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Amended claims in accordance with Rule 137(2)
EPC.

(54) **A lithographic printing plate precursor**

(57) A heat-sensitive positive-working lithographic printing plate precursor is disclosed which comprises on a support having a hydrophilic surface or which is provided with a hydrophilic layer, a heat and/or light-sensitive coating comprising a surfactant,

characterized in that said surfactant comprises a poly-ether block including a pendant fluoroalkylgroup and a urethane linking group.

EP 2 047 988 A1

Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a lithographic printing plate precursor.

BACKGROUND OF THE INVENTION

10 **[0002]** Lithographic printing presses use a so-called printing master such as a printing plate which is mounted on a cylinder of the printing press. The master carries a lithographic image on its surface and a print is obtained by applying ink to said image and then transferring the ink from the master onto a receiver material, which is typically paper. In conventional, so-called "wet" lithographic printing, ink as well as an aqueous fountain solution (also called dampening liquid) are supplied to the lithographic image which consists of oleophilic (or hydrophobic, i.e. ink-accepting, water-repelling) areas as well as hydrophilic (or oleophobic, i.e. water-accepting, ink-repelling) areas. In so-called driographic printing, the lithographic image consists of ink-accepting and ink-abhesive (ink-repelling) areas and during driographic printing, only ink is supplied to the master.

15 **[0003]** Printing masters are generally obtained by the image-wise exposure and processing of an imaging material called plate precursor. In addition to the well-known photosensitive, so-called pre-sensitized plates, which are suitable for UV contact exposure through a film mask, also heat-sensitive printing plate precursors have become very popular in the late 1990s. Such thermal materials offer the advantage of daylight stability and are especially used in the so-called computer-to-plate method wherein the plate precursor is directly exposed, i.e. without the use of a film mask. The material is exposed to heat or to infrared light and the generated heat triggers a (physico-) chemical process, such as ablation, polymerization, insolubilization by cross linking of a polymer, heat-induced solubilization or particle coagulation of a thermoplastic polymer latex.

25 **[0004]** The most popular thermal plates form an image by a heat-induced solubility difference in an alkaline developer between exposed and non-exposed areas of the coating. The coating typically comprises an oleophilic binder, e.g. a phenolic resin, of which the rate of dissolution in the developer is either reduced (negative working) or increased (positive working) by the image-wise exposure. During processing, the solubility differential leads to the removal of the non-image (non-printing) areas of the coating, thereby revealing the hydrophilic support, while the image (printing) areas of the coating remain on the support. Typical examples of such plates are described in e.g. EP-A 625728, 823327, 825927, 30 864420, 894622 and 901902. Negative working embodiments of such thermal materials often require a pre-heat step between exposure and development as described in e.g. EP-625,728.

35 **[0005]** Negative working plate precursors which do not require a pre-heat step may contain an image-recording layer that works by heat-induced particle coalescence of a thermoplastic polymer particle (latex), as described in e.g. EP-As 770 494, 770 495, 770 496 and 770 497. These patents disclose a method for making a lithographic printing plate comprising the steps of (1) image-wise exposing an imaging element comprising hydrophobic thermoplastic polymer particles dispersed in a hydrophilic binder and a compound capable of converting light into heat, (2) and developing the image-wise exposed element by applying fountain and/or ink.

40 **[0006]** Some of these thermal processes enable plate making without wet processing and are for example based on ablation of one or more layers of the coating. At the exposed areas the surface of an underlying layer is revealed which has a different affinity towards ink or fountain than the surface of the unexposed coating.

[0007] Other thermal processes which enable platemaking without wet processing are for example processes based on a heat-induced hydrophilic/oleophilic conversion of one or more layers of the coating so that at exposed areas a different affinity towards ink or fountain is created than at the surface of the unexposed coating.

45 **[0008]** JP 2006/330670 discloses a printing plate precursor containing a coating including a spreading agent comprising a fluoroalkyl group.

[0009] Printing plate precursors are susceptible to damage caused by mechanical forces applied to the surface of the coating during transport, mechanical handling and/or manual handling. After coating and drying, the thermal printing plate precursors are cut, stacked and packed in boxes by means of specified packaging equipment. During transport of the packed printing plate precursors, the plates can move relatively to each other. The degree of this slipperiness can be determined by the static coefficient of friction as measured between two stacked precursors: a low static coefficient of friction between the surface of a printing plate precursor and the interleaf sheet on top of it, or between the surface of a printing plate precursor and the aluminum back side of the plate on top of it in case no interleaf sheets are used, results in slippery plates. Slippery plates do not only cause unsafe situations during transport, but also lead to damage on the surface of the plate precursor, such as for example formation of the well-known "scuff marks". Scuff marks are unacceptable from an aesthetic point of view but moreover, these areas of the coating often do not sufficiently take up ink during printing and result in a poor, sometimes unacceptable, printing quality. Printing plate precursors characterized by a surface having a high static coefficient of friction on the other hand, will be much less slippery, but in general, the

preparation - i.e. coatability - of such printing plate precursors is difficult under industrial coating- and drying conditions. As a result, a precursor with an uneven and non-uniform surface - also referred to in the art as a surface with bad coating cosmetics - is obtained. Thus, under industrial coating- and drying conditions it is very difficult to obtain a printing plate precursor with a surface characterized by excellent coating cosmetics and at the same time a high static coefficient of friction.

SUMMARY OF THE INVENTION

[0010] It is an object of the present invention to provide a printing plate precursor with a heat and/or light-sensitive coating which has a smooth, even and uniform surface, and which at the same time has a sufficiently high coefficient of friction; i.e. a coefficient of friction whereby stacked plate precursors do not easily move relative to each other during handling and/or transport.

[0011] This object is realized by claim 1, i.e. a heat-sensitive positive-working lithographic printing plate precursor which comprises on a support having a hydrophilic surface or which is provided with a hydrophilic layer, a heat- and/or light sensitive coating comprising a surfactant, characterized in that said surfactant comprises a polyether block including a pendant fluoroalkyl group and a urethane linking group.

[0012] It was surprisingly found that the surfactants used in the present invention, in contrast to surfactants of the prior art, not only provide a good coatability to the coating - i.e. good coating cosmetics or a coating with an even and smooth surface - but at the same time provide a coating with a sufficiently high coefficient of friction.

[0013] Other features, elements, steps, characteristics and advantages of the present invention will become more apparent from the following detailed description of preferred embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

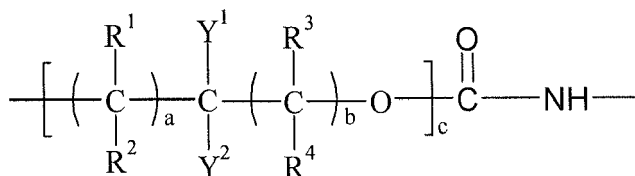
[0014] The lithographic printing plate precursor of the present invention comprises a heat and/or light sensitive coating on a support. The imaging mechanism of such printing plate precursors can be triggered by direct exposure to heat, e.g. by means of a thermal head, or by the light absorption of one or more compounds in the coating that are capable of converting light, more preferably infrared light, into heat.

[0015] The coating comprises a surfactant which comprises a polyether block including a pendant fluoroalkyl group and a urethane linking group. The fluoroalkyl group may be straight or branched and includes a $-(CF_2)-$ and/or a $-(CHF)-$ unit. The number of such units may be 1, i.e. $-(CF_3)$, $-(CHF_2)$ or $-(CH_2F)$; or more than 1, preferably less than 20; more preferably less than 15 and most preferably between 2 and 10.

[0016] In a preferred embodiment, the polyether block includes a pendant alkoxyfluoroalkyl group. The alkoxyfluoroalkyl group includes a $-[(CR^aR^b)_g-O-(CR^cR^d)_h-fluoroalkyl]-$ unit wherein R^a , R^b , R^c and R^d independently represent hydrogen, an alkyl or a fluoroalkyl group and g and h independently represent an integer ≥ 0 .

[0017] The urethane linking group present in the surfactant may be linked to the polyether block including a pendant fluoroalkyl group and/or alkoxyfluoroalkyl group; or may be linked to another polymeric block such as a polyether, polyester, polyurethane or polyvinyl alcohol block optionally present in the surfactant.

[0018] The surfactant used in the present invention preferably comprises the structural unit represented by the following formula (I):



(I)

wherein

a and b independently represent an integer ≥ 0 ;

c represents an integer ranging between 1 and 40, preferably an integer ranging between 2 and 20;

Y¹ represents a fluoroalkyl group or an alkoxyfluoroalkyl group;

Y² represents hydrogen; an optionally substituted alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl or pentyl group, a fluoroalkyl group or an alkoxyfluoroalkyl group;

R¹ to R⁴ independently represent hydrogen, fluoride, an optionally substituted alkyl group such as for example a methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl or pentyl group; a fluoroalkyl group or an optionally substituted aryl group.

The optional substituents on the alkyl or aryl group may be a halogen such as F, Cl, Br or I; an alkyl group or a fluoroalkyl group. The fluoroalkyl group and the alkoxyfluoroalkyl group are defined above.

[0019] In a more preferred embodiment, the surfactant comprises the structural unit represented by the formula (I) wherein:

a and b independently represent an integer ≥ 0 ;

c represents an integer ranging between 1 and 40, preferably an integer ranging between 2 and 20;

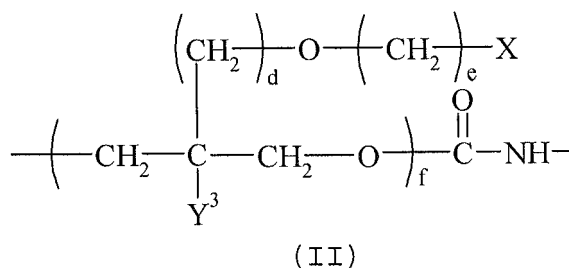
Y¹ represents a fluoroalkyl group or an alkoxyfluoroalkyl group;

Y² represents hydrogen; an optionally substituted alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl or pentyl group;

R¹ to R⁴ independently represent hydrogen, fluoride, an optionally substituted alkyl group such as for example a methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl or pentyl group; a fluoroalkyl group or an optionally substituted aryl group. The optional substituents on the alkyl or aryl group may be a halogen such as F, Cl, Br or I; an alkyl group or a fluoroalkyl group.

The fluoroalkyl group and the alkoxyfluoroalkyl group are defined above.

[0020] In a most preferred embodiment, the surfactant includes a polyether block including a pendant alkoxyfluoroalkyl group and a urethane linking group represented by the formula (II):



wherein d and e represent an integer ≥ 0 ;

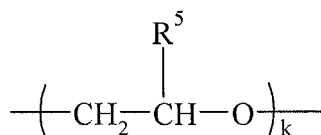
X represents a fluoroalkyl group;

Y³ represents hydrogen or an optionally substituted alkyl group such as a methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl or pentyl group;

and f represents an integer ranging between 1 and 40, preferably an integer ranging between 2 and 20.

The optional substituents on the alkyl group may be a halogen such as F, Cl, Br or I; an alkyl group or a fluoroalkyl group.

[0021] The surfactant used in the present invention may further comprise one or more polyether blocks as represented by formula (III):



(III)

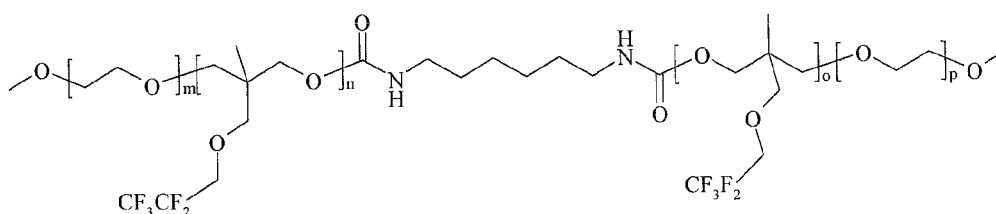
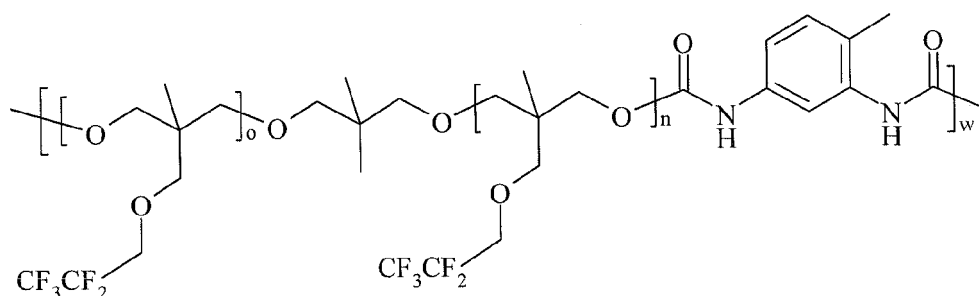
wherein R⁵ represents hydrogen; an optionally substituted

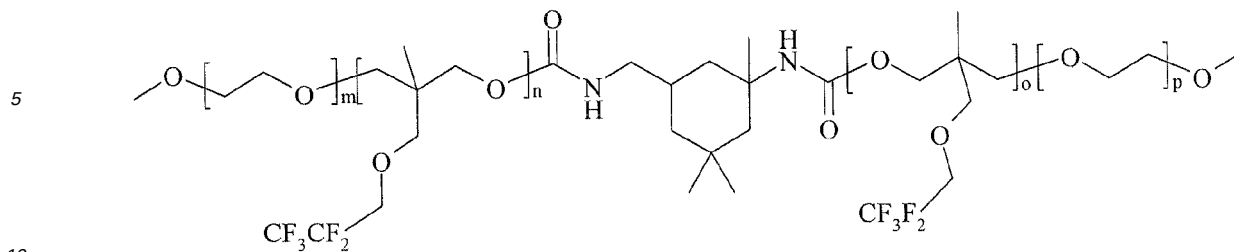
alkyl or cycloalkyl group such as methyl, ethyl, propyl, isopropyl, cyclopentyl; an optionally substituted aryl, aralkyl or heteroalkyl group;

and k represents an integer ranging between 1 and 40, preferably an integer ranging between 2 and 20. The optional substituents on the alkyl or aryl group may be a halogen such as F, Cl, Br or I; an alkyl group or a fluoroalkyl group.

