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(54) **Lithographic printing plate precursor, plate making method thereof and lithographic printing method thereof**

Lithographiedruckplattenvorläufer, Plattenherstellungsverfahren dafür und Lithographiedruckverfahren  
dafür

Précurseur de plaque d'impression lithographique, procédé de fabrication de plaque correspondant et  
procédé d'impression lithographique correspondant

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(56) References cited:

**JP-A- 2004 317 543**   **JP-A- 2007 249 036**

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**Description****FIELD OF THE INTENTION**

5 [0001] The present invention relates to a lithographic printing plate precursor, a plate making method thereof and a lithographic printing method thereof. More particularly, it relates to a lithographic printing plate precursor which is capable of undergoing a so-called direct plate making in which the plate making is directly conducted based on digital signals, for example, from a computer using various kinds of lasers, a plate making method thereof and a lithographic printing method thereof.

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**BACKGROUND OF THE INVENTION**

15 [0002] In general, a lithographic printing plate is composed of an oleophilic image area accepting ink and a hydrophilic non-image area accepting dampening water in the process of printing. Lithographic printing is a printing method utilizing the nature of water and oily ink to repel with each other and comprising rendering the oleophilic image area of the lithographic printing plate to an ink-receptive area and the hydrophilic non-image area thereof to a dampening water-receptive area (ink-unreceptive area), thereby making a difference in adherence of the ink on the surface of the lithographic printing plate, depositing the ink only to the image area, and then transferring the ink to a printing material, for example, paper.

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[0003] In order to produce the lithographic printing plate, a lithographic printing plate precursor (PS plate) comprising a hydrophilic support having provided thereon an oleophilic photosensitive resin layer (image-recording layer) is used. Specifically, the PS plate is exposed through a mask, for example, a lith film, and then subjected to development processing, for example, with an alkaline developer to remove the unnecessary image-recording layer corresponding to the non-image area by dissolving while leaving the image-recording layer corresponding to the image area, thereby obtaining the lithographic printing plate.

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[0004] Due to the recent progress in the technical field, nowadays the lithographic printing plate can be obtained by a CTP (computer-to-plate) technology. Specifically, a lithographic printing plate precursor is directly subjected to scanning exposure using laser or laser diode without using a lith film and developed to obtain a lithographic printing plate.

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[0005] With the progress described above, the issue on the lithographic printing plate precursor has transferred to improvements, for example, in image-forming property corresponding to the CTP technology, printing property or physical property. Also, with the increasing concern about global environment, as another issue on the lithographic printing plate precursor, an environmental problem on waste liquid discharged accompanying the wet treatment, for example, development processing comes to the front.

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[0006] In response to the environmental problem, simplification of development or plate making or non-processing has been pursued. As one method of simple plate making, a method referred to as "on-press development" is practiced. Specifically, according to the method after exposure of a lithographic printing plate precursor, the lithographic printing plate precursor is mounted as it is on a printing machine without conducting conventional development and removal of the unnecessary area of image-recording layer is performed at an early stage of printing step.

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[0007] Also, as a method of simple development, a method referred to as "gum development" is practiced wherein the removal of the unnecessary area of image-recording layer is performed using not a conventional high alkaline developer but a finisher or gum solution of near-neutral pH.

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[0008] In the simplification of plate making operation as described above, a system using a lithographic printing plate precursor capable of being handled in a bright room or under a yellow lump and a light source is preferred from the standpoint of workability. Thus, as the light source, a semiconductor laser emitting an infrared ray having a wavelength from 760 to 1,200 or a solid laser, for example, YAG laser, is used.

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[0009] As the lithographic printing plate precursor capable of undergoing on-press development or gum development, a lithographic printing plate precursor using a thermoplastic polymer fine particle in an image-forming layer and a plate making method are described in JP-A-9-123387 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") and JP-A-2003-255527. Also, a lithographic printing plate precursor using a thermoplastic polymer fine particle having a reactive group in an image-forming layer and a plate making method are described in JP-A-2001-260554 and JP-A-2003-316021. However, these techniques are still insufficient for obtaining both good development property and high printing durability.

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[0010] JP-A-2004317543 discloses a lithographic printing plate precursor comprising: an image-recording layer containing an infrared absorbing agent and a polymer compound; and a support having a hydrophilic surface, wherein the polymer compound is an alkali-soluble polymer having a star-like shape in which a main chain is branched to three or more branches and the branched main chains have a hydrophilic group in a side chain of the branched main chain. The image-recording layer further comprises a polymerizable compound and a polymerization initiator. The image is formed by polymerizing the polymerizable compound in the exposed regions.

**SUMMARY OF THE INVENTION**

[0011] An object of the present invention is to provide a lithographic printing plate precursor which can achieve both printing durability and development property, a plate making method using the lithographic printing plate precursor and a lithographic printing method using the lithographic printing plate precursor.

[0012] As a result of the intensive investigations, the inventor has achieved the above-described objects by incorporating a polymer compound (hereinafter, also referred to as a star polymer) having a star-like shape in which a main chain is branched to three or more branches and the branched main chains have a hydrophilic side chain into an image-recording layer containing a thermoplastic polymer fine particle.

[0013] The invention provides the following items 1 to 10.

1. A lithographic printing plate precursor comprising: an image-recording layer containing a thermoplastic polymer fine particle, an infrared absorbing agent and a polymer compound; and a support having a hydrophilic surface, wherein the polymer compound has a star-like shape in which a main chain is branched to three or more branches and the branched main chains have a hydrophilic group in a side chain of the branched main chain.
2. The lithographic printing plate precursor as described in the above item 1, wherein the hydrophilic group is at least any one of a carboxyl group or a salt thereof, a sulfo group or a salt thereof and a polyethylene oxy group.
3. The lithographic printing plate precursor as described in the above item 1 or 2, wherein the thermoplastic polymer fine particle has a crosslinkable group.
4. The lithographic printing plate precursor as described in the above item 3, wherein the polymer compound having the star-like shape has, in a side chain of the branched main chain, a group capable of reacting with the crosslinkable group of the thermoplastic polymer fine particle.
5. The lithographic printing plate precursor as described in the above item 4, wherein both the crosslinkable group of the thermoplastic polymer fine particle and the group capable of reacting with the crosslinkable group of the thermoplastic polymer fine particle are ethylenically unsaturated groups.
6. The lithographic printing plate precursor as described in any one of the above items 1 to 5, wherein the image-recording layer contains a polymerization initiator.
7. The lithographic printing plate precursor as described in any one of the above items 1 to 6, wherein the image-recording layer is capable of being removed with at least any of printing ink and dampening water.
8. A lithographic printing method comprising after either mounting the lithographic printing plate precursor as described in the above item 7 on a printing machine and exposing imagewise the lithographic printing plate precursor with laser or exposing imagewise the lithographic printing plate precursor as described in the above item 7 with laser and mounting the exposed lithographic printing plate precursor on a printing machine, supplying at least any of printing ink and dampening water on the exposed lithographic printing plate precursor to remove an unexposed area of the image-recording layer.
9. A plate making method of a lithographic printing plate precursor comprising after exposing imagewise the lithographic printing plate precursor as described in any one of the above items 1 to 6 with laser, developing the exposed lithographic printing plate precursor with an aqueous solution having pH from 2 to 12.
10. The plate making method of a lithographic printing plate precursor as described in the above item 9, wherein after the development of the exposed lithographic printing plate precursor with an aqueous solution having pH from 2 to 12, the developed lithographic printing plate precursor is subjected to a heat treatment.

[0014] The functional mechanism of the invention is not quite clear but it is estimated that due to using the star polymer as the polymer compound dispersibility of the thermoplastic polymer fine particle in the image-recording layer is improved in comparison with a conventional strait-chain polymer and the thermoplastic polymer fine particle is uniformly dispersed so that the development property is more improved and a heat fusion efficiency of the thermoplastic polymer fine particle increases to improve the printing durability.

[0015] According to the present invention, a lithographic printing plate precursor which can achieve both printing durability and development property, a plate making method using the lithographic printing plate precursor and a lithographic printing method using the lithographic printing plate precursor can be provided.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0016]

Fig. 1 is a view schematically showing a main chain structure of a star polymer.

Fig. 2 is a view explaining a structure of an automatic development processor.

[Description of reference numerals and signs]

**[0017]**

- 5 4: Lithographic printing plate precursor (PS plate)
- 6: Developing unit
- 10: Drying unit
- 16: Carrying-in roller
- 20: Developing tank
- 10 22: Transport roller
- 24: Brush roller
- 26: Squeeze roller (carrying-out roller)
- 28: Backup roller
- 36: Guide roller
- 15 38: Skewer roller

**DETAILED DESCRIPTION OF THE INVENTION**

[Image-recording layer]

20 **[0018]** The image-recording layer of the lithographic printing plate precursor according to the invention contains a thermoplastic polymer fine particle, an infrared absorbing agent and a polymer compound having a star-like shape in which a main chain is branched to three or more branches and the branched main chains have a hydrophilic side chain.

25 [Thermoplastic polymer fine particle]

**[0019]** According to the invention, it is preferred to incorporate a thermoplastic polymer fine particle having Tg of 60°C or higher. In case of mixing two or more kinds of thermoplastic polymer fine particles having different Tg, it is preferred that Tg of at least one kind of the thermoplastic polymer fine particles is 60°C or higher.

30 **[0020]** As the thermoplastic polymer fine particle having Tg of 60°C or higher, thermoplastic polymer fine particles described, for example, in Research Disclosure, No. 33303, January (1992), JP-A-9-123387, JP-A-9-131850, JP-A-9-171249, JP-A-9-171250 and European Patent 931,647 are preferably exemplified.

35 **[0021]** Specific examples of the polymer constituting the thermoplastic polymer fine particle include a homopolymer or copolymer of a monomer, for example, ethylene, styrene, vinyl chloride, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, vinylidene chloride, acrylonitrile or vinyl carbazole and a mixture thereof. Among them, polystyrene and polymethyl methacrylate are more preferred.

