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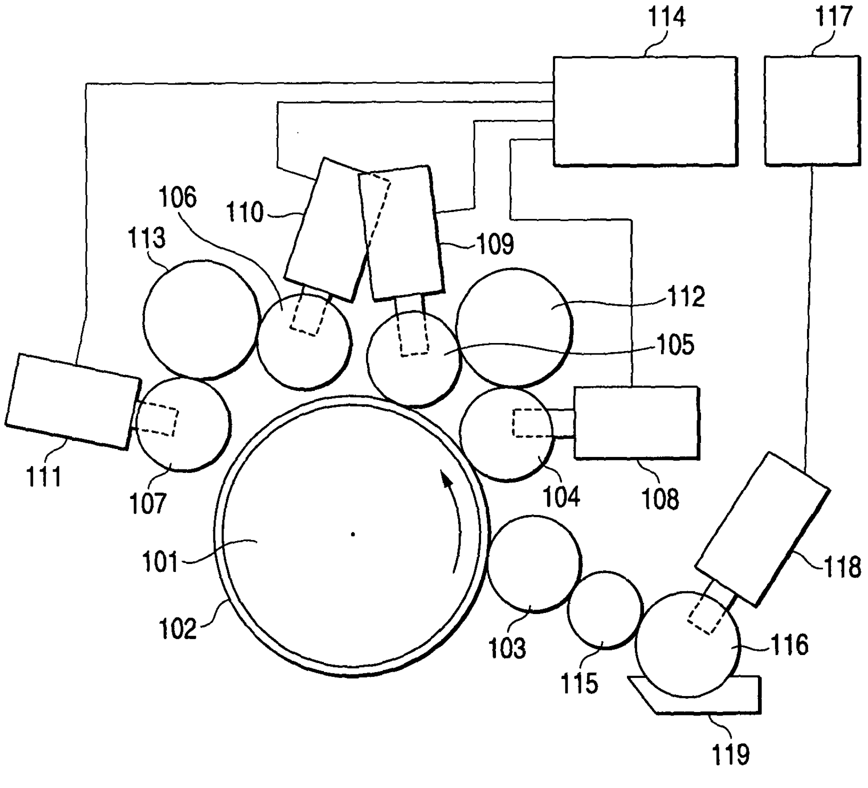
# (54) On-press development and printing method and printing apparatus

(57) A method of on-press developing and printing an on-press development type lithographic printing plate precursor by using a printing apparatus having a plurality of inking rollers, the method comprising an inking step in which at least one of said plurality of inking rollers is not in contact with a plate surface.

*FIG. 1*



EP 1 829 683 A2

## Description

## Background of the Invention

### 1. Field of the Invention

**[0001]** The present invention concerns an on-press development and printing method or a printing apparatus by using an on-press development type lithographic printing plate precursor.

### 2. Description of the Related Art

**[0002]** Generally, a lithographic printing plate has an oleophilic image area for receiving an ink and a hydrophilic non-image area for receiving a fountain solution in a printing process. Lithographic printing is a printing method of forming an oleophilic image portion as an ink receiving area and a hydrophilic non-image area as a fountain solution receiving area (non-ink receiving area) of the lithographic printing plate by utilizing the property that water and oily ink repel to each other, thereby causing difference in the ink depositability on the surface of the lithographic printing plate, depositing an ink only on the image area and transferring the ink to a material to be printed such as paper.

**[0003]** For preparing the lithographic printing plate, a lithographic printing plate precursor (PS plate) in which an oleophilic photosensitive resin layer (photosensitive layer) is disposed on a hydrophilic support has been used generally. Usually, after the lithographic printing plate precursor is exposed through an original such as a Lith film, plate making is conducted by a method of remaining a portion as the image area of the photosensitive layer and dissolving to remove other unnecessary photosensitive layer with a developer such as an aqueous alkali solution to expose the surface of a hydrophilic support thereby forming a non-image area, to obtain a lithographic printing plate.

**[0004]** As described above, while a wet processing step by a developer or the like is necessary in the existent plate making process for the lithographic printing plate precursor, it has become an important subject of saving or simplifying the wet treatment conducted additionally with a view point of making the plate making process reasonable and decreasing liquid wastes caused by the processing.

**[0005]** In view of the above, as one of simple plate making methods, it has been proposed a method referred to as a on-press development for obtaining a printing plate by using a photosensitive layer soluble or dispersible in fountain solution and/or ink and removing unnecessary portion of the photosensitive layer after exposure during a usual printing process on a printing machine (hereinafter also referred to simply as on-press development).

**[0006]** The developing mechanism for the on-press developing type lithographic printing plate precursor concerning the invention is considered as below. (1) water dipping step: fountain solution supplied from a dampening form roller to a plate surface penetrates in a photosensitive layer. As penetration proceeds, a layer of fountain solution is formed at the boundary between the photosensitive layer and a support to lower adhesion between the photosensitive layer and the support. (2) Inking deposition step: an inking rolled is brought into contact with a plate surface and the photosensitive layer reduced with the adhesion to the support is peeled and removed by the viscosity of an ink to complete development. After the completion of the development, printed matters are obtained successively by a usual printing process.

**[0007]** As specific example of such on-press development, JP-A Nos. 9-123387 and 9-123388 disclose a technique of attaching a lithographic printing plate precursor capable of on-press development after image formation to a printing machine cylinder, dropping a fountain solution roller of the printing machine to the plate surface to supply fountain solution to the lithographic printing plate precursor, then descending the ink roller after rotating the printing cylinder by 10 turns to supply an ink and obtaining providing printed matters with no stains on the non-image area after rotation by ten times.

**[0008]** However, number of printing paper sheets required till printed matters with no stains are obtained is increased by several times compared with the case of a lithographic printing plate obtained in general plate making by wet development. This increases the number of loss of paper sheets to result in a drawback in the on-press development type lithographic printing plate precursor.

**[0009]** As a method of promoting the on-press development and decreasing the number of loss sheets of paper, a method of increasing the amount of fountain solution supplies in the water dipping step of on-press development compared with the amount of supply upon completion of the on-press development or a method of changing the peripheral speed of a press cylinder (plate cylinder) during on-press developing (for example, refer to JP-A No. 2004-314530).

**[0010]** While the method of promoting on-press development described above is effective to some extent, it can not yet decrease the number of loss of paper sheets to such an extent as comparable with that in the lithographic printing plate obtained for plate making by the wetting process. The invention solves this problem. That is, the invention intends to shorten the time necessary for on-press development and greatly decrease the number of loss of paper sheets. More specifically, it intends to provide a on-press developing and printing method for attaining decrease in the number of loss of paper sheets comparable with that in the lithographic printing plate made by the wet process development, as well as a printing apparatus therefor.

## Summary of the Invention

**[0011]** As a result of an earnest study, the present inventor could overcome the problem described above by devising a method of bringing an inking roller into contact with a lithographic printing plate precursor on a plate cylinder in the inking step of on-press development. That is, the present invention is as follows:

(1) A method of on-press developing and printing an on-press development type lithographic printing plate precursor by using a printing apparatus having a plurality of inking rollers, the method comprising an inking step in which at least one of said plurality of inking rollers is not in contact with a plate surface.
(2) The method according to (1), further comprising a printing step after the inking step, wherein the number of the inking rollers being contact with the plate surface in the printing step is larger than the number of the inking rollers being contact with the plate surface in inking step.
(3) The method according to (2), wherein only one of said plurality of inking rollers is in contact with the plate surface in the inking step.
(4) The method according to (2) or (3), wherein all of said plurality of inking rollers are contact with the plate surface in the printing step.
(5) The method according to (1), further comprising: a water dipping step that initiates and keeps supplying a fountain solution to the an on-press development type lithographic printing plate precursor, before the inking step; and a printing step after the inking step, wherein the fountain solution is maintained to be supplied to the plate surface throughout from the water dipping step to the printing step, the fountain solution having been carried by way of a water fountain roller which is rotating, and wherein a rotational speed of the water fountain roller in the water dipping step is larger than that in the printing step.
(6) The method according to any one of (1) to (5), wherein the on-press development type lithographic printing plate precursor comprises, on a support, a photosensitive layer comprising a polymerization initiator, a polymerizable compound and a sensitizing dye.
(7) A printing apparatus comprising: three or more inking rollers, the inking rollers being divided two groups; and an inking roller attachment/detachment control means for separately controlling attachment/detachment of each of (i) one group of the inking roller(s) and (ii) the other group of the inking roller(s) to and from a plate surface of an on-press development type lithographic printing plate precursor.
(8) The printing apparatus according to (7), further comprising: a water fountain roller by way of which a fountain solution is supplied to the plate surface of the on-press development type lithographic printing plate precursor; and a water fountain roller rotational speed control means for varying a rotational speed of the water fountain roller.
(9) The printing apparatus according to (7) or (8), wherein the on-press development type lithographic printing plate precursor comprises, on a support, a photosensitive layer comprising a polymerization initiator, a polymerizable compound and a sensitizing dye.

**[0012]** The reason why the on-press development is promoted according to the invention is considered as below.

**[0013]** In the on-press development, fountain solution should penetrate for the entire print plate surface as far as the support/photosensitive layer boundary in the water dipping step to lower the adhesion between the support/photosensitive layer. However, in the on-press development by the existent process, it is considered that the fountain solution does not prevail over the entire support/photosensitive layer boundary only by the water dipping step, so that a place where the adhesion is not lowered is also present and such a portion where the adhesion is not lowered results in portion of failed development to increase the number of loss of paper sheets.

**[0014]** Accordingly, for completing on-press development in an early stage and decreasing the number of loss of paper sheets, it is necessary to supply a great amount of fountain solution to the plate also in the inking step. However, the substantial amount of plate surface fountain solution in the inking step is remarkably smaller than that in the water dipping step. This is because the fountain solution supplied by the dampening form roller to the plate surface is deprived by the inking roller (ink of the xoller).

**[0015]** In the invention, since the number of inking rollers in contact with the plate in the inking step is less than the number of inking rollers in contact with the plate in the printing step, the amount of dipping water deprived from the plate is decreased and a great amount of fountain solution is retained on the plate surface also in the inking step, penetration of the fountain solution to the photosensitive layer is fastened to promote development.

**[0016]** According to the invention, in the on-press development for the on-press development type lithographic printing plate precursor, a number of loss of sheets of paper comparable with that for the lithographic printing plate made by the existent wet development can be obtained.

## Brief Description of the Drawings

**[0017]**

Fig. 1 is a schematic view for an embodiment of a printing apparatus according to the invention;
Fig. 2 shows a printing apparatus in a state before starting;
Fig. 3 shows a printing apparatus in the water dipping step;
Fig. 4 shows a printing apparatus in the ink dip deposition step; and
Fig. 5 shows a printing apparatus in the printing step.

**[0018]** In the figures, 101 denotes a plate cylinder; 102 denotes a lithographic printing plate precursor; 103 denotes a dampening form roller; 104 denotes an inking roller; 105 denotes an inking roller; 106 denotes an inking roller; 107 denotes an inking roller; 108 denotes an actuator; 109 denotes an actuator; 110 denotes an actuator; 111 denotes an actuator; 112 denotes an ink leveling roller; 113 denotes an ink leveling roller; 114 denotes an inking roller attachment/detachment control device; 115 denotes a roller supplying a fountain solution to the dampening form roller; 116 denotes a water fountain roller; 117 denotes a water fountain roller rotational speed control device; 118 denotes an actuator; and 119 denotes a fountain solution bath.

## Detailed Description of the Invention

**[0019]** The on-press developing method, the printing apparatus, and the on-press development type lithographic printing plate precursor used in the method and the apparatus described above according to the invention are to be described.

(On-press developing and printing method)

**[0020]** According to the on-press developing and printing method of the invention, at least one of inking rollers is not in contact with the plate surface in the inking step of the on-press development and printing by a printing apparatus having a plurality of inking rollers.

**[0021]** On-press development is promoted by bringing the inking rollers into contact with the plate surface in the inking step by the number less than the number of the inking roller to be in contact with the plate surface in the printing step. This is considered that fountain solution supplied by the dampening form roller is less deprived by the ink of the inking roller as described above. For the promoting the on-press development, it gives scarce effect which rollers is brought into contact or which roller is kept from contact among the plurality of inking rollers. The on-press development promoting effect depends on the number of inking rollers in contact with the plate surface in the inking step and the effect is remarkable as the number of the rollers is smaller and it is most preferred to contact only one inking roller.

**[0022]** Further, in the on-press developing and printing method of the invention, it is preferred to increase the rotational speed of the water fountain roller in the water dipping step, compared to the rotational speed of the water fountain roller in the printing step. By increasing the rotational number of the water fountain roller, the amount of the supplied fountain solution is increased to promote the on-press development.

**[0023]** In the on-press developing and printing method of the invention, all the inking rollers are brought into contact with the plate surface in the printing step after the inking step to conduct the printing operation as usual.

**[0024]** As the fountain solution and the ink in the on-press developing and printing method of the invention, fountain solution and printing ink in usual offset printing can be used. The fountain solution may be simply water.

(Printing Apparatus)

**[0025]** The printing apparatus of the invention has a feature in that (1) it has: three or more inking rollers, the inking rollers being divided two groups; and an inking roller attachment/detachment control means for separately controlling attachment/detachment of each of (i) the inking roller(s) in one group and (ii) the inking roller(s) in the other group to and from a plate surface of an on-press development type lithographic printing plate precursor. Further, (2) it preferably further has a water fountain roller by way of which a fountain solution is supplied to the plate surface of the on-press development type lithographic printing plate precursor; and a rotational speed control means for varying a rotational speed of the water fountain roller.

**[0026]** Further, the printing apparatus of the invention is (3) preferably controlled such that one of the two groups is in contact with the lithographic printing plate precursor surface just after the water dipping step and then the other of them is in contact with the plate surface after the rotation of the plate cylinder by a predetermined number of rotation. Particularly, it is more preferred to be controlled such that one inking roller is in contact with the lithographic printing plate precursor surface just after the water dipping step.

**[0027]** An embodiment of the printing apparatus according to the invention is shown by a schematic view of a printing apparatus shown in Fig. 1.

**[0028]** The printing apparatus of the invention has three or more inking rollers, each inking roller conducts attachment/detachment to and from the lithographic printing plate precursor on a plate cylinder by a driving system (actuator), and attachment/detachment is controlled by a control device so as to be conducted for two groups separately.

Fig. 2 shows a state before starting the apparatus and the lithographic printing plate precursor surface on a plate cylinder from a dampening form roller and inking rollers are in a state not in contact with each other.
Fig. 3 shows a water dipping step in which the plate surface and a dampening form roller are in contact, while inking rollers are kept in a non-contact state.
Fig. 4 shows an inking step, and a dampening form roller and one inking roller are in contact with the plate surface.
Fig. 1 also shows the inking step in which the dampening form roller and two inking rollers are in contact with the plate surface.
Fig. 5 shows a printing step in which the dampening form roller and all the inking rollers are in contact with the plate surface.

**[0029]** According to the printing apparatus described above, the on-press developing and printing method of the invention described above can be conducted easily to attain decrease of loss of paper in on-press development.

[On-press development type lithographic printing plate precursor]

**[0030]** While the on-press development type lithographic printing plate precursor used in the invention has no particular restriction so long as it is a lithographic printing plate precursor capable of on-press development, a lithographic printing plate precursor having a polymerizable photosensitive layer on a support can be mentioned as being preferred. Since the polymerizable photosensitive layer can be removed by dissolution or dispersion with fountain solution and/or ink, good printing resistance as well as good on-press developability can be obtained.

**[0031]** A lithographic printing plate precursor having the polymerizable photosensitive layer is to be described.

(Photosensitive layer)

**[0032]** The photosensitive layer of an on-press developing type lithographic printing plate precursor used in the invention can contain a polymerization initiator, a polymerizable compound and a sensitizing dye. Further it can contain a binder polymer or other additive ingredients.

< Polymerization initiator >

**[0033]** The polymerization initiator used in the invention includes compounds generating radicals by the energy of light, heat or both of them and starting and promoting polymerization of compounds having polymerizable unsaturated groups. As the polymerization initiator usable in the invention, known heat polymerization initiators, compounds having bonding with a small bonding dissociation energy, photopolymerization initiators, etc. can be used. The radical generating compound used preferably in the invention means those compounds generating radicals by the heat energy and starting and promoting polymerization of compounds having polymerizable unsaturated groups. As the heat radial generators according to the invention, known polymerization initiators or compounds having bonding with small dissociation energy can be properly selected and used. Further, the radial generating compounds can be used each alone or in combination of two or more of them.

**[0034]** The radical generating compound includes, for example, organic halogenized compounds, carbonyl compounds, organic peroxide compounds, azo polymerization initiators, azide compounds, metallocene compounds, hexaaryl biimidazole compounds, organic boric acid compounds, disulfonic acid compounds, oxime ester compounds, and onium salt compounds.

**[0035]** The organic halogenated compounds include, specifically, those compounds described by Wakabayashi, et. al. in "Bull Chem. Soc Japan", 42, 2924 (1969), the specification of USP No. 3905815, JP-B No. 46-4605, JP-A Nos. 48-36281, 55-32070, 60-239736, 61-169835, 61-169837, 62-58241, 62-212401, 63-70243, and 63-298339, by M.P. Hutt, in "Journal of Heterocyclic Chemistry" 1 (No. 3), (1970)", etc. They includes, particularly, trihalomethyl group-substituted oxazole compounds; S-triazine compounds.

**[0036]** More preferably, they include s-triazine derivative in which at least one mono, di, or tri-halogen-substituted methyl group is bonded to the s-triazine ring, specifically, 2,4,6-tris(monochloromethyl)-s-triazine, 2,4,6-tris(dichloromethyl)-s-triazine, 2,4,6-tris(trichloromethyl)-s-triazxne, 2-methyl-4,6-bis(trichloromethyl)-s-triazine, 2-n-propyl-4, 6-bis (trichloromethyl)-s-triazine, 2- (α, a, β-trichloroethyl) - 4,6-bis(trichloromethyl)-s-triazine. 2-phenyl-4, 6-bis (trichloromethyl)-s-triazine, 2- (p-methoxyphenyl) -4, 6-bis (trichloromethyl) --s-triazine, 2-(3,4-epoxyphenyl)-4,6-bis(trichloromethyl)-s-triazine, 2-(p-chlorophenyl)-4,6-bis (trichloromethyl) -s-triaxine, 2-[1-p-methoxyphenyl)-2,4-butadienyl]-4,6-bis (trichloromethyl)-s-triazine, 2-styryl-4,6-bis(trichloromethyl)-s-triazine, 2-(p-methoxystyryl)-4,6-bis(trichloromethyl)-s-triazine, 2-(p-i-propyloxystyryl)-4,6-bis(trichloromethyl)-s-triazine, 2-(p-tolyl)-4,6-bis(trichloromethyl)-s-triazine, 2-(4-(natoxynaphtyl)-4,6-bis(trichloromethyl)-s-triazine, 2-phenylthio-4,6-bis(trichloromethyl)-s-triazine, 2-benzylthio-4, 6-bis (trichloromethyl)-s-triazine, 2,4,6-tris(dibromomethyl)-s-triazine, 2-4, 6-tris(tribromomethyl)-s-triazine, 2-methyl-4,6-bis (tribromomethyl)-s-triazine, 2-methoxy-4, 6-bis(tribromomethyl)-s-triazine, etc.

**[0037]** The carbonyl compounds include, benzophenone derivatives such as benzophenone, Michler's ketone, 2-methylbenzophenone, 3-methylbenzophenone, 4-methysbenzophenone, 2-chlorobanzophenone, 4-bromobenzophenone, and 2-carboxybenzophenone, acetophenone derivatives such as 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxyacetophenone, 1-hydroxycyclohexylphenylketone, α-hydroxy-2-methylphenyl propanone, 1-hydroxy-1-methylethyl-(p-isopropylphenyl)ketone, 1-hydroxy-1-(p-dodecylphenyl)ketone, 2-methyl-(4'-(methylthio)phenyl)-2-moxpholino-1-propanone, and 1, 1, 1-trichloromethyl-(p-butylphenyl)ketone, thioxantone derivatives such as thioxantone, 2-ethyl thioxantone, 2-isopropyl thioxantone, 2-chlorothio thioxantone, 2,4-dimethyl thioxantone, 2,4-diethyl thioxantone, and 2,4-diisopropyl thioxantone, and benzoic acid ester derivatives such as ethyl p-dimethyl aminobenzoate, and ethyl p-diethylamino benzoate.

**[0038]** As the azo compounds described above, azo compounds described, for example, in JP-A No. 8-108621 can be used.

**[0039]** The organic peroxide compounds include, for example, trimethylcyclohexanone peroxide, acetylacetone peroxide, 1,1-bis(tert-butyl peroxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert-butyl peroxy)cyclohexane, 2,2-bis(tert-butyl peroxy)butane, tert-butyl hydro peroxide, cumene hydroperoxide, diisopropyl benzene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, tert-butylcumyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-oxanoylperoxide, succinic acid peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, diisopropylperoxy dicarbonate, di-2-ethylhexyl peroxyl dicarbonate, di-2-ethoxyethyl peroxy dicarbonate, dimethoxy isopropy peroxycarbonate, di(3-methyl-3-methoxybutyl)peroxy dicarbonate, tert-butyl peroxyacetate, tert-butyl peroxypivalate, tert-butylperoxy neodecanoate, tert-butyl peroxyoctanoate, tert-butyl peroxylaurate, tert-butyl carbonate, 3,3',4,4'-tetra-(t-butyl peroxycabonyl)benzophenone, 3,3',4,4'-tetra(t-hexyl peroxycarbonyl)benzophenone, 3,3'4,4'-tetra-(p-isopropyl cumylperoxycarbonyl)benzophenone, carbonyl di(t-butylperoxy dihydrogen diphthalate), and carbonyl di (t-hexylperoxy dihydrogen diphthalate),

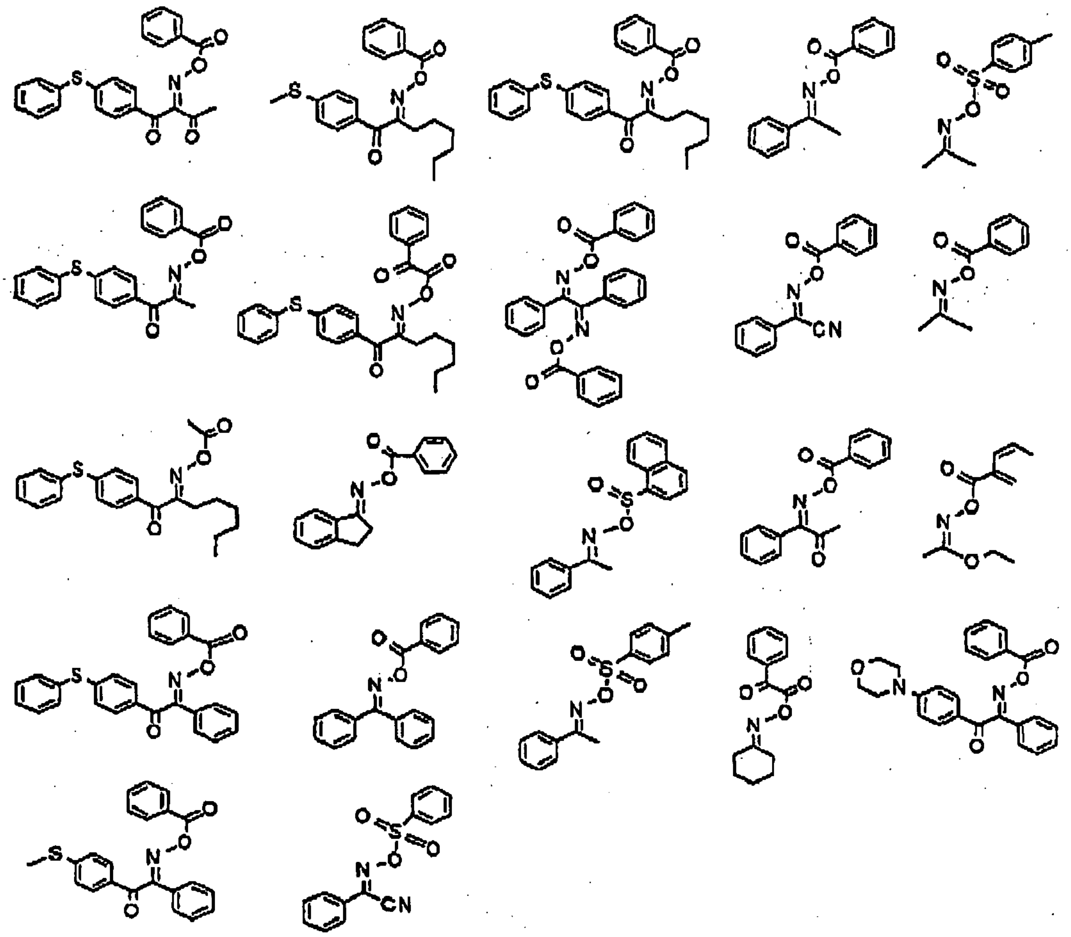
**[0040]** The metallocene compounds include various titanocene compounds described in JP-A Nos. 59-152396, 61-151191, 63-41484, 2-249, 2-4705, and 5-83588, for example, di-cyclopentadienyl-Ti-bis-phenyl, di-cyclopentadienyl-Ti-bis-2,6-difluoropheny-1-yl, di-cyclopentadienyl-Ti-bis-2,4-di-fluoropheny-1-yl, di-cyclopentadienyl-Ti-bis-2,4,6-trifluoropheny-1-yl, di-cyclopentadienyl-Ti-bis-2,3,5,6-tetrafluoropheny-1-yl, di-cyclopentadienyl-Ti-bis-2,3,4,5,6-pentafluoropheny-1-yl, di-methylcyclopentadienyl-Ti-bis-2,6-difluoropheny-1-yl, di-methylcyclopentadienyl-Ti-bis-2,4,6-trifluoropheny-1-yl, di-methylcyclopentadiethyl-Ti-bis-2,3,5,6-tetrafluoropheny-1-yl, di-methylcyclopentadiethyl-Ti-bis-2,3,4,5,6-pentafluoropheny-1-yl, and iron-arene complexes described in JP-A Nos. 1-304453, and 1-152109.

