

5 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

- 10 (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.

15 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.

20 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,

25 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

30 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.

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.

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.

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, not repeatable 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 however 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

5 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.

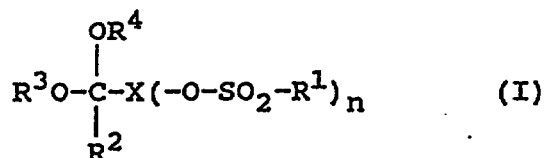
10 The use of onium salts, such as diazonium, phosphonium, sulfonium and iodonium salts, of non-nucleophilic acids such as HSbF_6 , HAsF_6 or HPF_6 as photolytic acid generators involves disadvantages which drastically restrict their possible uses in various fields of application. Thus, for example, many of the onium salts are toxic. Their solubility is inadequate in many solvents, which is why 15 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 microlithography. Moreover, the onium salts form 20 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 trichloromethyltriazine derivatives or trichloromethyl- 25 oxadiazole derivatives also form hydrohalic acids which have a severely corrosive action.

30 In more recent papers by F.M. Houlihan et al., SPIE 920, 67 (1988), it was shown by reference to positive-working systems that, in addition to the abovementioned acid generators, nitrobenzyl tosylates, which on exposure generate sulfonic acids having a low migration tendency, can be used in certain acid-unstable resist formulations. It can be deduced from these results that such compounds can also be used for photo-curable systems. The 35 sensitivities thus achieved, especially to UV radiation from 350 to 450 nm, and the thermal stability of the photoresists proved, however, to be inadequate.

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.

The object is achieved by means of radiation-sensitive and acid-cleavable compounds of the formula I



in which

- 20 R^1 is an alkyl, highly fluorinated alkyl, perfluoro-alkyl or aryl radical,
- R^2 is a hydrogen atom, an alkyl or aryl radical or one of the groups $(\text{R}^1-\text{SO}_2-\text{O})_n\text{X}-$ or $\text{R}^3\text{O}-$,
- R^3 and R^4 are identical or different and are alkyl, cyclo-alkylalkyl, cycloalkenylalkyl or aralkyl radicals,
- 25 in which 1 to 3 aliphatic CH_2 or CH groups can be replaced by NR^5 , O , S , CO , $\text{CO}-\text{O}$, $\text{CO}-\text{NH}$, $\text{O}-\text{CO}-\text{NH}$, $\text{CO}-\text{NH}-\text{CO}$, $\text{NH}-\text{CO}-\text{NH}$, SO_2 , SO_2-O or SO_2-NH , or alkenyl, alkynyl, cycloalkyl or cycloalkenyl radicals or are
- 30 mutually linked to form a heterocyclic ring,
- R^5 is an acyl radical,
- X is an alkanetriyl, cycloalkanetriyl or arenetriyl group or an alkanetetrayl or arenetetrayl group, and
- n is 2 or 3.

Those compounds of the formula I are preferred in which

- R^1 is an alkyl radical which has 1 to 6 carbon atoms and may be highly fluorinated, or an aryl radical which has 6 to 12 carbon atoms and
- 5 R^2 is a hydrogen atom or an R^3O radical.
- R^3 and R^4 are preferably identical and especially are alkyl, cycloalkylalkyl, cycloalkenylalkyl or aralkyl groups having less than 16 carbon atoms, it being possible for 1 to 3 aliphatic CH_2 or CH groups to be
- 10 replaced by NR^5 , O , S , CO , COO , $CONH$, $CONH$, $CONHCO$, $NHCONH$, SO_2 , SO_2O or SO_2NH , or alkenyl, alkynyl, cycloalkyl or cycloalkenyl radicals. If R^3 and R^4 together form a heterocyclic ring, this is preferably a 1,3-dioxolane or 1,3-dioxane ring.
- 15 R^5 can especially be an alkanoyl or aroyl, an alkyl-, alkenyl-, aralkyl- or aryl-sulfonyl or an alkyl-, alkenyl-, aralkyl- or aryl-phosphonyl radical having up to 12 carbon atoms, particularly preferably an alkanoyl radical having 2 to 6 carbon atoms or an
- 20 aroyl radical having 7 to 10 carbon atoms.
- X preferably is an alkyl group having 2 to 10 carbon atoms, a cycloalkyl group having 4 to 10 carbon atoms or an aryl group having 6 to 12 carbon atoms, each substituted by 1 to 3 sulfonyloxy groups
- 25 R^1-SO_2-O .

The aryl or arylene groups can be groups which are either unsubstituted or substituted by halogen atoms or by alkyl, alkoxy, nitro or cyano groups. Aralkyl groups are understood to be those which contain 1 to 2 aromatic

30 radicals linked through aliphatic groupings and bound via an aliphatic carbon atom.

Those compounds of the formula I are particularly preferred in which

- 35 R^1 is a methyl, ethyl, trifluoromethyl or hexafluoroisopropyl 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 appropriate combinations and

X is an aryl group which is substituted by 1 to 3 sulfonyloxy groups R^1-SO_2-O- .

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

R^2 is a hydrogen atom and

X is an aromatic six-membered ring substituted by 1 to 3 sulfonyloxy groups R^1-SO_2-O .

The method of preparing such compounds is known per se. This can be carried out, for example, analogously to the synthesis instructions given in EP-A 0,312,751, where the appropriate sulfonic acid ester derivative must be prepared in a preceding stage. Further suitable synthesis instructions are to be found in DE-A 2,610, 842, depending on the nature of the substituents R^2 , R^3 and R^4 . The synthesis of typical and preferred representatives of these classes of compounds is described below by reference to individual examples.

Preparation Example 1:

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 $-5^\circ C$. 125.8 g (0.66 mol) of p-toluenesulfonic acid chloride, dissolved in 330 ml of tetrahydrofuran and precooled to $-5^\circ C$, were added dropwise to the above mixture at -8 to $-5^\circ C$. 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 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)-benzaldehyde (white solid having a melting point of 70 to 72°C.).

2nd stage: 7.2 g (0.026 mol) of 4-(toluene-4-sulfonyloxy)-benzaldehyde were heated under reflux together with 7.2 g (0.052 mol) of phenoxyethanol, 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, 12.9 g (93%) of a pale yellow oil remained, which proved to be the desired 4-(toluene-4-sulfonyloxy)benzaldehyde bis(2-phenoxyethyl)acetal (compound No. 1 on the attached formula pages).

$C_{30}H_{30}O_7S$	calc.:	C 67.40	H 5.66	S 6.00
[534.62]	found:	C 67.7	H 5.7	S 5.9

Preparation Example 2:

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. 75.3 g (0.66 mol) of methanesulfonic acid chloride, dissolved in 330 ml of tetrahydrofuran and 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 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 84 g (63.7%) of 4-methanesulfonyloxybenzaldehyde (white solid having a melting point of 61 to 63°C.).

5 2nd stage: 5.2 g (0.026 mol) of 4-methanesulfonyloxybenzaldehyde were heated in an oil bath to 130°C together with 7.6 g (0.052 mol) of a urethane alcohol prepared by
10 condensing 1 mol of ethylene carbonate with 1 mol of n-propylamine, 4.25 g (0.0286 mol) of triethyl orthoformate and 100 mg of p-toluenesulfonic acid. In this process a highly mobile liquid distilled off. After 2 hours, the distillation was assisted for about 45 minutes by applying a vacuum of 1 mm Hg. The cooled-down residue was taken up in methylene chloride, washed twice with 2%
15 sodium hydroxide solution and deionized water each time, and the organic phase was dried. After removal of the solvent, 11.7 g (93%) of 4-methanesulfonyloxybenzaldehyde bis[2-(N-propylcarbamoyloxy)ethyl]acetal (amber-colored melt; Compound No. 2) remained. The compound shows a
20 single ¹H-NMR signal for the acetal group at 5.65 ppm.