**[0022]** The thermoplastic polymer fine particle contained in the image-recording layer of the lithographic printing plate precursor according to the invention may comprise two or more kinds of the thermoplastic polymer fine particles having different particle sizes or two or more kinds of the thermoplastic polymer fine particles having different Tg.

40 **[0023]** By using two or more kinds of the thermoplastic polymer fine particles as described above, film curing property of the image area is more improved and when a lithographic printing plate is prepared, printing durability is more improved.

45 **[0024]** For instance, in case of using the thermoplastic polymer fine particles having the same particle size, since voids exist in some extent between the thermoplastic polymer fine particles, the film curing property may not reach the desired level in some cases even when the thermoplastic polymer fine particles are fused and solidified, for example, by heat mode exposure. On the contrary, in case of using the thermoplastic polymer fine particles having different particle sizes, a void ratio between the thermoplastic polymer fine particles can be reduced and as a result, the film curing property of the image area after the heat mode exposure can be improved.

50 **[0025]** Also, in case of using the thermoplastic polymer fine particles having the same Tg, when temperature elevation of the image-recording layer, for example, by heat mode exposure is insufficient, the thermoplastic polymer fine particles are not sufficiently fused and solidified and the film curing property may not reach the desired level in some cases. On the contrary, in case of using the thermoplastic polymer fine particles having different Tg, the film curing property of the image area can be improved even when the temperature elevation of the image-recording layer, for example, by heat mode exposure is insufficient.

55 **[0026]** The average particle size of the thermoplastic polymer fine particle is preferably from 0.005 to 2.0  $\mu\text{m}$ . The value is also applied to the case in which two or more kinds of the thermoplastic polymer fine particles are used as a mixture. The average particle size thereof is more preferably from 0.01 to 1.5  $\mu\text{m}$ , and particularly preferably from 0.05 to 1.0  $\mu\text{m}$ . When the average particle size is extremely large, resolution may decrease in some cases, whereas when it is extremely small, time lapse stability may decrease in some cases. In case of mixing two or more kinds of the

thermoplastic polymer fine particles, a polydispersity is preferably 0.2 or more. In case of using a mixture comprising the particle of a large particle size and the particle of a small particle size, the occurrence of void at the heat fusion decreases and high printing durability can be achieved. The polydispersity and average particle size are determined by a laser scattering method.

5 [0027] The Tg of at least one kind of the thermoplastic polymer fine particles is preferably 60°C or higher, more preferably from 70 to 140°C, and still more preferably from 80 to 120°C. In case of mixing two or more kinds of the thermoplastic polymer fine particles having different Tg, difference of the Tg is preferably 10°C or more, and more preferably 20°C or more. The content of the thermoplastic polymer fine particles having Tg of 60°C or higher is preferably 70% by weight or more based on the total thermoplastic polymer fine particles. When the content is 70% by weight or more, deterioration of the on-press development property due to the lapse of time is preferably more reduced.

10 [0028] The thermoplastic polymer fine particle contained in the image-recording layer of the lithographic printing plate precursor according to the invention may have a crosslinkable group. The crosslinkable group may be a functional group which undergoes any reaction as long as a chemical bond is formed and includes, for example, an ethylenically unsaturated group (for example, an acryloyl group, a methacryloyl group, a vinyl group or an allyl group) undergoing a polymerization reaction, an isocyanate group or a blocked form thereof undergoing an addition reaction and a functional group having an active hydrogen atom (for example, an amino group, a hydroxy group or a carboxyl group) as the reaction partner thereof, an epoxy group also undergoing an addition reaction and an amino group, a carboxyl group or a hydroxy group as the reaction partner thereof, a carboxyl group undergoing a condensation reaction and a hydroxy group or an amino group as the reaction partner thereof, and an acid anhydride undergoing a ring opening addition reaction and an amino group or a hydroxyl group as the reaction partner thereof.

15 [0029] The thermoplastic polymer fine particle having a thermo-reactive functional group contained in the image-recording layer of the lithographic printing plate precursor according to the invention specifically includes that having an acryloyl group, a methacryloyl group, a vinyl group, an allyl group, an epoxy group, an amino group, a hydroxy group, a carboxyl group, an isocyanate group, an acid anhydride and a protected group thereof. The introduction of the functional group into the thermoplastic polymer fine particle may be conducted at the time of polymerization of the polymer fine particle or may be conducted by utilizing a polymer reaction after the polymerization of the polymer fine particle.

20 [0030] In the case of introducing the crosslinkable group at the time of polymerization of the polymer fine particle, a monomer having the crosslinkable group may preferably be subjected to emulsion polymerization or suspension polymerization.

25 [0031] Specific examples of the monomer having the crosslinkable group include allyl methacrylate, allyl acrylate, vinyl methacrylate, vinyl acrylate, glycidyl methacrylate, glycidyl acrylate, 2-isocyanateethyl methacrylate or a blocked isocyanate thereof, for example, with an alcohol, 2-isocyanateethyl acrylate or a blocked isocyanate thereof, for example, with an alcohol, 2-aminoethyl methacrylate, 2-aminoethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, acrylic acid, methacrylic acid, maleic anhydride, a divalent acrylate and a divalent methacrylate, but the invention should not be construed as being limited thereto.

30 [0032] The polymer reaction used in the case of conducting the introduction of the crosslinkable group after the polymerization of polymer fine particle includes, for example, a polymer reaction described in WO 96/34316.

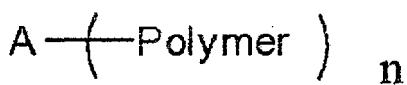
35 [0033] The polymer fine particles may be reacted with each other via the crosslinkable groups or with a reactive group introduced into a side chain of the polymer having a star-like shape or a low molecular weight polymerizable compound added to the image-recording layer. Also, different kinds of crosslinkable groups capable of undergoing thermal reaction with each other are introduced into two or more kinds of polymer fine particles so that the thermoplastic polymer fine particles are reacted with each other. The reaction involved therein includes a polymerization reaction by an unsaturated group, an addition reaction between an isocyanate group or a blocked form thereof and a compound having an active hydrogen atom (for example, an amine, an alcohol or a carboxylic acid), an addition reaction between an epoxy group and an amino group, a carboxyl group or a hydroxy group, a condensation reaction between a carboxyl group and a hydroxy or an amino group, and a ring opening addition reaction between an acid hydride and an amino group or a hydroxy group. However, any reaction may be used as long as a chemical bond can be formed.

40 [0034] The amount of the thermoplastic polymer fine particle for use in the invention to the image-recording layer is preferably from 40 to 95% by weight, more preferably from 50 to 90% by weight, particularly preferably from 60 to 85% by weight, based on the solid content of the image-recording layer.

[Star polymer]

45 [0035] The polymer compound for use in the invention is a star polymer in which a main chain is branched to three or more branches and a polymer compound which has a main chain structure as schematically shown in Fig. 1 and is represented by formula (1) shown below.

5 Formula (1):



[0036] In formula (1), A represents a branch unit (constituting unit including branch points) of the star polymer, Polymer represents a polymer chain constituting a main chain and has a hydrophilic group in its side chain, and n represents 3 or more.

10 [Polymer moiety]

[0037] The star polymer for use in the invention may be any polymer having the main chain structure as described above and a hydrophilic group in its side chain. The hydrophilic group is preferably contained in the Polymer moiety as 15 a repeating unit having the hydrophilic group in its side chain.

<Repeating unit having hydrophilic group>

[0038] The hydrophilic group includes -COOM<sup>1</sup> (a carboxyl group or a salt thereof), -SO<sub>3</sub>M<sup>1</sup> (a sulfo group or a salt 20 thereof), -OH, -OSO<sub>3</sub>M<sup>1</sup>, -CONR<sup>1</sup>R<sup>2</sup>, -SO<sub>2</sub>NR<sup>1</sup>R<sup>2</sup>, -NR<sup>1</sup>SO<sub>3</sub>M<sup>1</sup>, -P(=O)(OM<sup>1</sup>)(OM<sup>2</sup>), -OP(=O)(OM<sup>1</sup>)(OM<sup>2</sup>), a group containing an ethylene oxide structure, for example, a hydroxyethyl group or a polyethylene oxy group, and a group containing an propylene oxide structure, for example, a hydroxypropyl group or a polypropylene oxy group. In the formulate above, M<sup>1</sup> and M<sup>2</sup> each represents a hydrogen ion, a metal ion, an ammonium ion or a phosphonium ion, and R<sup>1</sup> and R<sup>2</sup> each independently represents a hydrogen atom, an alkyl group, an alkenyl group or an aryl group.

[0039] In the case where any one of M<sup>1</sup> and M<sup>2</sup> represents the metal ion, specific examples of the metal ion include 25 Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cu<sup>+</sup>. Of the metal ions, Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> are particularly preferred.

[0040] In the case where any one of M<sup>1</sup> and M<sup>2</sup> represents the ammonium ion, any ordinary ammonium ion can be 30 preferably used and an ammonium ion having a number of carbon atoms of 24 or less per molecule is preferred and an ammonium ion having a number of carbon atoms of 16 or less per molecule is particularly preferred.

[0041] In the case where any one of M<sup>1</sup> and M<sup>2</sup> represents the phosphonium ion, any ordinary phosphonium ion can be 35 preferably used and a phosphonium ion having a number of carbon atoms of 24 or less per molecule is preferred and a phosphonium ion having a number of carbon atoms of 16 or less per molecule is particularly preferred.