**[0041]** The hexa-aryl biimidazole compounds include, for example, various compounds described in each of the publications of JP-B No. 6-29285, USP Nos. 3479185, 4311783, and 4622286, specifically, 2,2'-bis(o-chlorophenyl)-4,4'-5,5'-tetraphenyl biimidazole, 2,2'-bis(o-bromophenyl))4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(p-dichlorophenyl)-4,4',5,5'-tetraphenyl biimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(m-methoxyphenyl)biimidazole, 2,2'-bis(o,o'-dichlorophenyl)-4,4',5,5'-tetraphenyl biimidazole, 2,2'-bis(o-nitrophenyl)-4,4',5,5'-tetraphenyl biimidazole, 2,2'-bis(o-methylphenyl)4,4',5,5'-tetraphenyl biimidazole, and 2,2'-bis(o-trifluorophenyl)-4,4',5,5'-tetraphenyl biimidazole.

**[0042]** The organic boric acid salt compounds include organic boric acid salts described, for example, in each of the publications of JP-A Nos. 62-143044, 62-150242, 9-188685, 9-188686, 9-188710, 2000-131837, 2002-107916, JP No. 2764769, and JP-A No. 2002-116539, and Kunz, Martin, "Rad Tech'98. Proceeding April 19-22, 1988, Chicago", organic boron sulfonium complexes or organic boron oxosulfonium complexes described in JP-A Nos. 157623, and 6-175564, organic boron iodonium complexes described in JP Nos. 6-175554, and 6-175553, organic boron phosphonium complexes described in JP-A Nos. 9-188710, and organic boron transition metal coordinate complex for example, in JP-A Nos. 6-348011, 7-128785, 7-140589, 7-306527, and 7-292014 as specific examples.

**[0043]** The disulfone compounds include, compounds described, for example, in JP-A Nos. 61-166544, and 2003-328465.

**[0044]** The oxime ester compounds include compounds described in J.C.S. Perkin II (1979) 1653-1660, J.C.S.Perkin II (1979) 156-162, Journal of Photopolymer Science and Technology (1995) 202-232, compounds described in JP-A No. 2000-66385, and compounds described in JP-A 2000-80068 and they include specifically the compounds shown by the following structural formulae.



**[0045]** The onium salt compounds include, for example, onium salts such as diazonium salts described in S.I. Schlesinger, Photogr. Sci. Eng., 18,387 (1974), T.S.Bal et al, Polymer, 21, 423 (1980), ammonium salts described in the specification of USP No. 4069055, JP-A No. 4-365049, etc., phosphonium salts described in USP Nos. 4069055, and 4069056, iodonium salts described in each of the specification of EP No. 104143, USP Nos. 339049 and 410201, and JP-ANos. 2-150848, and 2-296514, sulfonium salts described in each of the specifications of EP Nos. 370693, 390214, 233567, 297443, 297442, USP Nos. 4933377, 161811, 410201, 339049, 4760013, 4734444, and 2833827, DEP Nos. 2904626, 3604580, and 3604581, selenonium salts described in J.V.Crivello et al, Macromolecules, 10(6), 1307 (1977), J.V. Crivello et al, J.Polymer Sci., Polymer Chem. Ed., 17, 1047 (1979), and arsonium salts described in C.S. Wen et al, Teh, Proc. Conf. Rad. Curing ASIA, p478 Tokyo, Oct (1988).

**[0046]** Particularly, they include the oxim ester compounds or the diazonium salts, iodonium salts, and sulfonium salts in view of the reactivity and stability. In the invention, the onium salts function not as an acid generator but as an ionic radical polymerization initiator.

**[0047]** The onium salts used suitably in the invention are onium salts represented by the following general formulae (RI-I) to (RI-III).

$$\mathrm{Ar}_{11}—\overset{+}{\mathrm{N}}\equiv\mathrm{N} \qquad \mathrm{Z}_{11}^{-} \qquad (\mathrm{RI-I})$$

$$\mathrm{Ar}_{21}—\overset{+}{\mathrm{I}}—\mathrm{Ar}_{22} \qquad \mathrm{Z}_{21}^{-} \qquad (\mathrm{RI-II})$$

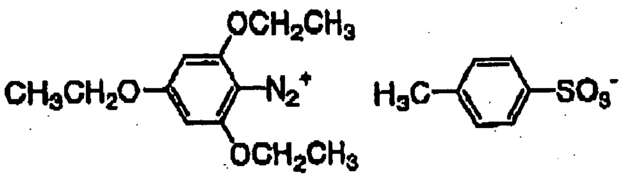
(RI-III)

**[0048]** In the formula (RI-I), $Ar_{11}$ represents an aryl group of 20 or less carbon atoms which may have 1 to 6 substituents and preferred substituents include alkyl groups of 1 to 12 carbon atoms, alkenyl groups of 1 to 12 carbon atoms, alkynyl groups of 1 to 12 carbon atoms, aryl groups of 1 to 12 carbon atoms, alkoxy groups of 1 to 12 carbon atoms, aryloxy groups of 1 to 12 carbon atoms, halogen atoms, alkyl amino groups of 1 to 12 carbon atoms, dialkyl amino groups of 1 to 12 carbon atoms, alkyl amido groups or aryl amido groups of 1 to 12 carbon atoms, carbonyl group, carboxyl group, cyano group, sulfonyl group, thioalkyl group of from 1 to 12 carbon atoms, and thioaryl group of from 1 to 12 carbon atoms. $Z_{11}^-$ represents a monovalent anion and includes specifically, halogen ion, perchlorate ion, hexafluorophosphate ion, tetrafluoroborate ion, sulfonate ion, sulfinate ion, thiosulfonate ion, and sulfate ion. Among them, persulfate ion, hexafluorophosphate ion, tetrafluoroborate ion, sulfanate ion and sulfinate ion are preferred in view of the stability.

**[0049]** In the formula (RI-II), $Ar_{21}$ and $Ar_{22}$ each represents independently an aryl group of 20 or less carbon atoms, which may have 1 to 6 substituents and preferred substituents include alkyl groups of 1 to 12 carbon atoms, alkenyl groups of 1 to 12 carbon atoms, alkynyl groups of 1 to 12 carbon atoms, aryl groups of 6 to 12 carbon atoms, alkoxy groups of 1 to 12 carbon atoms, aryloxy groups of 1 to 12 carbon atoms, halogen atom, alkylamino groups of 1 to 12 carbon atoms, dialkylamino groups of 1 to 12 carbon atoms, alkyl amido groups or arylamide groups of 1 to 12 carbon atoms, carbonyl group, carboxyl group, cyano group, sulfonyl group, thioalkyl groups of 1 to 12 carbon atoms, and thioaryl groups of 1 to 12 carbon atoms. $Z_{21}^-$ represents a monovalent anion and includes specifically, halogen ion, perchlorate ion, hexafluorophosphate ion, tetrafluoroborate ion, sulfonate ion, sulfinate ion, thiosulfonate ion, and sulfate ion. Among them, persulfate ion, hexafluorophosphate ion, tetrafluoroborate ion, sulfanate ion, and sulfinate ion are preferred in view of the stability.

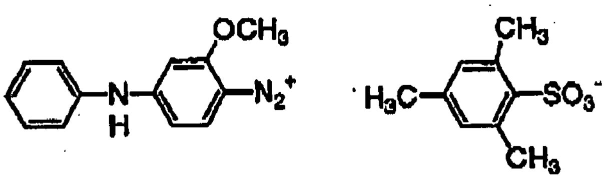
**[0050]** In the formula (RI-III), $R_{31}$, $R_{32}$, and $R_{33}$ each represents independently an aryl group, alkyl group, alkenyl group, or alkynyl group of 20 or less carbon atoms which may have 1 to 6 substituents. Among them, the aryl group is preferred in view of the reactivity and the stability. The substituent includes alkyl groups of 1 to 12 carbon atoms, alkenyl groups of 1 to 12 carbon atoms, alkynyl groups of 1 to 12 carbon atoms, aryl groups of 6 to 12 carbon atoms, alkoxy groups of 1 to 12 carbon atoms, aryloxy groups of 6 to 12 carbon atoms, halogen atoms, alkyl amino groups of 1 to 12 carbon atoms, dialkyl amino groups of 1 to 12 carbon atoms, alkyl amide groups or aryl amide groups of 1 to 12 carbon atoms, carbonyl group, carboxyl group, cyano group, sulfonyl group, thioalkyl group of 1 to 12 carbon atoms, and thioaryl groups of 6 to 12 carbon atoms. $Z_{31}$- represents a monovalent anion and includes specifically, halogen ion, perchlorate ion, hexafluorophosphate ion, tetrafluoroborate ion, sulfonate ion, sulfinate ion, thiosulfonate ion, sulfate ion and carboxylate. Among them, persulfate ion, hexafluorophosphate ion, tetrafluoroborate ion, sulfanate ion, sulfinate ion and carboxylate ion are preferred in view of the stability. More preferred include carboxylic acid ions described in JP-A No. 2001-343742 and particularly preferred include carboxylic acid ions described in JP-A No. 2002-148790.

**[0051]** Specific examples of the onium salt compounds suitable to the invention are to be described, but they are not restrictive.



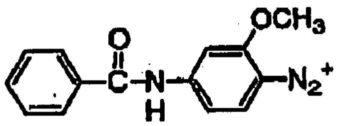
(N-1)

$PF_6^-$ (N-2)


(N-3)

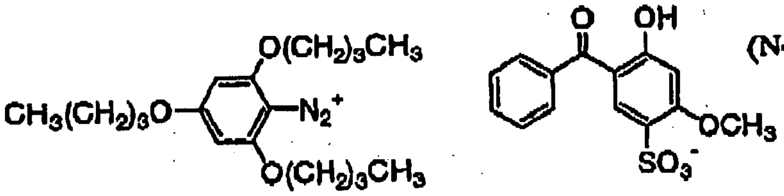
$ClO_4^-$ (N-4)

$PF_6^-$ (N-5)

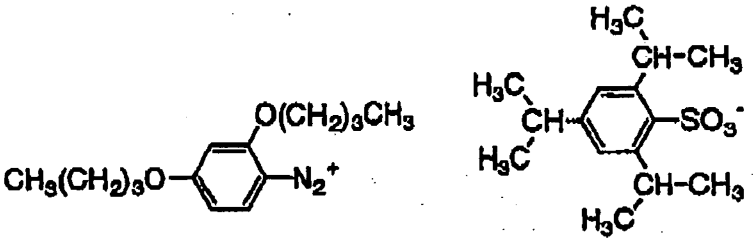


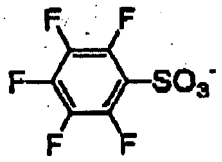
$CF_3SO_3^-$ (N-6)

$BF_4^-$ (N-7)

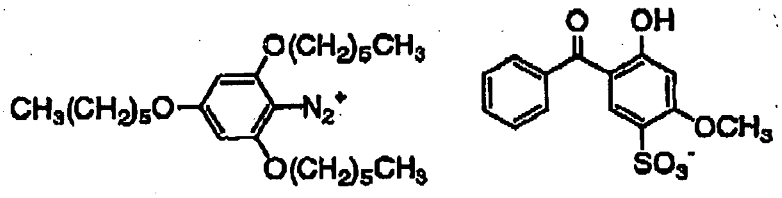

(N-8)

$ClO_4^-$ (N-9)


(N-10)

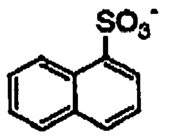

(N-11)

$PF_6^-$ (N-12)



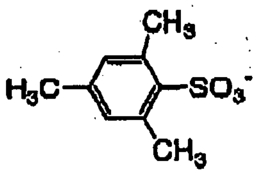
(N-13)

$ClO_4^-$ (N-14)



(N-15)

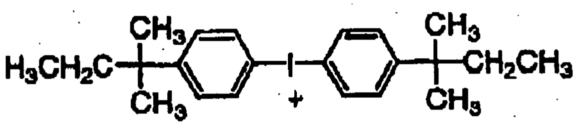
$PF_6^-$ (N-16)



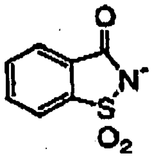
(N-17)

(I-1)

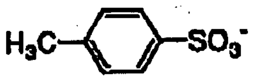
$PF_6^-$ (I-2)



$PF_6^-$ (I-3)

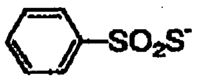


(I-9)



(I-4)

$ClO_4^-$ (I-5)



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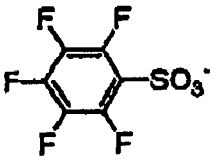

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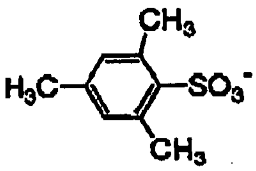

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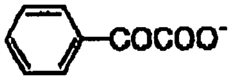
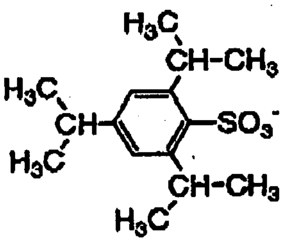
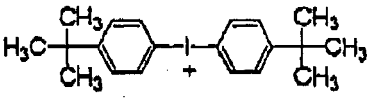


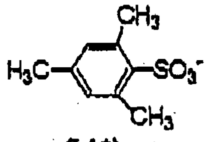
(I-7)

$CF_3SO_3^-$ (I-8)



(I-12)





(I-13)

$ClO_4^-$

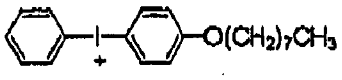
(I-14)

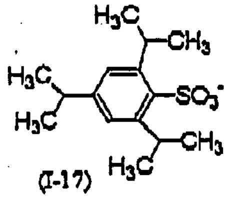
$PF_6^-$

(I-15)

$C_4F_9SO_3^-$

(I-16)





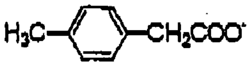
(I-17)

$CF_3COO^-$

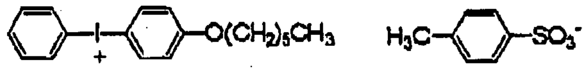
(I-18)

$CF_3SO_3^-$

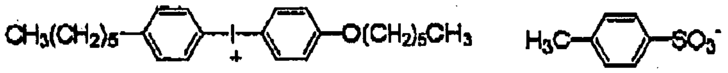
(I-19)



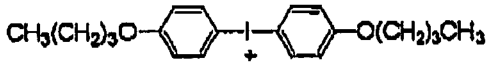
(I-20)



(I-21)

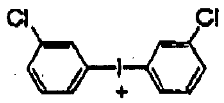


(I-22)



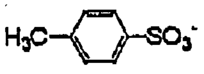
$C_4F_9SO_3^-$

(I-23)

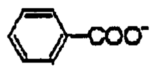


$BF_4^-$

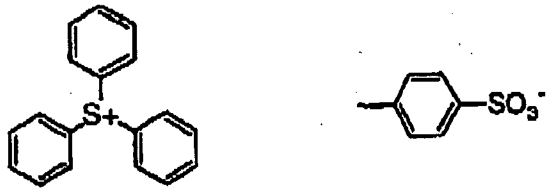
(I-24)



(I-25)



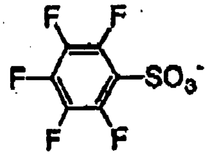
(I-26)



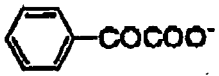
(S-1)

$PF_6^-$ (S-3)

$ClO_4^-$ (S-3)

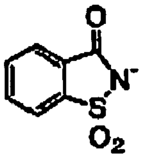


(S-4)

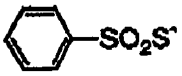


(S-5)

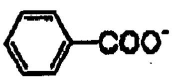
$CF_6SO_3^-$ (S-6)



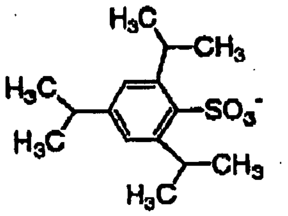
(S-7)



(S-8)



(S-9)



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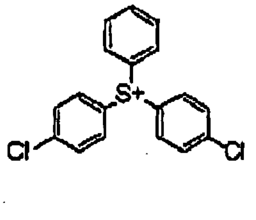
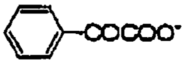
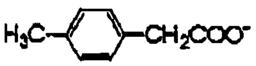




(S-11)



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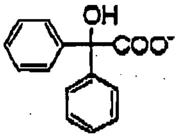

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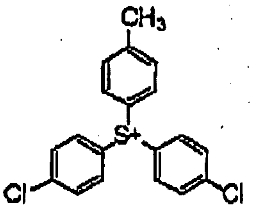

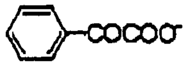

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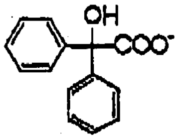
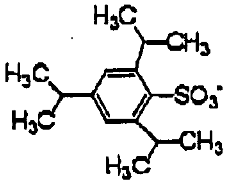
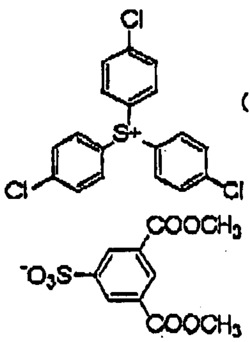


(S-15)

$BF_4^-$ (S-16)



(S-17)



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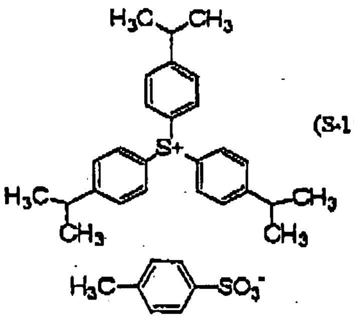


(S-19)

**[0052]** The polymerization initiators can be added to the entire solids constituting the photosensitive layer at a ratio, preferably, from 0.1 to 50 mass%, more preferably, from 0.5 to 30 mass%, particularly preferably, from 1 to 20 mass%. Within the range, good sensitivity and favorable less contamination property for non-image areas during printing can be obtained. The polymerization initiators may be used each alone or two or more of them may be used in combination. Further, the polymerization initiators may be added together with other ingredients in one identical layer, or may be added to a layer separately.

< Polymerizable compound >

**[0053]** The polymerizable compound used for the photosensitive layer in the invention is an addition polymerizable compound having at least one ethylenically unsaturated double bond and selected from compounds having at least one and, preferably, two or more of ethylenically unsaturated bonds. A group of such compounds is well-known in the relevant field of industry and they can be used with no particular restriction in the invention. They have chemical forms, for example, of monomers and prepolymers, that is, dimmers, trimers and oligomers, or mixtures thereof and copolymers thereof. Examples of the monomers and the copolymers thereof include unsaturated carboxylic acids (for example, acrylic acid, methacrylic acid, itaconic acid, protonic acid, isocrotonic acid, and maleic acid), or esters and amides thereof. Preferably, esters of unsaturated carboxylic acids and aliphatic polyhydric alcohol compounds or amides of unsaturated carboxylic acids and aliphatic polyvalent amine compounds are used. Further, addition reaction products of unsaturated carboxylic acid esters or amides having nucleophilic substituents such as hydroxyl group, amino group or mercapto group and monofunctional and polyfunctional isocyanates or epoxides, and dehydrogenating condensation reaction products thereof with monofunctional or polyfunctional carboxylic acids are also used suitably. Addition reaction products of unsaturated carboxylic acid esters or amides having electric substituents such as isocyanate group or epoxy group and monofunctional or polyfunctional alcohols, amines or thiols and, further, substitution reaction products of unsaturated carboxylic acid esters or amides having splitting substituents such as halogen group or tosyloxy group and monofunctional or polyfunctional group, amines or thiols are also suitable. Further, as other examples, a group of compounds formed by substituting the unsaturated carboxylic acids with unsaturated phosphoric acids, styrene, or vinyl ether can also be used.

**[0054]** Specific examples of the monomer of the aliphatic polyhydric alcohol compound and an unsaturated carboxylic acid include, for example, acrylic acid esters such as ethylene glycol diacrylate, triethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol diacrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, trimethylol propane triacrylate, trimethylol propane tri (acryloyloxypropyl) ether, trimethylol ethane triacrylate, hexanediol diacrylate, 1,4-cyclohexane diol diacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol diacrylate, dipentaerythritol hexaacrylate, sorbitol triacrylate, sorbitol tetraacrylate, sorbitol pentaacrylate, sorbitol hexaacrylate, tri(acryloyloxyethyl)isocyanurate, isocyanuric ethylene oxide (EO) modified triacrylate, polyester acrylate oligomer, and isocyanuric EO-modified triacrylate.

**[0055]** Methacrylic acid esters include, for example, tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, neopentyl glycol dimethacrylate, trimethylol propane trimethacrylate, trimethylol ethane trimethacryrate, ethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, hexanediol dimethacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol dimethacrylate, dipentaerythritol hexamethacrylate, sorbitol trimethacrylate, sorbitol tetramethacrylate, bis[p-(3-methacryloxy-2-hydroxypropoxy)phenyl] dimethylmethane, and bis[p-methacryloxyethoxy)phenyl]dimethyl methane.

**[0056]** Itaconic acid esters include, for example, ethylene glycol diitaconate, propylene glycol diitaconate, 1,3-butanediol diitaconate, 1,4-butanediol diitaconate, tetramethylene glycol diitaconate, pentaerythritol diitaconate, and sorbitol tetraitaconate. The crotonic acid esters include, for example, ethyleneglycol dicrotonate, tetramethylene glycol dicrotonate, pentaerythritol dicrotonate, and sorbitol tetradicrotonate. Isocrotonic acid esters include, for example, ethyleneglycol diisocrotonate, pentaerythritol diisocrotonate, sorbitol tetraisocrotonate. Maleic acid esters include, for example, ethylene glycol dimaleate, triethylene glycol dimaleate, pentaerythritol dimaleate, and sorbitol tetramaleate.

**[0057]** As examples of other esters, aliphatic alcoholic esters described, for example, in each of the publications of JP-B No. 51-47334, and JP-A No. 57-196231, those having aromatic skeleton described in each of the publications of JP-A Nos. 59-5240, 59-5241, and 2-226149, and those containing amino groups described in JP-A No. 1-165613 can also be used suitably. Further, the ester monomers described above can be used also as a mixture.

**[0058]** Further, specific examples of the monomers of the amides of aliphatic polyvalent amine compounds and the unsaturated carboxylic acids include, for example, methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, 1,6-hexamethylene bis-metharylamide, diethylene triamine trisacrylamide, xylylene bisacrylamide, and xylilene bismethacrylamide. Examples of other preferred amide type monomers include those having the cyclohexylene structure described in JP-B No. 54-21726.