[0022] The structural units represented by the formula's (I) and/or (II) may be linked together and/or they may be linked, optionally via a linking group, to a polyether block represented by formula (III), a polyester, polyurethane or polyvinyl alcohol block forming diblock copolymers. By further linking diblock copolymers, multiblock copolymers may be formed.

[0023] Such diblock copolymers may for example be prepared by reacting a mono-hydroxyterminated polyether comprising a pendant fluoroalkyl or alkoxyfluoroalkyl group with one, two or more isocyanate functional groups of a mono-, di or multi-isocyanate compound, optionally followed by a reaction of the remaining isocyanate functional group(s) with a polyether optionally comprising a pendant fluoroalkyl or alkoxyfluoroalkyl group, a polyester, polyurethane or polyvinyl alcohol. If the hydroxyterminated polyether comprising a pendant fluoroalkyl or alkoxyfluoroalkyl group contains two or more hydroxy endgroups, triblock or multiblock copolymers are obtained by reaction with mono-, di- and/or multi-isocyanate compounds. These tri- or multiblock copolymers may comprise for example the following structural units:

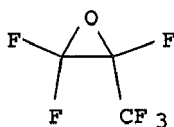




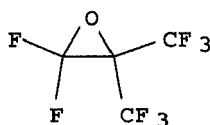
wherein independently in each of the structures above m, n, o, p and w independently represent an integer ranging between 1 and 40, preferably an integer ranging between 2 and 20.

[0024] Hydroxyterminated polyethers comprising a pendant fluoroalkyl or alkoxyfluoroalkyl group can be obtained by for example cationic ringopening polymerisation of a fluoroalkyl or an alkoxyfluoroalkyl substituted oxethane with an alcohol as initiator. The alcohol initiator may be a monofunctional alcohol or a multifunctional alcohol such as a diol, a triol or a tetra-alcohol. They may have a low molecular weight (i.e. non polymeric) or may be polymeric alcohols such as condensation polymers e.g. mono- or dihydroxy terminated polyurethanes, polyesters or polyethers or addition polymers e.g. polyvinyl alcohol. When the alcohols are mono-functional, mono-hydroxyterminated fluoroalkyl and/or alkoxyfluoroalkyl polyethers are obtained; when the alcohols are multifunctional, multi-hydroxyterminated fluoroalkyl and/or alkoxyfluoroalkyl polyethers are obtained such as for example bis-, tris- or tetra-hydroxyterminated (star branched) fluoroalkyl and/or alkoxyfluoroalkyl polyethers.

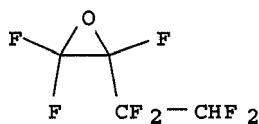
[0025] Suitable fluoroalkyl and alkoxyfluoroalkyl substituted oxethanes for the preparation of the surfactants include: hexafluoropropylene oxide:



perfluoroisobutene oxide:

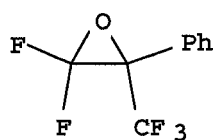


trifluoro(1,1,2,2-tetrafluoroethyl)- oxirane:



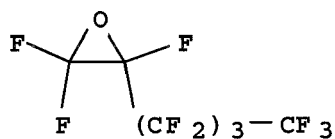
6-Hydroperfluoro-1,2-epoxyhexane:

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trifluoro(nonafluorobutyl)oxirane:

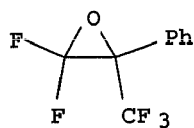
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2,2-difluoro-3-phenyl-3-(trifluoromethyl)- Oxirane:

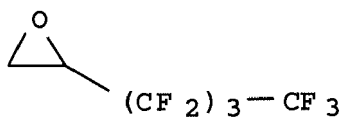
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(heptafluoropropyl)- oxirane,

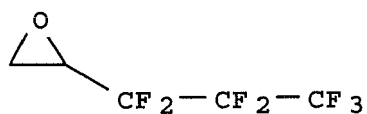
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(heptafluoropropyl)- oxirane:

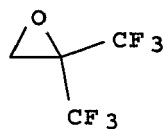
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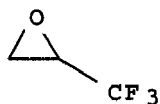
2,2-Bis(trifluoromethyl)oxirane:

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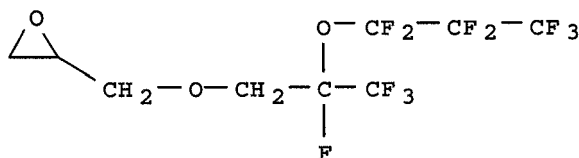


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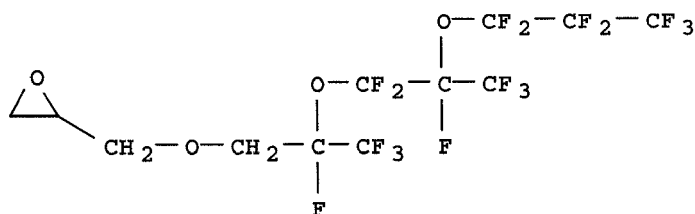
trifluoromethyloxirane:



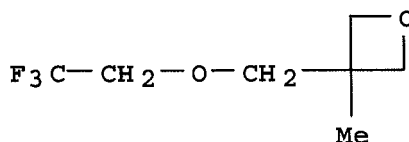
[[2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propoxy]methyl]-oxirane:



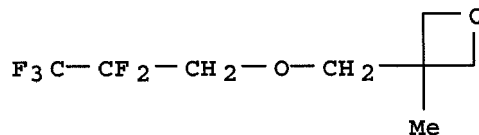
[[2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]propoxy]propoxy]methyl]- Oxirane:



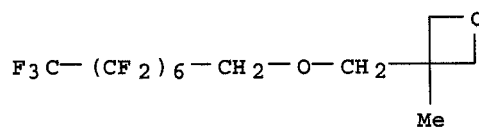
3-(2,2,2-Trifluoroethoxymethyl)-3-methyloxetane:



3-methyl-3-[(2,2,3,3,3-pentafluoropropoxy)methyl]oxetane:

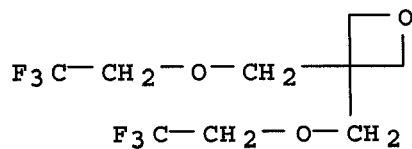


3-methyl-3-[[2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)oxy]methyl]- Oxetane:



3,3-bis[(2,2,2-trifluoroethoxy)methyl]- Oxetane:

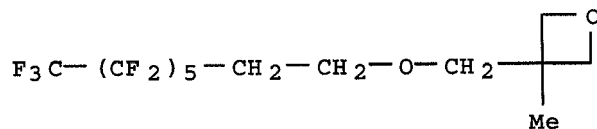
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3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyloxymethyl-3-methyloxetane:

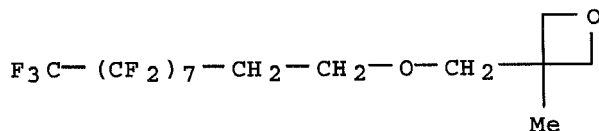
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3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyloxymethyl-3-methyloxetane:

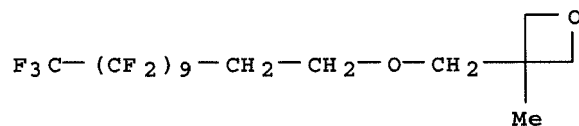
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3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heneicosafuorododecyloxymethyl-3-methyloxetane:

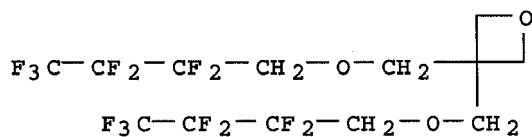
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3,3-Bis(2,2,3,3,4,4,4-heptafluorobutoxymethyl)-3-oxetane:

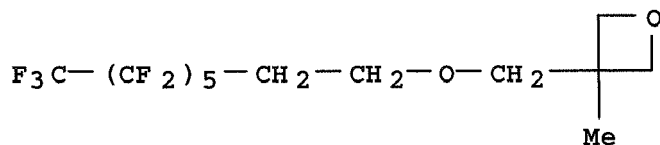
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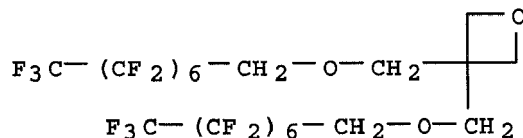
3-methyl-3-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) oxy] methyl] oxetane:

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3,3-bis[[[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl) oxy] methyl] -oxetane:

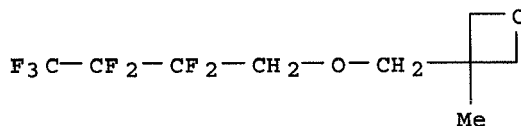
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3-(2,2,3,3,4,4,4-Heptafluorobutoxymethyl)-3-methyloxetane:

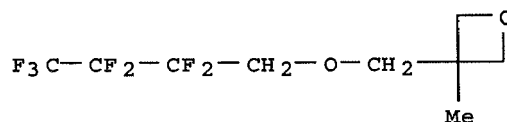
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3-[(2,2,3,3,4,4,4-heptafluorobutoxy)methyl]-3-methyloxetane:

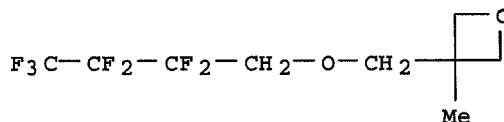
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3-[(2,2,3,3,4,4,4-heptafluorobutoxy)methyl]-3-methyloxetane:

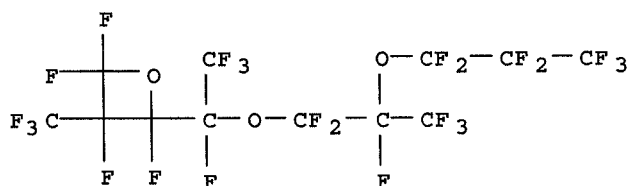
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2,2,3,4-tetrafluoro-4-[1,2,2,2-tetrafluoro-1-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]ethyl]-3-(trifluoromethyl)- Oxetane:

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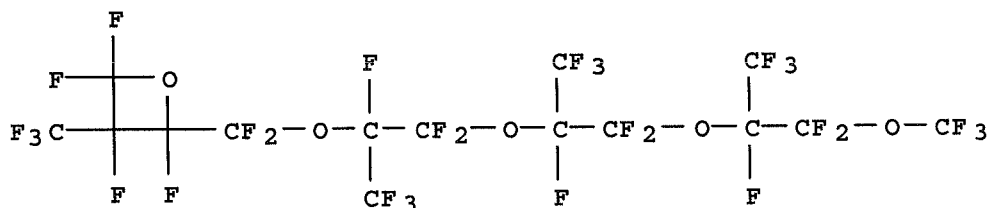
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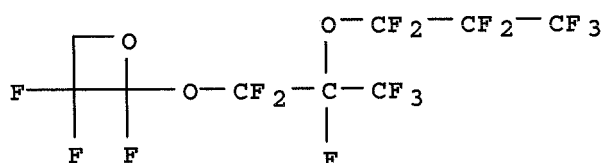
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2,2,3,4-tetrafluoro-4-[1,1,3,4,4,6,7,7,9,10,10,12,12,12-tetradecafluoro-3,6,9-tris(trifluoromethyl)-2,5,8,11-tetraoxadec-1-yl]-3-(trifluoromethyl)- Oxetane:

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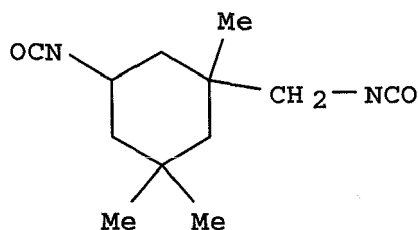


2,3,3-trifluoro-2-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]- Oxetane:



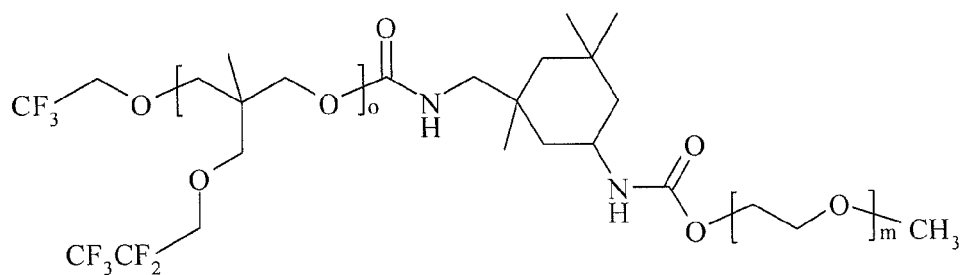
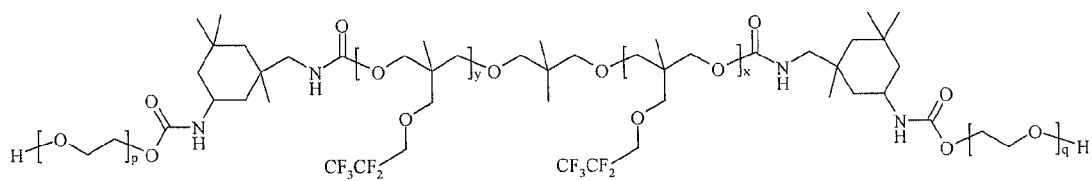
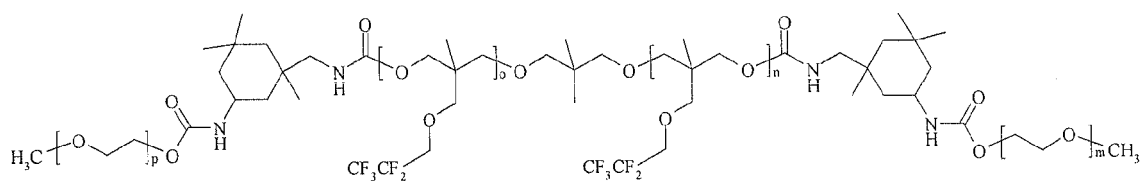
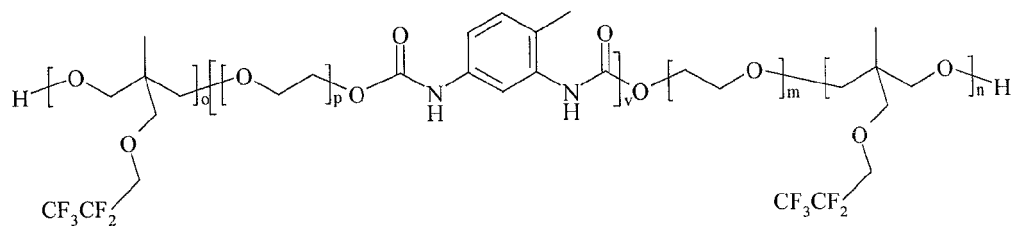
[0026] Suitable isocyanates for the preparation of the surfactants include monofunctional isocyanates such as phenyl isocyanate, stearyl isocyanate, 2-(methacryloxy)ethyl isocyanate, methyl isocyanate, isocyanatocyclohexane, ethyl isocyanate, 1-(isocyanatomethyl)benzene, 4-methoxyphenyl isocyanate, isopropyl isocyanate, m-anisyl isocyanate and 2-tolyl isocyanate; diisocyanates such as 1,6-hexylene diisocyanate, 4,4'-diphenylmethane diisocyanate, isophorone diisocyanate, tolylene diisocyanate, 4,4'-diisocyanatodicyclohexylmethane, 1,4-phenylene diisocyanate, tetramethylene isocyanate, 1 dodecamethylene diisocyanate, 1,5-naphthylene diisocyanate and m-xylylene diisocyanate; or multifunctional isocyanates such as the isocyanurate trimer of hexamethylenediisocyanate.