[0042] In the case where any one of R<sup>1</sup> and R<sup>2</sup> represents the alkyl group, any ordinary alkyl group can be used, and it may be a branched or cyclic form and may have a substituent, for example, a halogen atom, an ether group, a thioether 40 group, a hydroxy group, a cyano group, a keto group, a carboxyl group, a carboxylate group, a carbonic acid ester group, a carbonic acid amido group, a sulfo group, a sulfonate group, a sulfonic acid ester group, a sulfonamido group, a sulfoxide group, a phenyl group, a phosphonic acid group, a phosphonate group, a phosphoric acid group, a phosphate group, an amino group, an aminocarbonyl group, an amino carboxyl group or an aminosulfonyl group. As the alkyl group, an alkyl group having a total number of carbon atoms of 12 or less is particularly preferred.

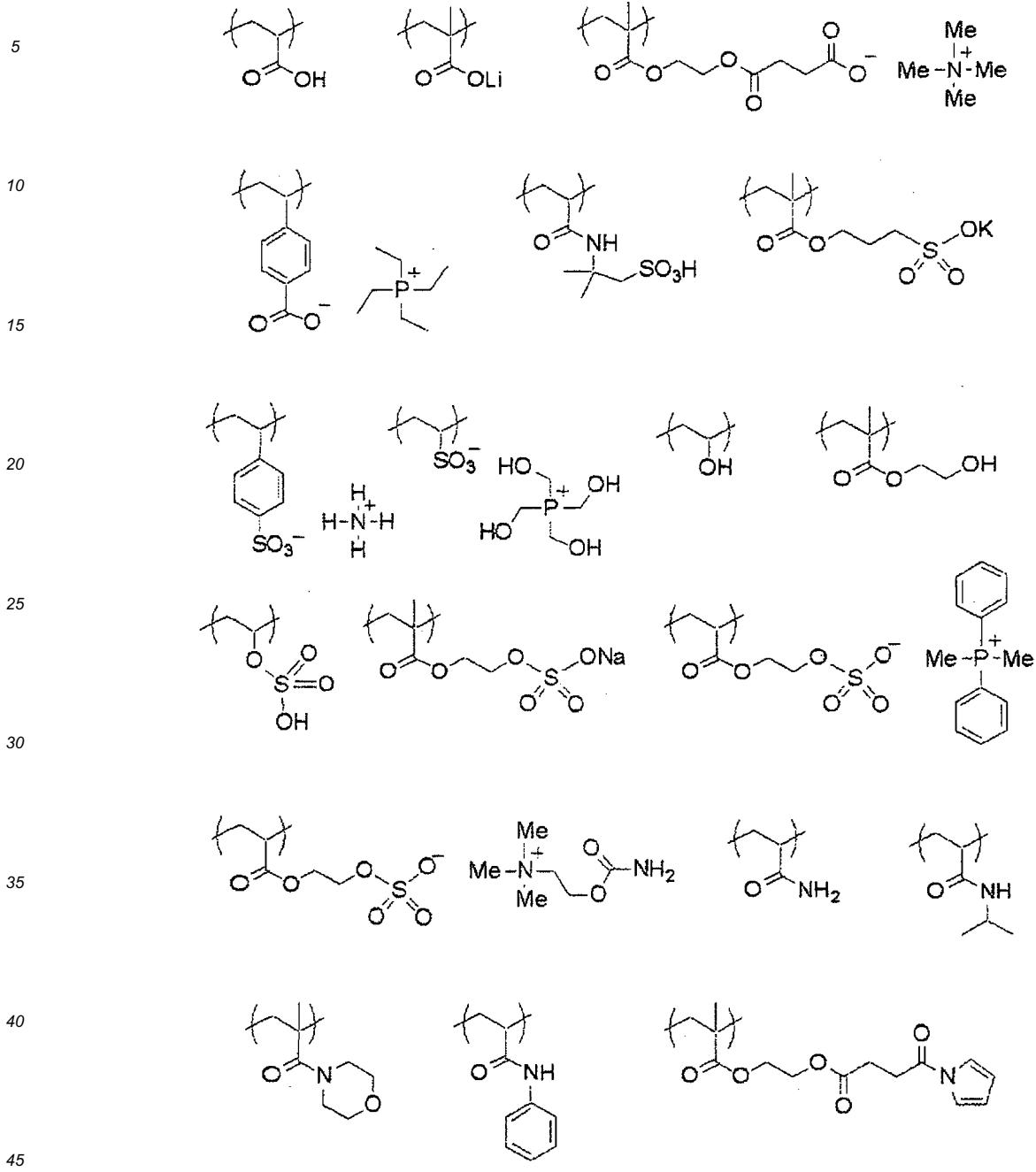
[0043] In the case where any one of R<sup>1</sup> and R<sup>2</sup> represents the alkenyl group, any ordinary alkenyl group can be used, and it may be a branched or cyclic form and may have a substituent, for example, a halogen atom, an ether group, a thioether group, a hydroxy group, a cyano group, a keto group, a carboxyl group, a carboxylate group, a carbonic acid ester group, a carbonic acid amido group, a sulfo group, a sulfonate group, a sulfonic acid ester group, a sulfonamido group, a sulfoxide group, a phenyl group, a phosphonic acid group, a phosphonate group, a phosphoric acid group, a phosphate group, an amino group, an aminocarbonyl group, an amino carboxyl group or an aminosulfonyl group. As the alkenyl group, an alkenyl group having a total number of carbon atoms of 12 or less is particularly preferred.

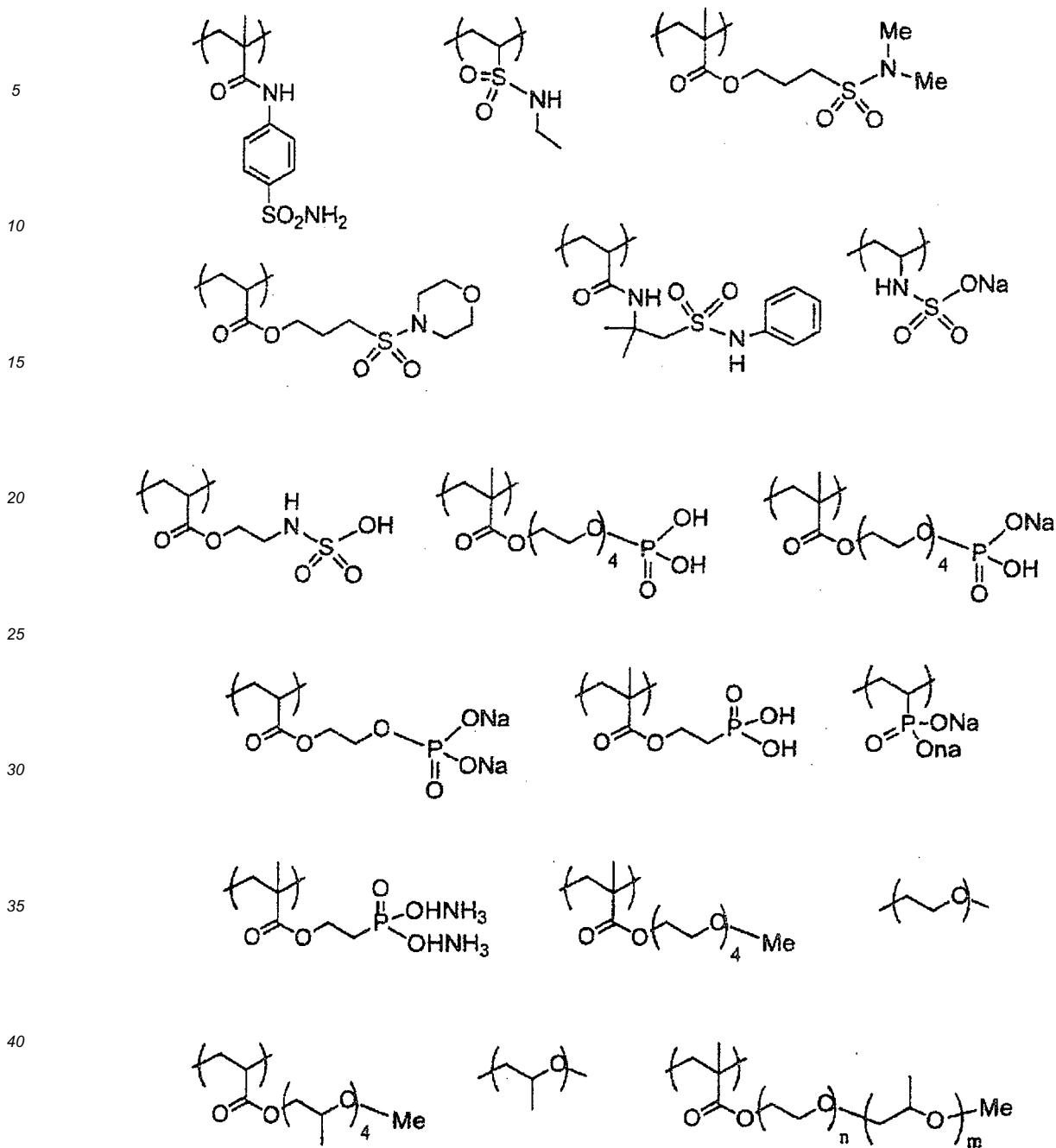
[0044] In the case where any one of R<sup>1</sup> and R<sup>2</sup> represents the aryl group, any ordinary aryl group can be 50 preferably used. The aryl group may have a substituent, for example, a halogen atom, an ether group, a thioether group, a hydroxy group, a cyano group, a nitro group, a keto group, a carboxyl group, a carboxylate group, a carbonic acid ester group, a carbonic acid amido group, a sulfo group, a sulfonate group, a sulfonic acid ester group, a sulfonamido group, a sulfoxide group, a phenyl group, a phosphonic acid group, a phosphonate group, a phosphoric acid group, a phosphate group, an amino group, an aminocarbonyl group, an amino carboxyl group or an aminosulfonyl group. As the aryl group, an aryl group having a total number of carbon atoms of 12 or less is particularly preferred.