**[0059]** Further, urethane type addition polymerizable compounds prepared by using an addition reaction of isocyanate and hydroxyl group are also preferred and specific examples thereof include vinyl urethane compounds containing two or more polymerizable vinyl groups in one molecule in which a vinyl monomer containing a hydroxyl group represented by the following general formula (A) is added to a polyisocyanate compound having two or more isocyanate groups in one molecule described, for example, in JP-B No. 48-41708.

$$CH_2{=}C\,(R_4)\,COOCH_2CH\,(R_5)\,OH \qquad (A)$$

(in which $R_4$ and $R_5$ each represents H or $CH_3$)

**[0060]** Further, urethane acrylates described in JP-A No. 51-37193, JP-B Nos. 2-32293, and 2-16765. and urethane compounds having ethylene oxide skeletons described in JP-B Nos. 58-49860, 56-17654, 62-39417, and 62-39418 are also suitable. Further, a photopolymerizable composition of extremely excellent in the sensitizing speed can be obtained by using addition polymerizable compounds having an amino structure or sulfide structure in the molecule as described in JP-A Nos. 63-277653, 63-260909, and 1-105238.

**[0061]** Other examples include polyfunctional acrylates or methacrylates such as polyester acrylates and epoxy acrylates formed by reacting epoxy resins and (meth)acrylic acid as described in each of the publications of JP-A No. 48-64183, 49-43191, and 52-30490. Further, they also include specified unsaturated compounds described in each of the publications of JP-B Nos. 46-43946, 1-40337, and 1-40336, and vinyl phosphonic type compounds described in JP-A No. 2-25493. Further, the structure containing a perfluoroalkyl group described in JP-A No. 61-22048 is sometimes used suitably. Further, those introduced in the Journal of Japan Adhesive Society Vol. 20, No. 7, 300 - 308 pages (1984) as photocurable monomers and oligomers can also be used.

**[0062]** For the polymerizable compounds, the structure thereof, details for the way of use, such as sole use or use in combination, and addition amount can be set optionally in accordance with the design performance of a final lithographic printing plate. For example, they are selected with the following viewpoint.

**[0063]** With the viewpoint of the sensitivity, a structure with a more content of unsaturated groups per one molecule is preferred and di or higher functionality is often preferred. Further, for increasing the strength of an image area, that is, a hardened film, those of tri- or higher functionality are preferred. Further, a method of controlling both the sensitivity and the strength by using those having different functionality and different polymerizable groups (for example, acrylic acid ester, methacrylic acid ester, styrenic compound, and vinyl etheric compound) in combination is also effective.

**[0064]** Further, selection and method of use for the polymerizable compound are also important factor for the compatibility and dispersibility relative to other ingredients in the photosensitive layer (for example, binder polymer, polymerization initiator, and colorant) and, for example, the solubility can sometimes be improved by the use of a low purity compound or combined use of two or more kinds of them. Further, with an aim of improving the adhesion with the support, a specified structure can also be selected.

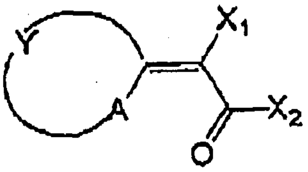
**[0065]** The polymerizable compound is used in the photosensitive layer within a range, preferably, from 5 to 80 mass% and, more preferably, from 25 to 75 mass%. Further, they may be used each alone or in combination of two or more of them. In addition, for the method of using the polymerizable compound, appropriate structure, blend, and addition amount can optionally be selected with a viewpoint of the degree of inhibition for polymerization with oxygen, resolution power, fogging property, change of refractive index, and surface adhesivity and, further, layer constitution or coating method such as undercoating or topcoating can also be practiced depending on the case.

## < sensitizing Dye >

**[0066]** The photosensitive layer of the invention can contain a sensitizing dye having an absorption wavelength corresponding to the wavelength of a laser used for exposure. Particularly, preferred sensitizing dyes include sensitizing dyes and IR-absorbent absorbing a light at 360 nm to 450 nm with a viewpoint of enabling to handle a lithographic printing plate in a bright room or under a yellow light.

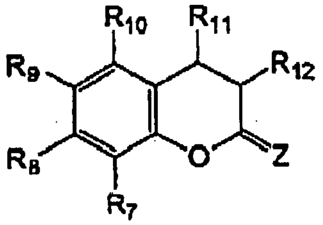
### (A) Sensitizing dye absorbing light at 360 nm to 450 nm

**[0067]** The sensitizing dye absorbing a light at 360 nm to 450 nm used in the invention preferably has an absorption maximum in a wavelength region of from 360 nm to 450 nm. Such sensitizing dyes include, for example, merocyanine dyes represented by the following general formula (I), benzopyranes and coumarines represented by the following general formula (II), aromatic ketones represented by the following general formula (III), and anthracenes represented by the following general formula (IV).

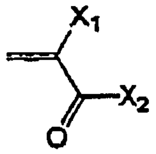


(I)

(where A represents an S atom or $NR_6$, $R_6$ represents a monovalent non-metal atom group, Y represents a non-metal atom group that forms a basic nuclei of a dye in corporation with adjacent A and adjacent carbon atom, $X_1$ and $X_2$ each represents independently a monovalent non-metal atom group, and $X_1$ and $X_2$ may joint to each other to form an acidic nuclei of a dye.

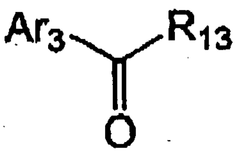


(II)



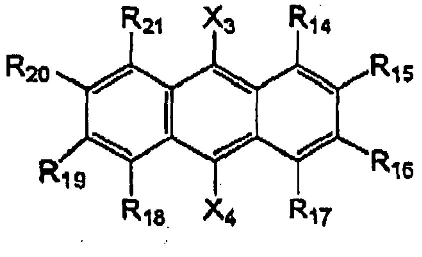
(I')

(where =Z represents a carbonyl group, thiocarbonyl group, imino group, or alkylidene group represented by the partial structural formula (I'), $X_1$ and $X_2$ have the same meanings as those in the general formula (II), and $R_7$ to $R_{12}$ each represents independently a monovalent non-metal atom group).



(III)

(where $Ar_3$ represents an aromatic group or heteroaromatic group which may have a substituent and $R_{13}$ represents a monovalent non-metal atom group. A more preferred $R_{13}$ is an aromatic group or heteroaromatic group, and $Ar_3$ and $R_{13}$ may join to each other to form a ring).



(IV)

($X_3$, $X_4$, and $R_{14}$ to $R_{21}$ each represents independently a monovalent non-metal atom group, and more preferred $X_3$, $X_4$ are electron donating groups having a negative Hammett's substituent constant).

**[0068]** Preferred examples of the monovalent non-metal atom groups represented by $X_1$ to $X_4$ and $R_6$ to $R_{21}$ in the general formulae (I) to (IV) include hydrogen atom, alkyl groups (for example, methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, hexadecyl group, octadecyl group, eicosyl group, isopropyl group, isobutyl group, s-butyl group, t-butyl group, isopentyl group, neopentyl group, 1-methylbutyl group, isohexyl group, 2-ethylhexyl group, 2-methylhexyl group, cyclohexyl group, cyclopentyl group, 2-norbornyl group, chloromethyl group, bromomethyl group, 2-chloroethyl group, trifluoromethyl group, methoxymethyl group, methoxyethoxyethyl group, allyloxymethyl group, phenoxymethyl group, methylthiomethyl group, tollylthiomethyl group, ethylaminoethyl group, diethylaminopropyl group, morpholinopropyl group, acetyloxymethyl group, benzoyloxymethyl group, N-cyclohexyl carbamoyloxyethy group, N-phenylcarbamoyloxyethyl group, acetylaminoethyl group, N-methylbenzoylaminopropyl group, 2-oxoethyl group, 2-oxopropyl group, carboxypropyl group, methoxycarbonylethyl group, allyloxycarbonyl butyl group, chlorophenoxycarbonylmethyl group, carbamoylmethyl group, N-methylcarbamoylethyl group, N, N-dipropylcarbamoylmethyl group, N-(methoxyphenyl)carbamoylethyl group, N-methyl-N-(sulfophenyl)carbamoylmethyl group, sulfobutyl group, sulfonatobutyl group, sulfamoylbutyl group, N-ethylsulfamoylmethyl group, N,N-dipropylsulfamoylpropyl group, N-tollylsulfamoyl propyl group, N-methyl-N-(phosphonophenyl)sulfamoyloctyl group, phosphonobutyl group, phosphonatehexyl group, diethylphosphonobutyl group, diphenyl phosphonopropoyl group, methylphosphonobutyl group, methylphosphonatobutyl group, tollylphosphonohexyl group, tollylphosphonatohexyl group, phosphonooxypropyl group, phosphonatooxybutyl group, benzyl group, phenetyl group, $\alpha$-methylbenzyl group, 1-methyl-1-phenylethyl group, p-methylbenzyl group, cinnamyl group, allyl group, 1-propenylmethyl group, 2-butenyl group, 2-methylallyl group, 2-methylpropenylmethyl group, 2-propynyl group, 2-butynyl group, and 3-butynyl group), aryl groups (for example, phenyl group, biphenyl group, naphthyl group, tollyl group, xylyl group, mesityl group, cumenyl group, chlorophenyl group, bromophenyl group, chloromethylphenyl group, hydroxyphenyl group, methoxyphenyl group, ethoxyphenyl group, phenoxyphenyl group, acetoxyphenyl group, benzoyloxyphenyl group, methylthiophenyl group, phenylthiophenyl group, methylaminophenyl group, dimethylaminophenyl group, acetylaminophenyl group, carboxyphenyl group, methoxycarbonylphenyl group, ethoxyphenylcarbonyl group, phenoxycarbonylphenyl group, N-phenylcarbamoylphenyl group, phenyl group, cyanophenyl group, sulfophenyl group, sulfonatophenyl group, phosphonophenyl group, and phosphonatophenyl group), heteroaryl groups (for example, thiophene, thiathrene, furan, pyran, isobenzofuran, chromene, xanethene, phenoxadine, pyrrole, pyrazole, isothiazole, isooxazole, pyrazine, pirimidine, pyridazine, indolidine, isoindolidine, indoyl, indazole, purine, quinolizine, isoquinoline, phthalazine, naphthyridine, quinazoline, sinoline, pteridine, carbazole, carboline, phenanthrene, acridine, perimidine, phenanthroline, phthalazine, phenalzadine, phenoxazine furazane, and phenoxadine), alkenyl groups (for example, vinyl group, 1-propenyl group, 1-butenyl group, cinnamyl group, and 2-chloro-1-ethenyl group), alkynyl groups (for example, ethynyl group, 1-propinyl group, 1-butynyl group, and trimethylsilyl ethynyl group), halogen atoms (-F, -Br-, -Cl, -I), hydroxyl group, alkoxy group, aryloxy group, mercapto group, alkylthio group, arylthio group, alkyldithio group, arylthio group, amino group, N-alkylamino group, N,N-dialkylamino group, N-arylamino group, N,N-diarylamino group, N-alkyl-N-arylamino group, acyloxy group, carbamoyloxy group, N-alkylcarbamoyloxy group, N-arylcarbamoyloxy group, N,N-dialkylcarbamoyloxy group, N,N-diarylcarbamoyloxy group, N-alkyl-N-arylcarbamoyloxy group, alkylsulfoxy group, arylsulfoxy group, acylthio group, acylamino group, N-alkylacylamino group, N-arylacylamino group, ureido group, N'-alkylureido group, N',N'-dialkylureido group, N'-arylureido group, N',N'-diarylureido group, N'-alkyl-N'-arylureido group, N'-alkylureido group, N-arylureido group, N'-alkyl-N-alkylureido group, N'-alkyl-N-arylureido group, N',N'-dialkyl-N-alkylureido group, N',N'-dialkyl-N-aryluzeido group, N'-aryl-N-alkylureido group, N'-aryl-N-arylureido group, N',N'-diaryl-N-alkylureido group, N'-N'-diaryl-N-arylureido group, N' -alkyl-N'-aryl-N-alkylureido group, N'-alkyl-N'-axyl-N-arylureido group, alkoxycarbonylamino group, aryloxycarbonylamino group, N-alkyl-N-alkoxycarbonylamino group, N-alkyl-N-aryloxycarbonylamino group, N-aryl-N-alkoxycarbonylamino group, N-aryl-N-aryloxycarbonylamino group, formyl group, acyl group, carboxyl group, alkoxycarbonyl group, aryloxycarbonyl group, carbamoyl group, N-alkylcarbamoyl group, N,N-dialkylcarbamoyl group, N-arylcarbamoyl group, N,N-diarylcarbamoyl group, N-alkyl-N-arylcarbamoyl group, alkylsulfinyl group, arylsulfinyl group, alkylsulfonyl group, arylsulfonyl group, sulfo group ($-SO_3H$ and conjugated base group thereof (hereinafter referred to as sulfonato group), alkoxysulfonyl group, aryloxysulfonyl group, sulfinamoyl group, N-alkylsulfinamoyl group, N,N-dialkylaulfinamoyl group, N-arylsulfinamoyl group, N,N-diarylsulfinamoyl group, N-alkyl-N-arylsulfinamoyl group, sulfamoyl group, N-alkylsulfamoyl group, N,N-dialkylsulfamoyl group, N-arylsulfamoyl group, N, N-diarylsulfamoyl group, N-alkyl-N-arylsulfamoyl group, phosphono group ($-PO_3H_2$) and a conjugated base group thereof (hereinafter referred to as phosphonato group), dialkylphosphono group ($-PO_3(alkyl)_2$), diarylphosphono group ($-PO_3(aryl)_2$), alkylarylphosphono group ($-PO_3(alkyl)aryl$), monoalkylphosphono group ($-PO_3H(alkyl)$) and a conjugated base group thereof (hereinafter referred to as alkylphosphonato group), monoarylphosphono group ($-PO_3H(aryl)$ and a conjugated base group thereof (hereinafter referred to as arylphosphonato group), phosphonooxy group ($-OPO_3H_2$) and conjugated base group thereof (hereinafter referred to as phosphonatooxy group), dialkylphosphonooxy group ($-OPO_3(alkyl)_2$), diarylphosphonooxy group ($-OP_3(aryl)_2$), alkylarylphosphonooxy group ($-OPO_3(alkyl)\ (aryl)$), monoalkylphosphonooxy group ($-OPO_3H(alkyl)$) and a conjugated base group thereof (hereinafter referred to as alkylphosphonatooxy group), monoarylphosphonooxy group ($-OPO_3H(aryl)$) and a conjugated base group thereof (hereinafter referred to as arylphosphonatooxy group), cyano group, and nitro group. Among the substituents described above, hydrogen atom, alkyl group, aryl group, halogen atom, alkoxy group, and acyl group are particularly preferred.

**[0069]** As the basic nuclei of a dye formed by incorporation of Y with an adjacent A and an adjacent carbon atom in the general formula (I) includes 5,6,7-membered nitrogen-containing and sulfur-containing heterocyclic rings which are, preferably, 5- or 6-membered heterocyclic rings.

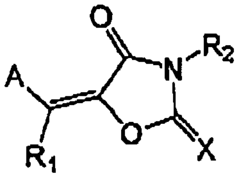
**[0070]** As the examples of the nitrogen-containing heterocyclic rings, any of those known to constitute the basic nuclei in the methalocyanine dyes described in L.G.Brooker et al., J.Am. Chem. Soc., 73, 5326-5358(1951) can be used suitably. Specific examples include thiazoles (for example, thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4,5-di(p-methoxyphenylthiazole), 4-(2-thienyl)thiazole), benzothiazoles (for example, benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methyl benzothiazole, 6-methyl benzothiazole, 5-bromo benzothiazole, 4-phenyl benzothiazole, 5-phenyl benzothiazole, 4-methoxy benzothiazole, 5-methoxy benzothiazole, 6-methoxy benzothiazole, 5-iodo benzothiazole, 6-iodo benzothiazole, 4-ethoxy benzothiazole, 5-ethoxy benzothiazole, tetrahydro benzothiazole, 5,6-dimethoxy benzothiazole, 5,6-dioxymethylene benzothiazole, 5-hydroxy benzothiazole, 6-hydroxy benzothiazole, 6-dimethylamino benzothiazole, 5-ethoxycarbonyl benzothiazole), naphthothiazoles (for example, naphtho[1,2]thiazole, naphtho[2,1]thiazole, 5-methoxynaphtho[2,1]thiazole, 5-ethoxynaphtho[2,1]thiazole, 8-mathoxynaphtho[1,2]thiazole, and 7-methoxynaphtho[1,2]thiazole), thianaphteno-7',6',4,5-thiazoles (for example, 4'-methoxythianaphteno-7',6',4,5-thiazole), oxazoles (for example, 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, and 5-phenyloxazole), benzooxazoles (benzooxazole, 5-chloro benzooxazole, 5-methyl benzooxazole, 5-phenyl benzooxazole, 6-methyl benzooxazole, 5,6-dimethyl benzooxazole, 4,6-dimethyl benzooxazole, 6-methoxy benzooxazole, 5-methoxy benzooxazole, 4-ethoxy benzooxazole, 5-chloro benzooxazole, 6-methoxy benzooxazole, 5-hydroxy benzooxazole, and 6-hydroxy benzooxazole), naphthooxazoles (for example, naphtha [1,2]oxazole, and naphtha [2,1]oxazole), selenazoles (for example, 4-methylselenazole, and 4-phenylselenazole), benzo selenazoles (for example, benzo selenazole, 5-chloro selenazole, 5-methoxybenzo selenazole, 5-hydroxybenzo selenazole, and tetrahydrobenzo selenazole, naphthoselenazoles (for example, naphtha[1,2]selenazole), and naphtha[2,1] selenazole, thiazolines (for example, thiazoline, and 4-methylthiazoline), 2-quinolines (for example, quinoline, 3-methylquinoline, 5-methylquinoline,7-methylquinoline, 8- methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, and 8-hydroxyquinoline), 4-quinolines (for example, quinoline, 6-methoxyquinoline, 7-methylquinoline and 8-methylquinoline), 1-isoquinolines (for example, isoquinoline, and 3,4-dihydroisoquinoline), 3-isoquinolines (for example, isoquinoline), benzimidazoles (for example, 1,3-dimethylbenzimidazole, and 1-ethyl-3-phenylbenzimidazole), 3,3-dialkylindolenines (for example, 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, and 3,3,7-trimethylindolenine), 2-pyridines (for example, pyridine, and 5-methylpyridine), and 4-pyridine (for example, pyridine).

**[0071]** Further, examples of the sulfur-containing heterocyclic rings include dithiol partial structures in the dyes described for example in JP-A No. 3-296759.

**[0072]** Specific examples include benzodithiols (for example, benzodithiol, 5-t-butyl benzodithiol, and 5-methyl benzodithiol), naphtho dithiols (for example, naphtho[1,2] dithiols, and naphtho[2,1]dithiol), dithiols (for example, 4,5-dimethyl dithiols, 4-phenyl dithiols, 4-methoxycarbonyl dithiols, 4,5-dimethoxycarbonylbenzo dithiols, 4,5-ditgrifluoromethyl dithiols, 4,5-dicyano dithiols, 4-methoxycarbonyl methyl dithiols, and 4-carboxymethyl dithiols).

**[0073]** In the descriptions used for explaining the heterocyclic rings described above, while names for the heterocyclic mother skeletons have been customarily used for the sake of convenience in a case where they constitute a partial basic skeleton structure of sensitizing dyes, they are introduced in the form of an alkylidene type substituent with the degree of unsaturation being decreased by the number of one, for example, as a 3-substituted-2(3H)-benzothiazolilidene group in a case of the benzothiazole skeleton.

**[0074]** Among the sensitizing dyes as the compounds having absorption maximum in the wavelength region from 360 to 450 nm, preferred dyes with a view point of high sensitivity are those dyes represented by the following general formula (V).



(V)

(in the general formula (V), A represents an aromatic ring or hetero ring which may have a substituent, and X represents an oxygen atom, sulfur atom, or =N($R_3$) . $R_1$, $R_2$ and $R_3$ each represents a hydrogen atom or monovalent non-metal atoms, and A and $R_1$, and $R_2$ and $R_3$ may be joined to each other for forming an aliphatic or aromatic ring).

**[0075]** The general formula (V) is to be described more specifically. $R_1$, $R_2$ and $R_3$ each represents independently a hydrogen atom or a monovalent non-metal atom group and, preferably, represents a substituted or not-substituted alkyl group, a substituted or not-substituted alkenyl group, a substituted or not-substituted aryl group, a substituted or not-substituted heteroaryl group, a substituted or not-substituted alkoxyl group, a substituted or not-substituted alkylthio group, hydroxyl group or halogen atom.

**[0076]** Preferred examples of $R_1$, $R_2$ and $R_3$ are to be described specifically. Examples of preferred alkyl group include linear, branched and cyclic alkyl groups of 1 to 20 carbon atoms and specific examples thereof include methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, hexadecyl group, octadecyl group, eicosyl group, isopropyl group, isobutyl group, s-butyl group, t-butyl group, isopentyl group, neopentyl group, 1-methylbutyl group, isohexyl group, 2-ethylhexyl group, 2-methylhexyl group, cyclohexyl group, cyclopentyl group, and 2-norbornyl group. Among them, linear alkyl groups of 1 to 12 carbon atoms, branched alkyl groups of 3 to 12 carbon atoms, and cyclic alkyl groups of 5 to 10 carbon atoms are more preferred.

**[0077]** As the substituents for the substituted alkyl groups, monovalent non-metal atom groups excluding hydrogen are used and preferred examples include halogen atoms (-F, -Br-, -Cl, - I), hydroxyl group, alkoxy group, aryloxy group, mercapto group, alkylthio group, arylthio group, alkyldithio group, arylthio group, amino group, N-alkylamino group, N, N-dialkylamino group, N-arylamino group, N,N-diarylamino group, N-alkyl-N-arylamino group, acyloxy group, carbamoyloxy group, N-alkylcarbamoyloxy group, N-arylcarbamoyloxy group, N,N-dialkylcarbamoyloxy group, N,N-diarylcarbamoyloxy group, N-alkyl-N-arylcarbamoyloxy group, alkylsulfoxy group, arylsulfoxy group, acylthio group, acylamino group, N-alkylacylamino group, N-arylacylamino group, ureido group, N'-alkylureido group, N',N'-dialkylureido group, N'-arylureido group, N',N'-diarylureido group, N'-alkyl-N'-arylureido group, N'-alkylureido group, N-arylureido group, N'-alkyl-N-alkylureido group, N'-alkyl-N-arylureido group, N',N'-dialkyl-N-alkylureido group, N',N'-dialkyl-N-arylureido group, N'-aryl-N-alkylureido group, N'-aryl-N-arylureido group, N',N'-diaryl-N-alkylureido group, N'-N'-diaryl-N-arylureido group, N'-alkyl-N'-aryl-N'-alkylureido group, N'-alkyl-N'-aryl-N-arylureido group, alkoxycarbonylamino group, aryloxycarbonylamino group, N-alkyl-N-alkoxycarbonylamino group, N-alkyl-N-aryloxycarbonylamino group, N-aryl-N-alkoxycarbonylamino group, N-aryl-N-aryloxycarbonylamino group, formyl group, acyl group, carboxyl group, alkoxycarbonyl group, aryloxycarbonyl group, carbamoyl group, N-alkylcarbamoyl group, N,N-dialkylcarbamoyl group, N-arylcarbamoyl group, N,N-diarylcarbamoyl group, N-alkyl-N-arylcarbamoy7. group, alkylsulfinyl group, arylsulfinyl group, alkylsulfonyl group, arylsulfonyl group, sulfo group ($-SO_3H$) and a conjugated base group thereof (hereinafter referred to as sulfonato group), alkoxysulfonyl group, aryloxysulfonyl group, sulfinamoyl group, N-alkylsulfinamoyl group, N,N-dialkylsulfinamoyl group, N-arysulfinamoyl group, N,N-diarylsulfinamoyl group, N-alkyl-N-arylsulfinamoyl group, sulfamoyl group, N-alkylsulfamoyl group, N,N-dialkylsulfamoyl group, N-arylsulfamoyl group, N,N-diarylsulfamoyl group, N-alkyl-N-arylsulfamoyl group, phosphono group ($-PO_3H_2$) and a conjugated base group thereof (hereinafter referred to as phosphonato group), dialkylphosphono group ($-PO_3(alkyl)_2$), diarylphosphono group ($-PO_3(aryl)_2$), alkylarylphosphono group ($-PO_3(alkyl)aryl$), monoalkylphosphono group ($-PO_3H(alkyl)$) and a conjugated base group (hereinafter referred to as alkylphosphonato group), monoarylphosphono group ($-PO_3H(aryl)$ and a conjugated base group thereof (hereinafter referred to as arylphosphonato group), phosphonooxy group ($-OPO_3H_2$) and a conjugated base group thereof (hereinafter referred to as phosphonatooxy group), dialkylphosphonooxy group ($-OPO_3(alkyl)_2$), diarylphosphonooxy group ($-OP_3(aryl)_2$), alkylarylphosphonooxy group ($-OPO_3(alkyl)\ (aryl)$), monoalkylphosphonooxy group ($-OPO_3H(alkyl)$) and a conjugated base group thereof (hereinafter referred to as alkylphosphonatooxy group), monoarylphosphonooxy group ($-OPO_3H(aryl)$) and a conjugated base group thereof (hereinafter referred to as arylphosphonatooxy group), cyano group, nitro group, aryl group, heteroaryl group, alkenyl group, and alkynyl group.