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
25 -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 thereto dropwise at -8 to -5°C. Stirring was continued for 2 hours at room temperature. The solution was poured into 1,000 ml of
30 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
35 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 7.44 g (0.052 mol) of N-(2-hydroxyethyl) succinimide, 4.25 g (0.0286 mol) of triethyl orthoformate and 100 mg of p-toluenesulfonic acid. In this process a highly mobile liquid distilled off. After 2 hours, the distillation was assisted for about 45 minutes by applying a vacuum of 1 mm Hg. 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, 16.9 g of an amber-colored melt remained, which was recrystallized from ethanol. This gave 12.8 g (90.6%) of 3,4-bis-(toluene-4-sulfonyloxy)benzaldehyde bis-(2-succinimidoethyl)-acetal (white crystals having a melting point of 127 to 128°C; Compound No. 3).

$C_{33}H_{33}N_2O_{12}S_2$	calc.	C 55.54	H 4.66	N 3.92	S 8.98
	found	C 55.9	H 4.5	N 4.0	S 9.0

Preparation Example 4:

1st stage: 15.4 g (0.1 mol) of 3,4,5-trihydroxybenzaldehyde were dissolved in 40 ml of tetrahydrofuran, 45.5 ml of triethylamine were added, and the mixture was cooled to -5°C. 57.2 g (0.3mol) of p-toluenesulfonic acid chloride, dissolved in 80 ml of tetrahydrofuran and precooled 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 1000 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 ethyl acetate with addition of active charcoal. This gave 46.8 g (75.9%) of 3,4,5-tris-(toluene-4-sulfonyloxy)-benzaldehyde (white)

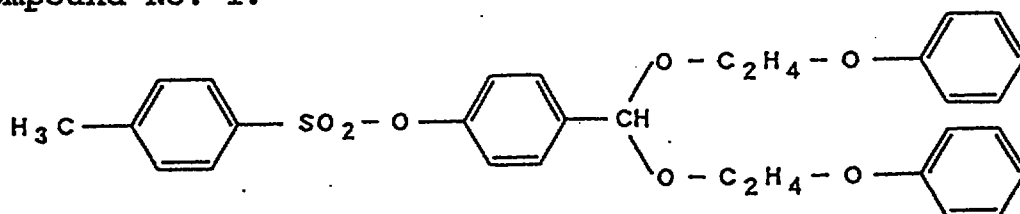
solid of melting point 159°C).

2nd stage: 18.5 g (0.03 mol) of 3,4,5-tris-(toluene-4-sulfonyloxy)-benzaldehyde were stirred at room temperature together with 5.2 g (0.035 mol) of triethyl orthoformate and 100 mg of p-toluenesulfonic acid in 150 ml of toluene. A slight evolution of heat was observed. The mixture was left to stand overnight, 8.84 g (0.065 mol) of 3-phenylpropanol and a further 100 mg of p-toluenesulfonic acid were added, followed by heating under reflux. The further procedure followed was as in Preparation Example 1. The cooled-down residue was taken up in methylenechloride, washed twice with 2% sodium hydroxide solution and deionised water each time, and the organic phase was dried. After removal of the solvent, 21.4 g (82%) of honey-colored melt reacted, which could not be made to crystallize. A thin-layer chromatogram (DC) showed that the desired 3,4,5-tris-(toluene-4-sulfonyloxy)-benzaldehyde bis-(3-phenylpropyl)-acetal (Compound No. 4) was more than 92% pure.

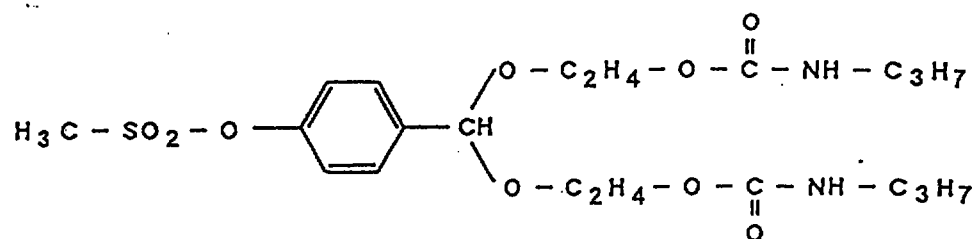
20	$C_{46}H_{46}O_{11}S_3$	calc.	C 63.39	H 5.39	S 11.03
	[871.58]	found	C 65.0	H 5.4	S 10.7

Further examples of compounds according to the invention are listed in the attached formula. These were synthesized analogously to processes known from the literature. Their authenticity was confirmed by elemental analysis and 1H -NMR.