[0045] Of the hydrophilic groups, -COOM<sup>1</sup> (a carboxyl group or a salt thereof), -SO<sub>3</sub>M<sup>1</sup> (a sulfo group or a salt thereof) 55 and a polyethylene oxy group are particularly preferred.

[0046] As the repeating unit having at least one hydrophilic group for forming the star polymer according to the invention, any repeating unit is preferably used as long as it is formed from a repeating unit having at least one of the hydrophilic groups. Specific examples of the repeating unit having a hydrophilic group which can be used in the invention are set

forth below, but the invention should not be construed as being limited thereto.





chain of the star polymer.

[0050] In the case where the thermoplastic polymer fine particle has an isocyanate group or a blocked form thereof undergoing an addition reaction, it is preferred to introduce a functional group having an active hydrogen atom (for example, an amino group, a hydroxy group or a carboxyl group), which is the reaction partner of the isocyanate group, into the side chain of the star polymer. In the case where the thermoplastic polymer fine particle has an epoxy group undergoing an addition reaction, it is preferred to introduce an amino group, a carboxyl group or a hydroxy group, which is the reaction partner of the epoxy group, into the side chain of the star polymer.

[0051] Also, in the case where the thermoplastic polymer fine particle has a crosslinkable group having an active hydrogen atom (for example, an amino group, a hydroxy group or a carboxyl group), it is preferred to introduce an isocyanate group or a blocked form thereof undergoing an addition reaction or an epoxy group also undergoing an addition reaction into the side chain of the star polymer.

[0052] Similarly, with respect to a combination of a carboxyl group and a hydroxyl group or an amino group undergoing a condensation reaction, a combination of an acid anhydride and an amino group or a hydroxyl group undergoing a ring opening addition reaction or the like, it is preferred for the star polymer to have a functional group, which is a reaction partner of the functional group included in the thermoplastic polymer fine particle.

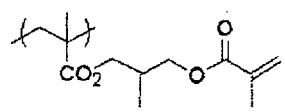
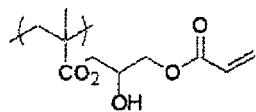
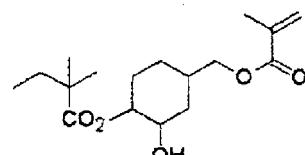
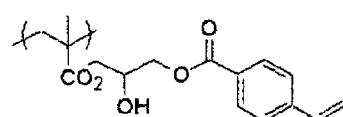
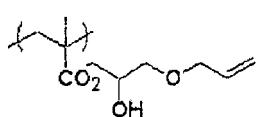
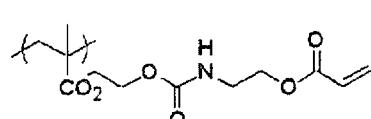
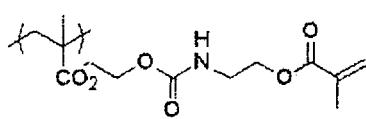
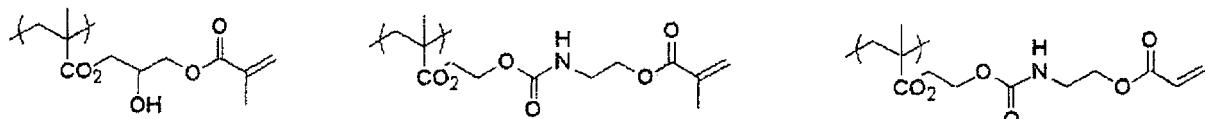
[0053] According to the invention, it is preferred to form crosslinkage between the polymer molecules by an ethylenically unsaturated group and to accelerate curing.

(1) Ethylenically unsaturated group

[0054] As the ethylenically unsaturated group, for example, a (meth)acryloyl group, a vinyl group or an allyl group is preferred. The ethylenically unsaturated group can be introduced into the polymer by a polymer reaction or copolymerization. For instance, a reaction between an acrylic polymer having a carboxyl group in its side chain and glycidyl methacrylate, a reaction between a polymer having an epoxy group and a carboxylic acid having an ethylenically unsaturated group, for example, methacrylic acid, or a reaction between a polymer having a hydroxy group and a methacrylate having an isocyanate group can be utilized.

[0055] From the standpoint of preservation stability of the polymer compound and film strength, a (meth)acryloyl group is preferred.

[0056] Specific examples of the repeating unit having a reactive group for use in the invention are set forth below, but the invention should not be construed as being limited thereto.



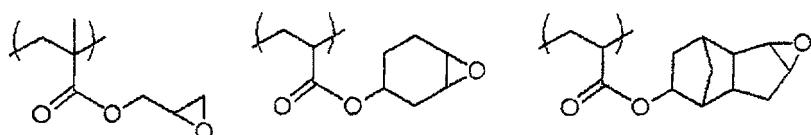
[0057] The content of the ethylenically unsaturated group in the polymer compound according to the invention is preferably from 0.1 to 10.0 mmol, more preferably from 0.25 to 7.0 mmol, most preferably from 0.5 to 5.5 mmol, per 1 g of the polymer compound.

(2) Other reactive group

[0058] Specific examples of the repeating unit having other reactive group include repeating units shown below.

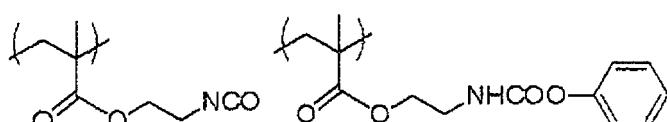
[0059] Epoxy group (which reacts with an amino group, a hydroxy group or a carboxyl group of the thermoplastic polymer fine particle)

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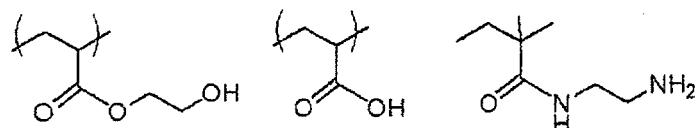
10 [0060] Isocyanate group or blocked isocyanate group (which reacts with an amino group, a hydroxy group or a carboxyl group of the thermoplastic polymer fine particle)

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20 [0061] Hydroxy group, carboxyl group or amino group (which reacts with an epoxy group, an isocyanate group or a blocked isocyanate group of the thermoplastic polymer fine particle)

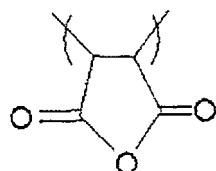
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[0062] Compound having acid anhydride skeleton (which reacts with an amino group or a hydroxy group of the thermoplastic polymer fine particle)

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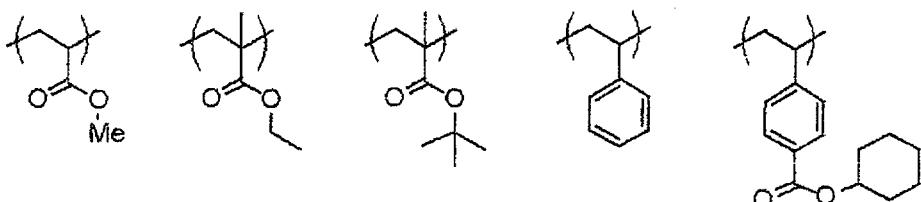
<Other repeating unit>

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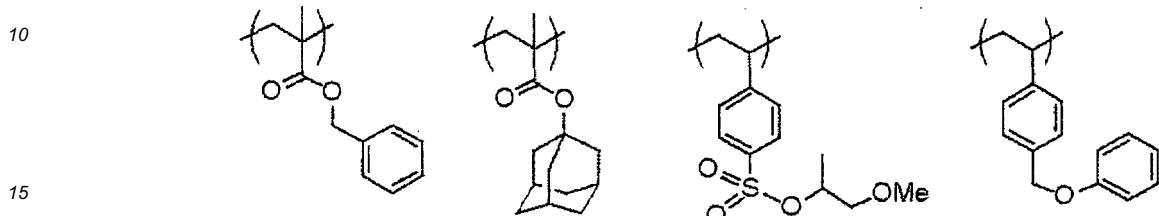
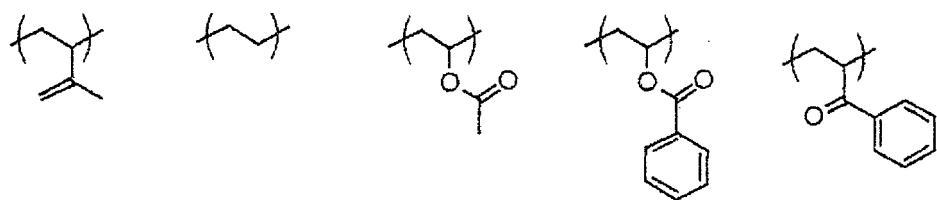
[0063] The star polymer for use in the invention may contain other repeating unit. Specific examples of the other repeating unit are set forth below, but the invention should not be construed as being limited thereto.