**[0078]** Specific examples for the alkyl groups in the substituents include the alkyl groups described above. Specific examples for the aryl groups include phenyl group, biphenyl group, naphthyl group, tollyl group, xylyl group, mesityl group, cumenyl group, chlorophenyl group, bromophenyl group, chloromethylphenyl group, hydroxyphenyl group, methoxyphenyl group, ethoxyphenyl group, phenoxyphenyl group, acetoxyphenyl group, benzoyloxyphenyl group, methylthiophenyl group, phenylthiophenyl group, methylaminophenyl group, dimethylaminophenyl group, acetylaminophenyl group, carboxyphenyl group, methoxycarbonylphenyl group, ethoxyphenylcarbonyl group, phenoxycarbonylphenyl group, N-phenylcarbamoylphenyl group, phenyl group, cyanophenyl group, sulfophenyl group, sulfonatophenyl group, phosphonophenyl group, and phosphonatophenyl group.

**[0079]** As preferred heteroaryl groups as $R_1$, $R_2$ and $R_3$, monocyclic or polycyclic aromatic rings containing at least one of nitrogen, oxygen and sulfur atoms are used, and examples of particularly preferred heteroaryl groups include, for example, thiophene, thiathrene, furan, pyran, isobenzofuran, chromene, xanethene, phenoxadine, pyrrole, pyrazole, isothiazole, isooxazole, pyrazine, pirimidine, pyridazine, indolidine, isoindolidine, indoyl, indazole, purine, quinolizine, isoquinoline, phthalazine, naphthyridine, quinazoline, sinoline, pteridine, carbazole, carboline, phenanthrene, acridine, perimidine, phenanthroline, phthalazine, phenalzadine, phenoxazine, furazan, and phenoxadine, which may be further put to condensation with benzo ring or which may have a substituent.

**[0080]** Examples of preferred alkenyl groups for $R_1$, $R_2$ and $R_3$ include, for example, vinyl group, 1-propenyl group, 1-butenyl group, cinnamyl group, and 2-chloro-1-athenyl group, and examples of the alkynyl groups include, for example, ethynyl group, 1-propinyl group, 1-butynyl group, and trimethylsilyl ethynyl group. G1 in the acyl group ($G1CO^-$) includes hydrogen, as well as the alkyl groups and the aryl groups described above. Among the substituents, more preferred include halogen atoms (-F, -Br, -Cl, and -I), alkoxy group, aryloxy group, alkylthio group, arylthio group, N-alkylamino group, N,N-dialkylamino group, acyloxy group, N-alkylcatbamoyloxy group, N-arylcarbamoyloxy group, acylamino group, formyl group, acyl group, carboxyl group, alkoxycarbonyl group, aryloxycarbonyl group, carbamoyl group, N-alkylcarbamoyl group, N,N-dialkylcarbamoyl group, N-arylcarbamoyl group, N-alkyl-N-arylcarbamoyl group, sulfo group, sulfonato group, sulfamoyl group, N-alkylsulfamoyl group, N,N-dialkylsulfamoyl group, N-arylsulfamoyl group, N-alkyl-N-arylsulfamoyl group, phosphono group, phosphonato group, dialkyl phosphono group, diarylphosphono group, monoalkylphosphono group, alkylphosphonato group, monoarylphosphono group, arylphosphonato group, phosphonooxy group, phosphonatooxy group, aryl group, and alkenyl group.

**[0081]** On the other hand, the alkylene groups in the substituted alkyl groups include those formed by removing one of hydrogen atoms on the alkyl groups of 1 to 20 carbon atoms described above into a bivalent organic residue and, preferably, include linear alkylene groups of 1 to 12 carbon atoms, branched alkylene groups of 3 to 12 carbon atoms and cyclic alkylene groups of 5 to 10 carbon atoms.

**[0082]** Specific examples of preferred substituted alkyl groups as $R_1$, $R_2$ and $R_3$ obtained by the combination of the substituent and the alkylene group include chloromethyl group, bromomethyl group, 2-chloroethyl group, trifluoromethyl group, methoxymethyl group, methoxyethoxyethyl group, allyloxymethyl group, phenoxymethyl group, methylthiomethyl group, tollylthiomethyl group, ethylaminoethyl group, diethylaminopropyl group, morpholinopropyl group, acetyloxymethyl group, benzoyloxymethyl group, N-cyclohexyl carbamoyloxyethy group, N-phenylcarbamoyloxyethyl group, acetylaminoethyl group, N-methylbenzoylaminopropyl group, 2-oxoethyl group, 2-oxopropyl group, carboxypropyl group, methoxycarbonylethyl group, allyloxycarbonyl butyl group, chlorophenoxycarbonylmethyl group, carbamoylmethyl group, N-methylcarbamoylethyl group, N,N-dipropylcarbamoylmethyl group, N-(methoxyphenyl)carbamoylethyl group, N-methyl-N-(sulfophenyl)carbaxnoylmethyl group, sulfobutyl group, sulfonatobutyl group, sulfamoylbutyl group, N-ethylsulfamoylmethyl group, N,N-dipropylsulfamoylpropyl group, N-tollylsulfamoyl propyl group, N-methyl-N-(phosphonophenyl)sulfamoyloctyl group, phosphonobutyl group, phosphonatohexyl, group, diethylphosphonobutyl group, diphenyl phosphonopropoyl group, methylphosphonobutyl group, methylphosphonatobutyl group, tollylphosphonohexyl group, tollylphosphonatohexyl group, phosphonooxypropyl group, phosphonatooxybutyl group, benzyl group, phenetyl group, $\alpha$-methylbenzyl group, 1-methyl-1-phenylethyl group, p-methylbenzyl group, cinnamyl group, allyl group, 1-propenylmethyl group, 2-butenyl group, 2-methylallyl group, 2-methylpropenylmethyl group, 2-propynyl group, 2-butynyl group, and 3-butynyl group.

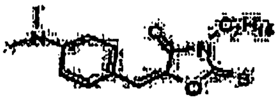
**[0083]** Specific examples of preferred aryl groups as $R_1$, $R_2$ and $R_3$ include those in which 1 to 3 benzene rings form a condensed ring and those in which a benzene ring and a 5-membered unsaturated ring form a condensed ring. Specific examples include phenyl group, naphthyl group, anthryl group, phnantollyl group, indenyl group, acenaphthenyl group, and fluolenyl group. Among them, phenyl group and naphtyl group are more preferred.

**[0084]** As specific examples of substituted aryl groups which are preferred as $R_1$, $R_2$ and $R_3$, those having a monovalent non-metallic atomic group excluding hydrogen as a substituent on the ring-forming carbon atoms of the aryl groups are used. Examples of the preferred substituents include the alkyl groups, substituted alkyl groups, and those previously shown as the substituents in the substituted alkyl groups. Specific preferred examples of such substituted aryl groups include biphenyl group, tollyl group, xylyl group; mesityl group, cumenyl group, chlorophenyl group, bromophenyl group, fluorophenyl group, chloromethylphenyl group, trifluoromethylphenyl group, hydroxyphenyl group, methoxyphenyl group, methoxyethoxyphenyl group, allyloxyphenyl group, phenoxyphenyl group, methylthiophenyl group, tollylthiophenyl group, ethylaminophenyl group, diethylaminophenyl group, morpholinophenyl group, acetyloxyphenyl group, benzoyloxyphenyl group, N-cyclohexyl carbamoyloxyphenyl group, N-phenylcarbamoyloxyphenyl group, acetylaminophenyl group, N-methylbenzoylaminophenyl group, carboxyphenyl group, methoxycarbonylphenyl group, allyloxycarbonylphenyl group, chlorophenoxycarbonylphenyl group, carbamoylphenyl group, N-methylcarbamoylphenyl group, N,N'-dipropylcarbamoylphenyl group, N-(methoxyphenyl)carbamoylphenyl group, N-methyl-N-sulfonyl)carbamoyl phenyl group, sulfophenyl group, sulfonatophenyl group, sulfamoylphenyl group, N-ethylsulfamoylphenyl group, N,N-dipropylsulfamoylphenyl group, N-tollylsulfamoylphenyl group, N-methyl-N-(phosphonophenyl)sulfamoylphenyl group, phosphonophenyl group, phosphonatophenyl group, diethylphosphonophenyl group, diphenylphosphonophenyl group, methylphosphonophenyl group, methylphosphonatophenyl group, tollylphosphonophenyl group, tollylphosphonatophenyl group, allyl group, 1-propenylmethyl group, 2-butenyl group, 2-methylallylphenyl group, 2-methylpropenylphenyl group, 2-propinylphenyl group, 2-butynylphenyl group, 3-butynylphenyl group, etc.

**[0085]** Then, A in the general formula (V) is to be described. A represents an aromatic ring or a hetero ring which may have a substituent and specific examples of the aromatic ring or hetero ring which may have a substituent include members identical with those described for $R_1$, $R_2$, and $R_3$ in the general formula (V).

**[0086]** The sensitizing dyes represented by the general formula (V) are obtained by condensating reaction of the acidic nuclei or acidic nuclei having an active methylene group as shown above and substituted or not-substituted aromatic rings or hetero rings and they can be synthesized with reference to JP-B No. 59-28329.

**[0087]** Preferred specific examples (Dl) to (D41) of the compounds represented by the general formula (V) are to be shown below. Further, isomers with respect to the double bonds connecting the acidic nuclei and the basic nuclei are not restricted to any one of the isomers.



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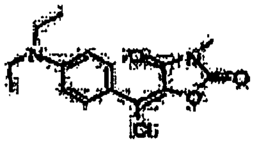

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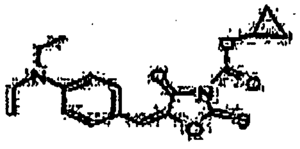

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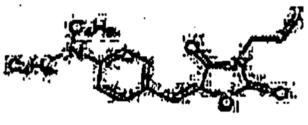

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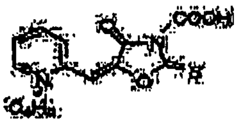

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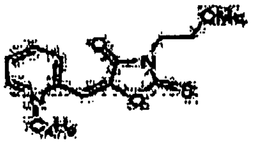

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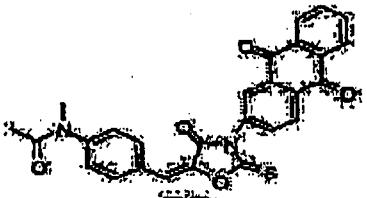

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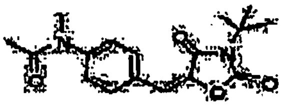

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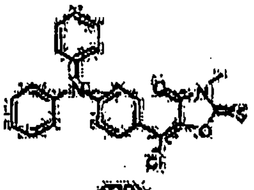

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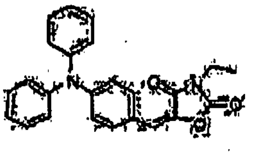

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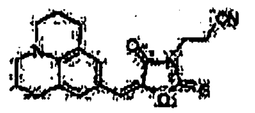
(D11)



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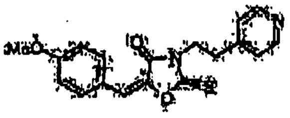
(D13)

(D14)



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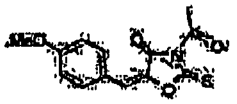

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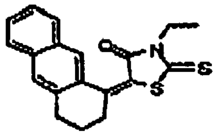

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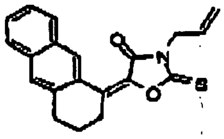

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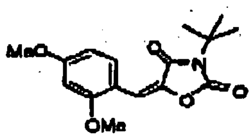

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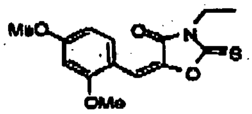

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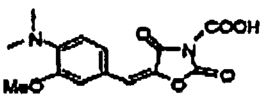

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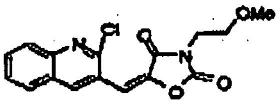

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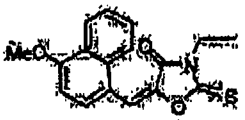

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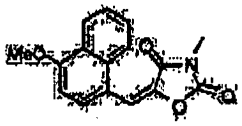

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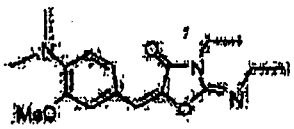

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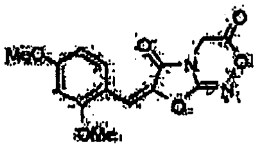

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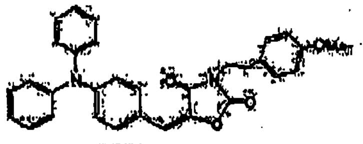

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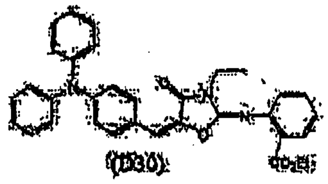

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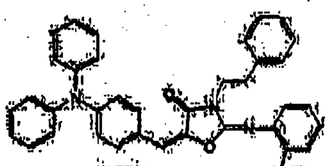

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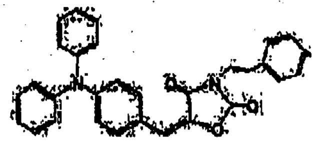

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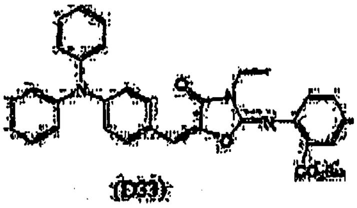

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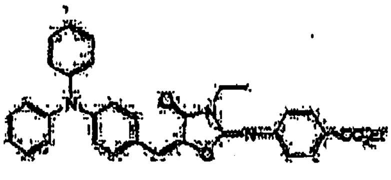

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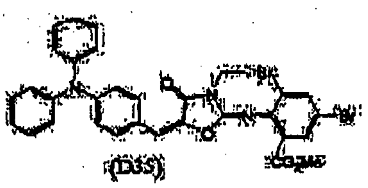

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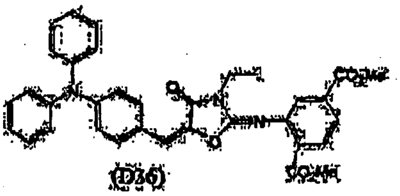

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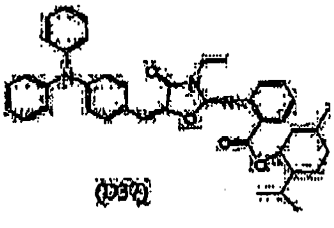

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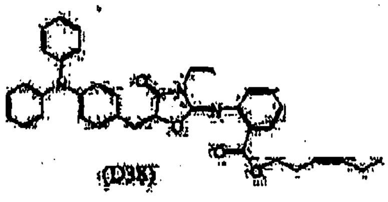

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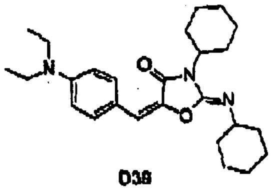
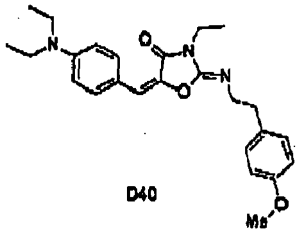
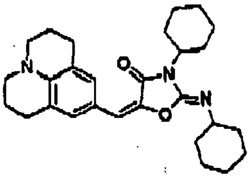


D39



D40



D41

**[0088]** The sensitizing dye absorbing a light from 360 nm to 450 nm is preferably used within a range from 1.0 to 10.0 mass% based on the entire solids of the photosensitive layer. More preferably, it is within a range from 1.5 to 5.0 mass%.

(B) IR-ray absorbent

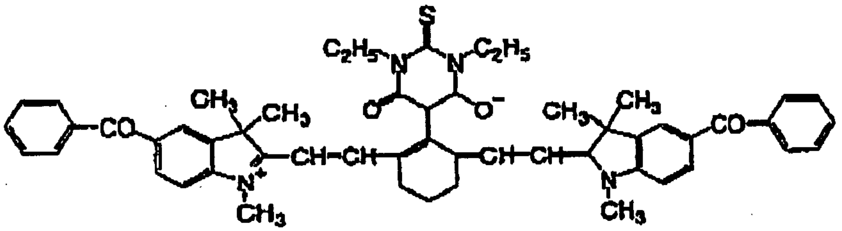
**[0089]** The IR-ray ray absorbent used in the invention has a function of converting absorbed infrared rays into heat. The infrared ray absorbent used in the invention is preferably a dye or a pigment having an absorption maximum at a wavelength from 760 to 1200 nm.

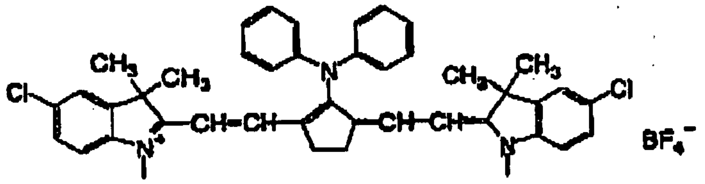
**[0090]** As the dye, commercially available dyes and known dyes as described in the literatures, for example, "Dye Manual" (edited by The Society of Organic Synthetic Chemistry, published in 1970) can be utilized. They include specifically those dyes, for example, azo dyes, metal complex salt azo dyes, pirazolon azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methyine dyes, cyanine dyes, squalilium dyes, pyrylium salts, and metal thiolate complexes.

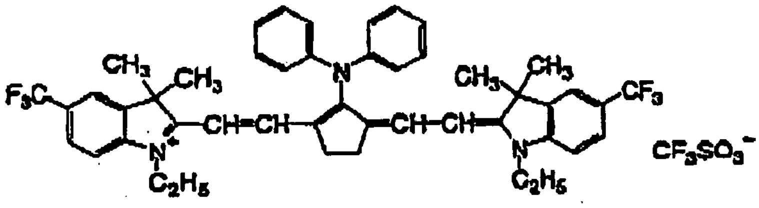
**[0091]** Preferred dyes include, for example, cyanine dyes described in JP-A Nos. 58-125246, 59-84356, and 60-78787, methine dyes described in JP-A Nos. 58-173696, 58-181690, and 58-194595, naphthoquionone dyes described in JP-A Nos. 58-112793, 58-224793, 59-48187, 59-73996, 60-52940, and 60-63744, squalilium dyes described in JP-A No. 58-112792, and cyanine dyes described in the specification of BP No. 434875.

**[0092]** Further, near infrared ray absorbing sensitizers described in the specification of USP No. 5156938 are also use suitably, and substituted aryl benzo(thio)pililium salts described in the specification of USP No. 3881924, trimethine thiapyrilium salts described in JP-A No. 57-142645 (specification of USP No. 4327169), pyrilium type compounds described in JP-A Nos. 58-181051, 58-220143, 59-41363, 59-84248, 59-84249, 59-146063, and 59-146061, cyanine dyes described in JP-A No. 59-216146, pentamethine thiopyrilium salts described in the specification of USP No. 4283475, and pyrilium compounds described in JP-B Nos. 5-13514, and 5-19702 are also used preferably. Further, another preferred examples of the dye include near infrared absorbing dyes described as formulae (I) and (II) in the specification of USP No. 4756993.

**[0093]** Further, other preferred examples of the infrared ray absorbing dyes include specified indolenine cyanine dyes described in JP-No. 2002-278057 exemplified below.



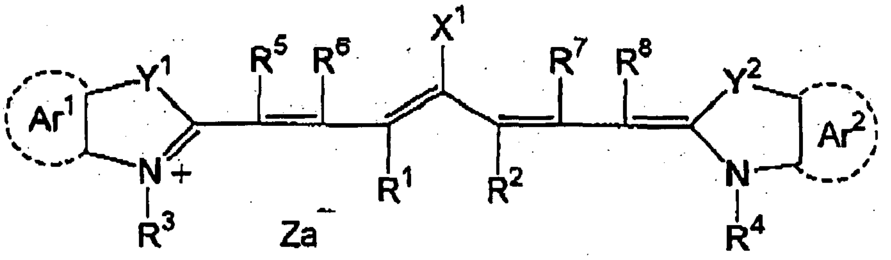




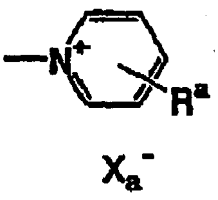
**[0094]** Among the dyes, particularly preferred include cyanine dyes, squalilium dyes, pyrilium salts, nickel thiolate complexes, and indolenine cyanine dyes. Further, cyanine dyes and indolenine cyanine dyes are preferred and one of particularly preferred examples includes a cyanine dye represented by the following general formula (VI).

General formula (VI)

**[0095]**



**[0096]** In the general formula (VI), $X^1$ represents a hydrogen atom, halogen atom, $-NPh_2$, $X^2$-$L^1$ or groups shown below. $X^2$ represents an oxygen atom, nitrogen atom, or sulfur atom, and $L^1$ represents a hydrocarbon group of 1 to 12 carbon atoms, an aromatic ring having a hetero atom, and a hydrocarbon group of 1 to 12 carbon atoms containing a hetero-atom. The hetero-atom means N, S, O, halogen atom, and Se. $Xa^-$ is defined in the same manner as for $Za^-$ to be described later, and $R^a$ represents a substituent selected from a hydrogen atom, alkyl group, aryl group, substituted or not-substituted amino group, and halogen atom.



**[0097]** $R^1$ and $R^2$ each represents independently a hydrocarbon group of 1 to 12 carbon atoms. In view of the store stability of the recording layer coating solution, it is preferred that each of $R^1$ and $R^2$ is a hydrocarbon group of 2 or more carbon atoms and, further, it is particularly preferred that $R^1$ and $R^2$ join to each other to form a 5- or 6-membered ring.

**[0098]** $Ar^1$ and $Ar^2$ may be identical or different with each other and represents an aromatic hydrocarbon group which may have a substituent. Preferred aromatic hydrocarbon groups include a benzene ring and a naphthalene ring. Preferred substituents include hydrocarbon groups of 12 or less carbon atoms, halogen atoms and alkoxy groups of 12 or less carbon atoms. $Y^1$ and $Y^2$ may be identical or different with each other and each represents a sulfur atom or a dialkylmethylene groups of 12 or less carbon atoms. $R^3$ and $R^4$ may be identical or different with each other and each represents a hydrocarbon group of 20 or less carbon atoms which may have a substituent. Preferred substituents include alkoxy groups of 12 or less carbon atoms, carboxy group and sulfo groups. $R^5$, $R^6$, $R^7$, and $R^8$ may be identical or different with each other and each represents a hydrogen atom or a hydrocarbon atom of 12 or less carbon atoms. They are preferably hydrogen atom in view of the availability of the starting material. Further, $Za^1$ represents a counter anion. However, $Za^-$ is not necessary in a case where the cyanine dye represented by the general formula (IV) has an anonic substituent in the structure and does not require neutralization for charges. Preferred $Za^-$ is a halogen ion, perchlorate ion, tetrafluoro borate ion, hexafluorophosphate ion, and sulfonate ion and, particularly preferably, perchlorate ion, hexafluorophosphate ion, and arylsulfonate ion in view of the store stability of the recording layer coating solution.

**[0099]** Specific examples of the cyanine dyes represented by the general formula (VI) that can be used suitably in the invention include those described in column Nos. [0017] to [0019] in JP-A No. 2001-133969.

**[0100]** Further, particularly preferred other examples include specified indolenin cyanine dyes described in JP-A 2002-278057.

**[0101]** As the pigments used in the invention, commercially available pigments and those pigments described in the Color Index C.I.) manual, "Modern pigment manual" (edited by the Society of Pigment Technology in Japan, published in 1977), "Modern Pigment Applied Technique", (CMC Publishing Co., Ltd., published in 1986), "Printing Ink Technique", CMC Publishing Co., Ltd., published in 1984).

