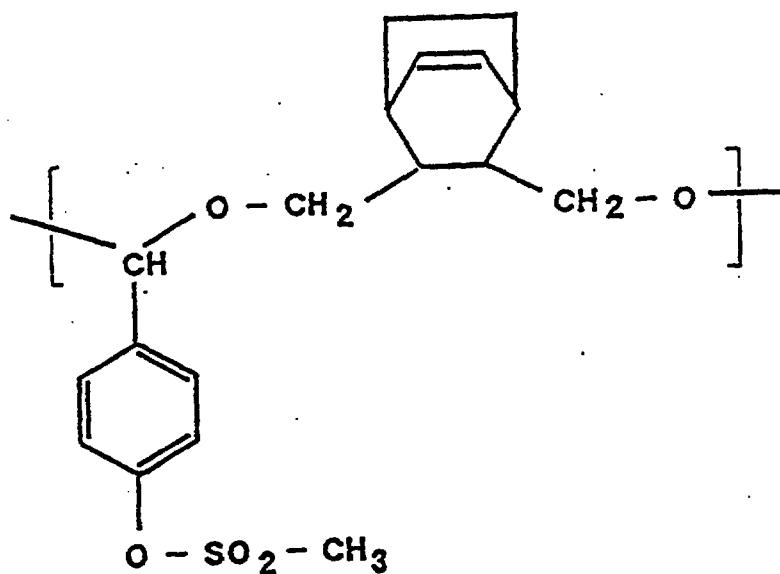
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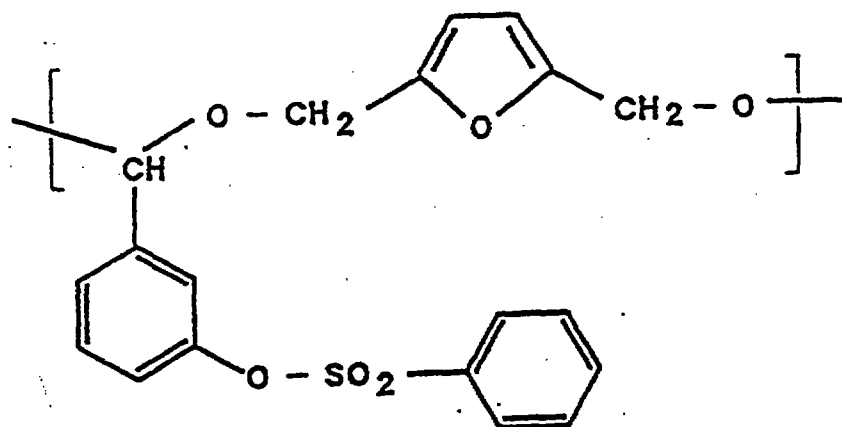
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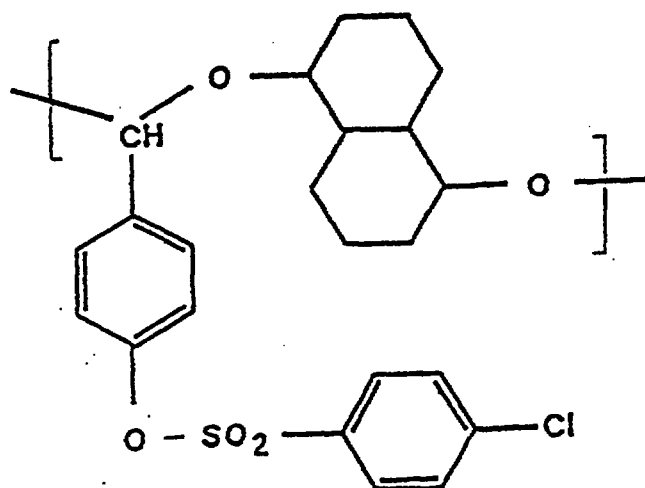
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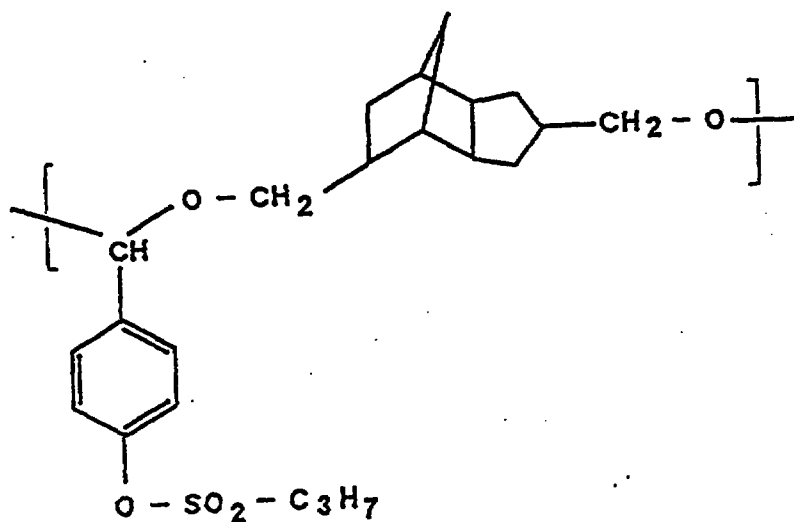
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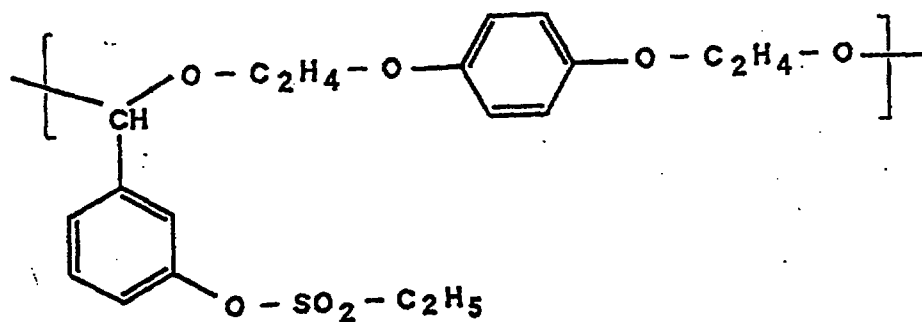