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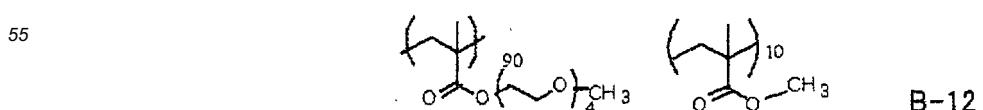
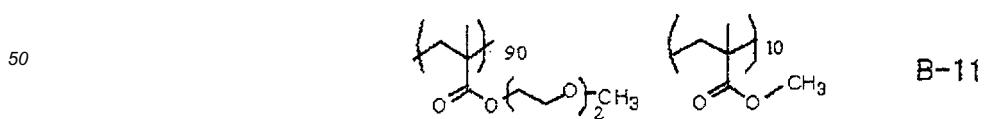
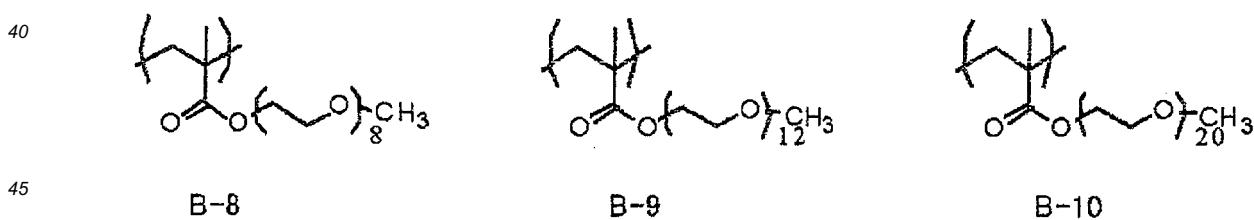
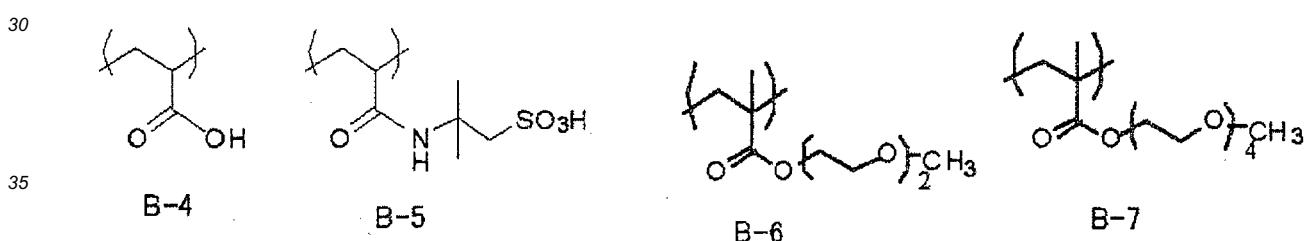
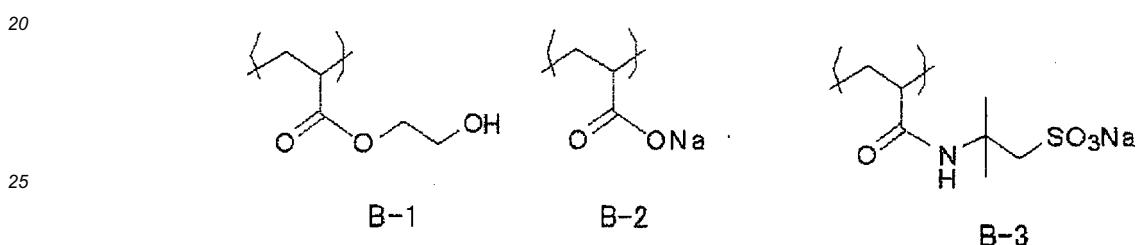
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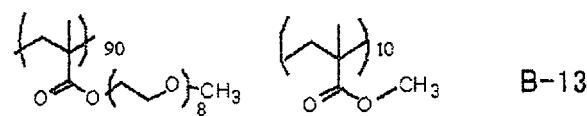


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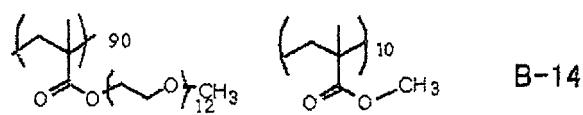


[0064] Specific examples of the structure of the Polymer moiety in formula (1) are set forth below.

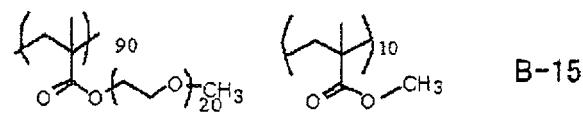




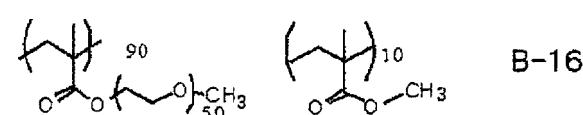
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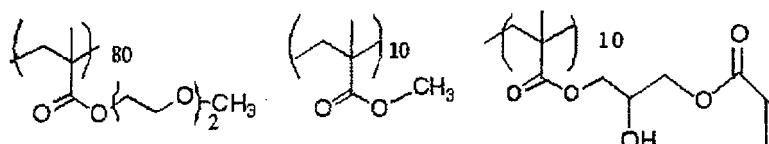
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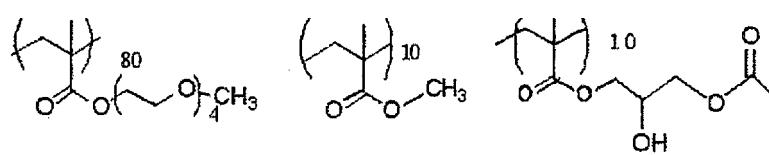
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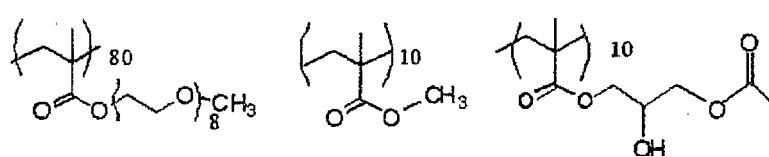
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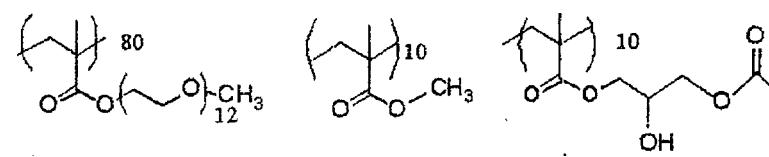
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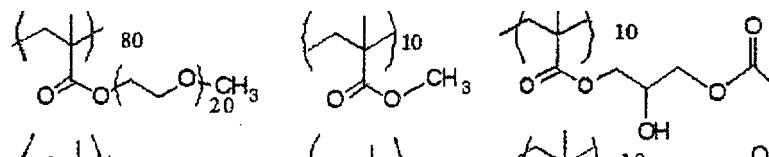
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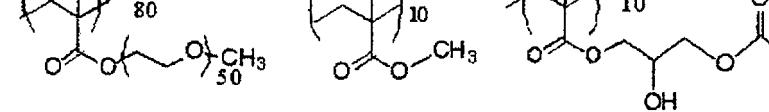
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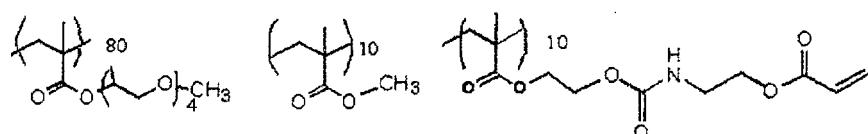


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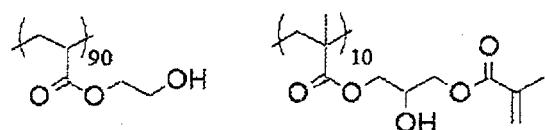
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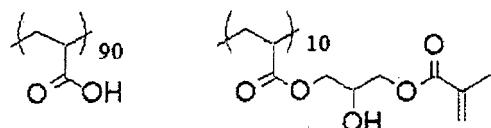
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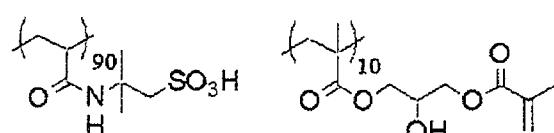
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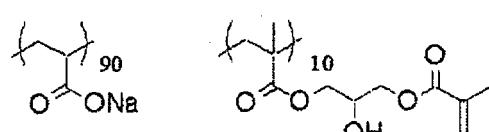
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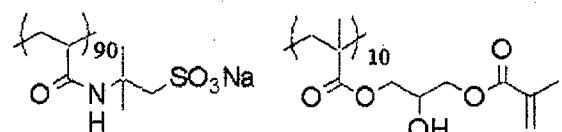
B-26

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B-27

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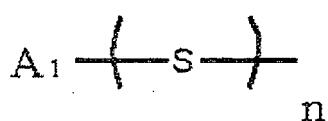
B-28

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[Branch unit A]

40 [0065] The branch unit represented by A in formula (1) is not particularly restricted and is preferably a branch unit having a hub portion, which is a residue of a three or higher functional thiol. In the idealized structure, a main chain of an addition polymer extends from each thio part of the hub portion and thus, three or more main chains extend from the thio parts. Specifically, the branch unit A has preferably a structure represented by formula (2) shown below.

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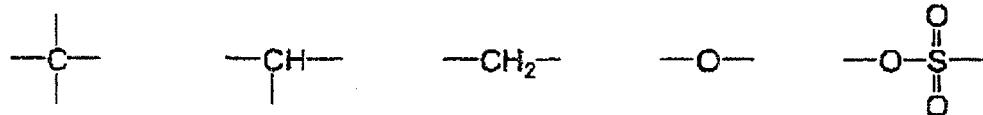


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[0066] In formula (2), A<sub>1</sub> represents a trivalent or higher valent organic group, and n represents an integer of 3 or more. Specific examples of A<sub>1</sub> include structures shown below and organic groups composed of combination of two or more of these structures, n is preferably an integer from 3 to 6, and particularly preferably an integer from 4 to 6.