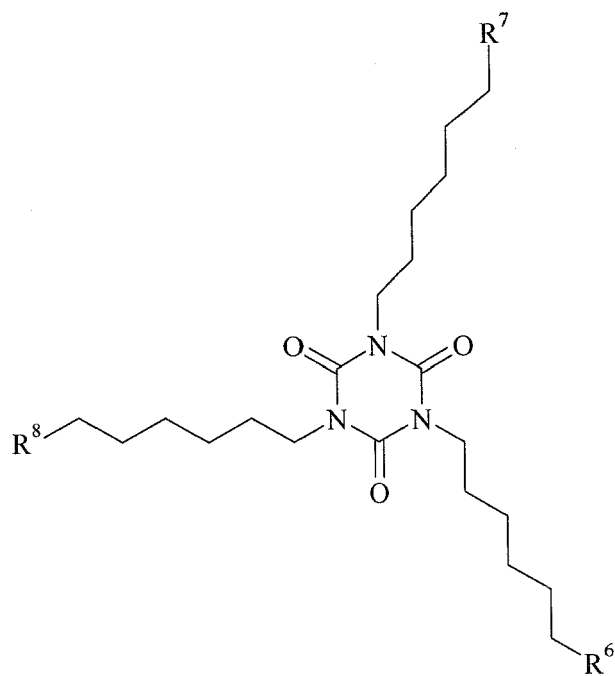
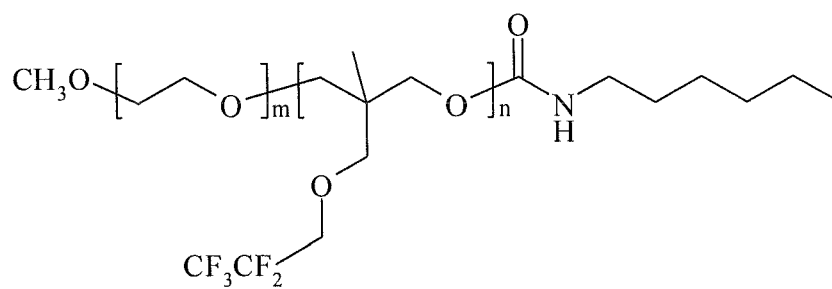
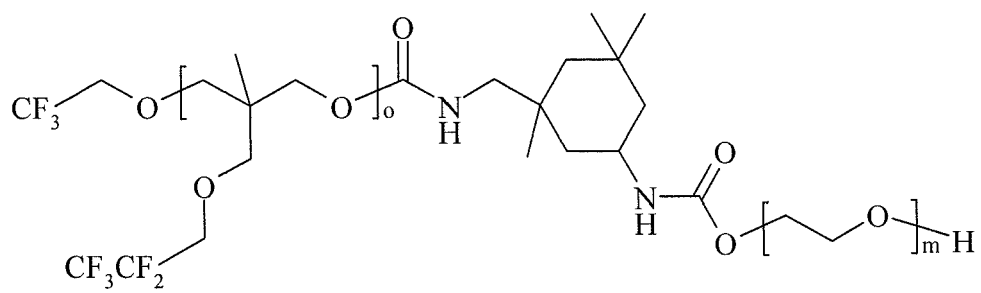
[0027] A specific di-isocyanate of interest is the following isophorone di-isocyanate:



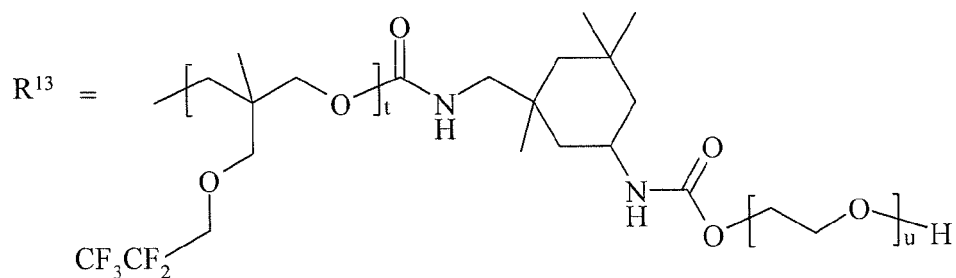
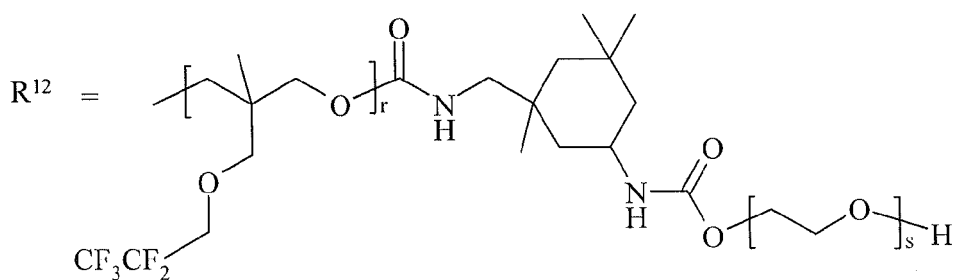
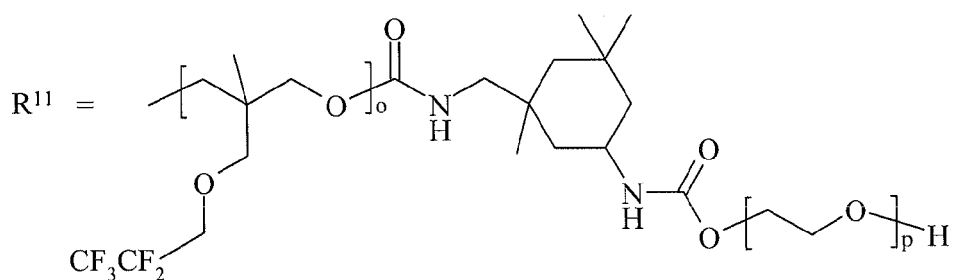
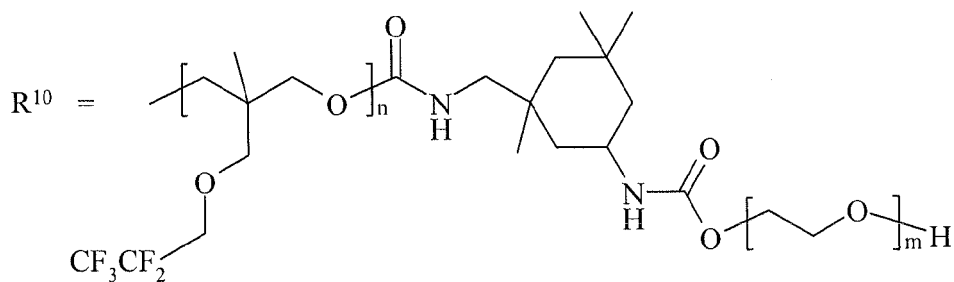
[0028] The linking group which may link the structural units represented by the formula's (I), (II) and/or (III) and/or other polymeric blocks such as for example polyester, polyurethane or polyvinyl alcohol blocks, may have up to 20 carbon atoms and may contain at least one atom selected from C, H, N, O and S. Preferred linking groups are a linear alkylene group having 1 to 18 carbon atoms, a linear, branched, or cyclic group having 3 to 18 carbon atoms, an alkynylene group having 2 to 18 carbon atoms and an arylene group having 6 to 20 atoms, -O-, -S-, -CO-, -CO-O-, -O-CO-, -CS-, -NRⁿR^o-, -CO-NRⁿ-, -NRⁿ-CO-, -NRⁿ-CO-O-, -O-CO-NRⁿ-, -NRⁿ-CO-NR^o-, -NRⁿ-CS-NR^o-, a phenylene group, a naphthalene group, an anthracene group, a heterocyclic group, or combinations thereof, wherein Rⁿ and R^o each independently represent hydrogen or an optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, heterocyclic, aryl, heteroaryl, aralkyl or heteroaralkyl group. Preferred substituents on the latter groups are an alkoxy group having up to 12 carbon atoms, a halogen or a hydroxyl group.

[0029] Suitable examples of diblock and multiblock surfactants include the following surfactants:









wherein independently in each of the structures above $m, n, o, p, r, s, t, x, y, u, q$ and v independently represent an integer ranging between 1 and 40, preferably an integer ranging between 2 and 20.

[0030] The amount of surfactant in the coating is preferably ranging between 0.05 %wt and 5 %wt, more preferably between 0.1 %wt and 3 %wt and most preferably between 0.15 %wt and 1.5 %wt.

[0031] The thermal printing plate precursor comprises a heat and/or light sensitive coating and is positive working. Its working mechanism is based on a heat-induced solubilization of an oleophilic resin. The oleophilic resin is preferably a polymer that is soluble in an aqueous developer, more preferably an aqueous alkaline developing solution with a pH between 7.5 and 14. Preferred polymers are phenolic resins e.g. novolac, resoles, polyvinyl phenols and carboxy sub-

stituted polymers. Typical examples of these polymers are described in DE 4007428, DE 4027301 and DE 4445820. The amount of phenolic resin present in the coating is preferably at least 50% by weight, preferably at least 80% by weight relative to the total weight of all the components present in the coating. The oleophilic resin is preferably a phenolic resin wherein the phenyl group or the hydroxy group is chemically modified with an organic substituent. The phenolic resins which are chemically modified with an organic substituent may exhibit an increased chemical resistance against printing chemicals such as fountain solutions or plate treating liquids such as plate cleaners. Examples of such chemically modified phenolic resins are described in EP 934 822; EP 1 072 432; US 5,641,608; EP 982 123; WO 99/01795; EP 2 102 446, EP 2 102 444; EP 2 102 445; EP 2 102 443; EP 3 102 522; WO04/035310; WO04/035686; WO04/035645; WO04/035687 or EP 1 506 858. The modified resins described in EP 2 102 446, are preferred, especially those resins wherein the phenyl-group of said phenolic resin is substituted with a group having the structure -N=N-Q, wherein the -N=N- group is covalently bound to a carbon atom of the phenyl group and wherein Q is an aromatic group.

[0032] The novolac resin or resol resin may be prepared by polycondensation of at least one member selected from aromatic hydrocarbons such as phenol, o-cresol, p-cresol, m-cresol, 2,5-xyleneol, 3,5-xyleneol, resorcinol, pyrogallol, bisphenol, bisphenol A, trisphenol, o-ethylphenol, p-ethylphenol, propylphenol, n-butylphenol, t-butylphenol, 1-naphtol and 2-naphtol, with at least one aldehyde or ketone selected from aldehydes such as formaldehyde, glyoxal, acetaldehyde, propionaldehyde, benzaldehyde and furfural and ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone, in the presence of an acid catalyst. Instead of formaldehyde and acetaldehyde, paraformaldehyde and paraldehyde may, respectively, be used.

[0033] The weight average molecular weight, measured by gel permeation chromatography using universal calibration and polystyrene standards, of the novolac resin is preferably from 500 to 150,000 g/mol, more preferably from 1,500 to 50,000 g/mol.

[0034] The poly(vinylphenol) resin may also be a polymer of one or more hydroxy-phenyl containing monomers such as hydroxystyrenes or hydroxy-phenyl (meth)acrylates. Examples of such hydroxystyrenes are o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, 2-(o-hydroxyphenyl)propylene, 2-(m-hydroxyphenyl)propylene and 2-(p-hydroxyphenyl)propylene. Such a hydroxystyrene may have a substituent such as chlorine, bromine, iodine, fluorine or a C₁₋₄ alkyl group, on its aromatic ring. An example of such hydroxy-phenyl (meth)acrylate is 2-hydroxy-phenyl methacrylate.

[0035] The poly(vinylphenol) resin may usually be prepared by polymerizing one or more hydroxy-phenyl containing monomer in the presence of a radical initiator or a cationic polymerization initiator. The poly(vinylphenol) resin may also be prepared by copolymerizing one or more of these hydroxy-phenyl containing monomers with other monomeric compounds such as acrylate monomers, methacrylate monomers, acrylamide monomers, methacrylamide monomers, vinyl monomers, aromatic vinyl monomers or diene monomers.

[0036] The weight average molecular weight, measured by gel permeation chromatography using universal calibration and polystyrene standards, of the poly(vinylphenol) resin is preferably from 1,000 to 200,000 g/mol, more preferably from 1,500 to 50,000 g/mol.

[0037] Examples of phenolic resins are:

- ALNOVOL™ SPN452, 40%wt of a novolac resin in Dowanol™ PM, commercially available from CLARIANT GmbH.
- ALNOVOL™ SPN400, 44%wt of a novolac resin in Dowanol™ PMA, commercially available from CLARIANT GmbH.
- ALNOVOL™ HPN100, novolac resin commercially available from CLARIANT GmbH.
- DURITE™ PD443, novolac resin commercially available from BORDEN CHEM. INC.
- DURITE™ SD423A, novolac resin commercially available from BORDEN CHEM. INC.
- DURITE™ SD126A, novolac resin commercially available from BORDEN CHEM. INC.
- BAKELITE™ 6866LB02, novolac resin commercially available from BAKELITE AG.
- BAKELITE™ 6866LB03, novolac resin commercially available from BAKELITE AG.
- KR 400/8, novolac resin commercially available from KOYO CHEMICALS INC.
- HRJ 1085, novolac resin commercially available from SCHNECTADY INTERNATIONAL INC.
- HRJ 2606, phenol novolac resin commercially available from SCHNECTADY INTERNATIONAL INC.