**[0102]** The type of pigments includes black pigment, yellow pigment, orange pigment, brown pigment, red pigment, purple pigment, blue pigment, green pigment, fluorescent pigment, metal powder pigment, as well as polymer bonded pigments. Specifically, insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyaine pigments, anthraquinone pigments, perylene and perinone pigments, thioindigo pigments, quinacrydone pigments, dioxadine pigments, isoindolinone pigments, quinophthalone pigments, dying lake pigments., azine pigments, nitroso pigments, nitro pigments, natural pigments, phosphorescent pigments, inorganic pigments, and carbon black can be used. Among the pigments, described above preferred are carbon black.

**[0103]** The pigments may be used without surface treatment or may be used after applying the surface treatment. For the method of the surface treatment, a method of surface coating a resin or wax, a method of depositing a surfactant, or a method of bonding a reactive material (for example, silane coupling agent, epoxy compound, and polyisocyanate) to the pigment surface may be considered. The surface treatment methods described above are described in "Property and Application of Metal Soaps" Seiwa Shobo, "Printing Ink Technique" (CMC Publishing Co., Ltd., published in 1984) and "Modern Pigment Application Technique", (CMC Publishing Co., Ltd., published in 1986) .

**[0104]** The grain size of the pigment is, preferably, within a range from 0.01 to 10 μm, more preferably, within a range from 0.05 to 1 μm and, particularly preferably, within a range from 0.1 to 1 μm. Within the range described above, good stability of the pigment dispersion in the photosensitive layer coating solution and good uniformness of the photosensitive layer are obtained.

**[0105]** As a method of dispersing the pigment, known dispersion techniques used for ink production or toner production can be used. The dispersing machine includes, for example, sand mill, attritor, pearl mill, super mill, ball mill,impellar, disperser, KD mill, colloid mill, dynatron, three roll mill, and pressure kneader. Details are described in "Modern pigment Application Technique" (CMC Publishing Co., Ltd. in 1986).

**[0106]** The infrared absorbers may be added in a layer identical with that for other ingredients, or may be added to a layer separately from that for other ingredients by constituting the photosensitive layer with two or more layers. Further, the absorbents can also be added being incorporated in microcapsules.

**[0107]** It is added preferably such that the absorbance of the photosensitive layer at the maximum absorption wavelength in a range of the wavelength from 760 nm to 1200 nm upon preparation of a negative type lithographic printing plate precursor, by a reflection measuring method is within a range from 0.3 to 1.2 and it is more preferably within a range from 0.4 to 1.1. Within a range described above, polymerizing reaction proceeds uniformly in the direction of the depth of the photosensitive layer to obtain good film strength for an image area and adhesion to a support. The absorbance of the light sensitive layer can be controlled depending on the amount of the infrared ray absorbent to be added to the photosensitive layer and the thickness of the photosensitive layer. The absorbance can be measured by a customary method. The measuring method includes, for example, a method of forming a photosensitive layer on a reflective support made of aluminum or the like at such a thickness that the coating amount after drying is properly determined for the lithographic printing plate, and measuring the reflection density by an optical densitometer or a method of measuring by a photospectrometer according to a reflection method using an integrating sphere.

< Microcapsule and Microgel >

**[0108]** In the invention, for the method of incorporating the constituent ingredients of the photosensitive layer described above and other constituent ingredients in the photosensitive layer, several modes can be used. One of them is a molecule dispersion type photosensitive layer of coating the constituent ingredients being dissolved in an appropriate solvent, for example, as described in JP-A No. 2002-287334. Another mode is a microcapsule type photosensitive layer in which the constituent ingredients are contained in the photosensitive layer while being entirely or partially incorporated in the microcapsules as described in JP-A Nos. 2001-277740 and 2001-277742. Further, the constituent ingredients can be incorporated to the outside of the microcapsules in the microcapsule type photosensitive layer. In this case, in a preferred mode of the microcapsule type photosensitive layer, hydrophobic constituent ingredients are incorporated in the microcapsules and hydrophilic constituent ingredients are contained to the outside of the microcapsules. Further, other modes include those containing cross linked resin particles, that is, microgel in the photosensitive layer. The microgel can contain a portion of the constituent ingredients in and/or the surface thereof. Particularly, a mode having the polymerizable compound on the surface thereof thereby forming reactive microgels is preferred with the view point of image forming sensitivity and printing resistance.

**[0109]** For obtaining more preferred on-press developability, the photosensitive layer is preferably a microcapsule type or microgel type photosensitive layer.

**[0110]** As the method of forming the light sensitive constituent ingredient into the microcapsule form or the microgel form, known methods can be applied.

**[0111]** For example, the method of manufacturing the microcapsules includes a method of utilizing coacervation described in the specification of US. Patent Nos. 2800457, and 2800458, a method by an interface polymerization method described in the specification of USP No. 3287154, and in each of JP-B Nos. 38-19574 and 42-446, a method by the deposition of polymers as described in the specifications of US Patent Nos. 3418250, and 3660304, a method of using an isocyanato polyol wall material as described in the specification of US Patent No. 3796669, a method of using an isocyanato wall material as described in the specification of US Patent No. 3914511, a method of using urea-foraldehyde or ureaformaldehyde-resorcinol wall forming materials as described in each of the specifications of US Patent Nos. 4001140, 4087376, 4089802, a method of using wall materials such as melanine-formaldehyde resin, and hydroxycellulose as described in the specification of US Patent No. 4025445, an in-situ method by monomer polymerization as described in each of JP-B Nos. 36-9163, and 51-9079, a spray drying method as described in the specifications of BP No. 930422 and USP No. 3111407, and an electrolytic dispersion cooling method as described in each of the specifications of BP Nos. 952807 and.967074, but they are not restrictive.

**[0112]** Preferred microcapsule walls in the invention are those having three-dimensional crosslinking and having a property of swelling with a solvent. With the viewpoint described above, the wall material for the microcapsule is preferably polyurea, polyurethane, polyester, polycarbonate, polyamide, and a mixture thereof and, particularly preferably, polyurea and polyurethane. Further, a compound having a crosslinkable functional group such as an ethylenically unsaturated bond that can be introduced to a binder polymer to be described later may also be introduced to the microcapsule wall.

**[0113]** On the other hand, as a method of preparing the microgel, it is possible to utilize pelleting by interface polymerization as described in the specifications of JP-B Nos. 38-19574, and 42-446, and pelleting by non-aqueous dispersion polymerization as described in the specification of JP-A No. 5-61214. However, the method is not restricted to such methods.

**[0114]** As a method of utilizing the interface polymerization, the known microcapsule production methods described above can be applied.

**[0115]** A preferred microgel used in the invention is pelleted by interface polymerization and has three-dimensional crosslinking. With such a viewpoint, the material to be used is preferably polyurea, polyurethane, polyester, polycarbonate, polyamide, and a mixture thereof and, particularly, polyurea and polyurethane are preferred.

**[0116]** The average grain size of the microcapsule or the microgel is preferably from 0.01 to 3.0 $\mu$m. It is, more preferably, from 0.05 to 2.0 $\mu$m and preferably, from 0.10 to 1.0 $\mu$m. Within the range described above, good resolution power and aging stability can be obtained.

< Other ingredients >

**[0117]** In the photosensitive layer of the invention, other ingredients such as a binder polymer, surfactant, etc. can be incorporated further. They are to be described below.

(a) Binder polymer

**[0118]** In the invention, a binder polymer can be used for improving the film property of the photosensitive layer and the on-press developability. As the binder polymer those known so far can be used with no restriction and polymers having a film forming property are preferred. Examples of such binder polymer include acryl resin, polyvinyl acetal resin, polyurethane resin, polyurea resin, polyimide resin, polyamide resin, epoxy resin, methacryl resin, polystyrene resin, novolac phenol resin, polyester resin, synthetic rubber, and natural rubber.

**[0119]** For improving the film strength in the image area, the binder polymer may have a crosslinking property. For providing the binder polymer with the crosslinking property, a crosslinkable functional group such as an ethylenically unsaturated bond may be introduced into the main chain or the side chain. The crosslinkable functional group may also be introduced by copolymerization.

**[0120]** Examples of the polymer having the ethylenically unsaturated bond in the main chain of the molecule include, for example, poly-1,4-butadiene and poly-1,4-isoprene.

**[0121]** Examples of the polymer having the ethylenically unsaturated bonds in the chain of the molecule include polymers of esters or amides of acrylic acid or methacrylic acid in which the residue of the ester or the amide (R is -COOR or -CONHR) has an ethylenically unsaturated bond.

**[0122]** Examples of the residue having the ethylenically unsaturated bond (R) described above include - $(CH_2)_nCR^1=CR^2R^3$ $-(CH_2O)_nCH_2CR^1=CR^2R^3$, - $(CH_2CH_2O)_nCH_2CR^1=CR^2R^3$,- $(CH_2)_n$-NH-CO-O-$CH_2CR^1=CR^2R^3$,- $(CH_2O)_n$-O-CO-$CR^1=CR^2R^3$ and - $(CH_2CH_2O)$-X (in which $R^1$ to $R^3$ each represents a hydrogen atom, halogen atom, or alkyl group, aryl group, alkoxy group, aryloxy group of 1 to 20 carbon atoms, and $R^1$ and $R^2$ or $R^3$ may join to each other to from a ring. n represents an integer of 1 to 10. X represents a dicyclopentadienyl residue).

**[0123]** Specific examples of the ester residue include - $CH_2CH=CH_2$ (described in JP-B No. 7-21633) -$CH_2CH_2O$-$CH_2CH=CH_2$, -$CH_2C(CH_3)=CH_2$, -$CH_2CH=CH$-$C_6H_5$, -$CH_2CH_2OCOCH=CH$-$C_6H_5$, -$CH_2CH_2$-NHCOO-$CH_2CH=CH_2$ and -$CH_2CH_2O$-X (in which X represents a dicyclopentadienyl residue).

**[0124]** Specific examples of the amide residue include - $CH_2CH=CH_2$, -$CH_2CH_2$-Y (in which Y represents a cyclohexene residue), and -$CH_2CH_2$-OCO-$CH=CH_2$.

**[0125]** The binder polymer having the crosslinking property is hardened, for example, by addition of free radicals (polymerization initiation radicals or growing radicals in the polymerization process of polymerizable compounds) and by addition polymerization directly or by way of a polymer chain of the polymerizable compounds to form crosslinking between the polymer molecules. Alternatively, it is hardened by extraction of atoms in the polymer (for example, hydrogen atoms on the carbon atom adjacent with the functional crosslinking group) by free radicals to form polymer radicals and bonding of them to each other to form crosslinking between the molecules.

**[0126]** The content of the crosslinking group in the binder polymer (content of the radical polymerizable unsaturated double bonds according to iodine titration) is, preferably, from 0.1 to 10.0 mmol, more preferably, from 1.0 to 7.0 mmol and, most preferably, from 2.0 to 5.5 mmol per 1 g of the binder polymer. Within the range described above, good sensitivity and good store stability can be obtained.

**[0127]** Further, with a view point of the on-press developability of the non-exposed area of the photosensitive layer, it is preferred that the binder polymer has high solubility or dispersibility to an ink and/or fountain solution.

**[0128]** For improving the solubility or dispersibility to the ink, the binder polymer is preferably oleophilic. For improving the solubility or dispersibility to the fountain solution, the binder polymer is preferably hydrophilic. Accordingly, in the invention, it is also effective to use an oleophilic binder polymer and a hydrophilic binder polymer in combination.

**[0129]** The hydrophilic binder polymer includes preferably, for example, those having hydrophilic groups such as hydroxyl group, carboxyl group, carboxylate group, hydroxyethyl group, polyoxyethyl group, hydroxypropyl group, polyoxypropyl group, amino group, aminoethyl group, aminopropyl group, ammonium group, amide group, carboxymethyl group, sulfonate group, and phosphate group.

**[0130]** Specific examples include, for example, gum Arabic, casein, gelatin, starch derivative, carboxymethylcellulose and sodium salts thereof, cellulose acetate, sodium alginate, vinylacetate-maleic acid copolymers, styrene-maleic acid copolymers, polyacrylic acids and salts thereof, polymethacrylic acids and salts thereof, homopolymers and copolymers of hydroxyethyl methacrylate, homopolymers and copolymers of hydroxyethyl acrylate, homopolymers and copolymers of hydroxypropyl methacrylate, homopolymers and copolymers of hydroxypropyl acrylate, homopolymers and copolymers of hydroxyl butyl methacrylate, homopolymers and copolymers of hydroxybutyl acrylate, polyethylene glycols, hydroxypropylene polymers, polyvinyl alcohols, hydrolyzed polyvinyl acetate polyvinyl formal, polybutyral, polyvinyl pyrrolidone and acrylamide having hydrolysis degree of 60 mol% or more and, preferably, 80 mol% or more, homopolymers and copolymers of methacrylamide, homopolymers and copolymers of methacrylamide, homopolymers and copolymers of N-methylol acrylamide, and polyethers of polyvinyl pyrrolidone, alcohol soluble nylon, and 2,2-bis-4-hydroxyphenyl)-propane with epichlorohydrin.

**[0131]** The binder polymer has a mass average molecular weight, preferably, of 5000 or more and, more preferably, of 10000 to 300000 and has a number average molecular weight, preferably, 1000 or more, and more preferably, from 2000 to 250000. It is preferred that polydispersion degree (mass average molecular weight/number average molecular weight) is from 1.1 to 10.

**[0132]** The content of the binder polymer to the entire solids of the photosensitive layer is, preferably, from 5 to 90 mass%, more preferably, from 5 to 80 mass% and, further preferably, 10 to 70 mass%. Within the range described above, good strength of the image area and image forming property can be obtained.

**[0133]** Further, the polymerizable compound and the binder polymer is preferably used in an amount from 0.5/1 to 4/1 by mass ratio.

(b) Surfactant

**[0134]** In the invention, for promoting the on-press developability upon starting and improving the coating surface state, it is preferred to use a surfactant for the photosensitive layer. The surfactant includes, for example, nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, and fluoro surfactants. The surfactants may be used each alone or two or more of them may be used in combination.

**[0135]** The nonionic surfactants used in the invention are not particularly restricted and those known so far can be used. For example, they include polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene polystyryl phenyl esters, polyoxyethylene polyoxypropylene alkyl ethers, glycerin fatty acid partial esters, sorbitane fatty acid partial esters, pentaerythritol fatty aid partial esters, propylene glycol monofatty acid esters, sacrose fatty acid partial esters, polyoxyethylene sorbitane fatty acid partial esters, polyoxyethylene sorbitol fatty acid partial esters, polyoxyethylene glycol fatty acid esters, polyglycerin fatty acid partial esters, polyoxyethylenated castor oils, polyoxyethylene glycerin fatty acid partial esters, fatty acid diethanol amides, N,N-bis-2-hydroxyalkylamines, polyoxyethylene alkylamine, triethanolamine fatty acid ester, trialkylamine oxide, polyethylene glycol, and copolymers of polyethylene glycol and polypropyleneglycol.

**[0136]** The anionic surfactants used in the invention are not particularly restricted and those known so far can be used. For example, they include fatty acid salts, abietate salts, hydroxyalkane sulfonate salts, alkane sulfonate salts, dialkyl sulfosuccinate salts, linear alkyl benzene sulfonate salts, branched alkylbenzene sulfonate salts, alkylnaphthalene sulfonate salts, alkylphenoxypoly oxyethylenepropyl sulfonate salts, polyoxyethylene alkylsulfophenyl ether salts, sodium salts of N-methyl-N-oleyl taurinate, disodium salts of N-alkylsulfosuccinate monoamide, petroleum sulfonate salts, sulfonated tallow oil, sulfate salts of fatty acid alkyl ester, alkyl sulfate salts, polyoxyethylene alkyl ether sulfate salts, fatty acid monoglyceride sulfate salts, polyoxyethylene alkylphenyl ether sulfate salts, polyoxyethylene styrylphenyl ether sulfate salts, alkyl phosphate salts, polyoxyethylene alkyl ether phosphate salts, polyoxyethylene alkylphenyl ether phosphate salts, partial saponified products of styrene/maleic acid anhydride copolymer, partial saponified products of olefin/maleic acid anhydride copolymers, and naphthalene sulfonate salt-formalin condensation products.

**[0137]** The cationic surfactants used in the invention are not particularly restricted and those known so far can be used. For example, they include alkylamine salts, quaternary ammonium salts, polyoxyethylene alkylamine salts, and polyethylene polyamine derivatives.

**[0138]** The amphoteric surfactants used in the invention are not particularly restricted and those known so far can be used. For example, they include carboxybetaines, aminocarboxylates, sulfobetaines, aminosulfate esters, and imidazolines.

**[0139]** In the surfactants described above, "polyoxyethylene" can be read as polyoxyalkylene" such as polyoxymethylene, polyoxypropylene or polyoxybutylene and such surfactant can also be used in the invention.

**[0140]** Further preferred surfactants include fluoro surfactants containing perfluoroalkyl groups in the molecule. Such fluoro surfactants include, for example, anionic type such as perfluoroalkyl carboxylate salts, perfluroalkyl sulfonate salts, and perfluoroalkyl phosphate esters; amphoteric type such as perfluoroalkyl betaines; cationic type such as perfluoroalkyl trimethyl ammonium salts; and nonionic types such as perfluoroalkylamine oxides, perfluoroalkylethylene oxide adducts, oligomers containing perfluoroalkyl groups and hydrophilic groups, oligomers containing perfluoroalkyl groups and oleophilic groups, oligomers containing perfluoroalkyl groups, hydrophilic groups, and oleophilic group, and urethane containing perfluoroalkyl groups and oleophilic groups. Further, they also include suitably fluoro surfactants as described in JP-A Nos. 62-170950, 62-226143, and 60-168144.

**[0141]** The surfactants may be used each alone or two or more may be used in combination.

**[0142]** The content of the surfactant to the entire solids of the photosensitive layer is, preferably, from 0.001 to 10 mass% and, more preferably, from 0.01 to 5 mass%..

(c) Printing out agent

**[0143]** In the photosensitive layer of the invention, compound that changes color by an acid or radical can be added for forming printing out images. However, since the not exposed area is removed by development in the printing machine, it is preferred not to have absorption substantially in the visible region before discoloration. Such compounds include, for example, various dyes such as diphenylmethane, triphenylmethane, tiazine, oxadine, xanthene, anthraquinone, iminoquinone, azo, and azomethine types.
**[0144]** In addition, leuco dyes known as the material for heat sensitive paper or pressure sensitive paper are also suitable. A preferred addition amount of the dye that changes color by acid or radical is preferably such that it has no substantial absorption in a visible region and, specifically, the absorbance at the absorption maximum is 0.1 or less.

(d) Polymerization inhibitor

**[0145]** In the photosensitive layer of the invention, a small amount of a heat polymerization inhibitor is preferably added in order to prevent unnecessary heat polymerization of (C) radical polymerizable compound during manufacture or storage of the photosensitive layer.
**[0146]** The heat polymerization inhibitors include, preferably, for example, hydroquinone, p-methoxyphenol, di-t-butyl-p-cresol, pyrogallol, t-butylcatechol, benzoquinone, 4,4-thiobis (3-methyl-6-t-butylphenol), 2,2'-methylenebis (4-methyl-6-t-butylphenol), and N-nitroso-N-phenylhydroxylamine aluminum salts.
**[0147]** The addition amount of the heat polymerization initiator to the entire solids of the photosensitive layer is preferably about from 0.01 to about 5 mass%.

(e) Higher fatty acid derivatives, etc.

**[0148]** In the photosensitive layer of the invention, higher fatty acid derivatives, etc. such as behenic acid or behenic amide and may be added and localized to the surface of the photosensitive layer in the course of drying after coating in order to prevent polymerization inhibition due to oxygen. The addition amount of the higher fatty acid derivative to the entire solids of the photosensitive layer is preferably about from 0.1 to about 10 mass%.

(f) Plasticizer

**[0149]** The photosensitive layer of the invention may contain a plasticizer for improving the on-press developability.
**[0150]** The plasticizer, preferably includes, for example, phthalate esters such as dimethyl phthalate, diethyl phthalate, dibutyl phthalate, diisobutyl phthalate, dioctyl phthalate, octyl caprylphthalate, dicyclohexyl phthalate, ditridecyl phthalate, butyl benzyl phthalate, diisodecyl phthalate, and diallylphthalate; glycol esters such as dimethylglycol phthalate, ethylphthalylethyl glycolate, methylphthalylethyl glycolate, butylphtharylbutyl glycolate, triethylene glycol dicaprylate esters; phosphate ester such as tricresyl phosphate, and triphenyl phosphate; fatty acid dibasic acid esters such as diisobutyladipate, dioctyl adipate, dimethyl sebacate, dibutyl sebacate, dioctyl azelate, and dibutyl maleate; polyglycidyl methacrylate, triethyl citrate, glycerin triacetyl ester, and butyl laurate.
**[0151]** The content of the plasticizer to the entire solids of the photosensitive layer is preferably about 30 mass% or less.

(g) Low molecular weight hydrophilic compound

**[0152]** The photosensitive layer of the invention may contain a hydrophilic low molecular weight compound for improving the on-press developability. The hydrophilic low molecular weight compound includes, for example, as water soluble organic compounds, glycols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, and tripropylene glycol, and ethers or ester derivatives thereof, polyhydroxyl compounds such as glycerin and pentaerythritol, organic amines such as triethanol amine, diethanol amine monoethanolamine, and salts thereof, organic sulfonic acids such as triene sulfonic acid, benzene sulfonic acid and salts thereof, organic phosphonic acids such as phosphonic acid and salts thereof, and organic carboxylic acids such as tartaric acids, oxalic acid, citric acid, and maleic acid, lactic acid, gluconic acid, and amino acids, and salts thereof.

< Formation of Photosensitive layer >

**[0153]** For the photosensitive layer of the invention, each of the necessary ingredients described above is dispersed or dissolved in a solvent to prepare a coating solution and coated. The solvent used herein includes, for example, ethylene dichloride, cyclohexanone, methylethylketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethyl acetoamide, N,N-dimethylformamide, tetramethyl urea, N-methyl pyrrolidone, dimethyl sulfoxide, sulfolane, $\gamma$-butyl lactone, toluene, and water, with no restriction,to them. The solvents may be used each alone or in admixture. The solid concentration of the coating solution is preferably from 1 to 50 mass%.

**[0154]** The photosensitive layer of the invention may also be formed by preparing a plurality of coating solution formed by dispersing or dissolving each of ingredients in identical or different solvents and repeating coating and drying by plural times.

**[0155]** Further, while the coating amount of the photosensitive layer (solid content) on the support obtained after coating and drying is different depending on the application use, it is generally from 0.3 to 3.0 g/m$^2$ preferably. Within the range described above, good sensitivity and preferred film property of the photosensitive layer can be obtained.

**[0156]** As the coating method, various methods can be used. For example, they include, bar coater coating, rotary coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, and roll coating.

(Protective Layer)

**[0157]** To the lithographic printing plate precursor of the invention, a protective layer (overcoat layer) may be optionally provided on the photosensitive layer optionally for providing oxygen shielding property, preventing occurrence of flaws at the photosensitive layer and preventing abrasion caused upon laser exposure at high luminance.

**[0158]** Usually, the exposure treatment to the lithographic printing plate is conducted in an atmospheric air. The image forming reaction in the photosensitive layer formed by the exposure treatment may possibly be hindered by low molecular weight compounds such as oxygen and basic substances present in the atmospheric air. The protective layer prevents the low molecular weight compounds such as oxygen or basic substances from intruding into the photosensitive layer and, as a result, suppresses image forming inhibitive reaction in the atmospheric air. Accordingly, the characteristic desired for the protective layer is to lower the permeability of low molecular weight compounds such oxygen and, further, it is excellent in the transmittance of light used for exposure, excellent in adhesion with the photosensitive layer and can be removed easily in the on-press developing step after exposure. The protective layer having such characteristics are described, for example, in the specification of USP No. 3458311 and JP-B No. 55-49729.

**[0159]** As the material used for the protective layer, any of water soluble polymers and water insoluble polymers may be properly selected and used. Specifically, they include, for example, water soluble polymers such as polyvinyl alcohol, modified polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl imidazole, polyacrylic acid, polyacrylamide, partial saponified product of polyvinyl acetate, ethylene-vinyl alcohol copolymer, water soluble cellulose derivative, gelatin, starch derivative, and gum Arabic, and polymers such as polyvinylidene chloride, poly(meth)acrylonitrile, polysulfone, polyvinyl chloride, polyethylene, polycarbonate, polystyrene, polyamide, and cellophane. Two or more of them can be used optionally in combination.