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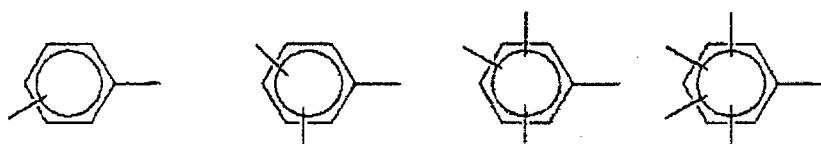


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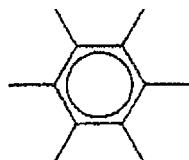


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Polyvalent naphtalene, Polyvalent anthracene

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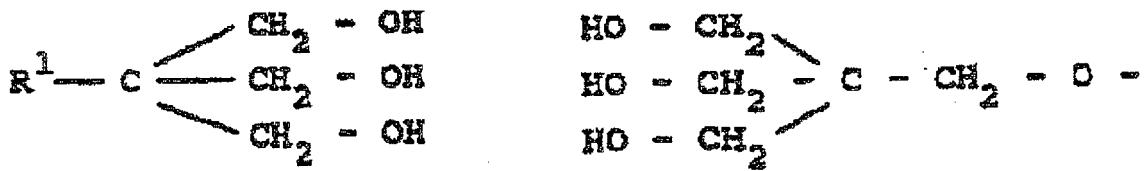
[0067] The three or higher functional thiol residue is derived from an aromatic or aliphatic thiol. Examples of the aromatic thiol include benzene-1,3,5-trithiol, 3,4,8,9-tetramercaptotetrathiafulvalene and 7-methyltrithiouric acid.

[0068] The thiol residue of the aliphatic thiol is preferably a residue of an ester formed from a three or higher functional alcohol and a mercaptoalkane acid having from 2 to 6 carbon atoms.

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[0069] Examples of the appropriate alcohol include glycerine, sorbitol, an alcohol represented by formula (3) and an alcohol having a group represented by formula (4). In particular, the alcohol represented by formula (3) and alcohol having a group represented by formula (4) are preferred.

40



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(3)

(4)

50 [0070] In formulae (3) and (4), R<sup>1</sup> represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms or a hydroxy-substituted alkyl group having from 1 to 4 carbon atoms. In particular, R<sup>1</sup> is preferably a methyl group, an ethyl group, a hydroxymethyl group or a hydroxyethyl group.

[0071] Examples of the mercaptoalkane acid having from 2 to 6 carbon atoms include 2-mercaptopropionic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 4-mercaptopbutyric acid, 5-mercaptopvaleric acid and 6-mercaptopcaproic acid. Among them, 2-mercaptopacetic acid and 3-mercaptopropionic acid are preferred.

55 [0072] Specific examples of the ester formed from a three or higher functional alcohol and a mercaptoalkane acid having from 2 to 6 carbon atoms include a compound having three mercapto groups, for example, 1,2,6-hexanetriol-trithioglycolate, 1,3,5-trithiocyanuric acid, 1,3,5-tris(3-mercaptopbutyryloxyethyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione,

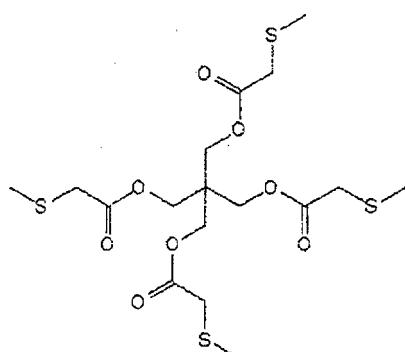
trimethylolpropane tris(3-mercaptopropionate), trimethylolpropane tristhioglycolate, trimethylolpropane tristhiopropionate, trihydroxyethyltriisocyanuric acid tristhiopropionate or tris-[(ethyl-3-mercaptopropionyloxy)ethyl] isocyanurate, and a compound having four mercapto groups, for example, pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), but the invention should not be construed as being limited thereto.

[0073] Commercially available products of the multifunctional thiol compound include trimethylolpropane tristhiopropionate (TMTG) (trademark) and pentaerythritol tetrakis(3-mercaptopropionate) (PETG) (trademark) (each produced by Yodo Kagaku Co., Ltd.), pentaerythritol tetrakis(3-mercaptopropionate) (KarenzMT PE1) (trademark) and 1,3,5-tris(3-mercaptopropionyloxyethyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (KarenzMT NR1) (trademark) (each produced by Showa Dekko K.K.), and trimethylolpropane tris(3-mercaptopropionate) (TMMP) (trademark), pentaerythritol tetrakis(3-mercaptopropionate) (PEMP) (trademark), dipentaerythritol hexakis(3-mercaptopropionate) (DPMP) (trademark) and tris-[(ethyl-3-mercaptopropionyloxy)ethyl] isocyanurate (TEMPIC) (trademark) (each produced by Sakai Chemical Industry Co., Ltd.), but the multifunctional thiol compound according to the invention should not be construed as being limited thereto.

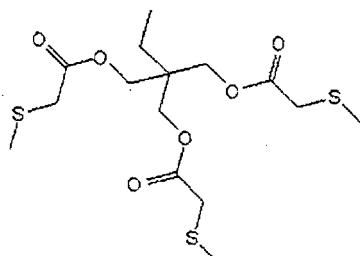
[0074] The branch unit represented by formula (2) includes structures shown below.

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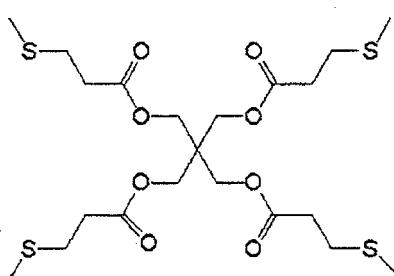


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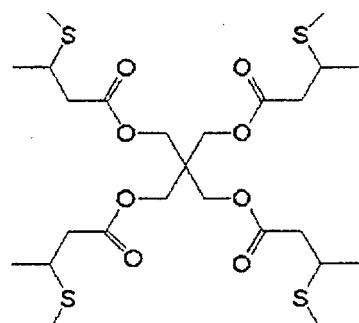
A-1

A-2

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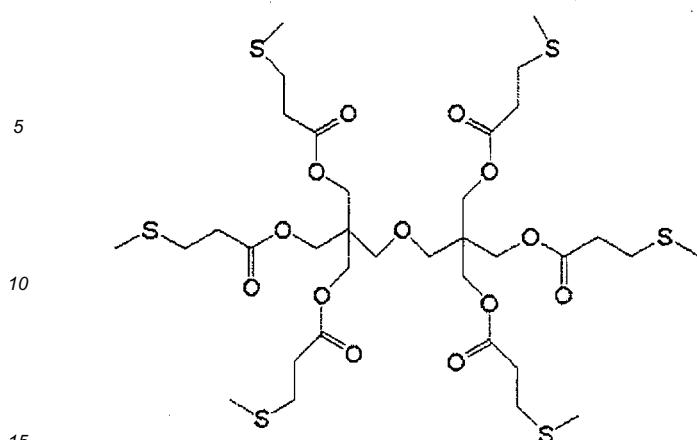
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A-3

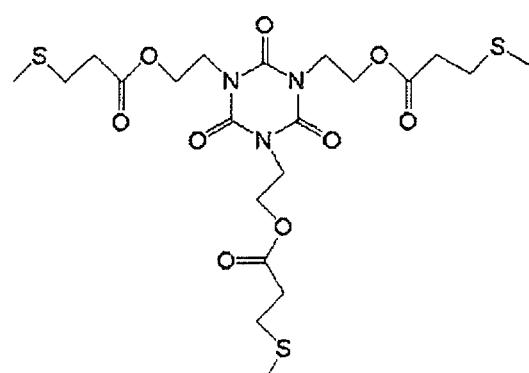
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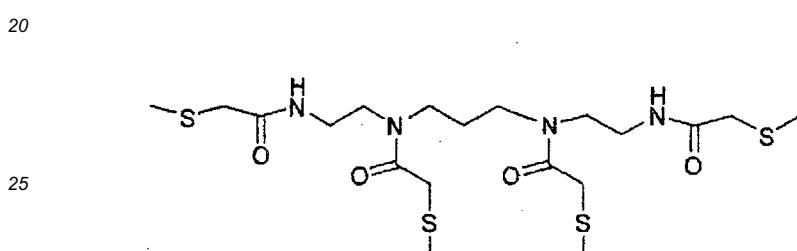
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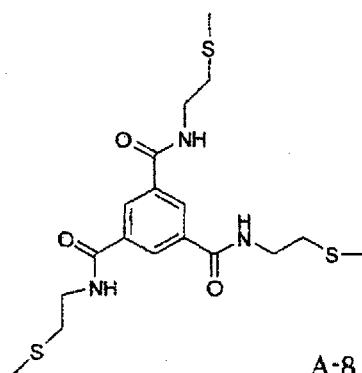
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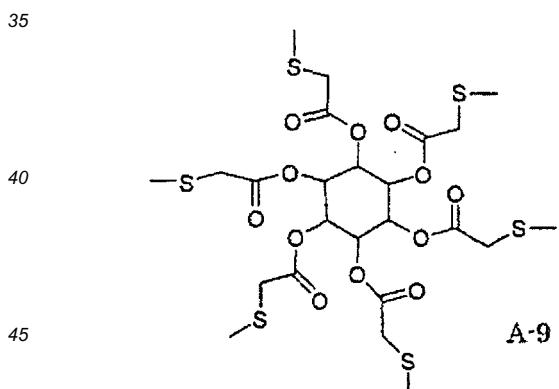
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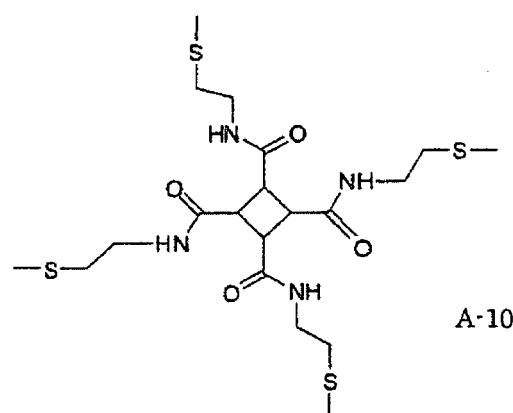
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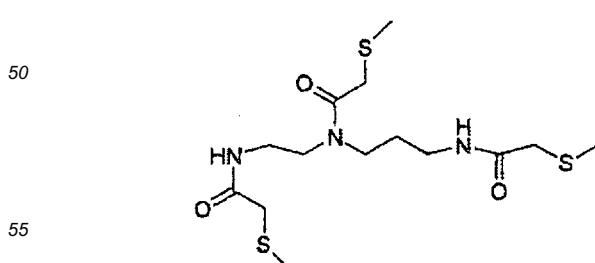
A-8



A-9



A-10



A-11

[0075] The weight average molecular weight (Mw) of the star polymer for use in the invention is preferably from 5,000

to 500,000, and more preferably from 10,000 to 250,000.