- LYNCUR™ CMM, copolymer of 4-hydroxy-styrene and methyl methacrylate commercially available from SIBER HEGNER.

[0038] The coating may comprise a second layer that comprises a polymer or copolymer (i.e.(co)polymer) comprising at least one monomeric unit that comprises at least one sulfonamide group. This layer is located between the layer described above comprising the oleophilic resin and the hydrophilic support. Hereinafter, 'a (co)polymer comprising at least one monomeric unit that comprises at least one sulfonamide group' is also referred to as "a sulphonamide (co) polymer". The sulphonamide (co)polymer is preferably alkali soluble. The sulphonamide group is preferably represented by -NR-SO₂-, -SO₂-NR- or -SO₂-NRR' wherein R and R' each independently represent hydrogen or an organic substituent.

[0039] The surfactant used in the present invention may be present in the first layer, the second layer or an optional other layer. Most preferably, the surfactant is present in the layer comprising the oleophilic resin.

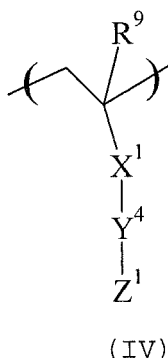
[0040] Sulfonamide (co)polymers are preferably high molecular weight compounds prepared by homopolymerization of monomeric units containing at least one sulfonamide group or by copolymerization of such monomeric units and other polymerizable monomeric units.

[0041] Examples of monomeric units containing at least one sulfonamide group include monomeric units further containing at least one polymerizable unsaturated bond such as an acryloyl, allyl or vinyloxy group. Suitable examples are disclosed in U.S. 5,141,838, EP 1 545 878; EP 909,657, EP 0 894 622 and EP 1,120,246.

[0042] Examples of monomeric units copolymerized with the monomeric units containing at least one sulfonamide group include monomeric units as disclosed in EP 1,262,318, EP 1,275,498, EP 909,657, EP 1,120,246, EP 0 894 622 and EP 1,400,351.

[0043] Suitable examples of sulfonamide (co)polymers and/or their method of preparation are disclosed in EP-A 933 682, EP-A 982 123, EP-A 1 072 432, WO 99/63407 and EP 1,400,351.

[0044] A highly preferred example of a sulfonamide (co)polymer is a homopolymer or copolymer comprising a structural unit represented by the following general formula (IV):



wherein:

R⁹ represents hydrogen or a hydrocarbon group having up to 12 carbon atoms; preferably R⁹ represents hydrogen or a methyl group;

X¹ represents a single bond or a divalent linking group. The divalent linking group may have up to 20 carbon atoms and may contain at least one atom selected from C, H, N, O and S. Preferred divalent linking groups are a linear alkylene group having 1 to 18 carbon atoms, a linear, branched, or cyclic group having 3 to 18 carbon atoms, an alkynylene group having 2 to 18 carbon atoms and an arylene group having 6 to 20 atoms, -O-, -S-, -CO-, -CO-O-, -O-CO-, -CS-, -NRⁿR⁰-, -CO-NRⁿ-, -NRⁿ-CO-, -NRⁿ-CO-O-, -O-CO-NRⁿ-, -NRⁿ-CO-NR⁰-, -NRⁿ-CS-NR⁰-, a phenylene group, a naphthalene group, an anthracene group, a heterocyclic group, or combinations thereof, wherein Rⁿ and R⁰ each independently represent hydrogen or an optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, heterocyclic, aryl, heteroaryl, aralkyl or heteroaralkyl group. Preferred substituents on the latter groups are an alkoxy group having up to 12 carbon atoms, a halogen or a hydroxyl group. Preferably X¹ is a methylene group, an ethylene group, a propylene group, a butylene group, an isopropylene group, cyclohexylene group, a phenylene group, a tolylene group or a biphenylene group;

Y⁴ is a bivalent sulphonamide group represented by -NR^p-SO₂- or -SO₂-NR^q- wherein R^p and R^q each independently

represent hydrogen, an optionally substituted alkyl, alkanoyl, alkenyl, alkynyl, cycloalkyl, heterocyclic, aryl, heteroaryl, aralkyl or heteroaralkyl group or a group of the formula $-C(=N)-NH-R^{10}$, wherein R^{10} represents hydrogen or an optionally substituted alkyl or aryl group;

Z^1 represents a terminal group preferably represented by hydrogen or an optionally substituted linear, branched, or cyclic alkylene or alkyl group having 1 to 18 carbon atoms such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, a t-butyl group, a s-butyl group, a pentyl group, a hexyl group, a cyclopentyl group, a cyclohexyl group, an octyl group, an optionally substituted arylene or aryl group having 6 to 20 carbon atoms; an optionally substituted hetero-arylene or heteroaryl group; a linear, branched, or cyclic alkenylene or alkenyl group having 2 to 18 carbon atoms, a linear, branched, or cyclic alkynylene or alkynyl group having 2 to 18 carbon atoms or an alkoxy group.

Examples of preferred substituents optionally present on the groups representing Z^1 are an alkyl group having up to 12 carbon atoms, an alkoxy group having up to 12 carbon atoms, a halogen atom or a hydroxyl group.

[0045] The structural unit represented by the general formula (IV) has preferably the following groups:

X^1 represents an alkylene, cyclohexylene, phenylene or tolylene group, $-O-$, $-S-$, $-CO-$, $-CO-O-$, $-O-CO-$, $-CS-$, $-NR^nR^o$, $-CO-NR^n$, $-NR^n-CO-$, $-NR^n-CO-O-$, $-O-CO-NR^n$, $-NR^n-CO-NR^o$, $-NR^n-CS-NR^o$, or combinations thereof, and wherein R^n and R^o each independently represent hydrogen or an optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, heterocyclic, aryl, heteroaryl, aralkyl or heteroaralkyl group. Preferred substituents on the latter groups are an alkoxy group having up to 12 carbon atoms, a halogen or a hydroxyl group;

Y^4 is a bivalent sulphonamide group represented by $-NR^p-SO_2-$, $-SO_2-NR^q-$ wherein R^p and R^q each independently represent hydrogen, an optionally substituted alkyl, alkanoyl, alkenyl, alkynyl, cycloalkyl, heterocyclic, aryl, heteroaryl, aralkyl or heteroaralkyl group;

Z^1 is a terminal group represented by hydrogen, an alkyl group such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, a t-butyl group, a s-butyl group, a pentyl group, a hexyl group, a cyclopentyl group, a cyclohexyl group or an octyl group, a benzyl group, an optionally substituted aryl or heteroaryl group, a naphthyl group, an anthracenyl group, a pyridyl group, an allyl group or a vinyl group.

[0046] Specific preferred examples of sulphonamide (co)polymers are polymers comprising N-(p-aminosulfonylphenyl) (meth)acrylamide, N-(m-aminosulfonylphenyl) (meth)acrylamide and/or N-(o-aminosulfonylphenyl) (meth)acrylamide. A particularly preferred sulphonamide (co)polymer is a polymer comprising N-(p-aminosulfonylphenyl) methacrylamide wherein the sulphonamide group comprises an optionally substituted straight, branched, cyclic or heterocyclic alkyl group, an optionally substituted aryl group or an optionally substituted heteroaryl group.

[0047] The layer comprising the sulphonamide (co)polymer may further comprise additional hydrophobic binders such as a phenolic resin (e.g. novolac, resoles or polyvinyl phenols), a chemically modified phenolic resin or a polymer containing a carboxyl group, a nitrile group or a maleimide group.

[0048] The dissolution behavior of the coating can be fine-tuned by optional solubility regulating components. More particularly, development accelerators and development inhibitors can be used. In the embodiment where the coating comprises more than one layer, these ingredients can be added to the first layer, to the second layer and/or to an optional other layer of the coating.

[0049] Development accelerators are compounds which act as dissolution promoters because they are capable of increasing the dissolution rate of the coating. For example, cyclic acid anhydrides, phenols or organic acids can be used in order to improve the aqueous developability. Examples of the cyclic acid anhydride include phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endoxy-4-tetrahydro-phthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride, alpha-phenylmaleic anhydride, succinic anhydride, and pyromellitic anhydride, as described in U.S. Patent No. 4,115,128. Examples of the phenols include bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxy-benzophenone, 4-hydroxybenzophenone, 4,4',4''-trihydroxy-triphenylmethane, and 4,4',3'',4''-tetrahydroxy-3,5,3',5'-tetramethyltriphenylmethane, and the like. Examples of the organic acids include sulphonic acids, sulfinic acids, alkylsulfuric acids, phosphonic acids, phosphates, and carboxylic acids, as described in, for example, JP-A Nos. 60-88, 942 and 2-96,755. Specific examples of these organic acids include p-toluenesulphonic acid, dodecylbenzenesulphonic acid, p-toluenesulfinic acid, ethylsulfuric acid, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluic acid, 3,4-dimethoxybenzoic acid, 3,4,5-trimethoxybenzoic acid, 3,4,5-trimethoxycinnamic acid, phthalic acid, terephthalic acid, 4-cyclohexene-1,2-dicarboxylic acid, erucic acid, lauric acid, n-undecanoic acid, and ascorbic acid. The amount of the cyclic acid anhydride, phenol, or organic acid contained in the coating is preferably in

the range of 0.05 to 20% by weight, relative to the coating as a whole. Polymeric development accelerators such as phenolic-formaldehyde resins comprising at least 70 mol% meta-cresol as recurring monomeric units are also suitable development accelerators.

[0050] In a preferred embodiment, the coating also contains developer resistance means, also called development inhibitors, i.e. one or more ingredients which are capable of delaying the dissolution of the unexposed areas during processing. The dissolution inhibiting effect is preferably reversed by heating, so that the dissolution of the exposed areas is not substantially delayed and a large dissolution differential between exposed and unexposed areas can thereby be obtained. The compounds described in e.g. EP-A 823 327 and WO97/39894 are believed to act as dissolution inhibitors due to interaction, e.g. by hydrogen bridge formation, with the alkali-soluble resin(s) in the coating. Inhibitors of this type typically comprise at least one hydrogen bridge forming group such as nitrogen atoms, onium groups, carbonyl (-CO-), sulfinyl (-SO-) or sulfonyl (-SO₂-) groups and a large hydrophobic moiety such as one or more aromatic rings. Some of the compounds mentioned below, e.g. infrared dyes such as cyanines and contrast dyes such as quaternized triarylmethane dyes can also act as a dissolution inhibitor.

[0051] Other suitable inhibitors improve the developer resistance because they delay the penetration of the aqueous alkaline developer into the coating. Such compounds can be present in the first layer and/or, if present, in the second layer as described in e.g. EP-A 950 518, and/or in a development barrier layer on top of said layer, as described in e.g. EP-A 864 420, EP-A 950 517, WO 99/21725 and WO 01/45958. In the latter embodiment, the solubility of the barrier layer in the developer or the penetrability of the barrier layer by the developer can be increased by exposure to heat or infrared light.

[0052] Preferred examples of inhibitors which delay the penetration of the aqueous alkaline developer into the coating include the following:

(a) A polymeric material which is insoluble in or impenetrable by the developer, e.g. a hydrophobic or water-repellent polymer or copolymer such as acrylic polymers, polystyrene, styrene-acrylic copolymers, polyesters, polyamides, polyureas, polyurethanes, nitrocellulosics and epoxy resins; or polymers comprising siloxane (silicones) and/or perfluoroalkyl units.

(b) Bifunctional compounds such as surfactants comprising a polar group and a hydrophobic group such as a long chain hydrocarbon group, a poly- or oligosiloxane and/or a perfluorinated hydrocarbon group. A typical example is Megafac F-177, a perfluorinated surfactant available from Dainippon Ink & Chemicals, Inc. A suitable amount of such compounds is between 10 and 100 mg/m², more preferably between 50 and 90 mg/m².

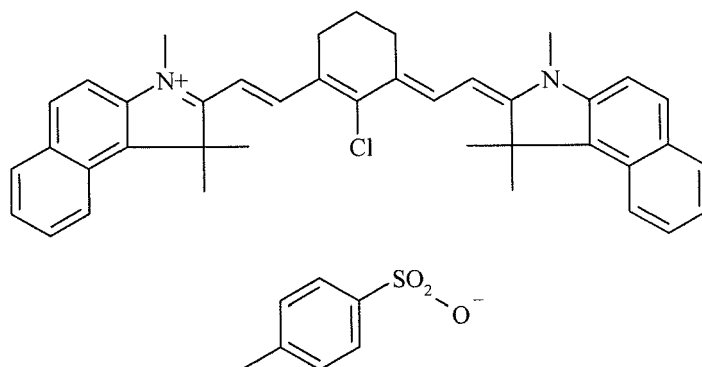
(c) Bifunctional block-copolymers comprising a polar block such as a poly- or oligo(alkylene oxide) and a hydrophobic block such as a long chain hydrocarbon group, a poly- or oligosiloxane and/or a perfluorinated hydrocarbon group. A suitable amount of such compounds is between 0.5 and 25 mg/m², preferably between 0.5 and 15 mg/m² and most preferably between 0.5 and 10 mg/m². A suitable copolymer comprises about 15 to 25 siloxane units and 50 to 70 alkyleneoxide groups. Preferred examples include copolymers comprising phenylmethylsiloxane and/or dimethylsiloxane as well as ethylene oxide and/or propylene oxide, such as Tego Glide 410, Tego Wet 265, Tego Protect 5001 or Silikophen P50/X, all commercially available from Tego Chemie, Essen, Germany. Said poly- or oligosiloxane may be a linear, cyclic or complex cross-linked polymer or copolymer. The term polysiloxane compound shall include any compound which contains more than one siloxane group -Si(R,R')-O-, wherein R and R' are optionally substituted alkyl or aryl groups. Preferred siloxanes are phenylalkylsiloxanes and dialkylsiloxanes. The number of siloxane groups in the polymer or oligomer is at least 2, preferably at least 10, more preferably at least 20. It may be less than 100, preferably less than 60.