**[0160]** In the materials described above, relatively useful materials include water soluble high molecular weight compounds of excellent crystallinity. Specifically, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl imidazole, water soluble acrylic resins such as polyacrylic acid, gelatin and gum Arabic are suitable. Among them, polyvinyl alcohol, polyvinyl pyrrolidone, and polyvinyl imidazole are preferred in that they can be coated using water as a solvent and can be removed easily by fountain solution during printing. Among them, polyvinyl alcohol (PVA) provides a best result for basic characteristics such as oxygen shielding property and developer removing property.

**[0161]** The polyvinyl alcohol usable for the protective layer may be partially substituted with ester, ether, and acetal so long as it contains a substantial amount of not-substituted vinyl alcohol units having necessary water solubility. Further, it may contain other copolymerization ingredients in a portion thereof. For example, polyvinyl alcohols of various polymerization degrees having various hydrophilic modified portions, for example, an anionic modified portion modified with an anion such as carboxyl group or sulfo group, a cation modified portion modified with a cation such as amino group or ammonium group, silanol modified portion, and thiol modified portion at random, and polyvinyl alcohols of various polymerization degrees having various modified portions, for example, the anion modified portion, the cation modified portion, the silanol modified portion, the thiol modified portion described above and, further, an alkoxyl modified portion, a sulfide modified portion, an ester modified portion of polyvinyl alcohol and various organic acids, an ester modified portion of the anion modified portion and alcohols, an epoxy modified portion, etc. to the terminal ends of the polymer chain can also be used preferably.

**[0162]** The modified polyvinyl alcohols include suitably those compounds having a polymerization degree within a range of 300 to 2400 and hydrolyzed by 71 to 100 mol%. Specifically, they include, for example, PVA-105, PVA-110, PVA-117, PVA-117H, PVA-120, PVA-124, PVA124H, PVA-CS, PVA-CST, PVA-HC, PVA-203, PVA-204, PVA-205, PVA-210, PVA-217, PVA-220, PVA-224, PVA-217EE, PVA-217E, PVA-220E, PVA-224E, PVA-405, PVA-420, PVA-613, and L-8 manufactured by Kuraray Co. Ltd. Further, the modified polyvinyl alcohols include LK-318, LK-118, KM-618, KM-118, SK-5102 having the anion modified portion, C-318, C-118, CM-318 having the cation modified portion, M-205 and M-115 having the end thiol modified portion, MP-103, MP-203, MP-102, and MP-202 having the terminal end sulfide modified portion, HL-12E, HL-1203 having the ester modified portion with the higher fatty acid at the terminal end, as well as R-1130, R-2105, and R-2130 having the reactive silane modified portion.

**[0163]** Further, for the protective layer in the lithographic printing plate precursor of the invention, an inorganic layered compound is preferably contained with an aim of improving the oxygen shielding property or surface protectivity for the photosensitive layer. The inorganic layered compound is particles having a thin planar shape which include, for example, group of micas such as natural mica and synthetic mica represented by the following general formula:

$$A\ (B,\ C)_{2\text{-}5}D_4O_{10}\ (OH,\ F,\ O)_2$$

[in which A is one of K, Na, and Ca, and each of B and C is one of Fe(II), Fe (III), Mn, Al, Mg, and V, and D is Si or Al], talc represented by the formula $3MgO \cdot 4SiO \cdot H_2O$, taeniolite, montmolillonite, saponite, hectolite, zirconium phosphate, etc.

**[0164]** In the group of micas described above, the natural mica includes white mica, soda mica, gold mica, black mica, and scale mica. The synthetic mica includes non-swelling micas such as fluorogold mica $KMg_3(AlSi_3O_{10})F_2$, potassium tetrasilicate mica $KMg_{2.5}(Si_4O_{10})F_2$ and swelling micas such as Na tetrasilicic mica: $NaMg_{2.5}\ (Si_4O_{10})F_2$, Na or Li taeniolite $(Na, Li)\ Mg_2Li(Si_4O_{10})F_2$, montmolillonite type Na or Li hectolite $(Na, Li)_{1/8}Mg_{2/5}Li_{1/8}\ (Si_4O_{10})F_2$. Further, synthetic smectite is also useful.

**[0165]** In the invention, the fluoro-swelling mica as the synthetic inorganic layered compounds is particularly useful among the inorganic layered compounds described above. That is, the swelling synthetic mica and the swelling mineral clay such as montmolillonite, saponite, hectoliter, and bentonite have a laminate structure comprising unit crystal lattice layers each of about 10 to 15 Å thickness, and the degree of intra-lattice metal atom substitution is remarkably larger than that of other clay minerals. As a result, the lattice layer causes insufficiency of positive charges and adsorbs cations such as $Na^+$, $Ca^{2+}$, $Mg^{2+}$ between the layers for compensating the same. Cations interposed between the layers are referred to as exchangeable cations and conduct exchange with various cations. Particularly in a case where the interlayer cations are $Li^+$ or $Na^+$, since the ionic radius is small, bonding between the layered crystal lattices is weak and they are swollen more greatly with water. When share is applied in this state, they easily cleave to form a stable sol in water. Bentonite and swellable synthetic mica have an intense trend and are useful in the invention and, particularly, swellable synthetic micas are used preferably.

**[0166]** As the shape of the inorganic layered compound used in the invention, the thickness is preferably as small as possible with a view point of diffusion control and the planar size is preferably as large as possible so long as it does not hinder the smoothness on the coating surface and transmittance to actinic rays. Accordingly, the aspect ratio is 20 or more, preferably 100 or more and, particularly preferably, 200 or more. The aspect ratio is a ratio of the thickness to the major diameter of a particle and can be measured, for example, according to a projection view by a microscopic photograph for the particle. As the aspect ratio is larger, the obtained effect is larger.

**[0167]** As the grain size of the inorganic layered compound used in the invention, it has an average major diameter of from 0.3 to 20 μm, preferably, from 0.5 to 10 μm and, particularly preferably, from 1 to 5 μm. Further, the average thickness of the grains is 0.1 μm or less, preferably, 0.05 μm or less and, particularly preferably, 0.01 μm or less. For example, the size of the swellable synthetic micas as the typical compound among the inorganic layered compounds is from 1 to 50 nm in the thickness and about from 1 to 20 μm in the planar size.

**[0168]** In a case of incorporating the particles of the inorganic layered compound with such a large aspect ratio into the protective layer, since the coating film strength is improved and the permeation of oxygen or water content can be prevented effectively, degradation of the protective layer due to deformation or the like can be prevented and the lithographic printing plate precursor does not suffer from deterioration of the image forming property due to the change of humidity even after long time storage under a high humidity condition and is excellent in the store stability.

**[0169]** The content of the inorganic layered compound in the protective layer is preferably from 5/1 to 1/100 by mass ratio relative to the amount of the binder used in the protective layer. Also in a case of using a plurality kinds of inorganic layered compounds together, it is preferred that the total amount for the inorganic layered compounds provides the mass ratio described above.

**[0170]** Then, description is to be made to an examples of a general dispersing method of the inorganic layered compound used for the protective layer. At first, 5 to 10 mass parts of the swellable layered compound referred to as the preferred inorganic layered compound above is added to 100 mass parts of water and, after sufficient fitting with water and swelling, it is dispersed on a dispersing machine. The dispersing machine used herein includes, for example, various kinds of mills for mechanical dispersion with direct addition of force, high speed stirring type dispersing machines having a large shearing force, and dispersing machine providing supersonic energy at high intensity. Specifically, they include a ball mill, sand grinder mill, visco mill, colloid mill, homogenizer, dissolver, polytron, homomixer, homoblender, keddy mill, jet aditer, capillary tube type emulsifying apparatus, liquid siren electro magnetostrictive supersonic wave generator, and an emulsification apparatus having a Pohlmann whistle. 5 to 10 mass% dispersion of the inorganic layered compound dispersed by the method described above is in a highly viscous or gelled state, and the store stability is highly favorable. In a case of preparing a protective layer coating solution by using the dispersion, it is preferably diluted with water, stirred sufficiently and then prepared by being blended with a binder solution.

**[0171]** As other compositions of the protective layer, glycerin, dipropylene glycol, etc. may be added in an amount corresponding to several mass% to the (co)polymer to provide flexibility. Further, anionic surfactants such as sodium alkyl sulfate and sodium alkyl sulfonate; amphoteric surfactants such as alkylamino carboxylate salts and alkylamino dicarboxylate salt; and nonionic surfactant such as polyoxyethylene alkylphenyl ether can be added. The addition amount of the active agent can be from 0.1 to 100 mass% based on the (co)polymer.

**[0172]** For improving the adhesion with the image area, JP-A No. 49-70702 and the specification of BP-A No. 1303578 describe that an acrylic emulsion, water insoluble vinyl pyrrolidonevinyl acetate copolymer, etc. are mixed by from 20 to 60 mass% in a hydrophilic polymer mainly comprising polyvinyl alcohol and laminated on a photosensitive layer to obtain a sufficient adhesion property. In the invention, any of such known techniques can be used.

**[0173]** For the protective layer coating solution, known additives such as anionic surfactants, nonionic surfactants, cationic surfactants, or fluoro surfactants for improving the coatability and water soluble plasticizer, etc. for improving the physical property of the film can be added. The water soluble plasticizer includes, for example, propionic amide, cyclohexanediol, glycerin, and sorbitol. Further, water soluble (meth)acrylic polymer can also be added. Further, known additives may also be added to the coating solution for improving the adhesion with the photosensitive layer and aging stability of the coating solution.

**[0174]** The protective layer is formed by coating and drying the thus prepared protective coating solution on the photosensitive layer provided above the support. While the coating solvent can be selected properly in relation with the binder, it is preferred to use distilled water or purified water in a case of using the water soluble polymer. The coating method for the protective layer is not particularly restricted and known methods, for example, a method as described in the specification of US Patent No. 3458311 or JP B No. 55-49729 can be applied. Specifically, the protective layer is formed, for example, by a blade coating method, air knife coating method, gravure coating method, roll coating method, spray coating method, dip coating method, and bar coating method.

**[0175]** The coating amount of the protective layer is preferably within a range from 0.01 to 10 g/m$^2$, more preferably, within a range from 0.02 to 3 g/m$^2$ and, most preferably, within a range from 0.02 to 1 g/m$^2$ as the coating amount after drying.

(Support)

**[0176]** The support used for the lithographic printing plate precursor in the invention is not particularly restricted and any dimensionally stable plate-like material may be used. For example, the material includes paper, paper laminated with plastics (for example, polyethylene, polypropylene, and polystyrene), metal plate (for example, of aluminum, zinc, and copper), plastic film (for example, of cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, and polyvinyl acetal), and paper or plastic film laminated or vapor deposited with the metal described above. Preferred supports include polyester films and aluminum plates. Among all, the aluminum plate which is dimensionally stable and relatively inexpensive is preferred.

**[0177]** The aluminum plate is a pure aluminum plate, an alloy plate comprising aluminum as a main ingredient and containing a micro-amount of foreign elements, or a thin film of aluminum or aluminum alloy laminated with plastic material. The foreign element contained in the aluminum alloy includes silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, and titanium. The content of the foreign elements in the alloy is preferably 10 mass% or less. In the invention, while the pure aluminum plate is preferred, since it is difficult to prepare a completely pure aluminum in view of the refining technique, it may slightly contain foreign elements. The aluminum plate is not specified for the composition and publicly known and used materials can be utilized appropriately.

**[0178]** The thickness of the support is, preferably, from 0.1 to 0.6 mm, more preferably, from 0.15 to 0.4 mm and, further preferably, from 0.2 to 0.3 mm.

**[0179]** Before using the aluminum plate, surface treatment such as a roughening treatment or anodizing treatment is preferably applied. By the surface treatment, improvement for the hydrophilicity and insurance of adhesion between the photosensitive layer and the support are facilitated. Before the roughening treatment for the aluminum plate, a degreasing treatment, for example, with a surfactant, organic solvent or an aqueous alkaline solution is applied optionally for removing rolling lubricants on the surface.

**[0180]** The roughening treatment for the surface of the aluminum plate is applied by various methods and they include, for example, a mechanical roughening treatment, electrochemical roughening treatment (roughening treatment of electrochemically dissolving the surface), and chemical roughening treatment (roughening treatment of selectively dissolving the surface chemically).

**[0181]** As the mechanical surface treating method, known methods such as ball grinding method, brush grinding method, blast grinding method, and buff grinding method can be used.

**[0182]** The method of electrochemical roughening treatment includes, for example, a method conducted by AC or DC current in an electrolyte containing an acid such as hydrochloric acid or nitric acid. Further, it also includes a method of using a mixed acid as described in JP-A 54-63902.

**[0183]** The aluminum plate subjected to the roughening treatment is optionally applied with an alkali etching treatment by using an aqueous solution, for example, of potassium hydroxide or sodium hydroxide and, further, after neutralizing treatment, an anodizing treatment is optionally applied for improving the wear resistance.

**[0184]** As the electrolyte used for the anodizing treatment of the aluminum plate, various electrolytes forming porous oxide films can be used. Generally, sulfuric acid, hydrochloric acid, oxalic acid, chromic acid, or a mixed acid thereof is used. The concentration of the electrolyte is properly determined depending on the kind of the electrolyte.

**[0185]** While the conditions for the anodizing treatment can not be specified generally since they vary depending on the electrolyte to be used, it is generally preferred that the concentration of the electrolyte in the solution is from 1 to 80 mass%, the liquid temperature is from 5 to 70°C, the current density is from 5 to 60 A/dm$^2$, a voltage is from 1 to 100 V, and the electrolysis time is from 10 sec to 5 min. The amount of the anodized film formed is, preferably, from 1.0 to 5.0 g/m$^2$ and, more preferably, from 1.5 to 4.0 g/m$^2$. Within the range described above, good printing resistance and good scratch resistance of the non-image area of lithographic printing plate can be obtained.

**[0186]** For the support used in the invention, while a substrate applied with the surface treatment and having the anodized film as described above may be used as it is, an enlarging treatment or hole-sealing treatment for micropores in the anodizing film, a surface hydrophilic treatment of dipping into an aqueous solution containing a hydrophilic compound as described in JP-A 2001-253181 and 2001-322365, etc. can also be properly selected and applied for further improving the adhesion with the upper layer, the hydrophilicity, less contaminating property, and heat insulating property. The enlarging treatment or hole sealing treatment are not of course restricted to those described therein but any of methods known so far can also be applied.

**[0187]** For example, the hole sealing treatment can be applied by vapor hole sealing, as well as a treatment by using zirconic fluoride solely, a treatment with sodium fluoride and vapor hole sealing with addition of lithium chloride.

**[0188]** The hole sealing treatment used in the invention is not particularly restricted and methods known so far can be used. Among them, a hole sealing treatment with an aqueous solution containing an inorganic fluoro compound, a hole sealing treatment with steams, and a hole sealing treatment with hot water are preferred. The methods are to be described below.

**[0189]** The inorganic fluorocompounds used for the hole sealing treatment with an aqueous solution containing an inorganic fluorocompound includes suitably metal fluorides.

**[0190]** They include specifically, for example, sodium fluoride, potassium fluoride, calcium fluoride, magnesium fluoride, sodium fluorozirconate, potassium fluorozirconate, sodium fluorotitanate, potassium fluorotitanate, ammonium fluorozirconate, ammonium fluorotitanate, potassium fluorotitanate, fluorozirconic acid, fluorotitanic acid, hexafluorosilisic acid, nickel fluoride, iron fluoride, fluorophosphonic acid, and ammonium fluorophosphates. Among them, sodium fluorozirconate, sodium fluorotitanate, fluorozirconic acid, and fluorotitanic acid are preferred.

**[0191]** The concentration of the inorganic fluoro-compound in the aqueous solution is, preferably, 0.01 mass% or more and, more preferably, 0.05 mass% or more with a view point of sufficiently conducting micropore sealings in the anodized film and, in view of the contamination resistance, it is preferably 1 mass% or less and, more preferably, 0.5 mass% or less.

**[0192]** It is further preferred that the aqueous solution containing the inorganic fluorocompound further contains a phosphate salt compound. Since the hydrophilicity on the surface of the anodized film is improved by the incorporation of the phosphate salt compound, the on-press developability and the contamination resistance can be improved.

**[0193]** The phosphonic acid salts include suitably, for example phosphate salts of of metals such as alkali metals, and alkaline earth metals.

**[0194]** Specifically, preferred are, for example, zinc phosphate, aluminum phosphate, ammonium phosphate, hydrogen diammonium phosphate, dihydrogen ammonium phosphate, mono-ammonium phosphate, mono-potassium phosphate, mono-sodium phosphate, dihydrogen potassium phosphate, dipotassium phosphate, calcium phosphate, sodium hydrogen ammonium phosphate, magnesium hydrogen phosphate, magnesium phosphate, ferrous iron phosphate, ferric phosphate, sodium dihydrogen phosphate, sodium phosphate, disodium hydrogen phosphate, lead phosphate, diammonium phosphate, dihydrogen calcium phosphate, lithium phosphate, phosphorous wolfuramic acid, ammonium phosphorous wolfuramate, sodium phosphorous wolfuramate, ammonium phosphorous molybdate, and sodium phosphorous molybdate, sodium phosphite, sodium tripolyphosphate, and sodium pyrophosphate. Among them, dihydrogen sodium phosphate, hydrogen disodium phosphate, dihydrogen potassium phosphate, and hydrogen dipotassium phosphate are preferred.

**[0195]** While the combination of the inorganic fluoro-compound and the phosphate salt compound is not particularly restricted, the aqueous solution preferably contains at least sodium fluoro-zirconate as the inorganic fluoro compounds and contains,at least dihydrogen sodium phosphate as the phosphate salt compound.

**[0196]** The concentration of the phosphate salt compound in the aqueous solution is, preferably, 0.01 mass% or more and more preferably, 0.1 mass% or more with a view point of improving the on-press developability and the contamination resistance, and it is preferably 20 mass% or less and, more preferably, 5 mass% or less in view of the solubility.

**[0197]** The ratio of each of the compound in the aqueous solution is not particularly restricted and the mass ratio between the inorganic fluoro compound and the phosphate salt compound is, preferably, from 7./200 to 10/1 and, more preferably, from 1/30 to 2/1.

**[0198]** Further, the temperature of the aqueous solution is, preferably, 20°C or higher, more preferably, 40°C or higher and it is, preferably, 100°C or lower and, more preferably, 80°C or lower.

**[0199]** Further, the aqueous solution is, preferably, at pH 1 or higher and, more preferably, at pH 2 or higher, and preferably at pH 11 or lower and, more preferably, at pH 5 or lower.

**[0200]** The method of the hole sealing treatment with the aqueous solution containing the inorganic fluro-compound is not particularly restricted and includes, for example, a dipping method and a spray method. They may be used alone for once or plural times and two or more of the methods may be used in combination.

**[0201]** Among them, the dipping method is preferred. In a case of treatment by using the dipping method, the treating time is preferably, 1 sec or more and, more preferably, 3 sec or more, and it is, preferably, 100 sec or less, and, more preferably, 20 sec or less.

**[0202]** The hole sealing treatment with steams includes, for example, a method of bringing steams at an elevated pressure or a normal pressure into contact with the anodized film continuously or not continuously.

**[0203]** The temperature of the steams is, preferably, 80°C or higher and, more preferably, 95°C or higher, and it is, preferably, 105°C or lower.

**[0204]** The pressure of the steams is, preferably, within a range from (atmospheric pressure - 50 mmAq) to (atmospheric pressure + 300 mm) (from $1.008 \times 10^5$ to $1.043 \times 10^5$ Pa).

**[0205]** The time of contacting the steams is, preferably, from 1 sec or more and, more preferably, 3 sec or more, and it is, preferably, 1000 or less and, more preferably, 20 sec or less.

**[0206]** The hole sealing treatment by hot water includes, for example, a method of dipping an aluminum plate formed with an anodized film into hot water.

**[0207]** The hot water may also contain an inorganic salt, for example, a phosphate salt, or an organic salt.

**[0208]** The temperature of the hot water is, preferably, 80°C or higher and, more preferably, 95°C or higher and it is preferably 100°C or lower.

**[0209]** Further, the hot water dipping time is, preferably, 1 sec or more and, more preferably, 3 sec or more and it is, preferably, 100 sec or less and, more preferably, 20 sec or less.

**[0210]** In the invention, prior to the hole sealing, an enlarging treatment for micro-pores in the anodized film such as described in JP-A No. 2001-322365 can also be conducted. Further, after the hole sealing, a surface hydrophilic treatment can also be applied.

**[0211]** The hydrophilic treatment includes an alkali metal silicate method as described in each of the specifications of USP Nos. 2,714,066, 3,181,461, 3,280,734 and 3,902,734. In the method, the support is subject to a dipping treatment with an aqueous solution such as of sodium silicate, or to a electrolysis treatment. In addition, the treatment also includes a method of treating with potassium fluoro zirconate as described in JP-B No. Sho 36-22063, and a method of treating with polyvinyl phosphoric acid as described in each of the specifications of USP Nos. 3,276,868, 4,153,461, and 4,689,272.

**[0212]** In a case of using a support with an insufficient surface hydrophilic property such as a polyester film as a support in the invention, it is desirable to coat a hydrophilic layer to render the surface hydrophilic. Preferred hydrophilic layer includes a hydrophilic layer described in JP-A No. 2001-199175 of coating a coating solution containing a colloid of an oxide or a hydroxide of at least one element selected from beryllium, magnesium, aluminum, silicon, titanium, boron, germanium, tin, zirconium, iron, vanadium, antimony, and transition metals, a hydrophilic layer described in JP-A No. 2002-79772 having an organic hydrophilic matrix obtained by crosslinking or pseudo-crosslinking of an organic hydrophilic polymer, a hydrophilic layer having an inorganic hydrophilic matrix obtained by sol-gel conversion comprising hydrolysis or condensation reaction of polyalkoxysilane, titanate, zirconate, or aluminate, or a hydrophilic layer comprising an inorganic thin film having a surface containing a metal oxide. Among them, a hydrophilic layer formed by coating a coating layer containing a colloid of an oxide or hydroxide of silicon is preferred.

**[0213]** In a case of using a polyester film or the like as the support in the invention, an antistatic layer is formed preferably on the side of the hydrophilic layer, or on the opposite side or on both sides of the support. In a case of interposing the antistatic layer between the support and the hydrophilic layer, it contributes also to the improvement of adhesion with the hydrophilic layer. As the antistatic layer, a polymer layer or the like in which fine metal oxide particles and a matting agent are disposed as described in JP-A 2002-79772 can be used.

**[0214]** The center line average roughness of the support in the invention is preferably from 0.10 to 1.2 μm. Within the range described above, good adhesion with the light sensitive layer, good printing resistance, and good less contamination property can be obtained.

(Back coating layer)

**[0215]** After applying the surface treatment or forming the undercoating layer to the support, a back coating layer can also be provided optionally to the rear face of the support.

**[0216]** The back coat includes, preferably, coating layers comprising organic polymer compounds as described in JP-A No. 5-45885, and metal oxides obtained by hydrolysis and polycondensation of organic metal compounds or inorganic metal compounds as described in JP-A No. 6-35174. Among them, use of alkoxy compounds of silicon such as Si $(OCH_3)_4$, $Si(OC_2H_5)_4$, $Si(OC_3H_7)_4$, and $Si(OC_4H_9)_4$ is preferred with a view point of easy availability of starting materials at a reduced cost.

(Undercoat layer)

**[0217]** In the lithographic printing plate precursor of the invention, particularly, in a case of an on-press developing lithographic printing plate precursor, an undercoat layer can be optionally disposed between a light sensitive layer and a support. Since the undercoat layer facilitates peeling of the photosensitive layer from the support in the non-exposed area, the on-press developability is improved. Further, in a case of infrared laser exposure, since the undercoat layer functions as a heat insulative layer and, accordingly, heat generated by exposure does not diffuse to the support but can be utilized efficiently, this provides a merit capable of improving the sensitivity.

**[0218]** A compound for the undercoat layer (undercoating compound) specifically include preferably a silane coupling agent having an ethylenically double bond reactive group capable of addition polymerization as described in JP-A No. 10-282679 and a phosphorus compound having an ethylenically double bond reaction group as described in JP-A No. 2-304441.

**[0219]** Most preferred undercoat compound includes polymer resins formed by co-polymerization of monomers having support adsorptive group/monomers having hydrophilic groups/monomers having crosslinking groups.