**[0076]** Specific examples of the star polymer for use in the invention are set forth below, but the invention should not be construed as being limited thereto.

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**TABLE 1: Specific Examples of Star Polymer**

Star Polymer	Branch Unit	Polymer Chain	Mw
P-1	A-1	B-1	2.6 x 10 <sup>4</sup>
P-2	A-1	B-2	2.6 x 10 <sup>4</sup>
P-3	A-1	B-3	2.6 x 10 <sup>4</sup>
P-4	A-1	B-4	2.5 x 10 <sup>4</sup>
P-5	A-1	B-5	2.6 x 10 <sup>4</sup>
P-6	A-1	B-6	3.4 x 10 <sup>4</sup>
P-7	A-1	B-7	3.4 x 10 <sup>4</sup>
P-8	A-1	B-8	3.5 x 10 <sup>4</sup>
P-9	A-1	B-13	3.6 x 10 <sup>4</sup>
P-10	A-1	B-17	4.6 x 10 <sup>4</sup>
P-11	A-1	B-18	4.6 x 10 <sup>4</sup>
P-12	A-1	B-19	4.7 x 10 <sup>4</sup>
P-13	A-1	B-20	4.8 x 10 <sup>4</sup>
P-14	A-1	B-21	4.9 x 10 <sup>4</sup>
P-15	A-1	B-24	4.6 x 10 <sup>4</sup>
P-16	A-1	B-25	4.6 x 10 <sup>4</sup>
P-17	A-1	B-26	4.7 x 10 <sup>4</sup>
P-18	A-1	B-27	4.6 x 10 <sup>4</sup>
P-19	A-1	B-28	4.7 x 10 <sup>4</sup>
P-20	A-1	B-4	3.6 x 10 <sup>4</sup>
P-21	A-2	B-4	2.7 x 10 <sup>4</sup>
P-22	A-3	B-4	3.6 x 10 <sup>4</sup>
P-23	A-4	B-4	3.6 x 10 <sup>4</sup>
P-24	A-5	B-4	5.4 x 10 <sup>4</sup>
P-25	A-6	B-4	2.7 x 10 <sup>4</sup>
P-26	A-7	B-4	3.6 x 10 <sup>4</sup>
P-27	A-8	B-4	2.7 x 10 <sup>4</sup>
P-28	A-9	B-4	5.4 x 10 <sup>4</sup>
P-29	A-10	B-4	3.6 x 10 <sup>4</sup>
P-30	A-11	B-4	2.7 x 10 <sup>4</sup>
P-31	A-5	B-19	6.3 x 10 <sup>4</sup>
P-32	A-5	B-25	6.3 x 10 <sup>4</sup>
P-33	A-5	B-28	6.3 x 10 <sup>4</sup>

**[0077]** The star polymers according to the invention may be used only one kind or two or more kinds thereof in combination. The content of the star polymer according to the invention in the image-recording layer is preferably from

3 to 50% by weight, more preferably from 5 to 40% by weight, particularly preferably from 10 to 30% by weight, based on the total solid content of the image-recording layer.

**[0078]** The star polymer according to the invention can be synthesized by a known method, for example, radical polymerization of the monomer constituting the polymer chain described above in the presence of the multifunctional thiol compound described above.

[Infrared absorbing agent]

**[0079]** The lithographic printing plate precursor according to the invention contains an infrared absorbing agent in the image-recording layer thereof. The infrared absorbing agent may also be incorporated into a layer adjacent to the image-recording layer (an undercoat layer or an overcoat layer described hereinafter). The infrared absorbing agent is a substance which absorbs an infrared laser beam and various pigments, dyes and metal particles can be used. In particular, a light-absorbing substance having an absorption band at least partially in a wavelength range from 700 to 1,200 nm is preferred.

**[0080]** Examples of the kind of pigment include black pigments, brown pigments, red pigments, purple pigments, blue pigments, green pigments, fluorescent pigments, metal powder pigments and polymer-bonded dyes. Specific examples of usable pigment include insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyanine pigments, anthraquinone pigments, perylene and perynone pigments, thioindigo pigments, quinacridone pigments, dioxazine pigments, isoindolinone pigments, quinophthalone pigments, dying lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments and carbon black.

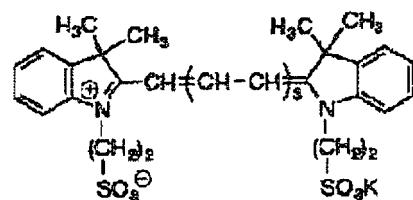
**[0081]** The pigment may be used without undergoing surface treatment or may be used after the surface treatment. For the surface treatment, there are, for example, a method of coating a hydrophilic resin or an oleophilic resin on the surface, a method of attaching a surfactant on the surface and a method of bonding a reactive substance (for example, a silica sol, an alumina sol, a silane coupling agent, an epoxy compound or an isocyanate compound) to the pigment surface. The surface treatment methods are described in Kinzoku Sekken no Seishitsu to Oyo (Properties and Applications of Metal Soap), Saiwai Shobo, Insatsu Ink Gijutsu (Printing Ink Technology), CMC Publishing Co., Ltd. (1984), and Saishin Ganryo Oyo Gijutsu (Newest Application on Technologies for Pigments), CMC Publishing Co., Ltd. (1986). Of the pigments, those absorbing an infrared ray are preferred because they are suitably utilized with a laser emitting an infrared ray. As the pigment absorbing an infrared ray, carbon black is preferred. The particle size of the pigment is preferably in a range from 0.01 to 1  $\mu\text{m}$ , and more preferably in a range from 0.01 to 0.5  $\mu\text{m}$ .

**[0082]** As the dye, commercially available dyes and known dyes described in literatures (for example, Senryo Binran (Dye Handbook) compiled by The Society of Synthetic Organic Chemistry, Japan (1970), Kinsekigai Kyushu Shikiso (Near Infrared Absorbing Dyes) on pages 45 to 51 of Kagaku Kogyo (Chemical Industry), May, 1986 and 90 Nen Dai Kinosei Shikiso no Kaihatsu to Shijo Doko (Development and Movement on Market of Functional Dyes in 90s), Chap. 2, Item 2.3, CMC Publishing Co., Ltd. (1990)) or patents can be used. Specifically, infrared absorbing dyes, for example, azo dyes, metal complex azo dyes, pyrazolone azo dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, polymethine dyes or cyanine dyes are preferred.

**[0083]** Further, cyanine dyes described, for example, in JP-A-58-125246, JP-A-59-84356 and JP-A-60-78787, methine dyes described, for example, in JP-A-58-173696, JP-A-58-181690 and JP-A-58-194595, naphthoquinone dyes described, for example, in JP-A-58-112793, JP-A-58-224793, JP-A-59-48187, JP-A-59-73996, JP-A-60-52940 and JP-A-60-63744, squarylium dyes described, for example, in JP-A-58-112792, cyanine dyes described in British Patent 434,875, dyes described in U.S. Patent 4,756,993, cyanine dyes described in U.S. Patent 4,973,572, dyes described in JP-A-10-268512, and phthalocyanine compounds described in JP-A-11-235 883 are exemplified.

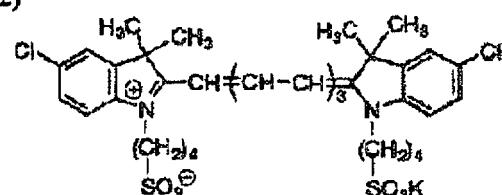
**[0084]** Also, near infrared absorbing sensitizers described in U.S. Patent 5,156,938 are preferably used as the dye. Further, substituted arylbenzo(thio)pyrylium salts described in U.S. Patent 3,881,924, trimethinethiopyrylium salts described in JP-A-57-142645, pyrylium compounds described in JP-A-58-181051, JP-A-58-220143, JP-A-59-41363, JP-A-59-84248, JP-A-59-84249, JP-A-59-146063 and JP-A-59-146061, cyanine dyes described in JP-A-59-216146, pentamethinethiopyrylium salts described in U.S. Patent 4,283,475, pyrylium compounds described in JP-B-5-13514 (the term "JP-B" as used herein means an "examined Japanese patent publication") and JP-B-5-19702, and EPOLIGHT III-178, EPOLIGHT III-130 and EPOLIGHT III-125 produced by Epolin, Inc. are also preferably used. Of the dyes, water-soluble dyes are preferred. In particular, water-soluble cyanine dyes are preferred, and cyanine dyes which become water-soluble by a sulfonate are more preferred. Specific examples thereof are set forth below.