[0053] It is believed that during coating and drying, the above mentioned inhibitor of type (b) and (c) tends to position itself, due to its bifunctional structure, at the interface between the coating and air and thereby forms a separate top layer even when applied as an ingredient of the coating solution of the first and/or of the optional second layer. Simultaneously, the surfactants also act as a spreading agent which improves the coating quality. The separate top layer thus formed seems to be capable of acting as the above mentioned barrier layer which delays the penetration of the developer into the coating.

[0054] Alternatively, the inhibitor of type (a) to (c) can be applied in a separate solution, coated on top of the first, optional second and/or other layers of the coating. In that embodiment, it may be advantageous to use a solvent in the separate solution that is not capable of dissolving the ingredients present in the other layers so that a highly concentrated water-repellent or hydrophobic phase is obtained at the top of the coating which is capable of acting as the above mentioned development barrier layer.

[0055] In addition, the first or optional second layer and/or other layer may comprise polymers that further improve the run length and/or the chemical resistance of the plate. Examples thereof are polymers comprising imido (-CO-NR-CO-) pendant groups, wherein R is hydrogen, optionally substituted alkyl or optionally substituted aryl, such as the polymers described in EP-A 894 622, EP-A 901 902, EP-A 933 682 and WO 99/63407.

[0056] The coating of the heat-sensitive printing plate precursor preferably also contains an infrared light absorbing dye or pigment which, in the embodiment where the coating comprises more than one layer, may be present in the first layer, and/or in the second layer, and/or in an optional other layer. Preferred IR absorbing dyes are cyanine dyes, merocyanine dyes, indoaniline dyes, oxonol dyes, pyrilium dyes and squarilium dyes. Examples of suitable IR dyes are described in e.g. EP-As 823327, 978376, 1029667, 1053868, 1093934; WO 97/39894 and 00/29214. A preferred compound is the following cyanine dye:



IR-1

[0057] The concentration of the IR-dye in the coating is preferably between 0.25 and 15.0 %wt, more preferably between 0.5 and 10.0 %wt, most preferably between 1.0 and 7.5 %wt relative to the coating as a whole.

[0058] The coating may further comprise one or more colorant(s) such as dyes or pigments which provide a visible color to the coating and which remain in the coating at the image areas which are not removed during the processing step. Thereby a visible image is formed and examination of the lithographic image on the developed printing plate becomes feasible. Such dyes are often called contrast dyes or indicator dyes. Preferably, the dye has a blue color and an absorption maximum in the wavelength range between 600 nm and 750 nm. Typical examples of such contrast dyes are the amino-substituted tri- or diarylmethane dyes, e.g. crystal violet, methyl violet, victoria pure blue, flexoblau 630, basonylblau 640, auramine and malachite green. Also the dyes which are discussed in depth in EP 400 706 are suitable contrast dyes. Dyes which, combined with specific additives, only slightly color the coating but which become intensively colored after exposure, as described in for example WO2006/005688 may also be used as colorants.

[0059] To protect the surface of the coating of the heat and/or light-sensitive printing plate precursors, in particular from mechanical damage, a protective layer may also optionally be applied. The protective layer generally comprises at least one water-soluble binder, such as polyvinyl alcohol, polyvinylpyrrolidone, partially hydrolyzed polyvinyl acetates, gelatin, carbohydrates or hydroxyethylcellulose, and can be produced in any known manner such as from an aqueous solution or dispersion which may, if required, contain small amounts - i.e. less than 5% by weight based on the total weight of the coating solvents for the protective layer - of organic solvents. The thickness of the protective layer can suitably be any amount, advantageously up to 5.0 μm , preferably from 0.1 to 3.0 μm , particularly preferably from 0.15 to 1.0 μm .

[0060] Optionally, the coating may further contain additional ingredients such as further surfactants, silicon or titanium dioxide particles or polymers particles such as matting agents and spacers.

[0061] Any coating method can be used for applying two or more coating solutions to the hydrophilic surface of the support. The multi-layer coating can be applied by coating/drying each layer consecutively or by the simultaneous coating of several coating solutions at once. In the drying step, the volatile solvents are removed from the coating until the coating is self-supporting and dry to the touch. However it is not necessary (and may not even be possible) to remove all the solvent in the drying step. Indeed the residual solvent content may be regarded as an additional composition variable by means of which the composition may be optimized. Drying is typically carried out by blowing hot air onto the coating, typically at a temperature of at least 70°C, suitably 80-150°C and especially 90-140°C. Also infrared lamps can be used. The drying time may typically be 15-600 seconds.

[0062] Between coating and drying, or after the drying step, a heat treatment and subsequent cooling may provide additional benefits, as described in WO99/21715, EP-A 1074386, EP-A 1074889, WO00/29214, and WO/04030923, WO/04030924, WO/04030925.

[0063] The support of the lithographic printing plate precursor may be a sheet-like material such as a plate or it may

be a cylindrical element such as a sleeve which can be slid around a print cylinder of a printing press. Preferably, the support is a metal support such as aluminum or stainless steel. The support can also be a laminate comprising an aluminum foil and a plastic layer, e.g. polyester film.

[0064] A particularly preferred lithographic support is an electrochemically grained and anodized aluminum support. The aluminum support has usually a thickness of about 0.1-0.6 mm. However, this thickness can be changed appropriately depending on the size of the printing plate used and/or the size of the plate-setters on which the printing plate precursors are exposed. The aluminum is preferably grained by electrochemical graining, and anodized by means of anodizing techniques employing phosphoric acid or a sulphuric acid/phosphoric acid mixture. Methods of both graining and anodization of aluminum are very well known in the art.

[0065] By graining (or roughening) the aluminum support, both the adhesion of the printing image and the wetting characteristics of the non-image areas are improved. By varying the type and/or concentration of the electrolyte and the applied voltage in the graining step, different type of grains can be obtained. The surface roughness is often expressed as arithmetical mean center-line roughness Ra (ISO 4287/1 or DIN 4762) and may vary between 0.05 and 1.5 μm . The aluminum substrate of the current invention has preferably an Ra value below 0.45 μm , more preferably below 0.40 μm and most preferably below 0.30 μm . The lower limit of the Ra value is preferably about 0.1 μm . More details concerning the preferred Ra values of the surface of the grained and anodized aluminum support are described in EP 1 356 926.

[0066] By anodising the aluminum support, its abrasion resistance and hydrophilic nature are improved. The micro-structure as well as the thickness of the Al_2O_3 layer are determined by the anodising step, the anodic weight (g/m^2 Al_2O_3 formed on the aluminum surface) varies between 1 and 8 g/m^2 . The anodic weight is preferably ≥ 3 g/m^2 , more preferably ≥ 3.5 g/m^2 and most preferably ≥ 4.0 g/m^2 .

[0067] The grained and anodized aluminum support may be subject to a so-called post-anodic treatment to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with a sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride.

Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or may be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulphonic acid, polyvinylbenzenesulphonic acid, sulphuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulphonated aliphatic aldehyde.

[0068] Another useful post-anodic treatment may be carried out with a solution of polyacrylic acid or a polymer comprising at least 30 mol% of acrylic acid monomeric units, e.g. GLASCOL E15, a polyacrylic acid, commercially available from Ciba Speciality Chemicals.

[0069] The support can also be a flexible support, which may be provided with a hydrophilic layer, hereinafter called 'base layer'. The flexible support is e.g. paper, plastic film or aluminum. Preferred examples of plastic film are polyethylene terephthalate film, polyethylene naphthalate film, cellulose acetate film, polystyrene film, polycarbonate film, etc. The plastic film support may be opaque or transparent.

[0070] The base layer is preferably a cross-linked hydrophilic layer obtained from a hydrophilic binder cross-linked with a hardening agent such as formaldehyde, glyoxal, polyisocyanate or a hydrolyzed tetra-alkylorthosilicate. The latter is particularly preferred. The thickness of the hydrophilic base layer may vary in the range of 0.2 to 25 μm and is preferably 1 to 10 μm . More details of preferred embodiments of the base layer can be found in e.g. EP-A 1 025 992.

[0071] The heat-sensitive plate precursor can be image-wise exposed directly with heat, e.g. by means of a thermal head, or indirectly by infrared light, preferably near infrared light. The infrared light is preferably converted into heat by an IR light absorbing compound as discussed above. The heat-sensitive lithographic printing plate precursor is preferably not sensitive to visible light i.e. no substantial effect on the dissolution rate of the coating in the developer is induced by exposure to visible light. Most preferably, the coating is not sensitive to ambient daylight.

[0072] The printing plate precursor can be exposed to infrared light by means of e.g. LEDs or a laser. Most preferably, the light used for the exposure is a laser emitting near infrared light having a wavelength in the range from about 750 to about 1500 nm, more preferably 750 to 1100 nm, such as a semiconductor laser diode, a Nd:YAG or a Nd:YLF laser.

The required laser power depends on the sensitivity of the plate precursor, the pixel dwell time of the laser beam, which is determined by the spot diameter (typical value of modern plate-setters at $1/e^2$ of maximum intensity: 5-25 μm), the scan speed and the resolution of the exposure apparatus (i.e. the number of addressable pixels per unit of linear distance, often expressed in dots per inch or dpi; typical value: 1000-4000 dpi).

[0073] Two types of laser-exposure apparatuses are commonly used: internal (ITD) and external drum (XTD) plate-setters. ITD plate-setters for thermal plates are typically characterized by a very high scan speed up to 500 m/sec and may require a laser power of several Watts. XTD plate-setters for thermal plates having a typical laser power from about 200 mW to about 1 W operate at a lower scan speed, e.g. from 0.1 to 10 m/sec. An XTD platesetter equipped with one or more laserdiodes emitting in the wavelength range between 750 and 850 nm is an especially preferred embodiment

for the method of the present invention.

[0074] The known plate-setters can be used as an off-press exposure apparatus, which offers the benefit of reduced press down-time. XTD plate-setter configurations can also be used for on-press exposure, offering the benefit of immediate registration in a multi-color press. More technical details of on-press exposure apparatuses are described in e.g. US 5,174,205 and US 5,163,368.

[0075] After exposure, the precursor is preferably developed by means of immersing the precursor in a developing solution; this may be combined with mechanical rubbing, e.g. by using a rotating brush. During the development the non-image areas of the coating are preferably removed with an aqueous alkaline developer solution. The developer solution preferably has a pH above 10, more preferably above 12. During the development step, any water-soluble layer present is preferably also removed. The development step is preferably carried out at temperatures ranging between 20 and 40°C in automated processing units as customary in the art.

[0076] More details concerning the development step can be found in for example EP 1614538, EP 1614539, EP 1614540 and WO/2004071767.

[0077] The developing solution preferably contains a buffer such as for example a silicate-based buffer or a phosphate buffer. The concentration of the buffer in the developer preferably ranges between 3 to 14%wt. Silicate-based developers which have a ratio of silicon dioxide to alkali metal oxide of at least 1 are advantageous because they ensure that the alumina layer (if present) of the substrate is not damaged. Preferred alkali metal oxides include Na₂O and K₂O, and mixtures thereof. A particularly preferred silicate-based developer solution is a developer solution comprising sodium or potassium metasilicate, i.e. a silicate where the ratio of silicon dioxide to alkali metal oxide is 1.

[0078] The developing solution may optionally contain further components as known in the art: other buffer substances, chelating agents, surfactants, complexes, inorganic salts, inorganic alkaline agents, organic alkaline agents, antifoaming agents, organic solvents in small amounts i.e. preferably less than 10%wt and more preferably less than 5%wt, nonreducing sugars, glycosides, dyes and/or hydrotropic agents. These components may be used alone or in combination.

[0079] To ensure a stable processing with the developer solution for a prolonged time, it is particularly important to control the concentration of the ingredients in the developer. Therefore a replenishing solution, hereinafter also referred to as replenisher, is often added to the developing solution. More than one replenishing solution containing different ingredients and/or different amounts of the ingredients may be added to the developing solution. Alkali metal silicate solutions having alkali metal contents of from 0.6 to 2.0 mol/l can suitably be used. These solutions may have the same silica/alkali metal oxide ratio as the developer (generally, however, it is lower) and likewise optionally contain further additives. It is advantageous that the (co)polymer of the present invention is present in the replenisher(s); preferably at a concentration of at least 0.5 g/l, more preferably in a concentration ranging between 1 and 50 g/l most preferably between 2 and 30 g/l.

[0080] The replenishing solution has preferably a pH value of at least 10, more preferably of at least 11, most preferably of at least 12.

[0081] The development step may be followed by a rinsing step, a gumming step, a drying step and/or a post-baking step.

[0082] The heat-sensitive printing plates can be used for conventional, so-called wet offset printing, in which ink and an aqueous dampening liquid are supplied to the plate. Another suitable printing method uses so-called single-fluid ink without a dampening liquid. Suitable single-fluid inks have been described in US 4,045,232; US 4,981,517 and US 6,140,392. In a most preferred embodiment, the single-fluid ink comprises an ink phase, also called the hydrophobic or oleophilic phase, and a polyol phase as described in WO 00/32705.

[0083] The printing plate precursor of the present invention can also be used for treating thermo-resists, for example on a PCB (printed circuit board) application as described in US 2003/0003406 A1.

EXAMPLES

1. Preparation of the lithographic support.

[0084] A 0.30 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 34 g/l of sodium hydroxide at 70°C for 6 seconds and rinsed with demineralized water for 3.6 seconds. The foil was then electrochemically grained during 8 seconds using an alternating current in an aqueous solution containing 15 g/l HCl, 15 g/l SO₄²⁻ ions and 5 g/l Al³⁺ at a temperature of 37°C and a current density of 100 A/dm². The aluminum foil was then desmuted by etching with an aqueous solution containing 145 g/l of sulfuric acid at 80°C for 5 seconds and rinsed with demineralized water for 4 seconds. The foil was subsequently subjected to anodic oxidation during 10 seconds in an aqueous solution containing 145 g/l of sulfuric acid at a temperature of 57°C and a current density of 25 A/dm², then washed with demineralized water for 7 seconds and post-treated for 4 seconds with a solution containing 2.2 g/l of polyvinylphosphonic acid at 70°C, rinsed with demineralized water for 3.5 seconds and dried at 120°C for 7 seconds.

[0085] The support thus obtained was characterized by a surface roughness Ra of 0.35-0.40 μm (measured with

interferometer NT1100) and an anodic weight of 3.0 g/m².