**[0220]** The essential ingredient of the polymer resin for undercoat is a support adsorbing group (adsorbing group to the surface of the hydrophilic support). Absence or presence of the adsorption property to the surface of the hydrophilic support surface can be judged by the method, for example, as shown below.

**[0221]** A coating solution formed by dissolving a test compound into an easily soluble solvent is prepared, the coating solution is coated and dried on a support such that the coating amount after drying is 30 mg/$m^2$. Then, after cleaning the support coated with a test compound sufficiently by using a easily soluble solvent, the remaining amount of the test compound not removed by cleaning is measured to calculate the adsorption amount on the support. Measurement for the remaining amount may be determined directly for the remaining amount of the compound, or may be calculated by the determination for the amount of the test compound dissolved in the cleaning solution. The compound can be determined quantitatively for example, by fluorescence X-ray measurement, reflection spectral absorptiometry, liquid chromatography, or the like. The compound having a support adsorption property is a compound which remains by 1 mg/$m^2$ or more even after conducting the cleaning treatment as described above.

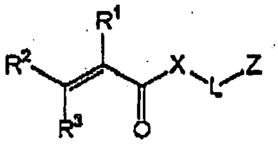
**[0222]** The adsorbing group to the hydrophilic surface of the support is a functional group capable of taking place chemical bonding (for example, ionic bond, hydrogen bond, coordination bond or intermolecular force bonding) with a substance (for example, metal or metal oxide) or a functional group (for example, hydroxyl group) present on the hydrophilic surface of the support. The adsorbing group is preferably an acid group or a basic group.

**[0223]** The acid group has preferably an acid association constant (pKa) of 7 or less. Examples of the acid group include phenolic hydroxyl group, carboxyl group, $-SO_3H$, $-OSO_3H$, $-PO_3H_2$, $-OPO_3H_2$, $-CONHSO_2$, $-SO_2NHSO_2-$, and $-COCH_2COCH_3$. Among all, $-OPO_3H_2$ and-$PO_3H_2$ are particularly preferred. The acid groups may be metal salts.

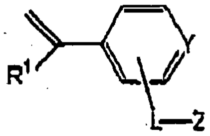
**[0224]** The basic group is preferably an onium salt. Examples of the onium salt include preferably ammonium group, phosphonium group, arsonium group, stibonium group, oxonium group, sulfonium group, solenonium group, stannonium group, and iodonium group. The ammonium group, phosphonium group, and sulfonium group are preferred, and ammonium group and phosphonium group are further preferred with the ammonium group being most preferred.

**[0225]** Particularly preferred examples of the monomer having the adsorbing group include the compound represented by the following general formula (VII) or (VIII).

(VII)



(VIII)



**[0226]** In the formula (VII), $R^1$, $R^2$, and $R^3$ each represents independently a hydrogen atom, halogen atom or alkyl group of 1 to 6 carbon atoms. $R^1$ and $R^2$, and $R^3$ each preferably represents independently a hydrogen atom or alkyl group of 1 to 6 carbon atoms, more preferably, the hydrogen atom or alkyl group of 1 to 3 carbon atoms and, most preferably, the hydrogen atom or methyl group. $R^2$ and $R^3$ each represents particularly preferably the hydrogen atom.

**[0227]** In the formula (VII), X is an oxygen atom (-O-) or imino (-NH-). X is more preferably an oxygen atom. In the formula (VII), L is a bivalent connection group. L is preferably a bivalent aliphatic group (alkylene group, substituted alkylene group, substituted alkenylene group, alkynylene group, and substituted alkynylene group), a bivalent aromatic group (arylene group and substituted arylene group) or bivalent heterocyclic group, or a combination thereof with an oxygen atom (-O-), sulfur atom (-S-), imino (-NH-), substituted imino (-NR-, in which R is an aliphatic group, aromatic group, or heterocyclic group), or carbonyl group (-CO-) in combination.

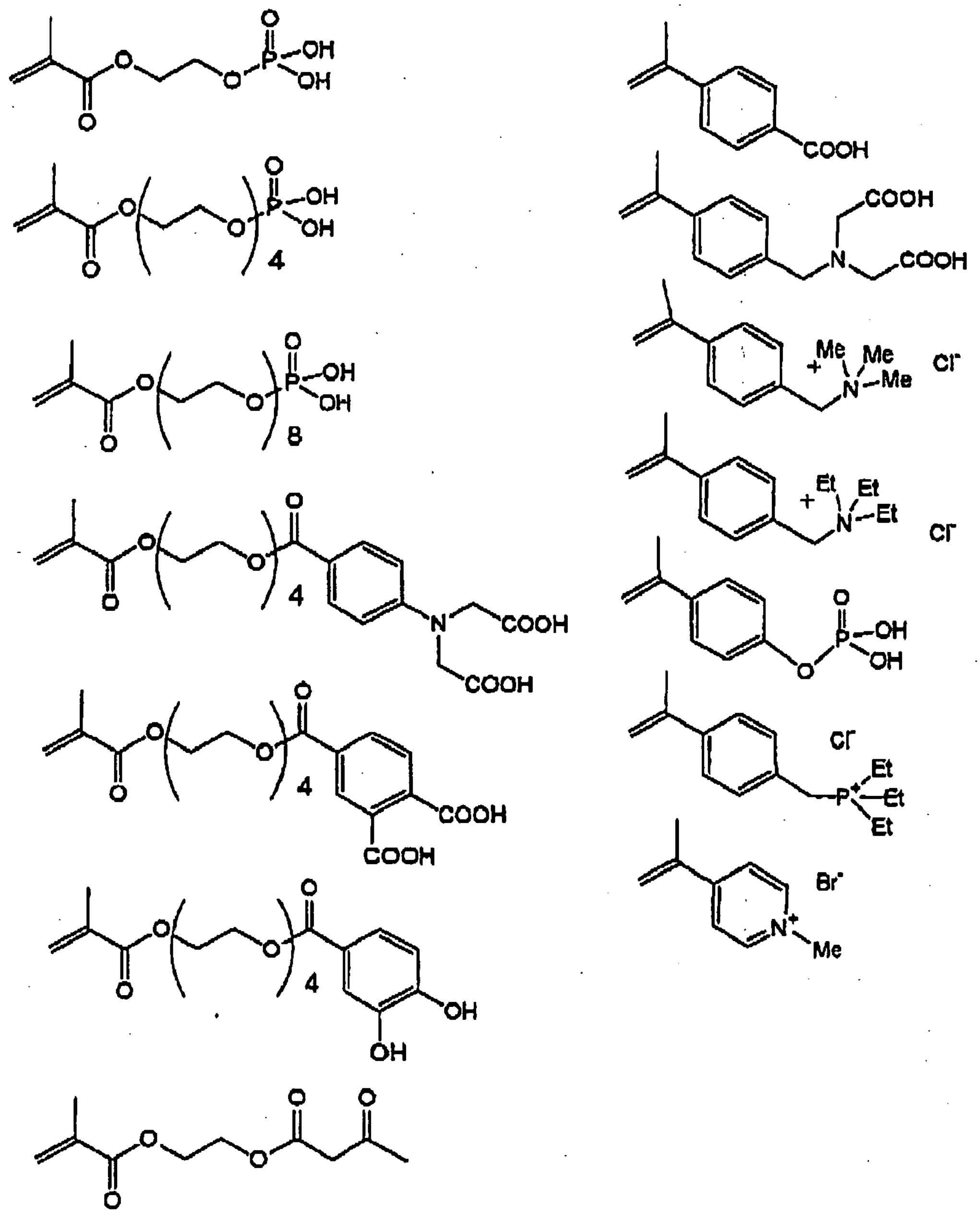
**[0228]** The aliphatic group may have a cyclic structure or branched structure. The number of carbon atoms of the aliphatic group is, preferably, from 1 to 20, more preferably, from 1 to 15 and, most preferably, from 1 to 10. For the aliphatic group, saturated aliphatic groups are preferred to unsaturated aliphatic groups. The aliphatic group may have a substituent. Examples of the substituent include, a halogen atom, hydroxyl group, aromatic group, and heterocyclic group.

**[0229]** The number of carbon atoms of the aromatic group is, preferably, from 6 to 20, more preferably, from 6 to 15, and, most preferably, from 6 to 10. The aromatic group may have a substituent. Examples of the substituent include a halogen atom, hydroxyl group, aliphatic group, aromatic group, and heterocyclic group. The heterocyclic group preferably has a 5-membered ring or 6-membered ring as the hetero ring. Other hetero ring, aliphatic ring, or aromatic ring may also be condensed to the hetero ring. The heterocyclic group may have a substituent. Examples of the substituent include a halogen atom, hydroxyl group, oxo group (=O), thiooxo group (=S), imino group (=NH), substituted imino group (=N-R, in which R is an aliphatic group, aromatic group or heterocyclic group), aliphatic group, aromatic group, and heterocyclic group.

**[0230]** L is preferably a bivalent connection group containing a plurality of polyoxyalkylene structures. The polyoxyalkylene structure is more preferably a polyoxyethylene structure. In other words, L preferably contain $-(OCH_2CH_2)_n-$ (n is an integer of 2 or greater).

**[0231]** In the formula (VII), Z is a functional group adsorbing to the hydrophilic surface of the support. Further, Y is a carbon atom or nitrogen atom. In a case where Y = nitrogen atom and L is connected on Y to form a quaternary prydinium salt, since this shows adsorbing property per se, Z is not essential.

**[0232]** Examples of typical monomers represented by the formula (VII) or (VIII) are shown below.



**[0233]** The hydrophilic group of the polymer resin for under coating usable in the invention preferably includes, for example, hydroxyl group, carboxyl group, carboxylate group, hydroxylethyl group, polyoxyethyl group, hydroxypropyl group, polyoxypropyl group, amino group, aminoethyl group, aminopropyl group, ammonium group, amide group, carboxymethyl group, sulfonate group, and phosphate group. Among them, monomers having sufonate group showing high hydrophilicity are preferred. Specific examples of the monomer having sulfonate group include sodium salts or amine salts of methalyl oxybenzene sulfonic acid, allyl oxybenzene sulfonic acid, allyl sulfonic acid, vinyl sulfonic acid, allyl sulfonic acid, p-styrene sulfonic acid, methalyl sulfonic acid, acrylamide t-butyl sulfonic acid, 2-acrylamide-2-methyl propane sufonic acid, and (3-acryloyloxypropyl)butyl sulfonic acid. Among them, sodium 2-acrylamide-2-methylpropane sulfonate salt is preferred in view of the hydrophilicity and handlability in the synthesis.

**[0234]** The water soluble polymer resin for undercoat layer in the invention preferably has crosslinking groups. Improvement for the adhesion with an image area can be obtained by the crosslinking group. For providing the polymer resin in for undercoat layer with the crosslinkability, crosslinking functional groups such as ethylenically unsaturated bond can be introduced into the side chains of the polymer or they can be introduced by forming a salt structure with a substituent having the counter charge to the polar substituent of the polymer resin, and a compound having an ethylenically unsaturated bond.

**[0235]** Examples of the polymer having the ethylenically unsaturated bonds in the side chain of the molecule include polymers of esters or amides of acrylic acid or methacrylic acid in which the residue of the ester or the amide (R in -COOR or -CONHR) has the ethylenically unsaturated bond.

**[0236]** Examples of the residue having the ethylenically unsaturated bond (R as described above) include -$(CH_2)_nCR_1=CR_2R_3$, -$(CH_2O)_nCH_2CR_1=CR_2R_3$, -$(CH_2CH_2O)_nCH_2CR_1=CR_2R_3$, -$(CH_2)_nNH$-CO-O-$CH_2CR_1=CR_2R_3$, $(CH_2)_n$-O-CO-$CR_1=CR_2R_3$, and - $(CH_2CH_2O)_2$-X (in which $R_1$ to $R_3$ each represents a hydrogen atom, halogen atom or alkyl group, aryl group, alkoxy group, or aryloxy group of 1 to 20 carbon atoms, $R_1$, $R_2$ or $R_3$ may join to each other to form a ring n represents an integer of 1 to 10, an X represents a dicyclopentadienyl residue).

**[0237]** Specific examples of the ester residue include -$CH_2CH=CH_2$ (described in JP-B No. 7-21633), -$CH_2CH_2O$-$CH_2CH=CH_2$, -$CH_2C(CH_3)=CH_2$, -$CH_2CH=CH$-$C_6H_5$, -$CH_2CH_2OCOCH=CH$-$C_6H_5$, -$CH_2CH_2NHCOO$-$CH_2CH=CH_2$ and -$CH_2CH_2O$-X (in which X represents a dicyclopentadienyl residue).

**[0238]** Specific examples of the amide residue include, $CH_2CH=CH_2$, -$CH_2CH_2O$-Y (in which Y represents a cyclehexene residue), and -$CH_2CH_2OCO$-$CH=CH_2$.

**[0239]** As the monomer having the crosslikable group of the polymer resin for undercoat layer, esters or amides of acrylic acid or methacrylic acid having the crosslinking groups are suitable.

**[0240]** The content of the crosslinkable group in the polymer resin for undercoat layer (content of unsaturated double bonds capable of radical polymerization by iodine titration) is, preferably, from 0.1 to 10.0 mmol, more preferably, from 1.0 to 7.0 mmol and, most preferably, from 2.0 to 5.5 mmol per 1 g of the polymer range. Within the resin described above, compatibility between the good sensitivity and the contaminating property, and good store stability can be obtained.

**[0241]** The polymer resin for undercoat layer has a mass average molecular weight of, preferably, 5,000 or more, more preferably, 10,000 to 300,000, and a number average molecular weight of 1,000 or more and, more preferably, from 2,000 to 250,000. The poly-dispersion degree (mass average molecular weight/number average molecular weight) is preferably from 1.1 to 10.

**[0242]** While the polymer resin for undercoat layer may be any of random polymers, block polymers, and graft polymers, it is preferably the random polymer.

**[0243]** The polymer resin for under coat may be used alone or two ore more of them may be used in admixture. The coating amount of the undercoat layer (solid content) is, preferably, from 0.1 to 100 mg/m$^2$ and, more preferably, from 1 to 30 mg/m$^2$.

**[0244]** It is a particularly preferred form that the compound having the polymerizable group further has the support adsorbing group and the hydrophilicity providing group in the molecule with a view point of further improving the adhesion property, and the on-press developability and the contamination property. The support adsorbing group is a group that causes bonding with a metal, metal oxide, hydroxyl group, etc. present on a support applied, for example, with an anodizing treatment or hydrophilic treatment generally by ionic bond, hydrogen bond, coordination bond or intermolecular force. As the support adsorbing group, an acid group or onium group is preferred. The acid group is preferably a group having an acid dissociation constant (pKa) of 7 or less and includes, specifically, -COOH, -$SO_3H$, -$OSO_3H$, -$PO_3H_2$, -$OPO_3H_2$, -$CONHSO_2$, and-$SO_2NHSO_2$-, etc. Among them, - $PO_3H_2$ is particularly preferred. Further, the onium group includes onium groups derived from atoms of the group 5B (group 15) or group 6B (group 16) of the periodical table and, more preferably, onium groups derived from nitrogen atom, phosphorus atom or sulfur atom and, particularly preferably, onium groups derived from the nitrogen atom. The hydrophilicity providing group includes ethylene oxide group (-$OCH_2CH_2$-), sulfonate group, etc.

**[0245]** The coating amount (solid content) of the undercoat layer is preferably from 0.1 to 100 mg/m$^2$ and, more preferably, from 3 to 30 mg/m$^2$.

## [Exposure]

**[0246]** Suitable light sources upon imagewise exposure of a lithographic printing plate precursor of the invention includes a carbon arc lamp, mercury lamp, xenone lamp, metal halide lamp, strobo, UV-rays, infrared rays, and laser lights. Lasers are particularly preferred and include solid lasers and semiconductor lasers emitting infrared rays of from 760 to 1200 nm, UV-semiconductor lasers emitting lights of 360 nm to 450 nm, and argon ion lasers and FD-YAG lasers emitting visible lights. Among them, with a view point of simplifying the plate making, lasers emitting infrared rays or ultraviolet rays that enable operation under white lamp or yellow lamp are preferred and lasers emitting infrared rays are particularly preferred.

**[0247]** The power of the infrared laser is preferably 100 mW or more. Further, for shortening the exposure time, use of a multi-beam laser device is preferred. The exposure time per 1 pixel is preferably within 20 $\mu$s. Further, irradiation amount of energy is preferably from 10 to 300 mJ/cm$^2$.

**[0248]** As the UV-ray lasers, specifically, InGaN type semiconductor lasers are suitable. While the exposure mechanism may be any of an inner surface drum system, an outer surface drum, a flat bed system or the like, a multi-beam exposure device so as to provide 20 mW or more of total power is preferred.

**[0249]** The on-press developing lithographic printing plate precursor is put to on-press development after imagewise exposure as described above.

[Example]

**[0250]** The present invention is to be described specifically by way of examples but the invention is not restricted to them. [Manufacture of on-press developing type lithographic printing plate precursor]

1. Preparation of a support

**[0251]** For removing a rolling lubricant on the surface of an aluminum plate (material 1050) of 0.3 mm thickness, after applying a degreasing treatment by using an aqueous solution of 10 mass% sodium aluminate at 50°C for 30 sec, the aluminum surface was sand-set by using three nylon brushes with a planted bundle of fibers each of a diameter of 0.3 mm and an aqueous suspension of pumice at a median diameter of 25 μm (specific gravity: 1.1 g/cm$^3$) and it was washed with water thoroughly. The plate was etched by being dipped in an aqueous solution of 25 mass% sodium hydroxide at 45°C for 9 sec and, after water washing, it was further dipped in 20 mass% nitric acid at 60°C for 20 sec and washed with water. In this case, the etching amount at the sand-set surface was about 3 g/m$^2$.

**[0252]** Then, a continuous electrochemical roughening treatment was applied by using an AC voltage at 60 Hz. The electrolyte in this case comprised an aqueous solution of 1 mass% nitric acid (containing 0.5 mass% of aluminum ions) at a liquid temperature of 50°C. An electrochemical roughening treatment was conducted with a carbon electrode as a counter-electrode using a trapezoidal rectangular wave AC current with a time TP of 0.8 mm sec for the current value to reach from 0 to a peak, at a duty ratio of 1:1 as the AC power source waveform. Ferrite was used for the auxiliary anode. The current density was 30 A/cm$^2$ at the peak value for the current and 5% of the current flowing from the power source was shunted to the auxiliary anode. The amount of electricity during nitric acid electrolysis was 175 C/dm$^2$ during operation of the aluminum plate as the anode. Then, water washing was conducted by spraying.

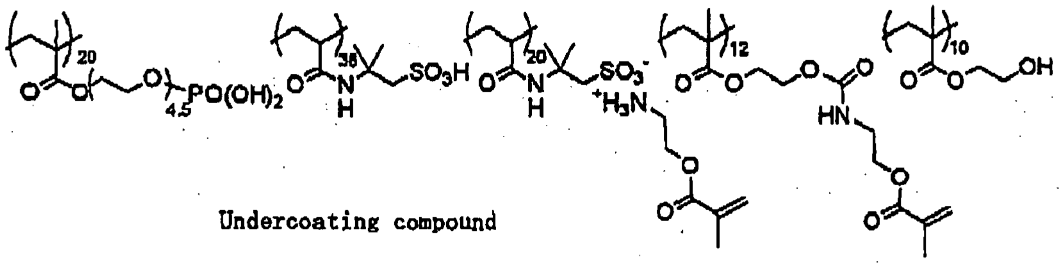
**[0253]** Then, an electrochemical roughening treatment was conducted by the same method as the nitric acid electrolysis using an electrolyte of an aqueous 0.5 mass% solution of hydrochloric acid (containing 0.5 mass% of aluminum ions) at a liquid temperature of 50°C under the conditions of 50 C/dm$^2$ of the electrolycity amount during operation of the aluminum plate as the anode and then water washing was conducted by spraying.

**[0254]** Then, after treating the plate at a current density of 15 A/dm$^2$ by using 15 mass% of sulfuric acid (containing 0.5 mass% of aluminum ions) as an electrolyte to form a 2.5 g/m$^2$ of a DC anodized film, it was water washed and dried to obtain a support A. When the center line average roughness (Ra) of the support was measured by using a needle of 2 μm diameter, it was 0.51 μm.

2. Preparation of undercoat layer

**[0255]** After coating the undercoating solution to the support by using a bar such that the dried coating amount was 10 mg/m$^2$, it was dried at 80°C for 20 sec in an oven to prepare an undercoat layer.

| Undercoating solution | |
|---|---|
| Undercoating compound described below | 0.017 g |
| Methanol | 9.00 g |
| Water | 1.00 g |



Undercoating compound

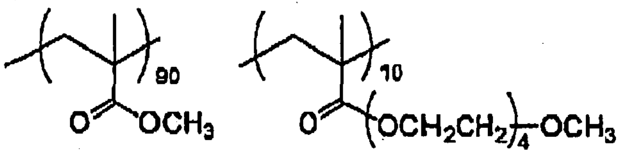
3. Preparation of photosensitive layer and protective layer

**[0256]** After coating a coating solution of photosensitive layer of the following composition on the obtained undercoat layer by bar coating, it was oven-dried at 100°C for 60 sec and a photosensitive layer with a dried coating amount of 1.0 g/m$^2$ was formed to obtain a lithographic printing plate precursor. Successively, a coating solution of the protective layer of the following composition was bar-coated on the photosensitive layer, oven-dried at 120°C for 60 sec, and a protective layer with a dried coating amount of 0.15 g/m$^2$ was formed to obtain a lithographic printing plate precursor.

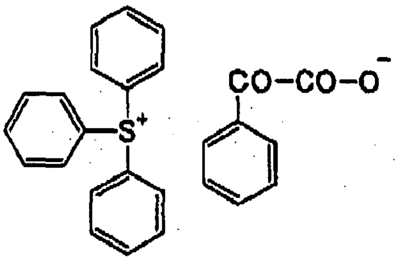
**[0257]** The coating solution of the photosensitive layer was obtained by mixing and stirring the following photosensitive solution (1) and a micro-gel solution (1) just before the coating,.

| | |
|---|---|
| Photosensitive solution (1) | |
| Binder polymer (1) | 0.162 g |
| Polymerization initiator (1) | 0.100 g |
| Infrared absorbing dye (1) | 0.020 g |
| Polymerizable monomer, ARONIX M-215 | |
| (manufactured by Toa Gosei Co. Ltd.) | 0.385 g |
| Fluoro surfactant (1) | 0.044 g |
| Methyl ethyl ketone | 1.091 g |
| 1-metoxy-2-propanol | 8.609 g |
| Micro-gel solution (1) | |
| Micro-gel solution synthesized as describe below | 2.640 g |
| Water | 2.425 g |

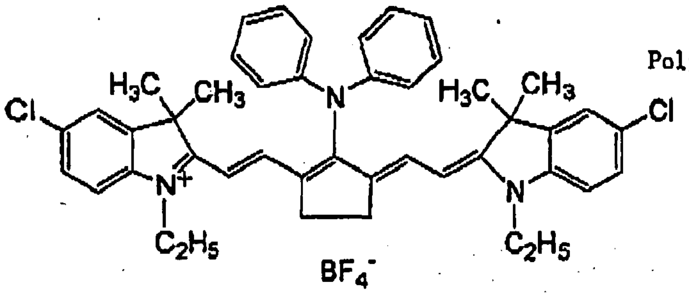
| | |
|---|---|
| Coating solution of protective layer | |
| The following aqueous dispersion of layered compound | 1.5 g |
| Polyvinyl alcohol PVA105 (manufactured by Kuraray, saponification degree: 98.5 mol%, polymerization degree: 500) | 0.06 g |
| Polyvinyl pyrrolidone K30 | 0.01g |
| (manufactured by Tokyo Kasei Industry Co, molecular weight Mw = 40,000) Vinyl pyrrolidone/vinyl acetate polymer LUVITEC VA64W(manufactured by ISP Co; | 0.01 g |
| polymerization ratio = 6/4) Nonionic surfactant Emalex 710 | 0.01 g |
| (Manufactured by Nihon Emulsion Co. Ltd.) Ion exchange water | 6.0 g |



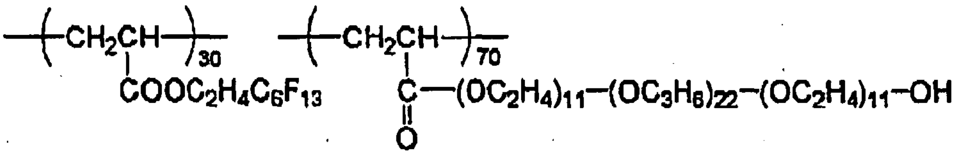
Binder polymer (1)



Polymerization initiator (1)



Infra-rod ray absorbont (1)



$$-\!\left(\mathrm{CH_2\underset{\displaystyle COOC_2H_4C_6F_{13}}{CH}}\right)_{30}\!-\quad-\!\left(\mathrm{CH_2\underset{\displaystyle \overset{\displaystyle \|}{\underset{\displaystyle O}{C}}-(OC_2H_4)_{11}-(OC_3H_6)_{22}-(OC_2H_4)_{11}-OH}{CH}}\right)_{70}\!-$$

Fluoro surfactant (1)

< Synthesis of micro-gel >

**[0258]** As an oil phase ingredient, 10 g of trimethylol propane and xylylene diisocyanate adduct (manufactured by Mitsui Takeda Chemicals Inc.: Takenate 17-110N, 75 mass% solution of ethyl acetate), 6.00 g of ARONIX M-215, manufactured by Toa Gosei Co. Ltd.) and 0.12 g of Pionine A-41C (manufactured by Takemoto Oil & Fat Co.) were dissolved in 16.67 g of ethyl acetate. As an aqueous phase ingredient, 37.5 g of an aqueous 4 mass% solution of PVA-205 was prepared. The oil phase ingredient and the aqueous phase ingredient were mixed and emulsified by using a homogenizer at 12,000 rpm for 10 min. The obtained emulsion was added to 25 g of distilled water and stirred at a room temperature for 30 min and then at 40°C for 2 hours. The thus obtained micro-gel solution was diluted by using distilled water such that the solid content concentration was 15 mass%. The average grain size was 0.2 μm.