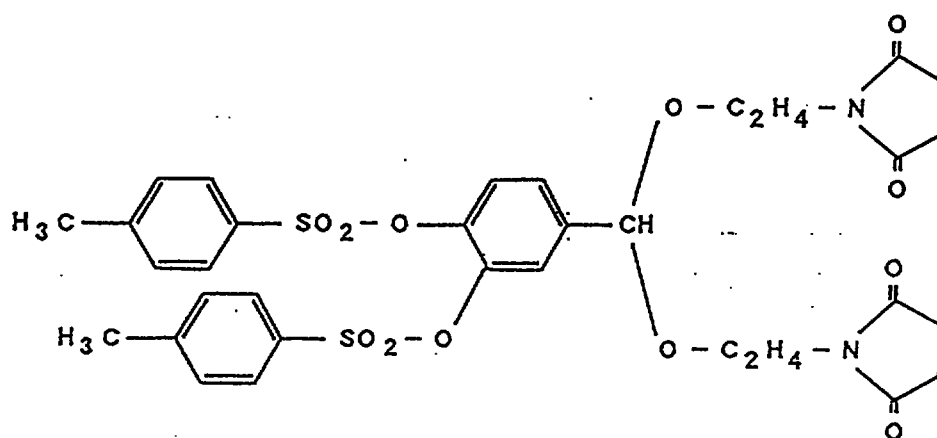
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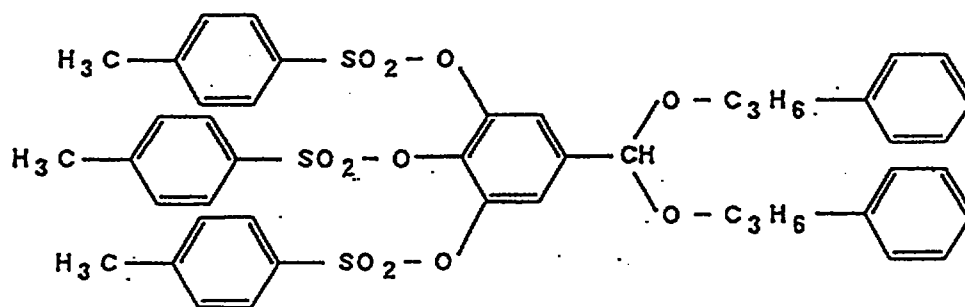
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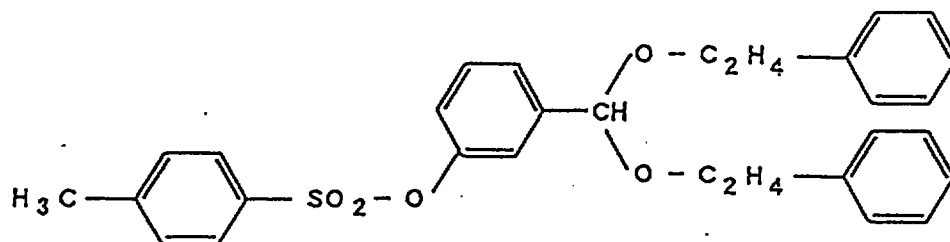
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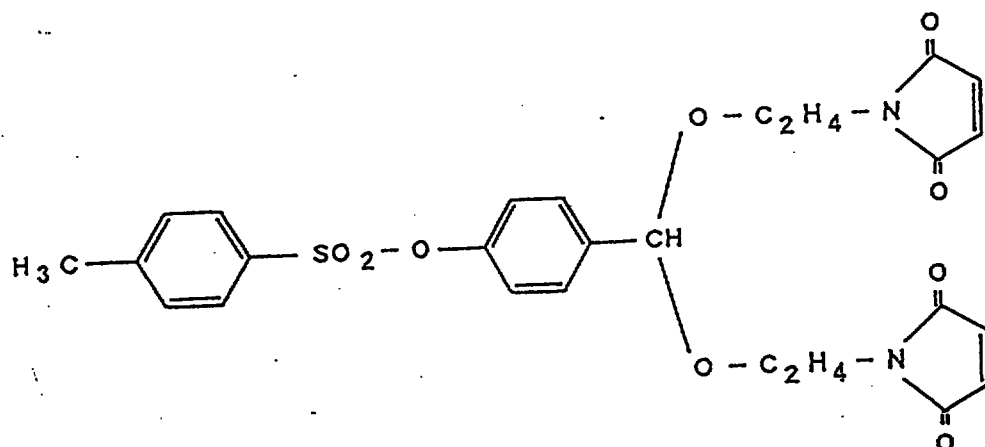
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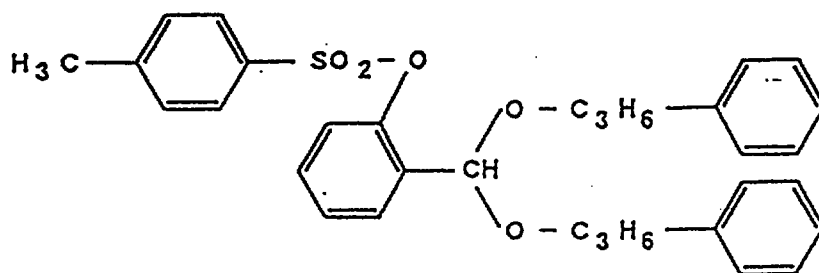
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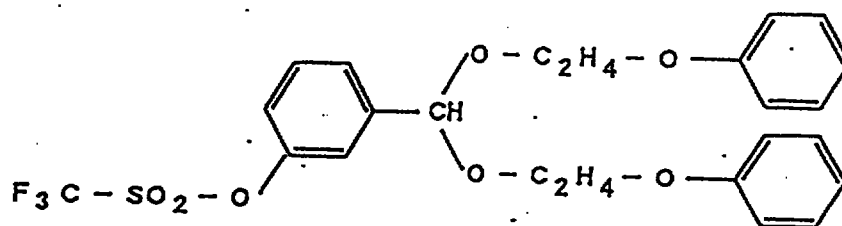
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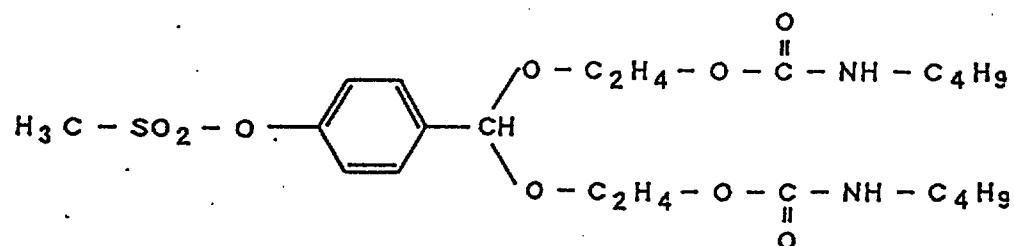
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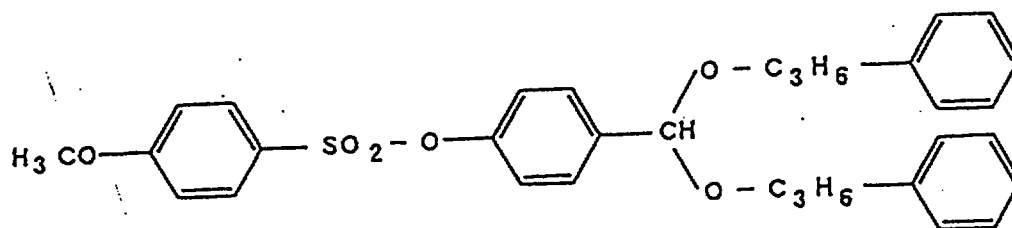
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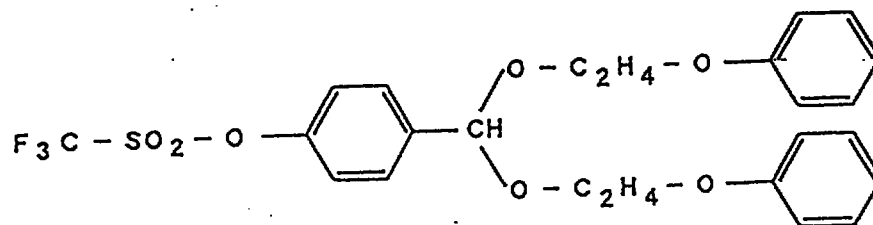
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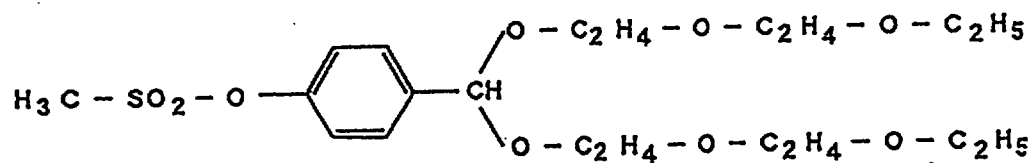
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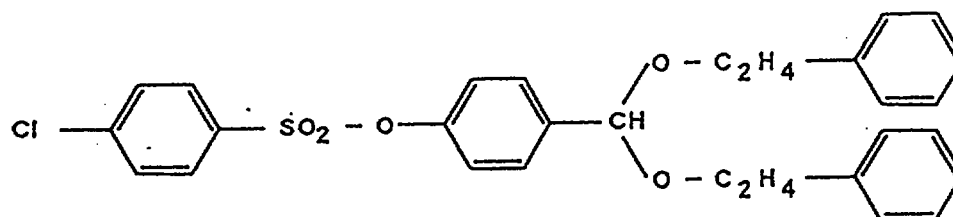
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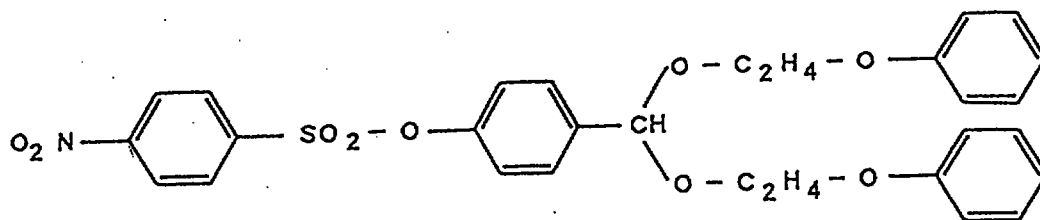
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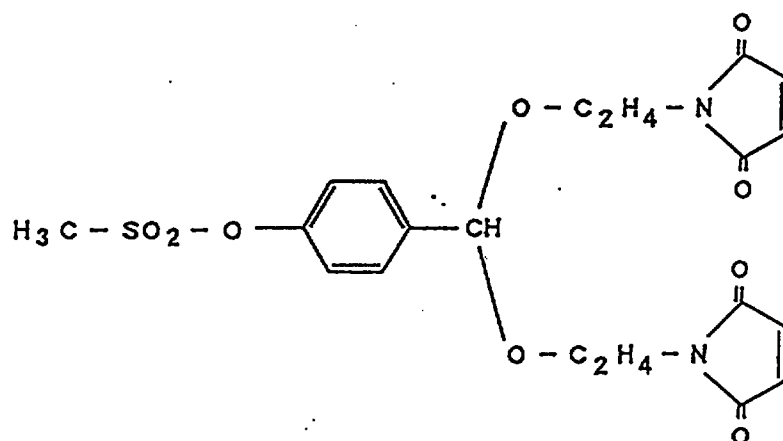
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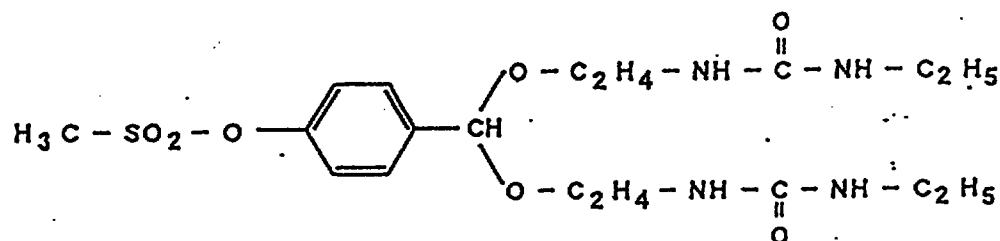