2. Printing Plate Precursors PPP-1 to PPP-16.

2.1. First layer.

[0086] A first layer was coated on an aluminum substrate (described above) with the first coating solution with the composition as defined in Table 1 at a wet coating thickness of 20 μm.

Table 1: composition of the first coating solution.

Composition first coating solution	g
Dowanol PM (1)	270.98
THF (2)	576.55
Binder-01(25 wt%) (3)	53.75
Crystal Violet (1 wt%) (4)	58.24
Tegoglide 410 (1 wt%) (5)	5.82
(1) Propyleneglycol-monomethylether (1-methoxy-2-propanol) commercially available from Dow Chemical Company; (2) THF is tetrahydrofuran; (3) Binder-01: preparation see 2.2; (4) 1 wt% solution of Crystal Violet in Dowanol PM, Crystal Violet is commercially available from Ciba-Geigy GmbH; (5) 1 wt% solution of Tegoglide 410 in Dowanol PM; Tegoglide 410 is a copolymer of polysiloxane and poly (alkylene oxide), commercially available from Tego Chemie Service GmbH.	

[0087] The total dry coating weight amounts to 0.671 g/m². The dry weight of the ingredients in the first coating is shown in Table 2.

Table 2: Dry coating weight of first coating.

Dry Weight first Coating*	mg/m ²
Binder-01	660
Crystal Violet	10
Tegoglide 410	1
* ingredients as defined in Table 1.	

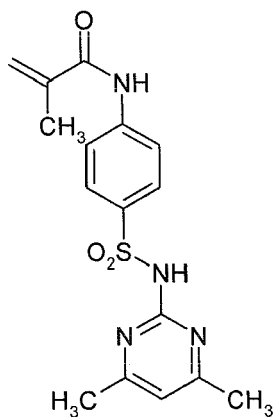
2.2. Preparation of Binder-01.

[0088] In a 250 ml reactor, 162 mmol of Monomer-01 (structure see below), 21.3g (132 mmol) benzyl acrylamide, 0.43 g (6 mmol) acrylic acid and 103g gamma-butyrolactone were added and the mixture was heated to 140°C, while stirring at 200 rpm. A constant flow of nitrogen was put over the reactor. After dissolution of all the components, the reactor was cooled to 100°C. 0.35 ml Trigonox™ DC50, commercially available from AKZO NOBEL, was added followed by the addition of 1.39 ml Trigonox™ 141, commercially available from AKZO NOBEL, in 3.43 ml butyrolactone. The polymerization was started and the reactor was heated to 140°C over 2 hours while dosing 1.75 ml Trigonox™ DC50. The mixture was stirred at 400 rpm and the polymerization was allowed to continue for 2 hours at 140°C. The reaction mixture was cooled to 120°C and the stirrer speed was enhanced to 500 rpm. 85.7 ml 1-methoxy-2-propanol was added and the reaction mixture was allowed to cool down to room temperature.

Binder-01 was analyzed with ¹H-NMR-spectroscopy and size exclusion chromatography, using dimethyl acetamide/0.21 % LiCl as eluent on a 3x mixed-B column and relative to polystyrene standards.

	M_n	M_w	PD
Binder-01	23500	67000	2.84

[0089] The reaction mixture was cooled to 40°C and the resulting 25 %wt polymer solution was collected in a drum.
[0090] Monomer-01:



2.3. Second layer.

[0091] Above the first layer, a second coating solution with the composition as defined in Table 3 (coating solutions 1 to 16) was coated at a wet coating thickness of 16 μm resulting in the printing plate precursors PPP-01 to PPP-16.

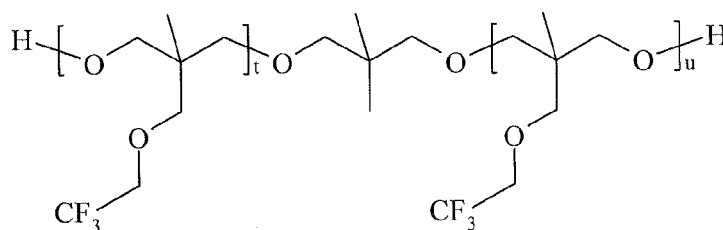
Table 3: composition of the second coating solutions.

Composition second coating solution	1 ref.	2 comp.	3 comp.	4 comp.	5 comp.	6 comp.	7 comp.	8 comp.
	g	g	g	g	g	g	g	g
Dowanol PM	306.76	306.76	306.76	306.76	306.76	306.76	306.76	306.76
MEK	473.35	473.35	473.35	473.35	473.35	473.35	473.35	473.35
Alnovol SPN402 (1)	106.33	106.33	106.33	106.33	106.33	106.33	106.33	106.33
TMCA (2)	40.12	40.12	40.12	40.12	40.12	40.12	40.12	40.12
Adagio (3)	1.79	1.79	1.79	1.79	1.79	1.79	1.79	1.79
Crystal Violet (4)	71.65	71.65	71.65	71.65	71.65	71.65	71.65	71.65
Tegoglide 410 (5)	-	35.85	-	-	-	-	-	-
PolyFox PF-636 (6)	-	-	35.85	71.65	-	-	-	-
PolyFox PF-6520 (7)	-	-	-	-	35.85	71.65	-	-
PolyFox-PF656 (8)	-	-	-	-	-	-	35.85	71.65
PolyFox-PF6320 (9)	-	-	-	-	-	-	-	-
PolyFox-PF159N (10)	-	-	-	-	-	-	-	-
PolyFox-PF652 (11)	-	-	-	-	-	-	-	-
PolyFox-PF651 (12)	-	-	-	-	-	-	-	-

Table 3 continued: composition of the second coating solutions.

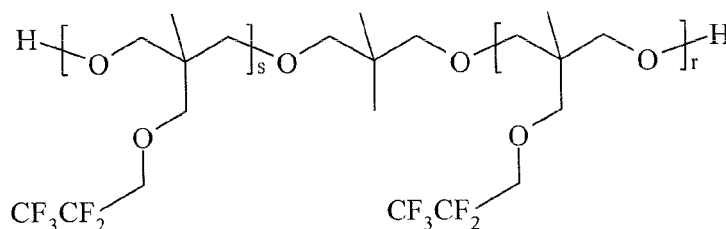
Composition second coating solution	9	10	11	12	13	14	15	16
	comp.	comp.	comp.	comp.	inv.	inv.	inv.	inv.
	g	g	g	g	g	g	g	g
Dowanol PM	306.76	306.76	306.76	306.76	306.76	306.76	306.76	306.76
MEK	473.35	473.35	473.35	473.35	473.35	473.35	473.35	473.35
Alnovol SPN402 (1)	106.33	106.33	106.33	106.33	106.33	106.33	106.33	106.33
TMCA (2)	40.12	40.12	40.12	40.12	40.12	40.12	40.12	40.12
Adagio (3)	1.79	1.79	1.79	1.79	1.79	1.79	1.79	1.79
Crystal Violet (4)	71.65	71.65	71.65	71.65	71.65	71.65	71.65	71.65
Tegoglide 410 (5)			-	-	-	-	-	-
PolyFox PF-636 (6)	-	-	-	-	-	-	-	-
PolyFox PF-6520 (7)	-	-	-	-	-	-	-	-
PolyFox-PF656 (8)	-	-	-	-	-	-	-	-
PolyFox-PF6320 (9)	35.85	71.56	-	-	-	-	-	-
PolyFox-PF159N (10)	-	-	35.85	71.65	-	-	-	-
PolyFox-PF652 (11)	-	-	-	-	35.85	71.85	-	-
PolyFox-PF651 (12)	-	-	-	-	-	-	35.85	71.85

- 1) Alnovol SPN402 is a 44.3 wt.% solution of novolac resin in Dowanol PM commercially available from Clariant GmbH..
- 2) 10 wt% solution of TMCA (3,4,5-trimethoxy cinnamic acid) in Dowanol PM.
- 3) Adagio is an IR absorbing cyanine dye, commercially available from FEW CHEMICALS, with the chemical structure IR-1 (see above).
- 4) 1 wt% solution of Crystal Violet in Dowanol PM, commercially available from Ciba-Geigy GmbH.
- 5) 1 wt % solution of Tegoglide 410 in Dowanol PM., copolymer of polysiloxane and poly(alkylene oxide), commercially available from TEGO Chemie Service GmbH.
- 6) 1 wt% solution of PolyFox PF-636 in Dowanol PM, commercially available from Omnova Solutions Inc. and containing the following chemical structure:



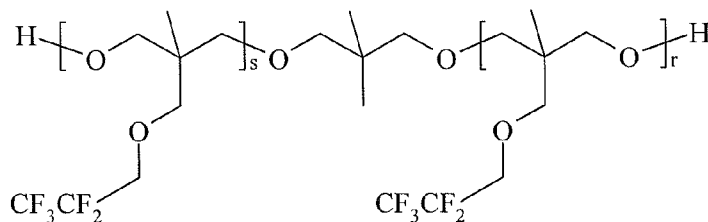
with a number average degree of polymerization $t+u$ equal to approximately 6.

- 7) wt% solution of PolyFox PF-6520 in Dowanol PM, commercially available from Omnova Solutions Inc. and containing the following chemical structure:



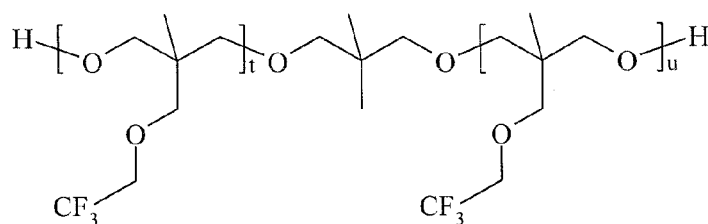
with a number average degree of polymerization $s+r$ equal to approximately 20.

- 8) 1 wt% solution of PolyFox PF-656 in Dowanol PM, commercially available from Omnova Solutions Inc. and containing the following chemical structure:



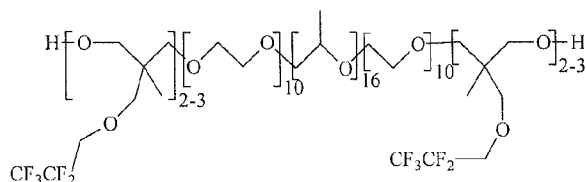
with a number average degree of polymerization $s+r$ equal to approximately 6.

- 9) 1 wt% solution of PolyFox PF-6320 in Dowanol PM, commercially available from Omnova Solutions Inc. and containing the following chemical structure:



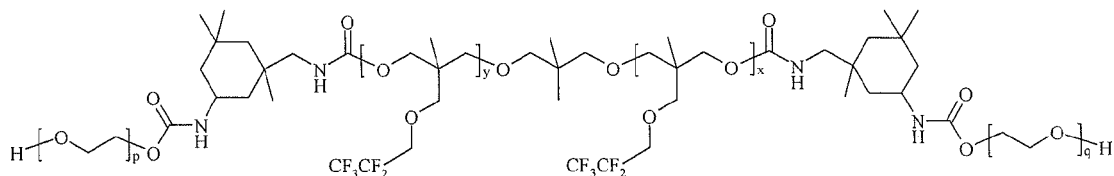
with a number average degree of polymerization $t+u$ equal to approximately 20.

- 10) 1 wt% solution of PolyFox PF-159N in Dowanol PM, commercially available from Omnova Solutions Inc. and containing the following chemical structure:



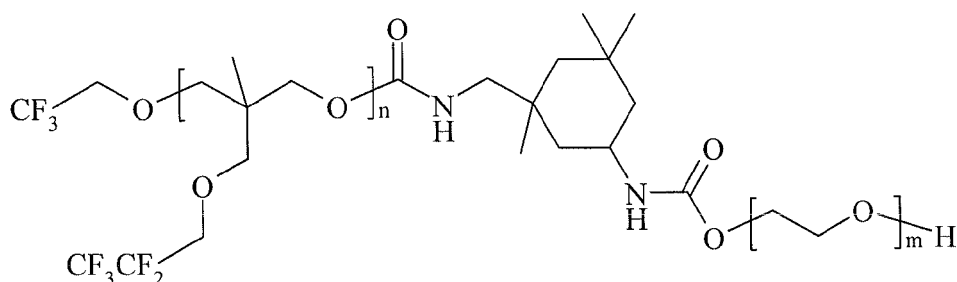
- 11) 1 wt% solution of PolyFox PF-652 in Dowanol PM,

commercially available from Omnova Solutions Inc. as a 50%
solution in isopropanol, PolyFox PF-652 containing the
following chemical structure:



with a number average degree of polymerization $x+y$ equal to
approximately 10 and a number average degree of polymerization
 $p+q$ equal to approximately 17.8.

12) 1 wt% solution of PolyFox PF-651 in Dowanol PM,
commercially available from Omnova Solutions Inc. as a 50%
solution in isopropanol containing the following chemical
structure :



a number average degree of polymerization n equal to
approximately 10 and a number average degree of polymerization
 m equal to approximately 8.9.

[0092] The total dry coating weight of the second coatings and their respective ingredients are given in Table 4.

Table 4: dry coating weight of the second coating.

Dry Weight second Coating *	mg/m ²
Alnovol SPN402	653.0
TMCA	56.0
Adagio	25.0
Crystal Violet	10.0
Perfluoro surfactant	5.0 or 10.0

(continued)

Dry Weight second Coating *	mg/m ²
Total:	749 or 754
*:the dry coating weight of the second coating of PPP-01 amounted to only 744 mg/m ² ; the ingredients of the coating are defined in Table 3.	

3. Exposure of the printing plate precursors 1 to 16.

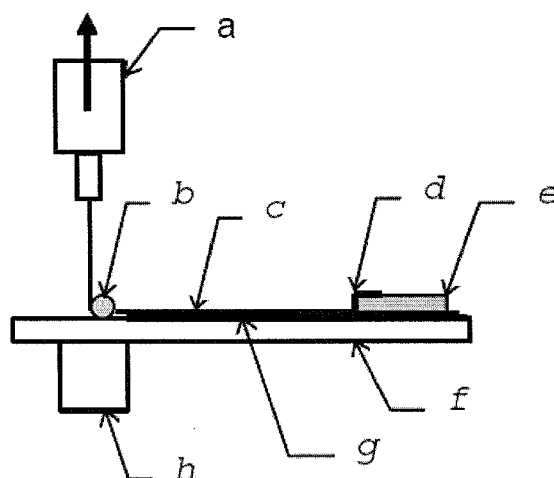
[0093] The printing plate precursors PPP-01 to PPP-16 were imaged on a Creo TrendSetter with a 40 W imaging head (commercially available from Kodak) at 140 rpm and 2400 dpi and then developed in an Agfa Autolith TP105 processor (commercially available from Agfa Graphics NV) with Agfa Energy Elite developer (commercially available from Agfa Graphics NV) in the developer section (temperature 23°C, dwell time 25 sec.) and tap water (room temperature) in the finisher section.