< Preparation of aqueous solution of layered compound)

**[0259]** 6.4 g of synthesis mica, Somashif ME-100 (manufactured by CO-OP Chemical Co.) to 193.6 g of ion exchanged water and dispersed till the average grain size was 3 μm (by laser scattering method) by using a homogenizer. The aspect ratio of the obtained inorganic dispersion particle was 100 or more.

[Printing Apparatus]

**[0260]** In the example, actuators were disposed additionally and relevant control systems, etc. were modified such that inking rollers could be attached to and detached from the lithographic printing plate precursor surface on a plate cylinder all independently to a lithographic printing machine DIA 1F (manufactured by Mitsubishi Heavy Industries Ltd.) and an offset printing machine of the embodiment shown in Fig. 1. was used as the printing apparatus.

[Exposure]

**[0261]** To the lithographic printing plate precursor obtained as described above, solid images (half tone area ratio: 100%) of 20 mm length were exposed in a GATF chart and printing direction by a 32 channel multi-head plate setter Luxel T6M (manufactured by Fuji Film Corp.) mounting semiconductor lasers at 1 W by the number of 32 at a power of 0.24 W/channel, the number of outer surface drum rotation of 10,000 rpm and at a resolution power of 2400 dpi.

[Control of printing press]

**[0262]** The amount of ink and a water scale were controlled such that the ink concentration (reflection density) on printed matter was 1.6 by using a lithographic printing plate obtained by on-press development of an exposed lithographic printing plate precursor under usual conditions. In this case, the water scale was at 50 in the scale from 1 to 100 (amount of water is more as the numerical value is larger). Water dilution liquid of ECORITY-2 (manufactured by Fuji Film Corp) (ECORITY-2/water = 4/96 vol. ratio) was used for fountain solution and GEOS-G(N) black ink (manufactured by Dai-Nippon Ink Chemical Industry Co.) was used as the ink.

**[0263]** The following experiments were conducted under the printing conditions unless the change of conditions are described.

[Example 1]

**[0264]** From the start of the printing press, a dampening form roller was brought into contact with the plate surface of an exposed lithographic printing plate precursor attached to a plate cylinder and, from the 10th rotation, two inking rollers nearer to the dampening form roller were brought into contact with the plate surface with the inking roller being as it was and, after 6 rotation thereof, remaining dampening form roller s were brought into contact with the plate surface.

[Example 2]

**[0265]** From the start of the printing press, a dampening form roller was brought into contact with the plate surface of the exposed lithographic printing plate precursor attached to the plate cylinder and, from the 10th rotation, one inking roller nearest to the dampening form roller was bought into contact with the plate surface and, after 6 rotation thereof, remaining inking rollers were brought into contact with the plate surface.

[Example 3]

**[0266]** From the start of the printing press, a dampening form roller was brought into contact with the plate surface of an exposed lithographic printing plate precursor attached to the plate cylinder and, from the 10th rotation, only one inking roller furthest from the dampening form roller was brought into contact with the plate surface and, after 6 rotation thereof, the remaining inking rollers were brought into contact with the plate surface.

[Example 4]

**[0267]** On-press development was conducted in the same manner as in Example 2 except for increasing the water scale to 80 during 10 rotations after contact the dampening form roller with the plate surface.

[Comparative Example 1]

**[0268]** From the start of the printing press, the dampening form roller was brought into contact with the plate surface of an exposed lithographic printing plate precursor attached to a plate cylinder and, from the 10th rotation, all the dampening form rollers were brought into contact with the plate surface while leaving the dampening form roller as it was and printing was started.

[Comparative Example 2]

**[0269]** On-press development was conducted in the same manner as in Comparative Example 1 except for increasing the water scale to 80 during 10 rotations after contact of the dampening form roller with the plate surface.

[Comparative Example 3]

**[0270]** After exposing the same images under the same conditions as in Example 1 to a thermal CTP plate HP-S (manufactured by Fuji Film Corporation), a developing treatment was conducted by using an automatic developing machine LP-1310 HII, a developer DT-2 (1:8 dilution), and a finisher solution FG-1 (1:1 dilution manufactured by Fuji film corp.) to obtain a lithographic printing plate.

**[0271]** The lithographic printing plate precursor was attached to the printing apparatus identical with that in Example 1, dampening form rollers were brought into contact with the plate surface from the start and, all the dampening form rollers were brought into contact with the plate surface, and printing was started while leaving the dampening form rollers as they were from the 10th rotation.

[Evaluation and result]

**[0272]** The number of printed sheets from the start of printing at which respective contaminations were removed for the non-image area of a large area and the non-image area in 90% meshed portion was examined. The result is shown in Table 1.

Table 1: Result of Evaluation

| | Number of plates upon removing contamination (plate) | |
|---|---|---|
| | Non-image area of large area | non-image area in 90% mesh |
| Example 1 | 13 | 21 |
| Example 2 | 5 | 11 |
| Example 3 | 5 | 11 |
| Example 4 | 4 | 9 |

(continued)

| | Number of plates upon removing contamination (plate) | |
|---|---|---|
| | Non-image area of large area | non-image area in 90% mesh |
| Comp. Example 1 | 33 | 43 |
| Comp. Example 2 | 25 | 32 |
| Comp. Example 3 | 3 | 9 |

**[0273]** From the result of Table 1, the effect of the invention is apparent. Further, by bringing only one roll adjacent with the water dipping rolls in the inking step into contact with the plate surface, it was shown that printing could be conducted with a number of loss paper sheet comparable with that for the lithographic printing plate formed by existing wet development and that the number of loss paper sheet could be decreased further by increasing the rotational speed of the water source roll together.

## Claims

1. A method of on-press developing and printing an on-press development type lithographic printing plate precursor by using a printing apparatus having a plurality of inking rollers, the method comprising

    an inking step in which at least one of said plurality of inking rollers is not in contact with a plate surface.

2. The method according to claim 1, further comprising a printing step after the inking step,
wherein the number of the inking rollers being contact with the plate surface in the printing step is larger than the number of the inking rollers being contact with the plate surface in inking step.

3. The method according to claim 2,
wherein only one of said plurality of inking rollers is in contact with the plate surface in the inking step.

4. The method according to claim 2 or 3,
wherein all of said plurality of inking rollers are contact with the plate surface in the printing step.

5. The method according to claim 1, further comprising:

    a water dipping step that initiates and keeps supplying a fountain solution to the an on-press development type lithographic printing plate precursor, before the inking step; and
    a printing step after the inking step,

    wherein the fountain solution is maintained to be supplied to the plate surface throughout from the water dipping step to the printing step, the fountain solution having been carried by way of a water fountain roller which is rotating, and wherein a rotational speed of the water fountain roller in the water dipping step is larger than that in the printing step.

6. The method according to any one of claims 1 to 5,
wherein the on-press development type lithographic printing plate precursor comprises, on a support, a photosensitive layer comprising a polymerization initiator, a polymerizable compound and a sensitizing dye.

7. A printing apparatus comprising:

    three or more inking rollers, the inking rollers being divided two groups; and
    an inking roller attachment/detachment control means for separately controlling attachment/detachment of each of (i) the inking roller(s) in one group and (ii) the inking roller(s) in the other group to and from a plate surface of an on-press development type lithographic printing plate precursor.

8. The printing apparatus according to claim 7, further comprising:

    a water fountain roller by way of which a fountain solution is supplied to the plate surface of the on-press

development type lithographic printing plate precursor; and
a water fountain roller rotational speed control means for varying a rotational speed of the water fountain roller.

**9.** The printing apparatus according to claim 7 or 8,
wherein the on-press development type lithographic printing plate precursor comprises, on a support, a photosensitive layer comprising a polymerization initiator, a polymerizable compound and a sensitizing dye.

FIG. 1

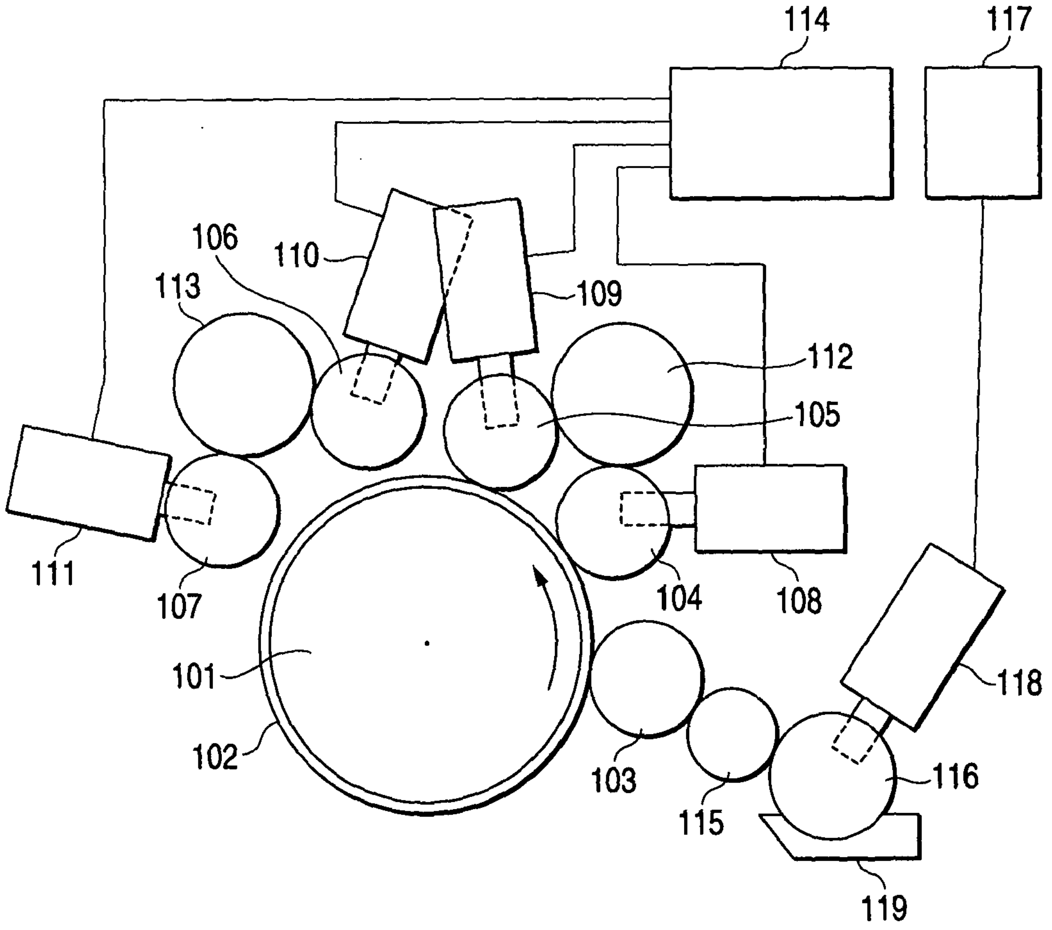

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FIG. 2

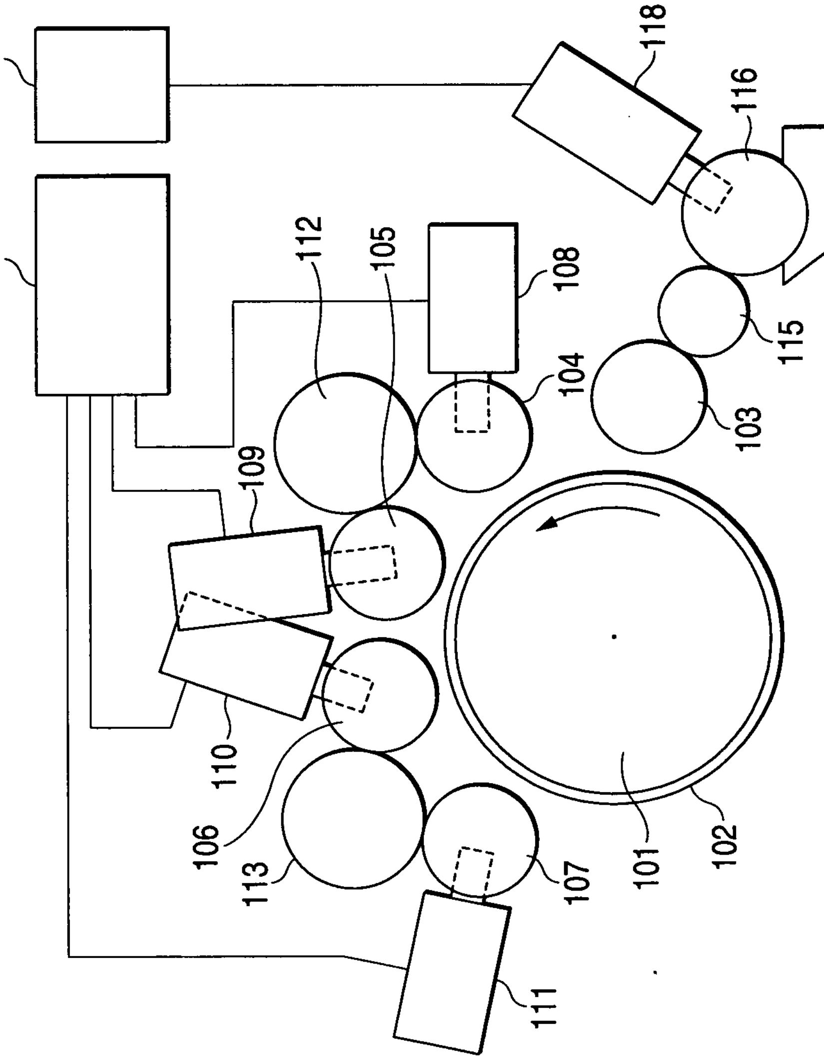
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FIG. 3

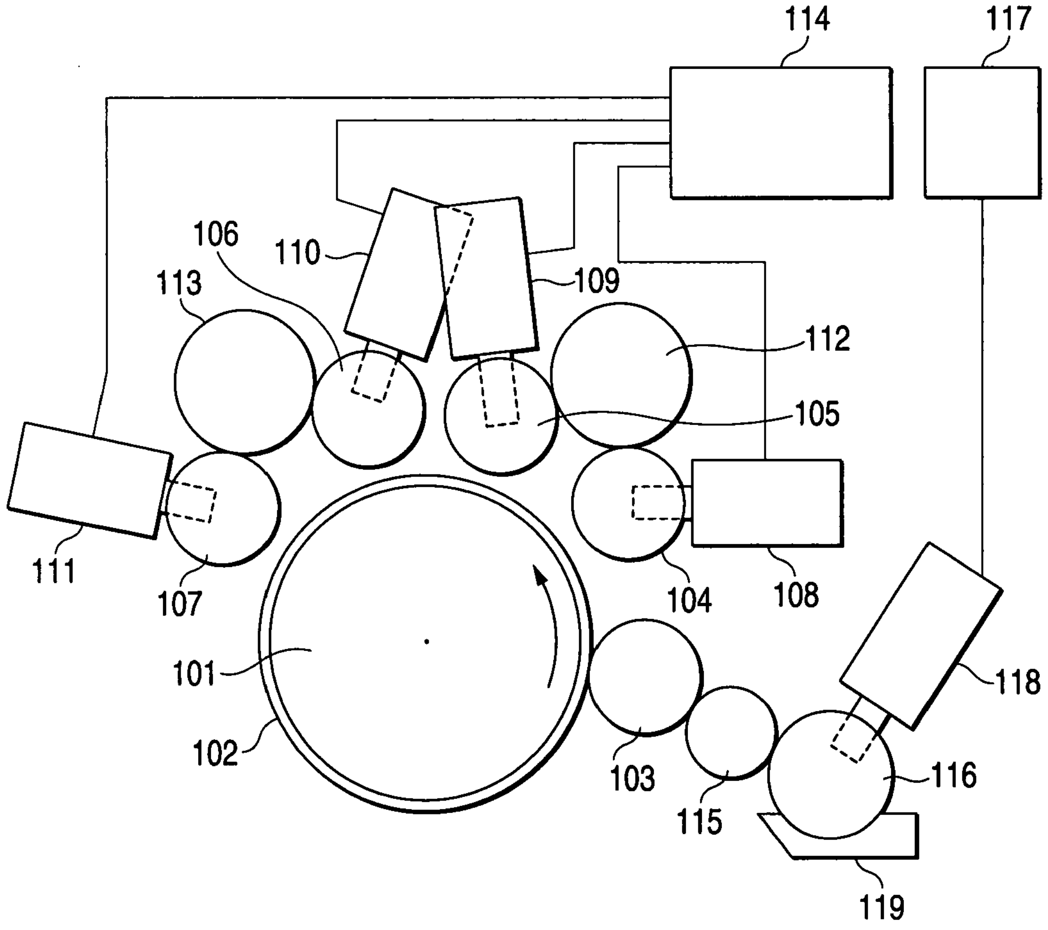
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FIG. 4

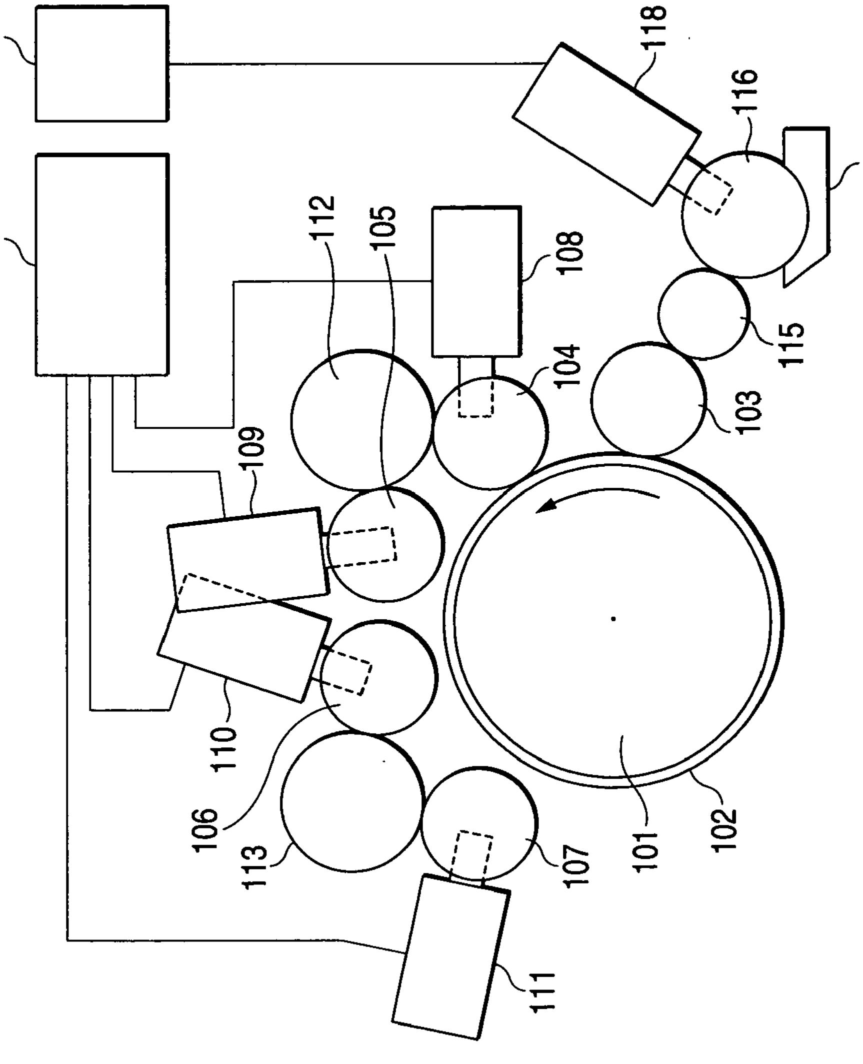
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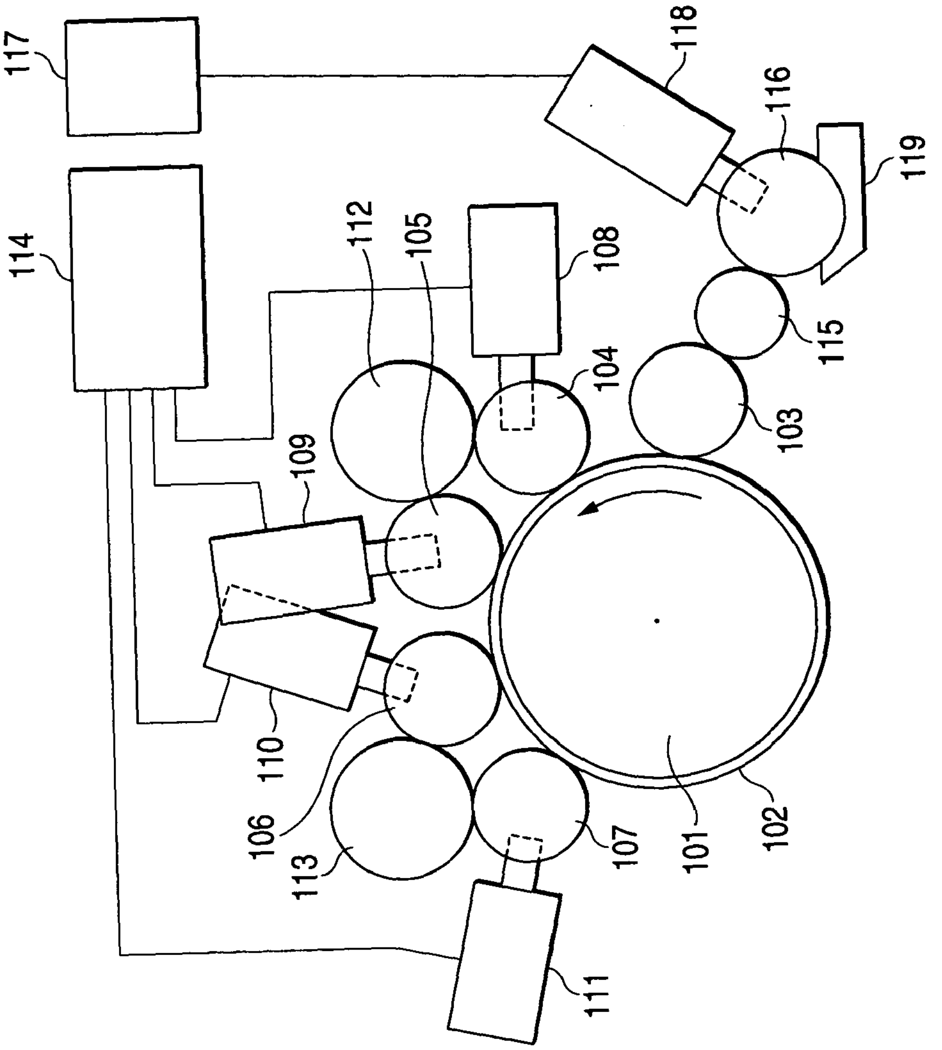
FIG. 5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