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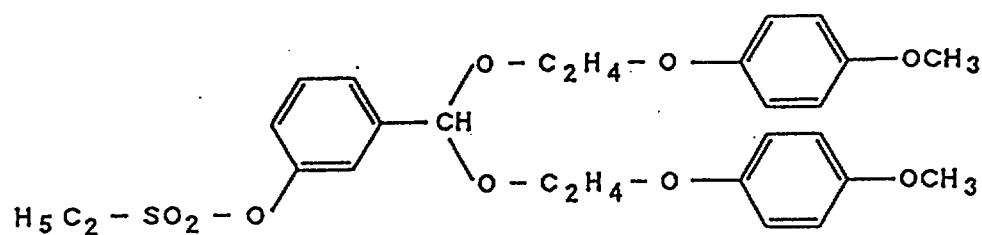
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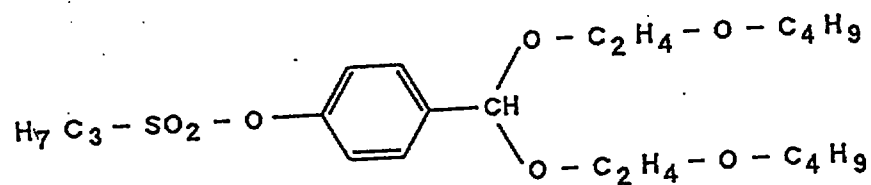
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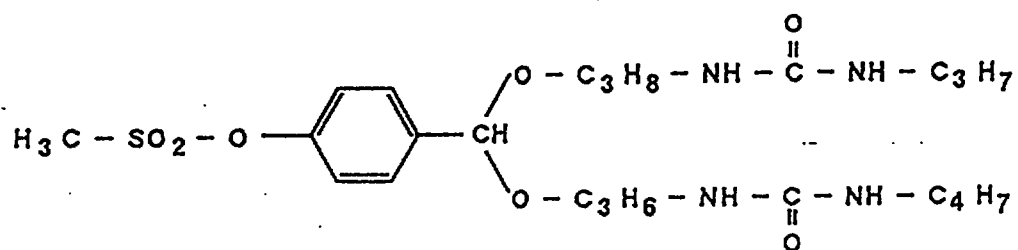
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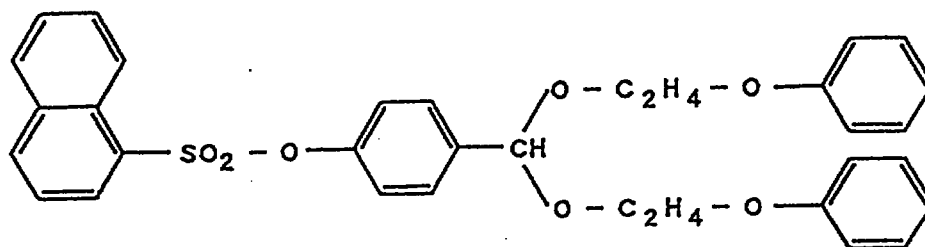
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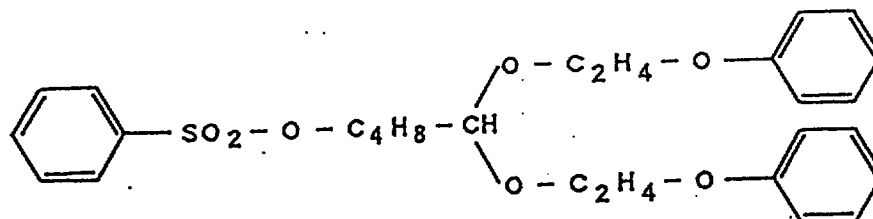
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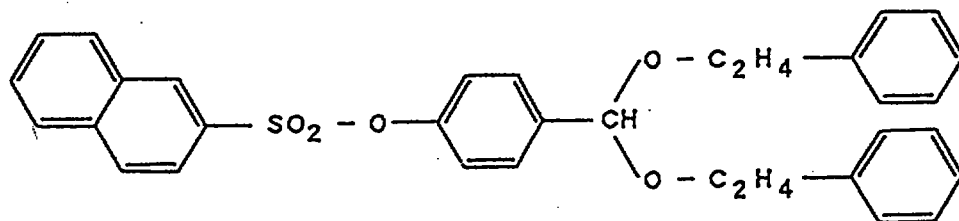
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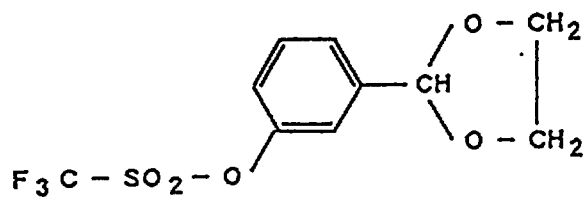
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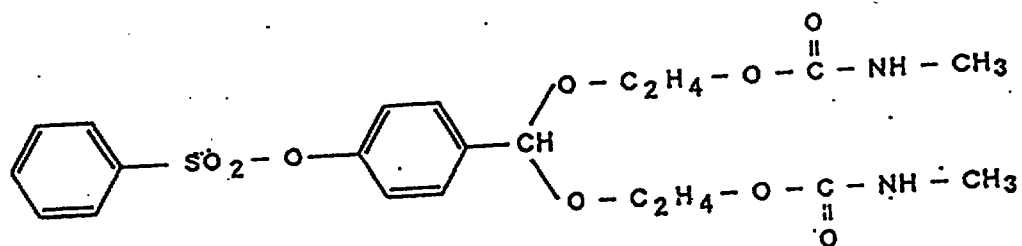
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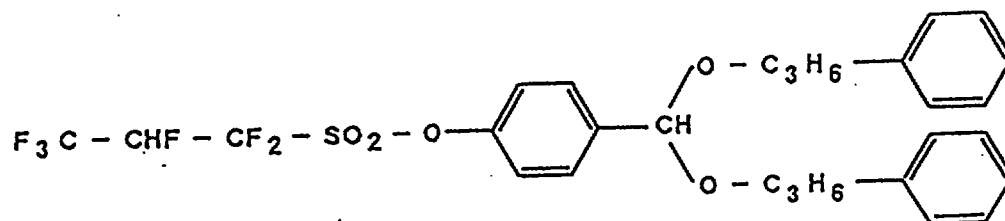
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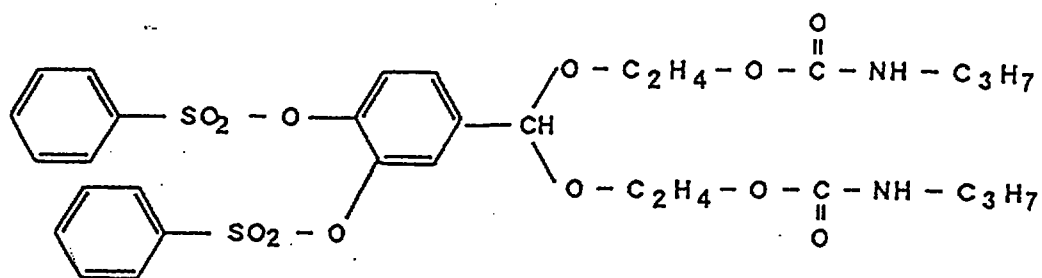
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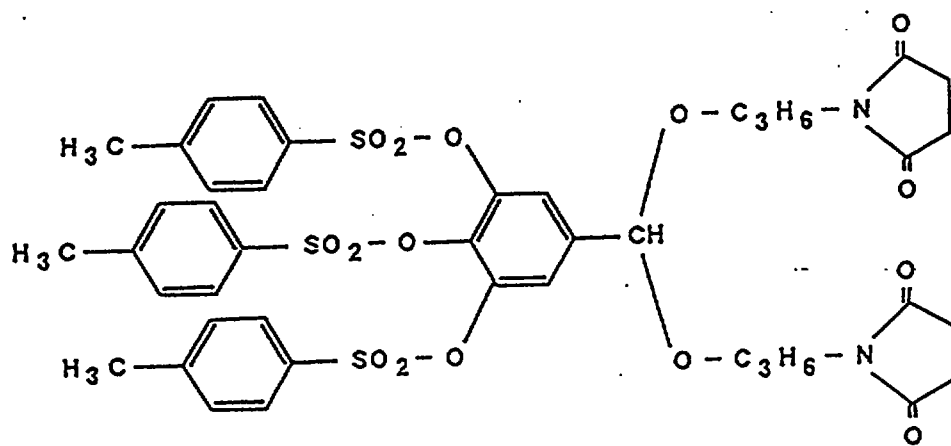
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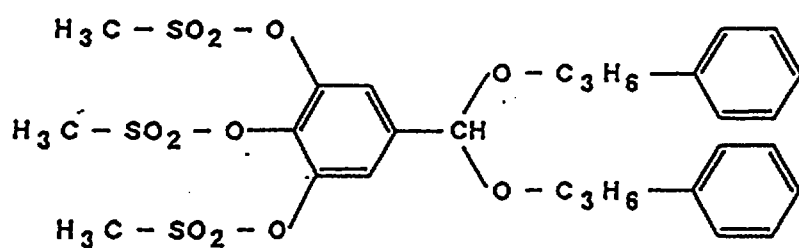
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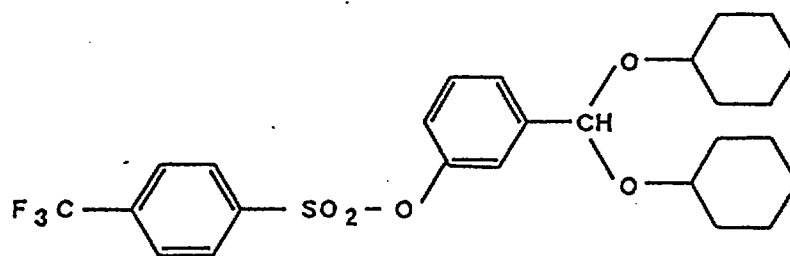
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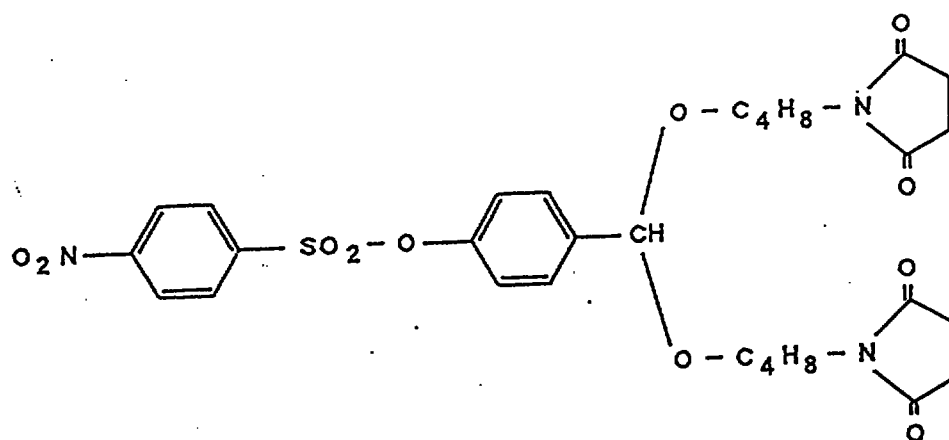