4. Evaluation of the printing plate precursors 1 to 16.

4.1. Evaluation of the coefficient of friction.

[0094] The static coefficient of friction of the surface of the precursors was measured. A value of at least 0.45 is required in order to prevent the occurrence of plates shifting over each other during transport, giving rise to "scuff mark" defects.

[0095] The static coefficient of friction was measured in line with standard ASTM D 1894. The following experimental set-up was used:



wherein

a: gauge which measures the frictional force between d and g; b: pulley;

c: nylon thread;

d: part of a typical interleaf paper (Pleiderer Pergo-Tec 37 g/m²) ;

e: stainless steel block;

f: support;

g: the printing plate precursor with the photosensitive layer facing upwards

[0096] The static coefficient of friction is defined as the maximum power (N) in order to move the stainless steel block e, divided by the weight of the stainless steel block.

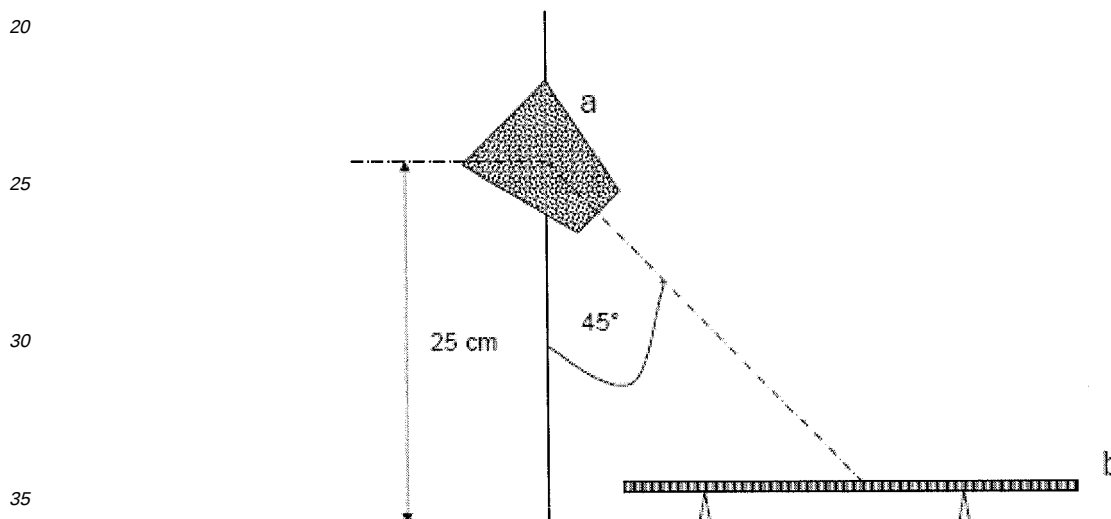
[0097] This assessment was performed 5 times for each of the printing plate precursors 1 to 16. The results of this evaluation (average value and standard deviation) are given in Table 5.

4.2. Evaluation of the coatability (cosmetics).

[0098] In order to evaluate the robustness of each of the second coating solutions with regards to coating and drying conditions, i.e. coatability, an additional coating test on an aluminum support as described under 1 was performed with each of the coating solutions 1 - 16 as described in 2.3 but using very critical drying conditions:

- step 1: drying for 30 seconds under the conditions described below;
- step 2: drying in a warm air (convection) oven for 3 minutes at 135°C.

[0099] Drying conditions used in step 1:



wherein

- a is a hair dryer (WIGO Taifun 110ch, power 1000W, commercially available from WIGO) used at the maximum available air blowing capacity setting 2.
- b is the printing plate precursor.

[0100] After coating and drying under the conditions described above, the obtained precursors were visually evaluated with regards to the coating uniformity using the following qualitative scale:

- 1= strongly cloudy coating
- 2= cloudy coating
- 3= slightly cloudy coating
- 4= nearly homogeneous coating
- 5= perfectly homogeneous coating

[0101] A value of at least 4 of the cosmetics or coatability of the surface is required in order to be able to coat the layer with sufficient latitude under industrial conditions.

4.3. Evaluation of the right exposure sensitivity.

[0102] The right exposure (RE) sensitivity is the energy density value (in mJ/cm²) where the 1x1 checkerboard pattern

on the plate after processing reads 52% (Gretag-MacBeth D19C densitometer, automatic colour filter setting).

[0103] The results of the right exposure sensitivity (RE), cosmetics level/coatability and coefficient of friction evaluations are given in Table 5.

Table 5: Static coeff. of friction and sensitivity results.

Printing plate precursor	"RE" sensitivity (mJ/cm ²)	static coefficient of friction *	coating cosmetics **	Dry coating weight of the surfactant (mg/m ²)
PPP 1; <i>reference</i>	111	0.60 ± 0.008	2	-
PPP 2; <i>comparative</i>	109	0.16 ± 0.009	5	5.0
PPP 3; <i>comparative</i>	na	na	1	5.0 0
PPP 4; <i>comparative</i>	na	na	1	10.0
PPP 5; <i>comparative</i>	98	0.36 ± 0.019	4	5.0
PPP 6; <i>comparative</i>	84	0.31 ± 0.010	4.5	10.0
PPP 7; <i>comparative</i>	na	na	3	5.0
PPP 8; <i>comparative</i>	na	na	3	10.0
PPP 9; <i>comparative</i>	83	0.46 ± 0.023	1	5.0
PPP 10; <i>comparative</i>	101	0.33 ± 0.016	1	10.0
PPP 11; <i>comparative</i>	na	na	1	5.0 0
PPP 12; <i>comparative</i>	na	na	1	10.0
PPP 13; <i>inventive</i>	97	0.58 ± 0.002	5	5.0
PPP 14; <i>inventive</i>	88	0.57 ± 0.004	4	10.0
PPP 15; <i>inventive</i>	108	0.56 ± 0.008	4.5	5.0
PPP 16; <i>inventive</i>	99	0.48 ± 0.008	4	10.0
na= data not available; * determined as described above; ** coating uniformity visually evaluated using the following qualitative scale: 1= strongly cloudy coating 2= cloudy coating 3= slightly cloudy coating 4= nearly homogeneous coating 5= perfectly homogeneous coating.				

[0104] The results in Table 5 show that the comparative printing plates either have a bad result for coatability (i.e. coating cosmetics level of 1 to 3), or, when the coatability is acceptable i.e. a coating cosmetics level of at least 4, the static coefficient of friction is not sufficiently high (below 0.45).

[0105] The inventive printing plate precursors comprising the surfactants PolyFox PF-652 and PolyFox PF-651, PPP-13 to PPP-16, allow for a good coatability - i.e. a coating cosmetics level of at least 4 - AND at the same time a sufficiently high static coefficient of friction - i.e. a static coefficient of friction of at least 0.45. PolyFox PF-652 has the additional feature that it shows a very consistent behaviour over the concentration range used.

[0106] The sensitivity results are comparable for all the printing plate precursors PPP-1 to PPP-16.

Claims

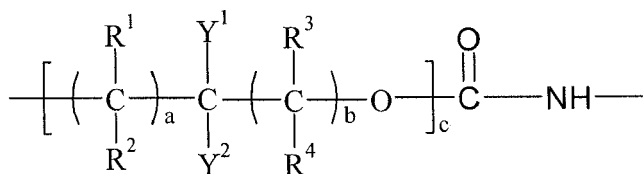
1. A heat-sensitive positive-working lithographic printing plate precursor which comprises on a support having a hy-

drophilic surface or which is provided with a hydrophilic layer, a heat and/or light-sensitive coating comprising a surfactant,

characterized in that the surfactant comprises a polyether block including a pendant fluoroalkyl group and a urethane linking group.

2. A printing plate precursor according to claim 1 wherein the fluoroalkyl group is an alkoxyfluoroalkyl group.

3. A printing plate precursor according to claims 1 or 2 wherein the surfactant comprises the following structural unit:



wherein

a and b independently represent an integer ≥ 0 ;

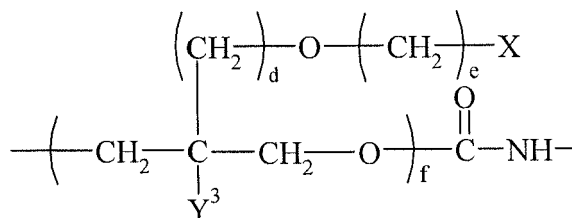
c represents an integer ranging between 1 and 40;

Y^1 represents a fluoroalkyl group or an alkoxyfluoroalkyl group;

Y^2 represents hydrogen, an optionally substituted alkyl group, a fluoroalkyl group or an alkoxyfluoroalkyl group;

R^1 to R^4 independently represent hydrogen, fluoride, a fluoroalkyl group, an optionally substituted alkyl group or an optionally substituted aryl group.

4. A precursor according to any of claims 1 to 3 wherein the surfactant comprises the following structural unit:



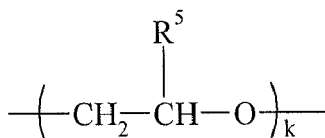
wherein d and e represent an integer ≥ 1 ;

X represents a fluoroalkyl group;

Y^3 represents hydrogen or an optionally substituted alkyl group;

and f represents an integer ranging between 1 and 40.

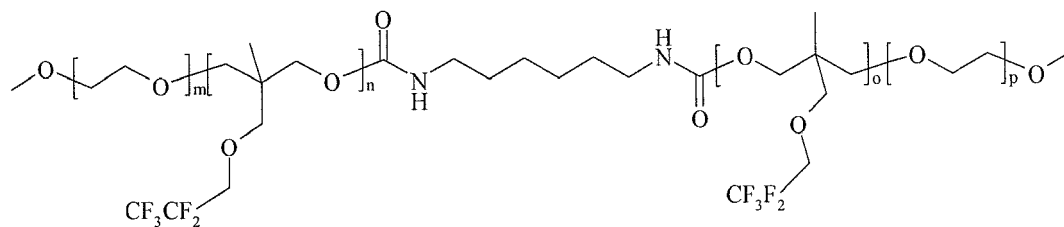
5. A printing plate precursor according to any of the preceding claims wherein the surfactant comprises the following structural unit:



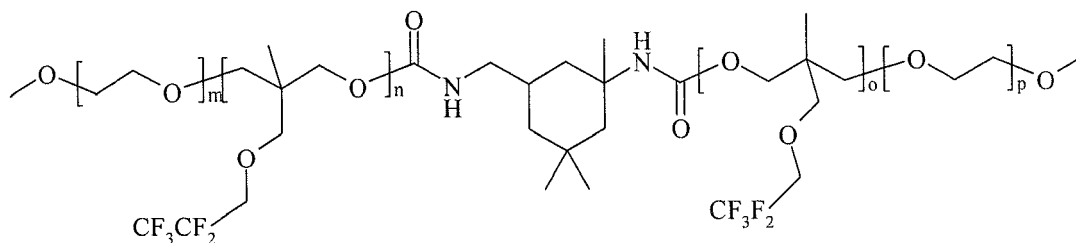
wherein R^5 represents hydrogen; an optionally substituted

alkyl or an optionally substituted aryl, aralkyl or heteroalkyl group;
and k represents an integer ranging between 1 and 40.

6. A printing plate precursor according to any of the preceding claims wherein the surfactant comprises the following structural unit:

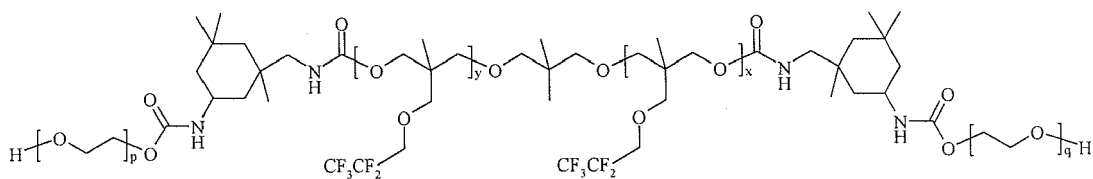
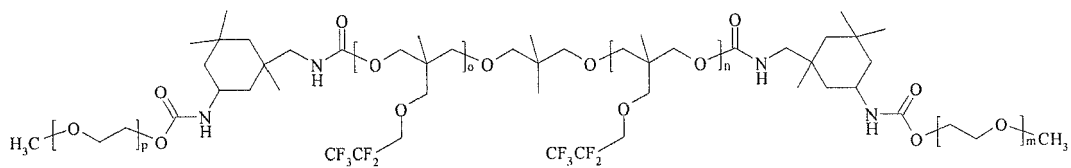


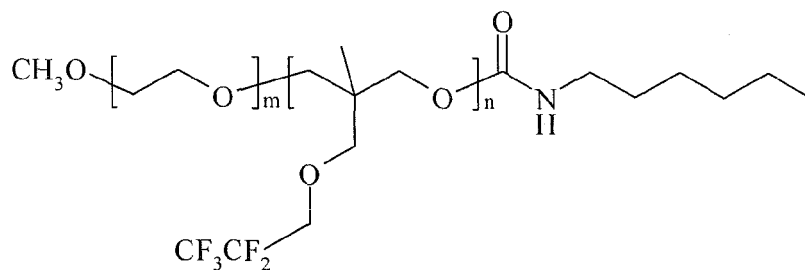
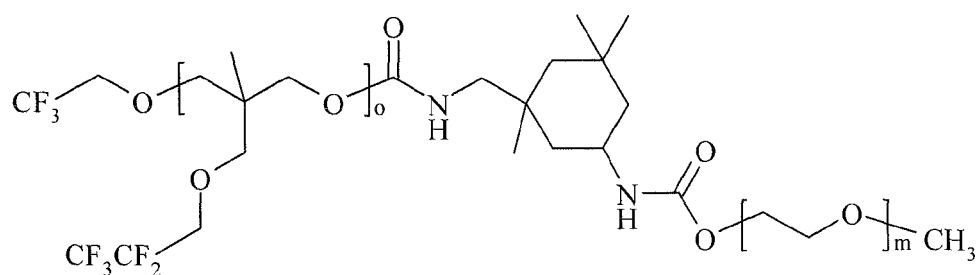
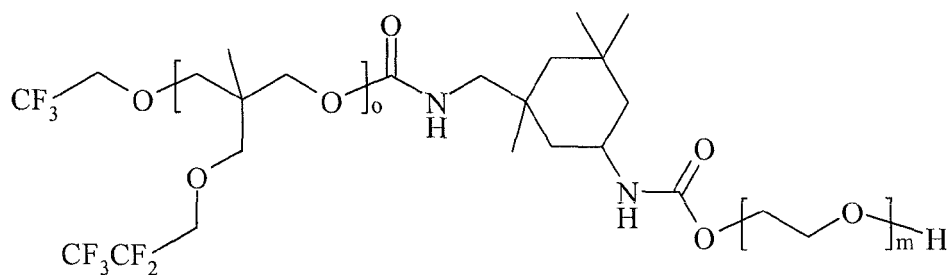
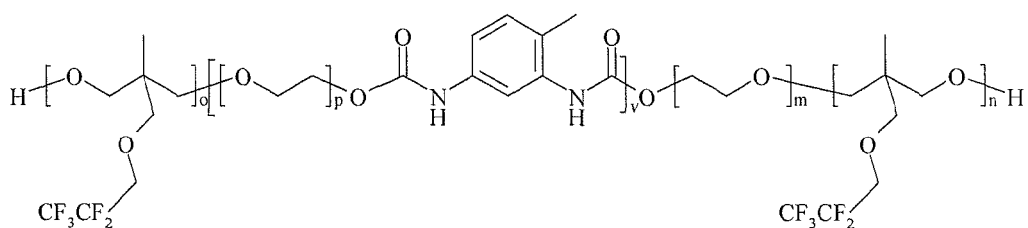
and/or



wherein m, n, o and p in each of the compounds independently represent an integer ranging between 1 and 40.