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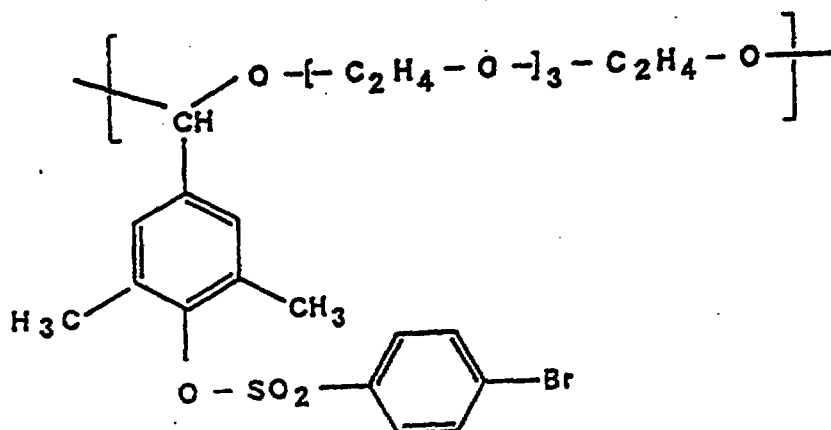
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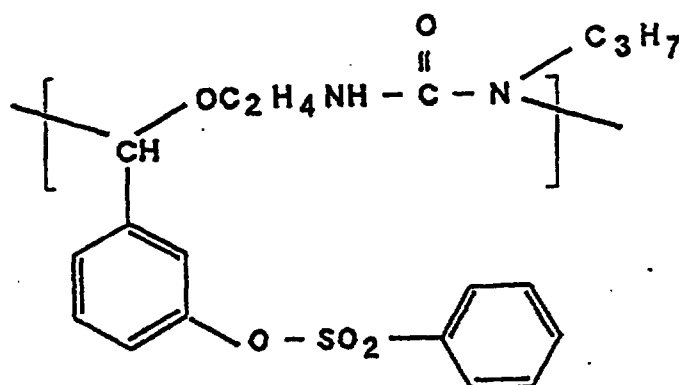
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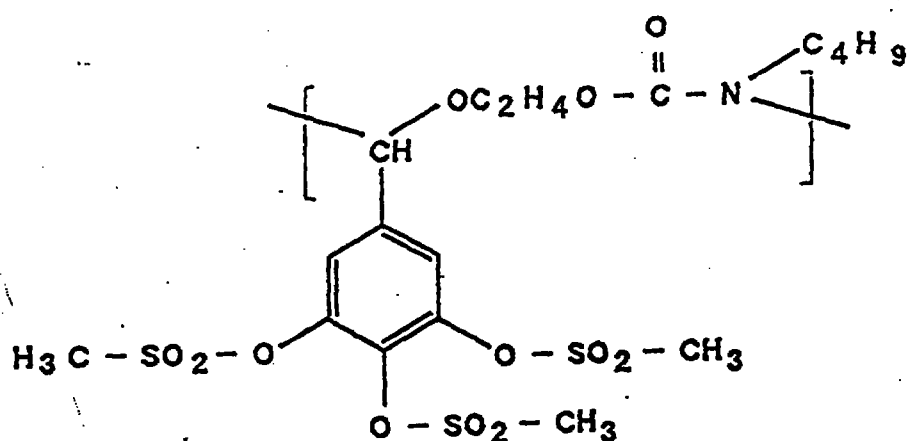
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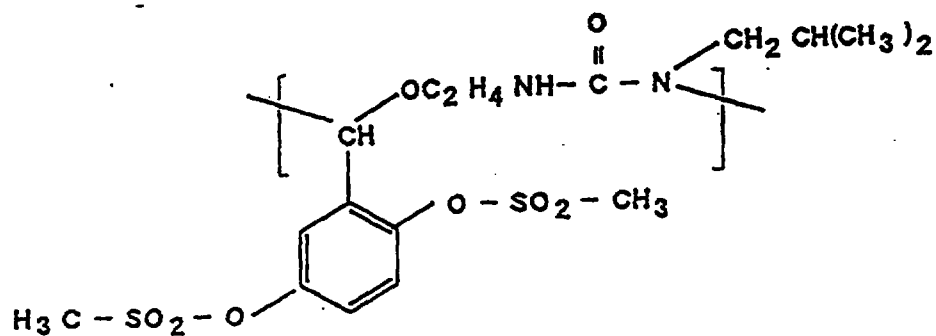
Compound No. 35:



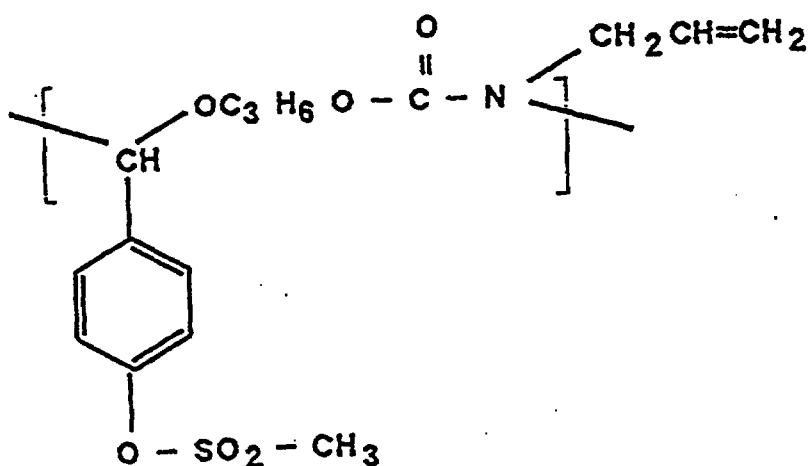
Compound No. 36:



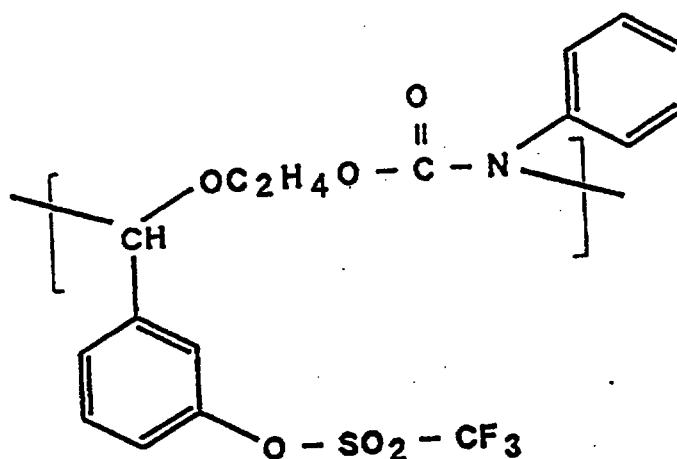
Compound No. 37:



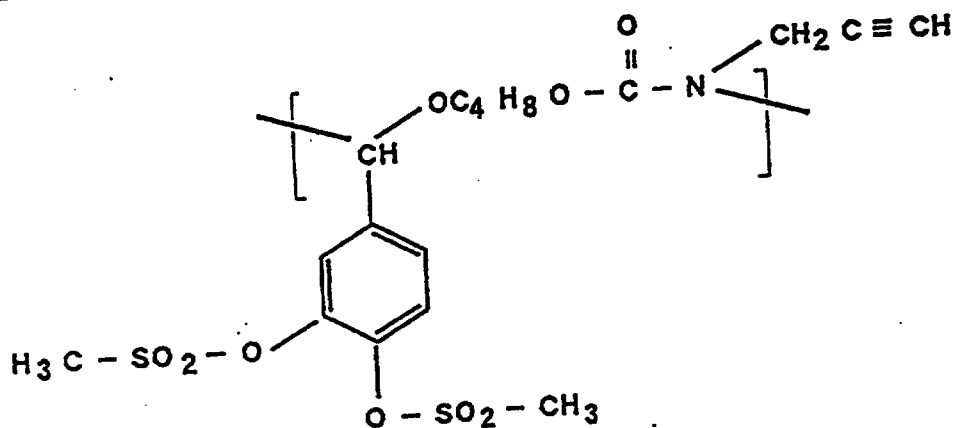
Compound No. 38:



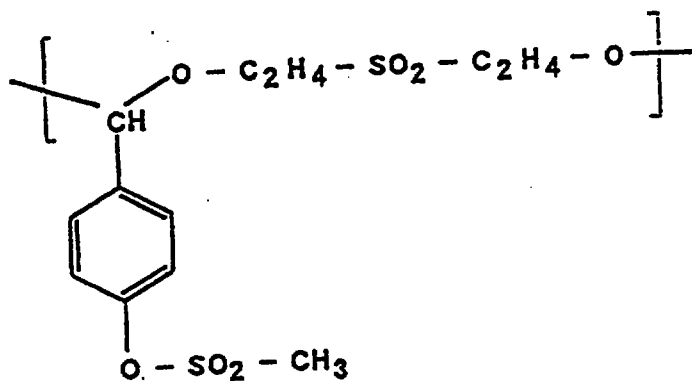
Compound No. 39:



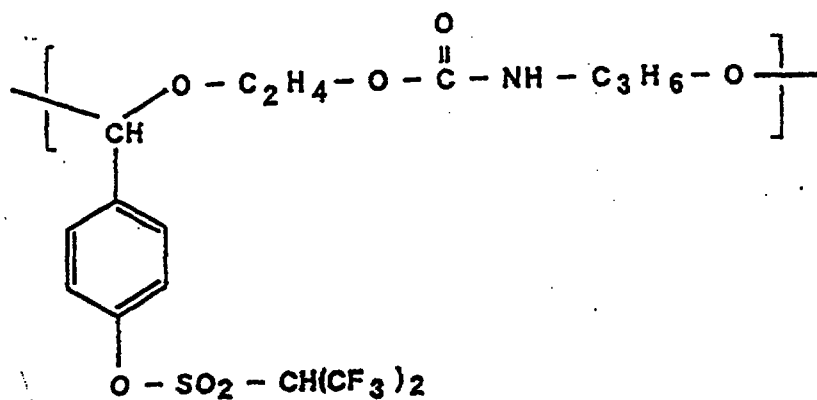
Compound No. 40:



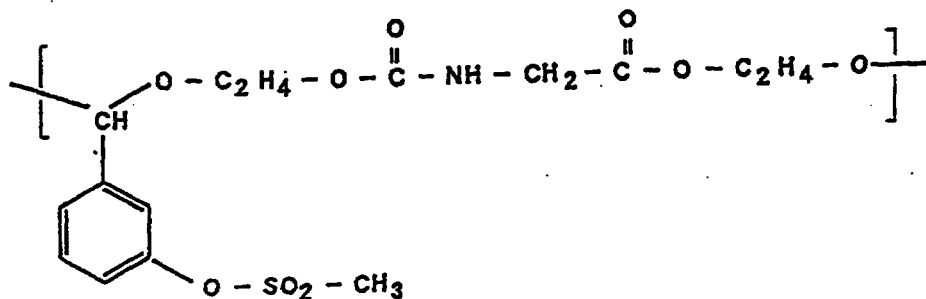
Compound No. 41:



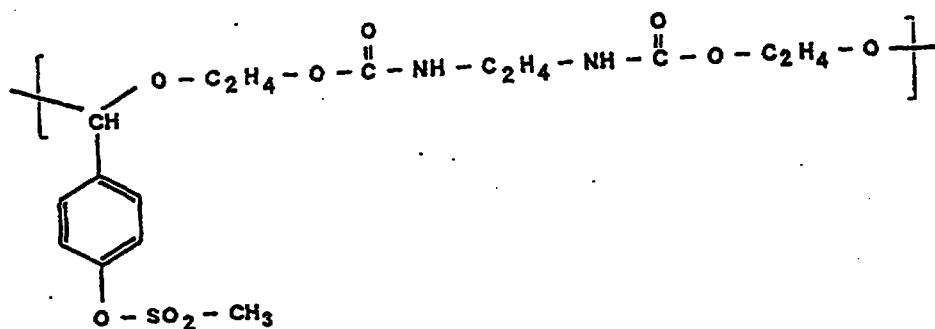
Compound No. 42:



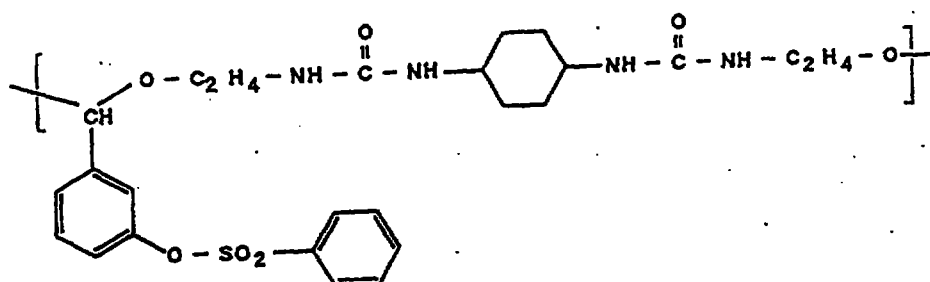
Compound No. 43:



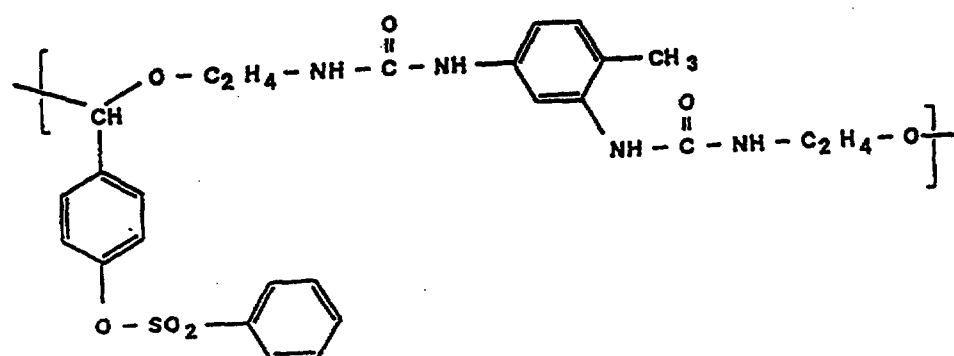
Compound No. 44:



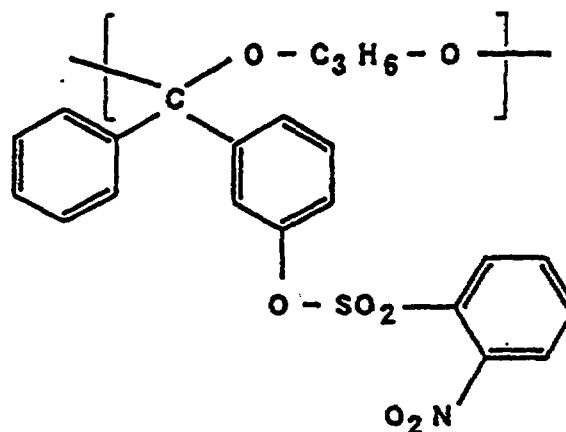
Compound No. 45:



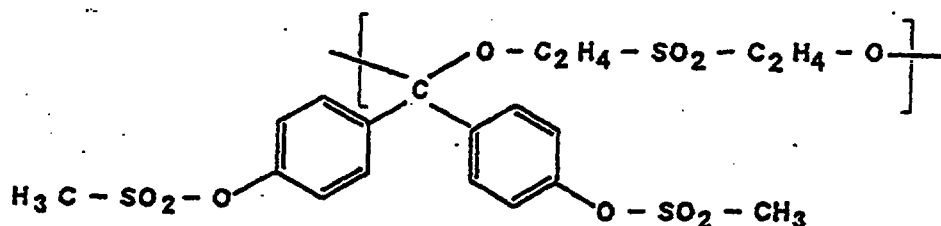
Compound No. 46:



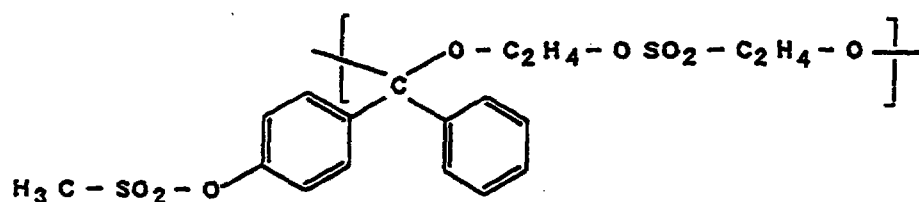
Compound No. 47:



Compound No. 48:



Compound No. 49:



These were synthesized analogously to processes known from the literature. Their authenticity was confirmed by elemental analysis and ¹H-NMR.

It is clear from the preparation methods that the resulting oligomeric compounds according to the invention of the formula I are formed by a condensation reaction. It is in the nature of such reactions that they form product mixtures which are composed of individual oligomers of different degrees of oligomerization. By means of a suitable polymer analysis, it was possible to prove that, as a result of optimized reaction control, more than 90% of the mixture has a degree of oligomerization of between 4 and 40, but monomeric, dimeric and trimeric compounds or compounds having a degree of oligomerization of > 40 are also always detectable in small quantities. The oligomer composition can, however, be made reproducible by using clearly fixed reaction conditions.

The above selection of compounds according to the invention of the formula I shows that those which have acetal structures are particularly preferred. This is to be

ascribed to the fact that they are very readily accessible and, in addition, are also extremely stable to hydrolysis both in solution and in layers, and that thus a stable recording material containing these compounds can be produced. As described in the Preparation Examples, the acetals according to the invention are based on certain aldehydes, of which the following are particularly preferred as starting compounds:

2-, 3- and 4-hydroxybenzaldehyde,
2,3-, 2,4-, 2,5- and 3,4-dihydroxybenzaldehyde,
2,3,4- and 3,4,5-trihydroxybenzaldehyde,
4-hydroxy-3-methyl-benzaldehyde,
2-hydroxy-4-methoxy-benzaldehyde,
2-hydroxy-5-methoxy-benzaldehyde,
3-hydroxy-4-methoxy-benzaldehyde,
4-hydroxy-3-methoxy-benzaldehyde,
4-hydroxy-3,5-dimethyl-benzaldehyde,
5-hydroxy-3,4-dimethoxy-benzaldehyde,
3-ethoxy-4-hydroxy-benzaldehyde,
2-hydroxy-5-nitro-benzaldehyde,
3-hydroxy-4-nitro-benzaldehyde,
4-hydroxy-3-nitro-benzaldehyde,
5-hydroxy-2-nitro-benzaldehyde,
2-hydroxy-naphthalene-1-carbaldehyde

These aldehydes are commercially available, while other hydroxyaldehydes suitable according to the invention as precursors can in general be prepared in a simple manner by the most diverse methods. A review of these is given in Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], vol. 7/1.

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

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

b) a compound which generates a strong acid under the action of actinic radiation and which has at least one acid-cleavable C-O-C bond,

5 wherein the compound (b) is a compound of the formula I described above.

10 The radiation-sensitive mixtures according to the invention, obtained with the use of compounds of the formula I, are distinguished by high sensitivities over a wide spectral range. They are very particularly suitable for irradiation with high-energy UV radiation, preferably with light of a wavelength from 190 to 350 nm. They show high thermal stability and make it possible accurately to reproduce even superfine structures of an original. No corrosive photolysis products are generated by the exposure, so that the mixture can also be used on sensitive substrate materials.

20 The acid-cleavable photolytic acid generators contained in the radiation-sensitive mixture according to the invention can be used alone or in combination with other acid-unstable acid generators of the said class according to the invention. However, combinations with other photolytic acid generators are also possible, for which even the onium salts mentioned at the outset, halogen compounds, especially trichloromethyltriazine derivatives or trichloromethyloxadiazole derivatives, o-quinonediazidesulfochlorides or organometal/organohalogen combinations are suitable. Overall, however, such combinations are not preferred since the disadvantages already mentioned can under certain circumstances reappear in such radiation-sensitive mixtures.