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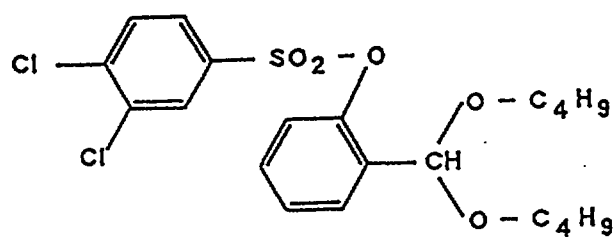
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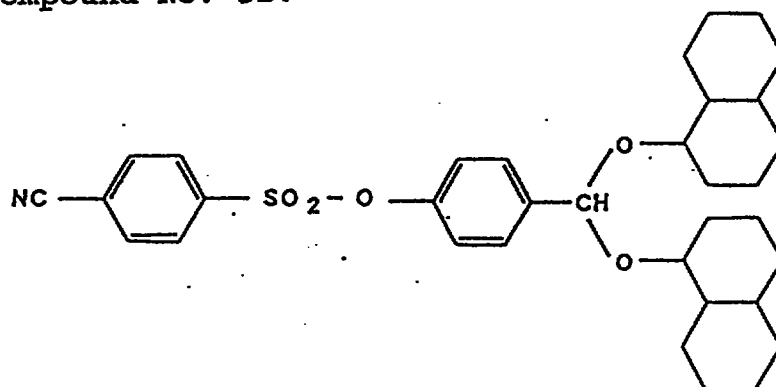
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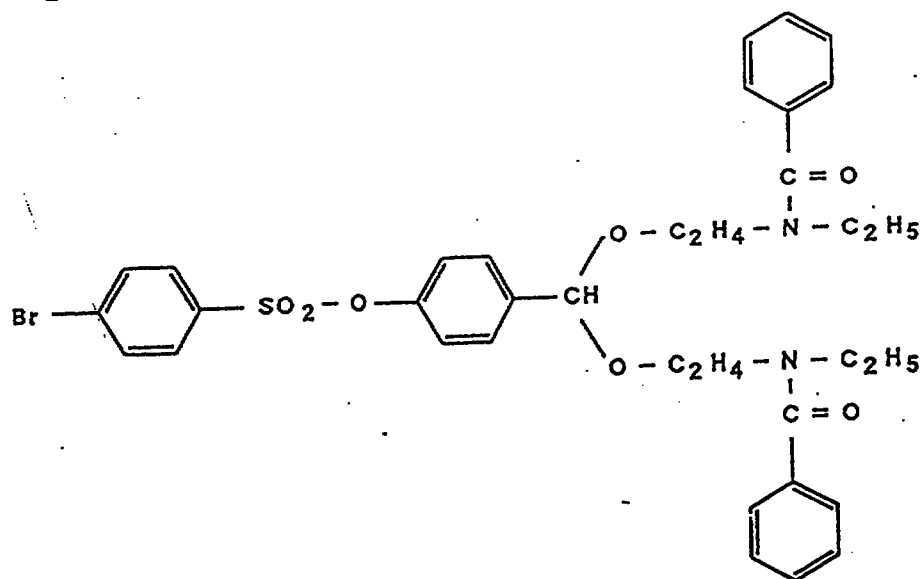
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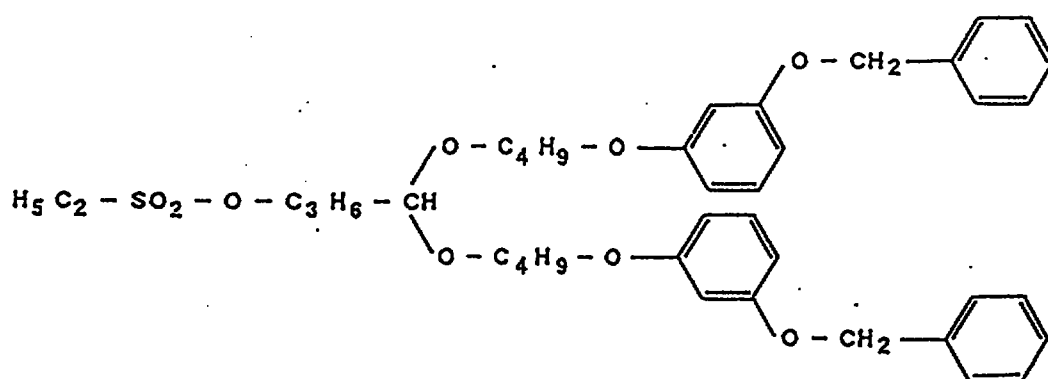
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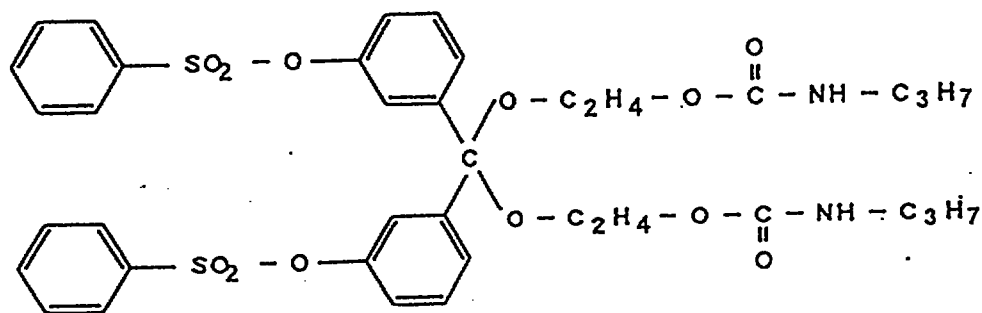
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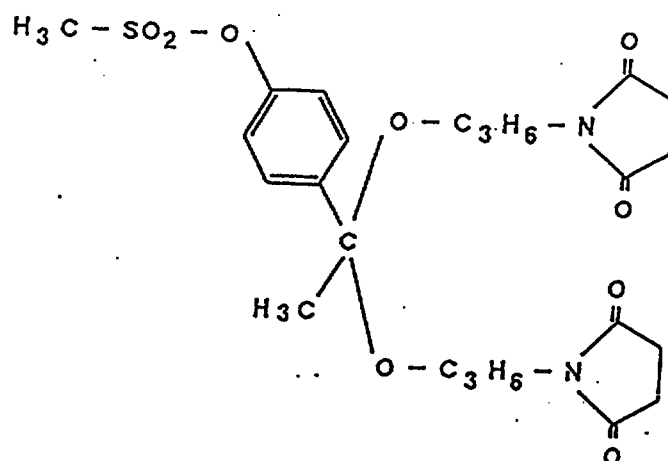
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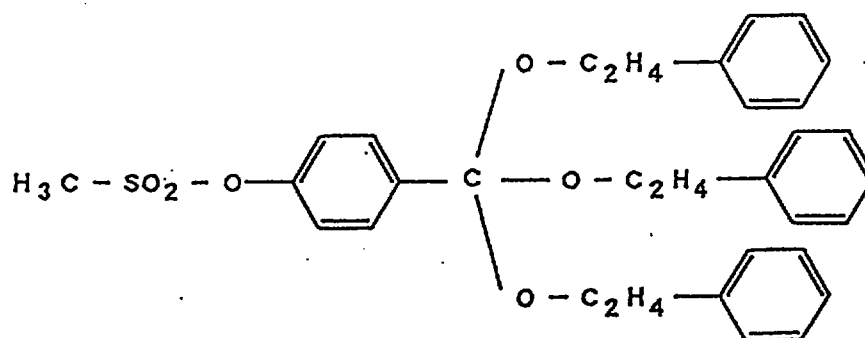
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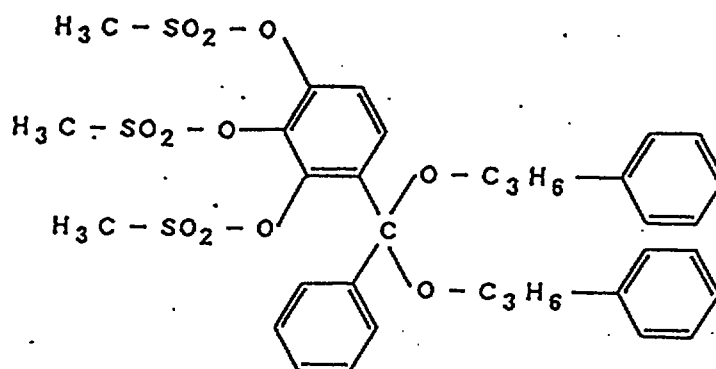
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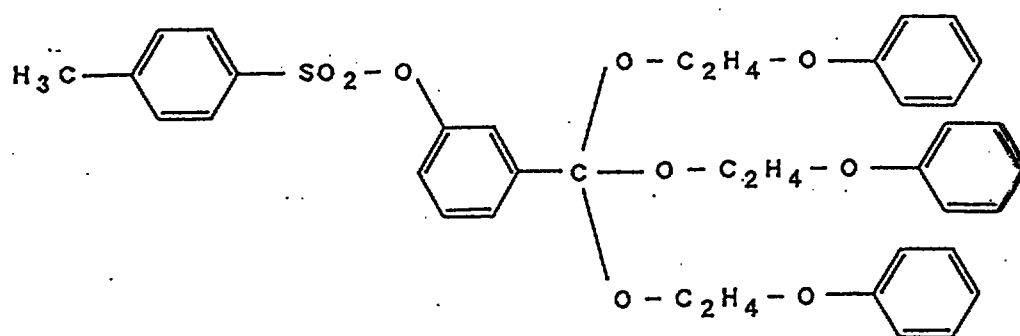
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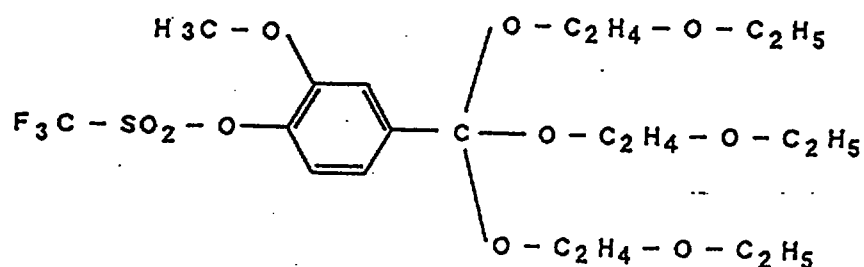
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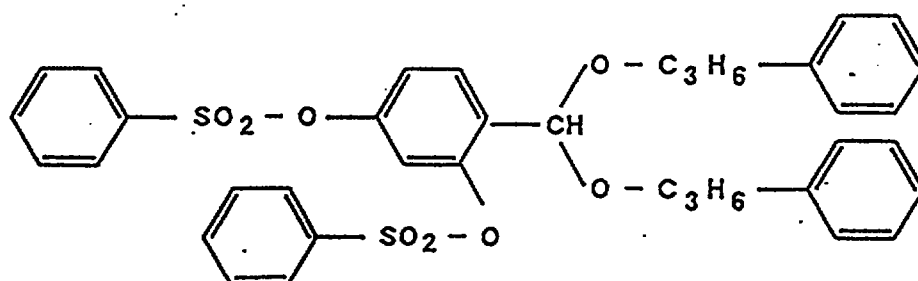
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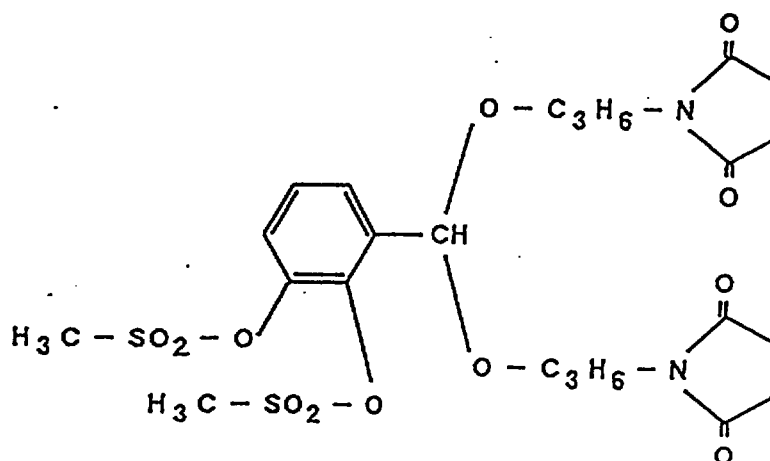
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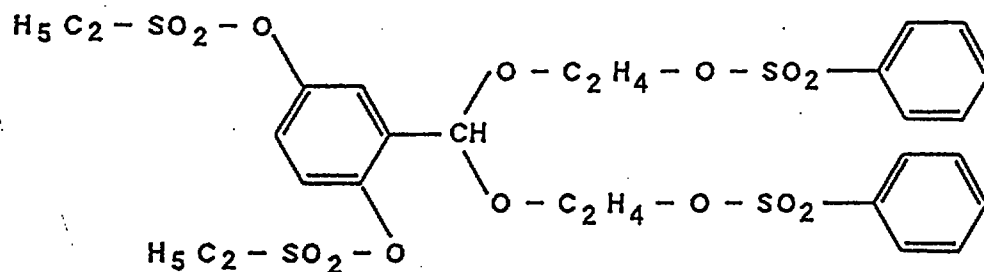
Compound No. 41:



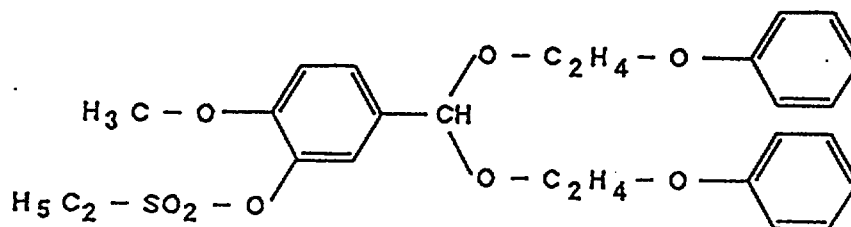
Compound No. 42:



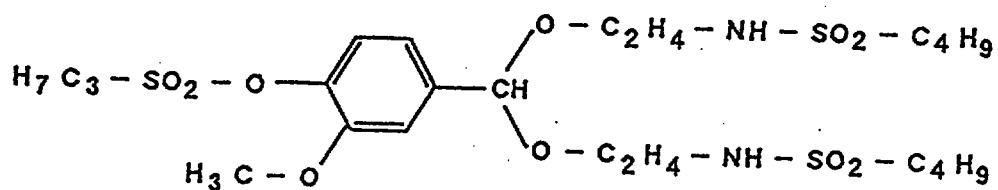
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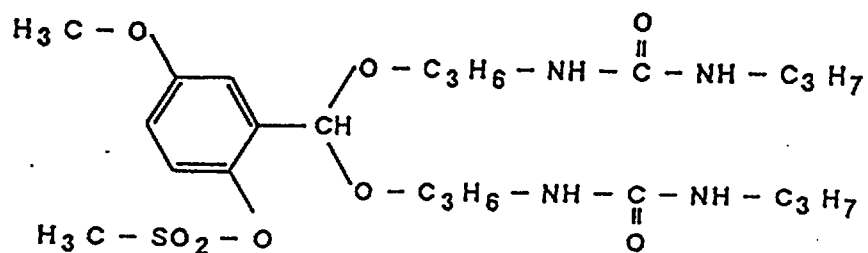
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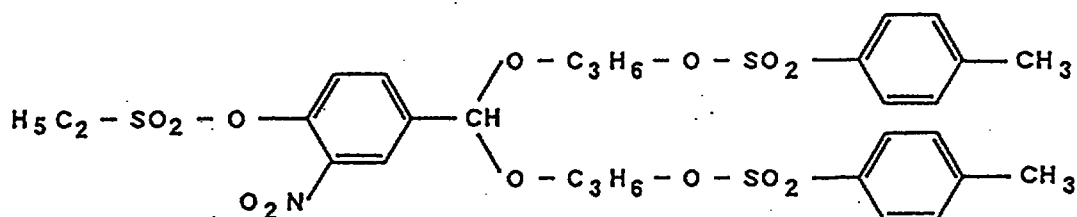
Compound No. 45:



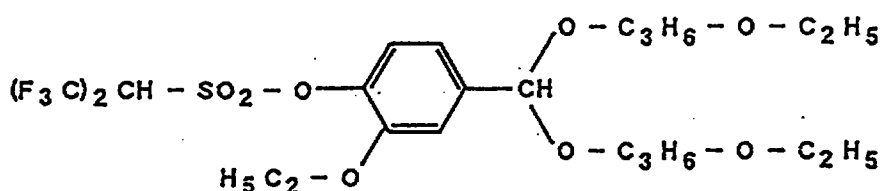
Compound No. 46:



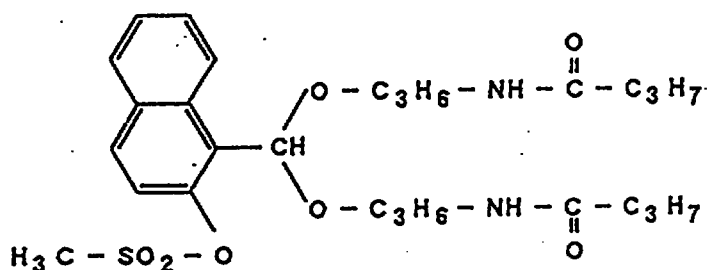
Compound No. 47:



Compound No. 48:



Compound No. 49:



5 The above selection of compounds according to the inven-
tion 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
10 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-methylbenzaldehyde,
5 2-hydroxy-4-, 2-hydroxy-5-, 3-hydroxy-4-, 4-hydroxy-3-
methoxybenzaldehyde, 3,5-dimethyl-4-, 3,4-dimethoxy-5-,
3-ethoxy-4-hydroxy-benzaldehyde, 2-hydroxy-5-, 3-hydroxy-4-,
4-hydroxy-3-, 5-hydroxy-2-nitrobenzaldehyde, 2-hydroxy-
naphthalene-1-carbaldehyde
- 10 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
15 of Organic Chemistry], vol. 7/1.

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

- 20 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,

25 wherein the compound (b) is a compound of the formula I
described above including such compounds, wherein X is an
alkylene, cycloalkylene or arylene group and n is 1.

30 The radiation-sensitive mixtures according to the inven-
tion, 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.

5 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
10 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
15 already mentioned can under certain circumstances reappear in such radiation-sensitive mixtures.

The content of acid-unstable acid generators of the formula I in the mixture according to the invention is in
20 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
25 suitable:

- (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
30 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
35 (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),
- 5 (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 silylenol ether groupings (DE-A 3,730,785 and 3,730,783),
- 10 (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
- 15 (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)].

20 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

25 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

30 150°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.

35 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 300 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.

Novalak 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.

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 of (meth)acrylic 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.

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

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

15 Finally, copolymers of styrene can, furthermore, also be 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.

20 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.

25 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.

30 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 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.