7. A printing plate precursor according to any of the preceding claims wherein the surfactant is one of the following compounds:





55 wherein m, n, o, p, x, y, q and v in each of the compounds independently represent an integer ranging between 1 and 40.

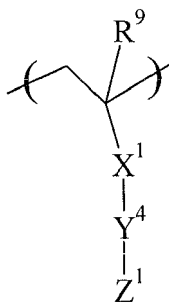
8. A printing plate precursor according to any of the preceding claims wherein the surfactant is present in the coating

in an amount ranging between 0.1 %wt and 3%wt.

- 9.** A printing plate precursor according to any of the preceding claims wherein the coating comprises at least two layers

- a layer comprising an oleophilic resin;
- another layer comprising a sulfonamide binder, which is located between the support and said layer comprising the oleophilic resin;
and wherein the surfactant is present in the layer comprising the oleophilic resin.

- 10.** A printing plate precursor according to claim 8 wherein the sulfonamide binder is represented by



wherein

R⁹ represents hydrogen or a hydrocarbon group having up to 12 carbon atoms;

X¹ represents a single bond or a divalent linking group;

Y⁴ is a bivalent sulphonamide group;

and Z^1 represents a terminal group.

- 11.** A method for making a lithographic printing plate precursor comprising the steps of

- applying a coating as defined in any of the preceding claims;
- drying the precursor.

- 12.** A method for making a lithographic printing plate comprising the steps of

- providing a printing plate precursor according to any of the preceding claims;
- exposing said precursor to heat and/or infrared light;
- developing the exposed precursor with an aqueous alkaline solution.

Amended claims in accordance with Rule 137(2) EPC.

1. A heat-sensitive positive-working lithographic printing plate precursor which comprises on a support having a hydrophilic surface or which is provided with a hydrophilic layer, a heat and/or light-sensitive coating which comprises a surfactant and at least two layers:

- a layer comprising an oleophilic resin;
- another layer comprising a sulfonamide binder, which is located between the support and said layer comprising the oleophilic resin;

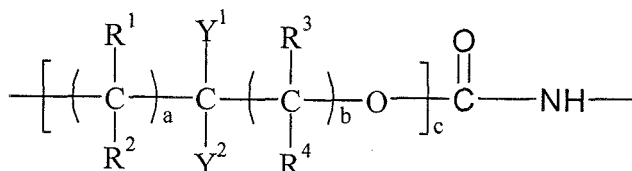
characterized in that the surfactant comprises a polyether block including a pendant fluoroalkyl group and a urethane linking group.

- 2.** A printing plate precursor according to claim 1 wherein the surfactant is present in the layer comprising the

oleophilic resin.

3. A printing plate precursor according to claims 1 or 2 wherein the fluoroalkyl group is an alkoxyfluoroalkyl group.

4. A printing plate precursor according to any of the preceding claims wherein the surfactant comprises the following structural unit:



wherein

a and b independently represent an integer ≥ 0 ;

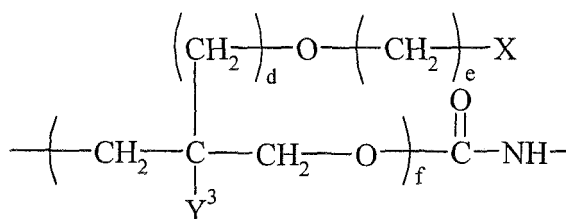
c represents an integer ranging between 1 and 40;

Y^1 represents a fluoroalkyl group or an alkoxyfluoroalkyl group;

Y^2 represents hydrogen, an optionally substituted alkyl group, a fluoroalkyl group or an alkoxyfluoroalkyl group;

R^1 to R^4 independently represent hydrogen, fluoride, a fluoroalkyl group, an optionally substituted alkyl group or an optionally substituted aryl group.

5. A precursor according to any of the preceding claims wherein the surfactant comprises the following structural unit:



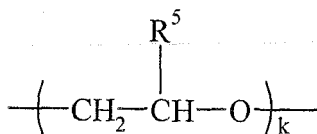
wherein d and e represent an integer ≥ 1 ;

X represents a fluoroalkyl group;

Y^3 represents hydrogen or an optionally substituted alkyl group;

and f represents an integer ranging between 1 and 40.

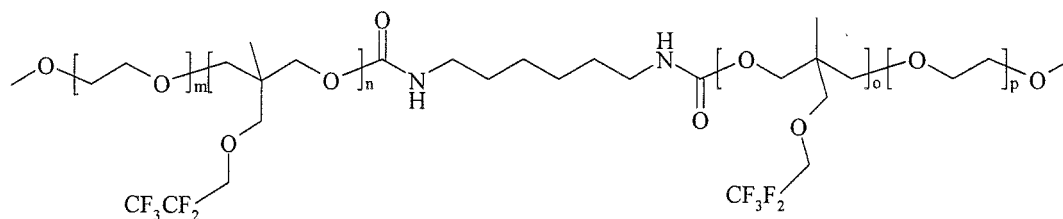
6. A printing plate precursor according to any of the preceding claims wherein the surfactant comprises the following structural unit:



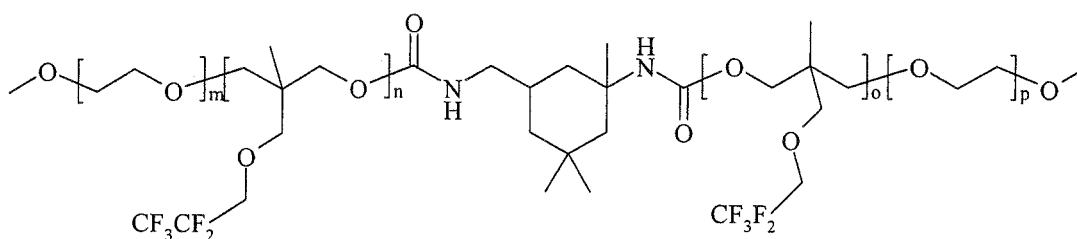
wherein R^5 represents hydrogen; an optionally substituted alkyl or an optionally substituted aryl, alkyl or heteroalkyl group;

and k represents an integer ranging between 1 and 40.

7. A printing plate precursor according to any of the preceding claims wherein the surfactant comprises the following structural unit:

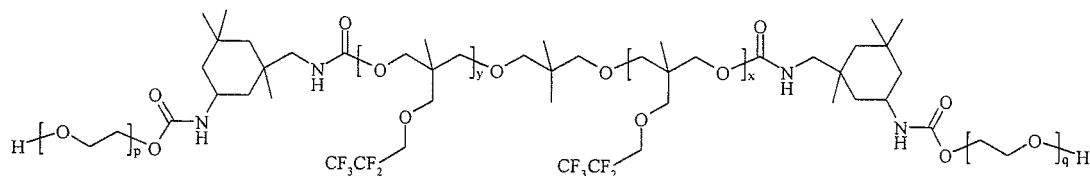
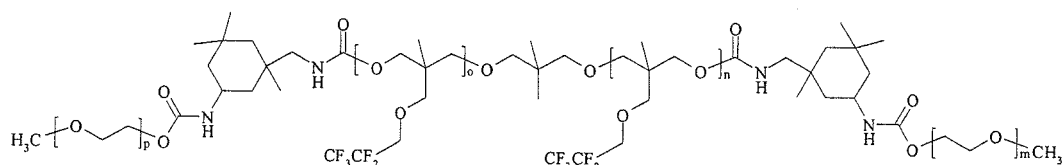


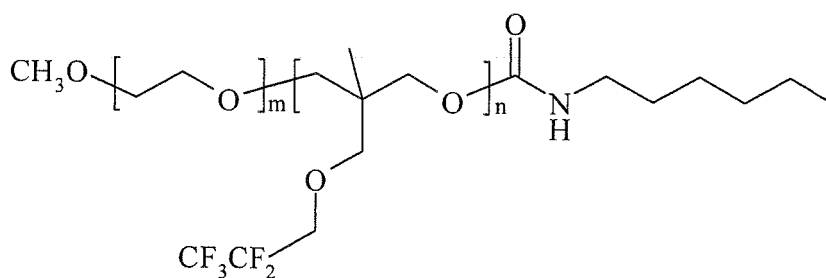
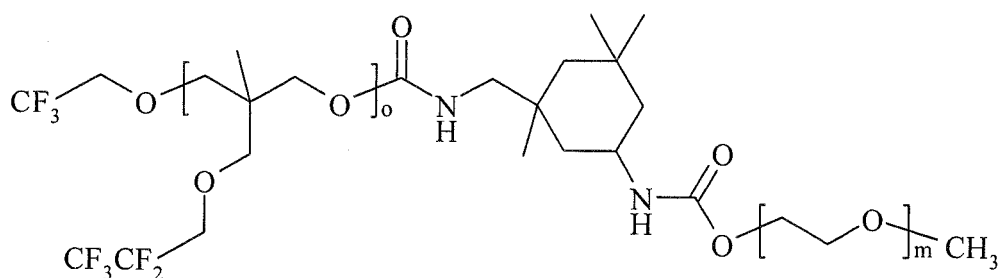
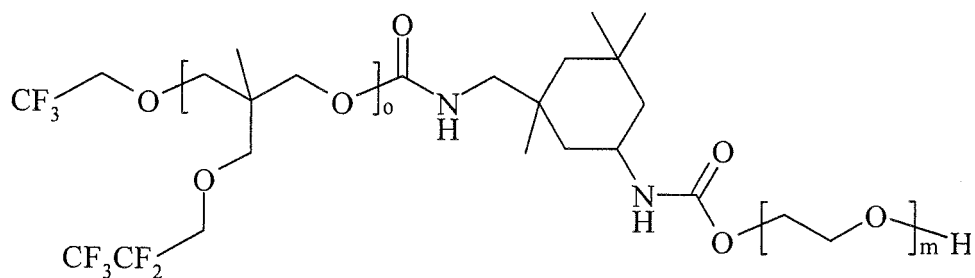
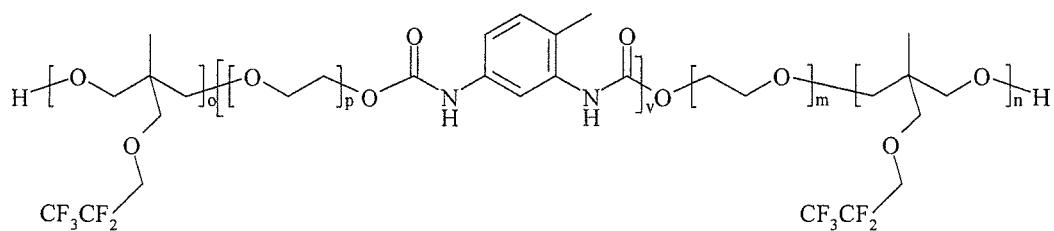
and/or



wherein m, n, o and p in each of the compounds independently represent an integer ranging between 1 and 40.

8. A printing plate precursor according to any of the preceding claims wherein the surfactant is one of the following compounds:

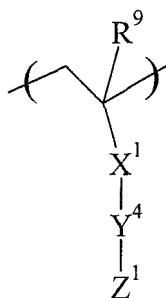




wherein m, n, o, p, x, y, q and v in each of the compounds independently represent an integer ranging between 1 and 40.

9. A printing plate precursor according to any of the preceding claims wherein the surfactant is present in the coating in an amount ranging between 0.1 %wt and 3%wt.

10. A printing plate precursor according to any of the preceding claims wherein the sulfonamide binder is represented by



wherein

R^9 represents hydrogen or a hydrocarbon group having up to 12 carbon atoms;

X^1 represents a single bond or a divalent linking group;

Y^4 is a bivalent sulphonamide group;

and Z^1 represents a terminal group.

11. A method for making a lithographic printing plate precursor comprising the steps of

- applying a coating as defined in any of the preceding claims;
- drying the precursor.

12. A method for making a lithographic printing plate comprising the steps of

- providing a printing plate precursor according to any of the preceding claims;
- exposing said precursor to heat and/or infrared light;
- developing the exposed precursor with an aqueous alkaline solution.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 07 11 8085

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			TECHNICAL FIELDS SEARCHED (IPC)
			B41C
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 12 March 2008	Examiner Markham, Richard
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 07 11 8085

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12-03-2008

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