35 The content of acid-unstable acid generators of the formula I in the mixture according to the invention is in general between 2 and 60% by weight, preferably 5 to 50% by weight and particularly preferably 10 to 40% by weight, each relative to the total weight of the layer.

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:

- 5 (1) those having at least one orthocarboxylic acid ester grouping and/or carboxylic acid amide-acetal grouping, the compounds also having a polymeric character and it being possible for the said groupings to occur as linking elements in the main
10 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),
- 15 (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),
- 20 (5) compounds having silyl ether groupings (DE-A 3,544,165 and 3,601,264),
- (6) compounds having silylenol ether groupings (DE-A 3,730,785 and 3,730,783),
- (7) monoacetals and monoketals, whose aldehyde or keto
25 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
30 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
35 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 (b) or the combination of compounds (b) is present in a concentration from 2 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 highly 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 350 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.

Novolak condensation resins can, however, 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 30% by weight, especially up to 20% by weight, of a novolak condensation resin.

5 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-
10 hydroxystyrene, or the esters of (meth)acrylic acid with
phenols, for example pyrocatechol, resorcinol,
hydroquinone, pyrogallol or aminophenols and the cor-
responding amides with aromatic amines. Polymerizable
compounds such as styrene, methyl methacrylate, methyl
15 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.
20 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
25 in the wavelength range described. Here again, the
comonomers preferably used are styrene, substituted
styrenes, vinylphenols, vinyl ethers, vinyl esters,
vinylsilyl compounds or (meth)acrylates.

Finally, copolymers of styrene can, furthermore, also be
30 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 be mixed with one another if

this does not impair the optical quality of the radiation-sensitive mixture. However, binder mixtures are not preferred.

5 The quantity of binder is in general 40 to 98% by weight, especially 50 to 95% by weight, preferably 60 to 90% by weight, relative to the total weight of the radiation-sensitive mixture.

10 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 $0.5 \mu\text{m}^{-1}$.

15 If appropriate, dyes, pigments, plasticizers, wetting 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.

20 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, 25 dimethylacetamide, hexamethylphosphoramide, N-methylpyrrolidone, butyrolactone, tetrahydrofuran and mixtures thereof] are particularly suitable for this purpose. Glycol ethers, aliphatic esters and ketones are particularly preferred.

30

5 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.

10 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.

15 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 doped, merit special mention. In addition, all other
20 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, for example, glass and indium-tin oxide and also metal
25 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 been thermally pretreated, superficially roughened, incipiently etched or, to improve desired properties, for
30 example to enhance the hydrophilic character, pretreated with chemicals.

35 To impart better cohesion and/or better adhesion of the 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 this purpose.

5 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, which may have been anodically oxidized, grained and/or
10 silicated beforehand, and also zinc and steel plates which may be chromium-plated, and also plastic films and paper.

15 The recording material according to the invention is exposed imagewise to actinic radiation. Suitable radiation sources are especially metal halide lamps, carbon arc lamps, xenon lamps and mercury vapor lamps. 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
20 from 190 to 260 nm, i.e. especially xenon lamps and mercury vapor lamps, are particularly preferred. Furthermore, 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
25 must show adequate emission in the said wavelength ranges.

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 .

30 The invention also relates to a process for producing a radiation-sensitive recording material. The radiation-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
35 that the radiation-sensitive layer remains on the surface

of the substrate. The removal of the solvent can be 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 used as temporary support can in principle be all those which are also suitable as support materials. Subsequently, the layer is irradiated imagewise and heated to intensify the cleavage reaction. The layer is then treated with a developer solution which dissolves and removes the irradiated areas of the layer, 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, if desired, 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.

5 The radiation-sensitive mixture according to the invention is used in the production of integrated circuits or of discrete electronic components by lithographic processes because they have a high light sensitivity, particularly on irradiation with light of a wavelength of between 190 and 350 nm. Since the mixtures bleach very well on exposure, finer structures can be achieved than
10 is possible with the known mixtures. 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
15 layer support.

Examples 1 to 10 which follow demonstrate the suitability of the mixture according to the invention for recording materials in microlithography, using high-energy radiation. The superiority of the mixtures according to
20 the invention over the state of the art is demonstrated by reference to Comparison Examples 11 and 12.

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
25 understood as being in weight units.

Example 1

A coating solution was prepared from

30 6.0 p.b.w. of a styrene/p-hydroxystyrene copolymer (molar ratio 30:70) having a mean molecular weight of 27,000,
1.5 p.b.w. of a cresol/formaldehyde novolak having a softening range from 105 to 120°C and
2.0 p.b.w. of Compound 1 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 3,300 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane).
5 After drying for 1 minute at 100°C on the hotplate, a layer thickness of 1.05 μm was obtained.

The recording material was exposed imagewise under an original to the UV radiation of a xenon-mercury vapor lamp (filter with a transmission from 240 to 260 nm) with
10 an energy of 78 mJ/cm² and stored for about 30 minutes at room temperature before development.

The recording material was developed using a 0.3 N alkaline developer of the following composition:

15 5.3 p.b.w. of sodium metasilicate $\times$ 9 H₂O,
3.4 p.b.w. of trisodium phosphate $\times$ 12 H₂O,
0.3 p.b.w. of sodium dihydrogen phosphate and
191 p.b.w. of deionized water.

After a developing time of 60 seconds, this gave a defect-free image of the mask with steep resist flanks,
20 structures of < 0.6 μm also being resolved in true detail. An examination of the flanks of the resist profiles by means of scanning electron microscopy proved that these were aligned virtually perpendicular to the substrate surface.