5 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
10 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
15 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
20 thereof are particularly suitable for this purpose. Glycol ethers, aliphatic esters and ketones are particularly preferred.

25 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.

30 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.

35 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 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, 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 been thermally pretreated, superficially roughened, incidentally 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 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.

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 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 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 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 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 1.0 and 10 μm .

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 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 improve 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
5 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
10 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.

15 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
20 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.

25 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
30 between 190 and 300 nm. Since the mixtures bleach very well on exposure, finer structures can be achieved than 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
35 support, the implantation of ions in the layer support or the precipitation of metals or other materials on the layer support.

5 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 the invention over the state of the art is demonstrated by reference to Comparison Examples 11 and 12.

10 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

15 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 4-(toluene-4-sulfonloxy)benzaldehyde bis(2-phenoxyethyl)acetal (Compound No. 1)
20 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 3,500 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 1.0 µm was obtained.

30 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 an energy of 80 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:

- 5 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.

10 After a developing time of 60 seconds, this gave a defect-free image of the mask with steep resist flanks, structures of $< 0.7 \mu\text{m}$ also being resolved in true detail. An examination of the flanks of the resist profiles by means of scanning electron microscopy proved that these were aligned virtually perpendicular to the substrate surface.

Example 2:

A coating solution was prepared from

- 15 7.5 p.b.w. of a styrene/p-hydroxystyrene copolymer (molar ratio 20:80) having a mean molecular weight of 32,000 and
 2.0 p.b.w. of 3,4-bis(toluene-4-sulfonyloxy)benzaldehyde bis(2-succinimidoethyl)acetal
20 (Compound No. 3) in
 42 p.b.w. of propylene glycol monomethyl ether acetate.

25 The solution was filtered through a filter of $0.2 \mu\text{m}$ 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 $1.22 \mu\text{m}$ was obtained.

30 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 76 mJ/cm^2 , 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 $< 0.7 \mu\text{m}$ being resolved in true detail.

5 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/cm^2 . After development, an image true to the original was obtained.

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 4-(toluene-4-sulfonyloxy)benzaldehydebis
15 (2-phenoxyethyl)acetal (Compound No. 1) in
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 3,100 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 $1.08 \mu\text{m}$ was obtained in both cases.

One of the coated wafers was exposed imagewise under an original to the UV radiation of an xenon-mercury vapor lamp at 240 to 260 nm with an energy of 80 mJ/cm^2 , heated for 75 seconds to 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 $< 0.7 \mu\text{m}$ being resolved in true detail.

5 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

10 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 4-(toluene-4-sulfonyloxy)benzaldehyde bis
42 (2-phenoxyethyl)acetal (Compound No. 1) in
p.b.w. of propylene glycol monomethyl ether-
acetate.

15 The solution was filtered through a filter of 0.2 μ m pore diameter and divided into two equal parts. One part was 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 1.08 μ m was
20 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 60 mJ/cm², heated for
75 seconds at 100°C and then processed using the
25 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 < 0.7 μ m being resolved in true
detail.

30 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:

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 4-methanesulfonyloxybenzaldehyde bis[2-
5 (N-propylcarbamoyl)ethyl]acetal (Compound
No. 2) 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 3,100 rpm onto a wafer treated with an adhesion promoter (hexamethyldisilazane). After drying at 100°C for 1 minute, a layer thickness of 1.08 μm was obtained.

15 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 60 mJ/cm², heated for 75 seconds at 100°C and then processed using the developer described in Example 1.

20 After a developing time of 60 seconds, this gave a defect-free image of the mask with high flank stability, here again structures of $< 0.7 \mu\text{m}$ being resolved in true detail.

Example 7:

The experiment of Example 4 was repeated twice, but
25 instead of 60 seconds at 100°C, heating was carried out
for 90 seconds at 90°C and for 60 seconds at 110°C
respectively. In both cases, the results were virtually
identical and were the same as those described in Example
4, which means that the recording material according to
30 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

5 2.0 p.b.w. of 3,4,5-tris(toluene-4-sulfonyloxy)-benzaldehyde bis(3-phenylpropyl)acetal (Compound No. 4) in

42 p.b.w. of cyclohexanone.

10 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.

15 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 120 mJ/cm² and heated for 60 seconds at 90°C.

20 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 0.7 µm were resolved in true detail.

25 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 2-(toluene-4-sulfonyloxy)benzaldehyde
bis(3-phenylpropyl)acetal (Compound No. 7)
30 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 1.00 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 67 mJ/cm² and heated for 60 seconds at 110°C.

10 The recording material was developed using a 0.02 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. The edge steepness of the image was excellent.

15 Example 10:

A coating solution was prepared from

7.5 p.b.w. of the copolymer described in Example 2 and
2.0 p.b.w. of trisphenethyl 4-methanesulfonyloxyortho-
benzoate (compound no. 37) in
20 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 3,500 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.

30 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 45 mJ/cm² and then stored for 20 minutes at room temperature.

The recording material was developed using a 0.27 N aqueous solution of tetramethylammonium hydroxide, the

5 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):

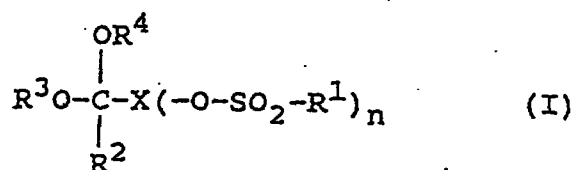
10 The resist formulation of Example 2 was modified in such a way that instead of 2.0 p.b.w. of Compound No. 3, 0.2 p.b.w. of the compounds, likewise known as acid generators, triphenylsulfonium hexafluorophosphate (Example 11) or 2-nitrobenzyl tosylate (Example 12) were added to the mixture. After coating and drying, it was
15 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 did not
20 differ from that of Example 2.

25 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 the formula I



in which

R^1 is an alkyl, highly fluorinated alkyl, perfluoroalkyl or aryl radical,

R^2 is a hydrogen atom, an alkyl or aryl radical or one of the groups $(\text{R}^1-\text{SO}_2-\text{O})_n\text{X}-$ or $\text{R}^3\text{O}-$,

R^3 and R^4 are identical or different and are alkyl, cycloalkylalkyl, cycloalkenylalkyl or aralkyl radicals, in which 1 to 3 aliphatic CH_2 or CH groups can be replaced by NR^5 , O, S, CO, CO-O, CO-NH, O-CO-NH, CO-NH-CO, NH-CO-NH, SO_2 , SO_2 -O or SO_2 -NH, or alkenyl, alkynyl, cycloalkyl or cycloalkenyl radicals or are mutually linked to form a heterocyclic ring,

R^5 is an acyl radical,

X is an alkanetriyl, cycloalkanetriyl or arenetriyl group or an alkanetetrayl, cycloalkanetetrayl or arenetetrayl group and

n is an integer from 1 to 3



2. A compound as claimed in claim 1, wherein R^1 is an alkyl, perfluoroalkyl or highly fluorinated alkyl radical having 1 to 6 carbon atoms, an aryl radical having 6 to 12 carbon atoms and R^2 is a hydrogen atom or an R^3O radical.
3. A compound as claimed in claim 1 or 2, wherein R^3 and R^4 are identical or different and are alkyl or arylalkyl groups having up to 15 carbon atoms.
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,

wherein the compound (b) is a compound as claimed in any of claims 1 to 3, comprising also compounds in which X is an alkylene, cycloalkylene or arylene group and in which n is 1.

5. A radiation-sensitive mixture as claimed in claim 4, wherein X is an alkylene group having 2 to 10 carbon atoms, a cycloalkylene group having 4 to 10 carbon atoms or an arylene group having 6 to 12 carbon atoms.
6. 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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7. A radiation-sensitive mixture as claimed in claim 4, which contains the compound (b) in a concentration from 2 to 60 % by weight.
8. A radiation-sensitive mixture as claimed in claim 4, 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 4, which contains the binder (a) in a concentration from 40 to 98 % by weight.
11. 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 10.