25 Example 2

A coating solution was prepared from

7.5 p.b.w. of a styrene/p-hydroxystyrene copolymer (molar ratio 20:80) having a mean molecular weight of 32,000 and
30 2.0 p.b.w. of Compound 2 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 3,300 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 UV radiation of a xenon-mercury vapor lamp at 240 to 260 nm with an energy of 82 mJ/cm², stored for about 30 minutes at room temperature and then processed using the developer described in Example 1.

After a developing time of 60 seconds, this gave a defect-free image of the mask with high flank stability, here again structures of < 0.6 μm being resolved in true detail.

15 Example 3

A wafer produced correspondingly to Example 1 was irradiated under an original with KrF-excimer laser radiation of 248 nm wavelength with an energy of 100 mJ/cm². After development, an image true to the original was obtained.

20

Example 4

A coating solution was prepared from

7.5 p.b.w. of the copolymer indicated in Example 2 and
2.0 p.b.w. of Compound 3 in
25 42 p.b.w. of propylene glycol monomethyl ether-
acetate.

30 The solution was filtered through a filter of 0.2 μm pore diameter and whirler-coated at 3,300 rpm onto two wafers in total, treated with an adhesion promoter (hexamethyldisilazane). After drying for 1 minute at 100°C on the hotplate, a layer thickness of 1.04 μm was obtained in both cases.

One of the coated wafers was exposed imagewise under an original to the UV radiation of a xenon-mercury vapor lamp at 240 to 260 nm with an energy of 60 mJ/cm², heated for 75 seconds at 100°C and then processed using a developer which was composed of 3% of tetramethylammonium hydroxide and 97% of deionized water.

After a developing time of 60 seconds, this gave a defect-free image of the mask with high flank stability, here again structures of < 0.6 μm being resolved in true detail.

The second wafer was exposed, heat-treated and developed as described above after 14 days. Virtually the same results as described above were obtained. This means that the mixture applied in the dried form to a substrate has excellent stability.

Example 5

A coating solution was prepared from

7.5 p.b.w. of a 3-methyl-4-hydroxystyrene homopolymer having a mean molecular weight of 25,000 and
2.0 p.b.w. of Compound 1 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 divided into two equal parts. One part was whirler-coated at 3,300 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 the radiation of a xenon-mercury vapor lamp at 240 to 260 nm with an energy of 80 mJ/cm², heated for 75 seconds at 100°C and then processed using the developer described in Example 4.

After a developing time of 60 seconds, this gave a defect-free image of the mask with high flank stability, here again structures of $< 0.6 \mu\text{m}$ being resolved in true detail.

5 The second part was subjected to the same procedure after storage for 20 weeks in the refrigerator. Identical results were obtained, which shows that the mixture has an extraordinarily high stability in solution.

Example 6

10 A coating solution was prepared from

7.5 p.b.w. of a 3,5-dimethyl-4-hydroxystyrene/4-hydroxystyrene copolymer (molar ratio 20:80) having a mean molecular weight of 25,000 and

2.0 p.b.w. of Compound 4 in

15 42 p.b.w. of propylene glycol monomethyl ether-acetate.

The solution was filtered through a filter of $0.2 \mu\text{m}$ pore diameter and whirler-coated at 3,300 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane).

20 After drying at 100°C for 1 minute, a layer thickness of $1.08 \mu\text{m}$ was obtained.

The recording material was exposed imagewise under an original to the UV radiation of a xenon-mercury vapor lamp at 240 to 260 nm with an energy of $72 \text{ mJ}/\text{cm}^2$, heated for 75 seconds at 100°C and then processed using the developer described in Example 1.

25 After a developing time of 60 seconds, this gave a defect-free image of the mask with high flank stability, here again structures of $< 0.6 \mu\text{m}$ being resolved in true detail.

30

Example 7

Example 4 was repeated twice, with the modification that,

instead of 60 seconds at 100°C, drying was carried out for 90 seconds at 90°C and for 60 seconds at 110 respectively. In both cases, the results were virtually identical and were the same as those described in Example 4. This means that the recording material according to the invention has a wide processing latitude.

Example 8

A coating solution was prepared from

7.5 p.b.w. of a styrene/maleimide copolymer (molar ratio 1:1) having a softening range from 165 to 180°C and

2.0 p.b.w. of Compound 4 in
42 p.b.w. of cyclohexanone.

The solution was filtered through a filter of 0.2 μm pore diameter and whirler-coated at 3,400 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 240 to 260 nm with an energy of 89 mJ/cm².

The recording material was developed using a 0.02 N aqueous solution of tetramethylammonium hydroxide, the exposed areas being detached without residues within 60 seconds.

A further time, a defect-free image of the mask with steep resist flanks was obtained. The loss in the dark was less than 20 nm; even structures smaller than 0.6 μm were resolved in true detail.

Example 9

A coating solution was prepared from

7.5 p.b.w. of the copolymer indicated in Example 8 and
2.0 p.b.w. of Compound 11 in
42 p.b.w. of cyclohexanone.

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.

10 The recording material was exposed imagewise under an original to the radiation of a xenon-mercury vapor lamp at 240 to 260 nm with an energy of 67 mJ/cm².

15 The recording material was developed using a 0.02 N aqueous solution of tetramethylammonium hydroxide, the exposed areas being detached without residues within 60 seconds and an image of the original in true detail being obtained. The edge steepness of the image was excellent.

Example 10

A coating solution was prepared from

20 7.5 p.b.w. of the copolymer described in Example 2 and
2.0 p.b.w. of Compound 23 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 3,100 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying for 1 minute at 100°C, a layer thickness of 1.07 μm was obtained.

30 The recording material was exposed imagewise under an original to the radiation of a xenon-mercury vapor lamp at 240 to 260 nm with an energy of 75 mJ/cm².

The recording material was developed using a 0.27 N

aqueous tetramethylammonium hydroxide solution, the exposed areas being detached without residues within 60 seconds and an image of the original in true detail being obtained. Lines and gaps down to 0.5 μ m were reproduced true to the mask. It was found that the solution of the material as produced still gave reproducible lithographic results identical to the first tests even after storage in the dark for 6 weeks.

Examples 11 and 12 (Comparison Examples)

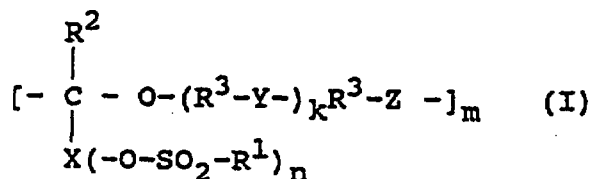
The resist formulation of Example 2 was modified in such a way that in each case 0.2 p.b.w. of the compounds, known as acid generators, triphenylsulfonium hexafluorophosphate (Example 11) and 2-nitrobenzyl tosylate (Example 12) were added to the mixture. After coating and drying, it was found that the formulation of Example 11 is about 10% more sensitive than the mixture according to the invention of Example 2, to KrF-excimer laser light of 248 nm wavelength under identical process conditions, while the sensitivity of the formulation of Example 12 does not differ from that of Example 2.

When the onium salt (Example 11) was used, however, structures having a so-called "coating foot" were obtained, i.e. residues of the resist adhere to the substrate in the exposed areas, whereas, when the tosyl ester was used (Example 12), surface crosslinkings were visible which partially overlapped the bared substrate surfaces. In both cases, acceptable structuring was thus not obtainable.



Patent claims

1. A compound of formula I



in which

- 5 R^1 is an alkyl, halogenoalkyl or aryl radical,
 R^2 is a hydrogen atom, an alkyl, alkenyl or aryl
 radical or the group $(\text{R}^1-\text{SO}_2-\text{O})_n\text{X}-$,
 R^3 is a cycloalkylenedialkyl, cycloalkenylenedialkyl, arylenedialkyl or heteroarylenedialkyl
10 group, or an alkylene, alkenylene, alkynylene, cycloalkylene or arylene group,
 X is an alkyl, cycloalkyl or aryl group substituted by 1 to 3 sulfonyloxy groups $\text{R}^1-\text{SO}_2-\text{O}-$,
 Y is O, S, CO, CO-O, SO_2 , SO_2-O , NR^4 , CO-NH,
15 O-CO-NR⁵, NH-CO-NR⁵ or NR⁵-CO-O,
 Z is O, CO-NR⁶, O-CO-NR⁶ or NH-CO-NR⁶,
 R^4 is an acyl radical,
 R^5 is a hydrogen atom or an alkyl, cycloalkyl, alkenyl, alkynyl or aryl radical,
20 R^6 is an alkyl, cycloalkyl, alkenyl, alkynyl or aryl radical,
 k is an integer from 0 to 4,
 m is an integer greater than 1 and
 n is an integer from 1 to 3,

25 where R^3 and Y in recurring groupings $(\text{R}^3-\text{Y}-)$ can have identical or different definitions.

2. A compound as claimed in claim 1, wherein R^1 is an alkyl, highly fluorinated alkyl or perfluoroalkyl radical having 1 to 6 carbon atoms or an aryl radical having 6 to 12 carbon atoms.
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3. A compound as claimed in claim 1, wherein X is an alkyl or cycloalkyl group having 2 to 10 carbon atoms and substituted by 1 to 3 sulfonyloxy groups R^1-SO_2-O- or an aryl group having 6 to 12 carbon atoms and substituted in this way.
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4. A positive-working radiation-sensitive mixture which contains essentially
- a) a binder which is insoluble in water and soluble or at least swellable in aqueous alkaline solutions, and
- b) a compound which generates a strong acid under the action of actinic radiation and which has at least one acid-cleavable C-O-C bond,
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- wherein the compound (b) is a compound as claimed in any of claims 1 to 3.
5. A radiation-sensitive mixture as claimed in claim 4, wherein the compound (b) is sensitive to light of a wavelength from 190 to 350 nm.
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6. A radiation-sensitive mixture as claimed in claim 4, which contains the compound (b) in a concentration from 2 to 60% by weight.
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7. A radiation-sensitive mixture as claimed in claim 4, wherein the binder (a) has an extinction of less than $0.5 \mu m^{-1}$ in the wavelength region of the sensitivity of compound (b).
8. A radiation-sensitive mixture as claimed in claim 7, wherein the binder is a polymer having phenolic hydroxy groups.
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9. A radiation-sensitive mixture as claimed in claim 4, which contains the binder (a) in a concentration from 40 to 98% by weight.
10. 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 4 to
9.