(I-1)



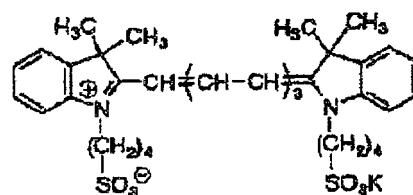
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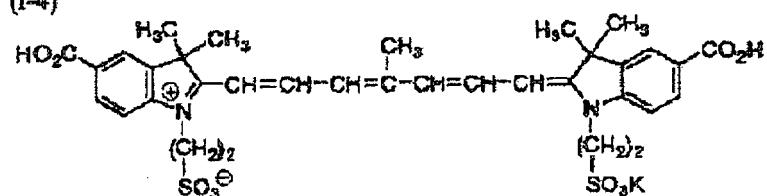
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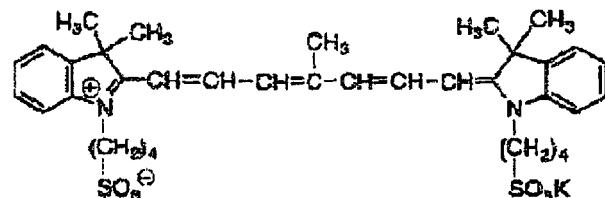
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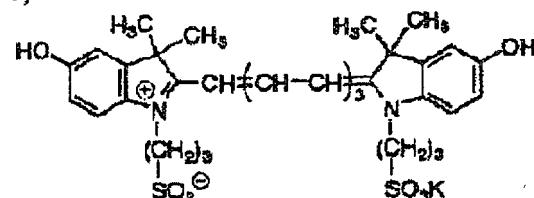
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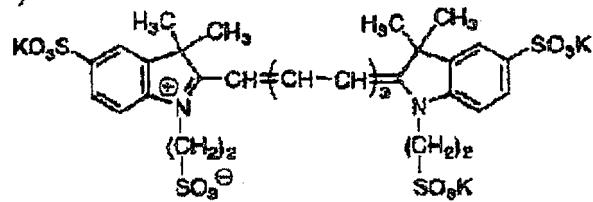


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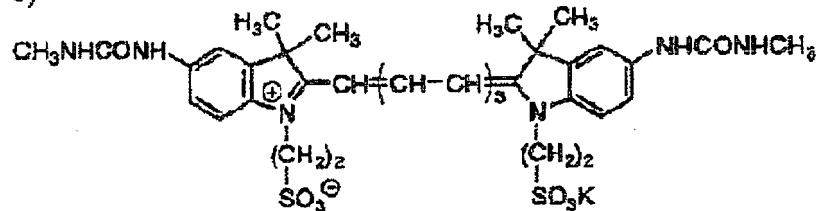


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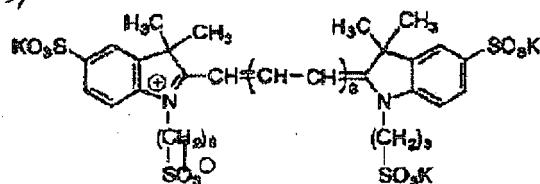
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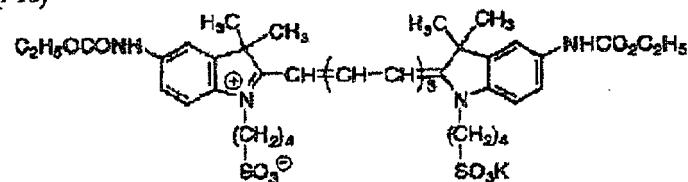
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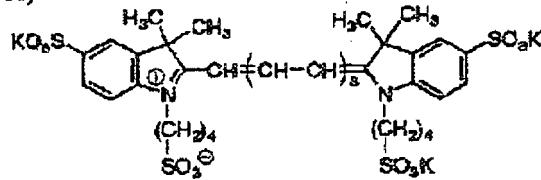
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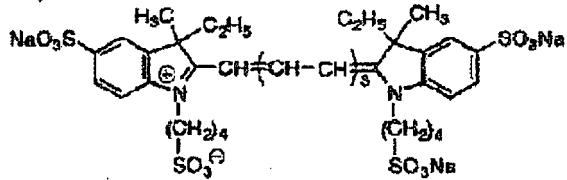
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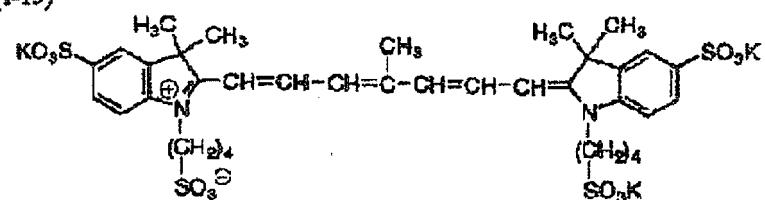


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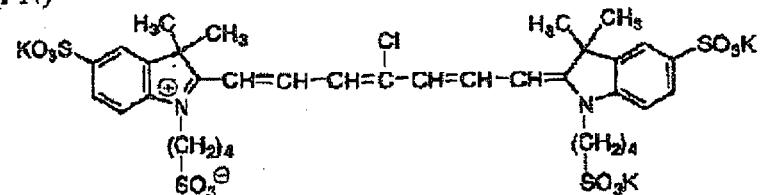
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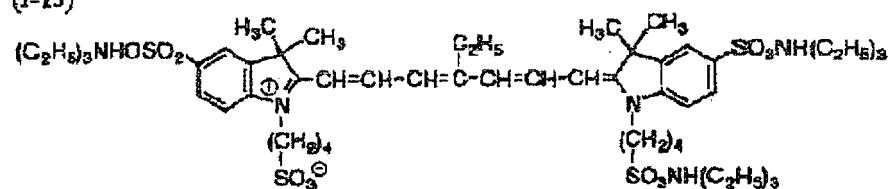
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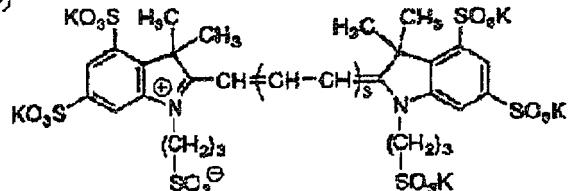
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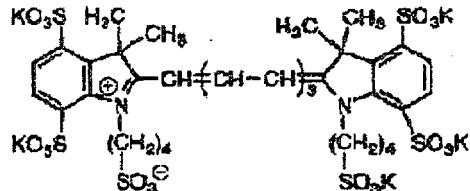
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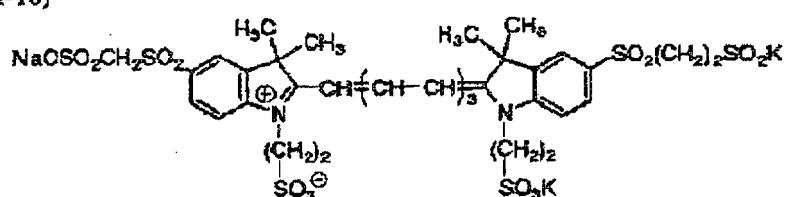
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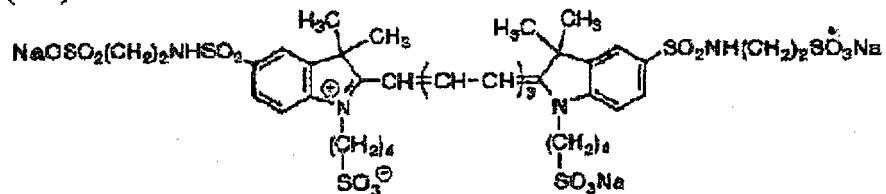
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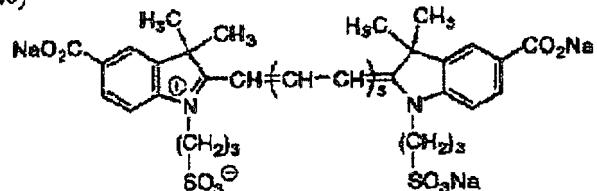


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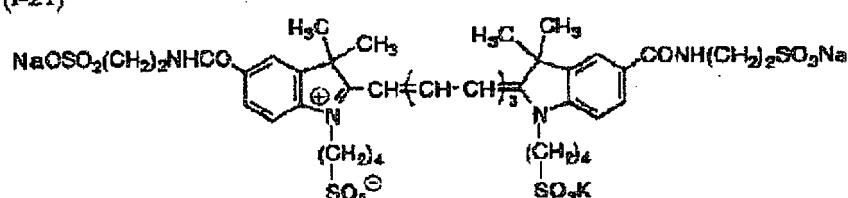
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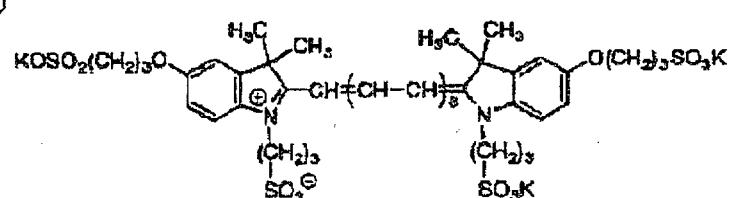
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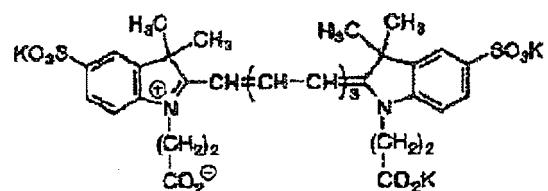
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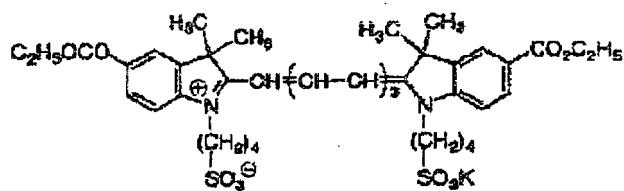
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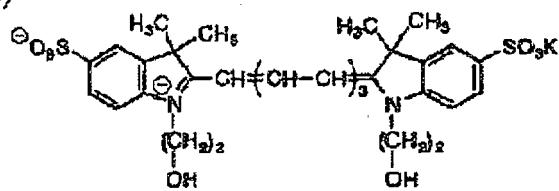
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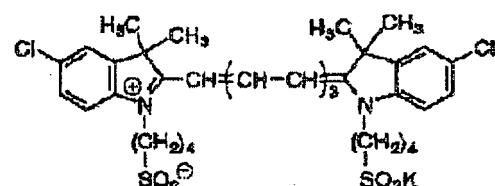


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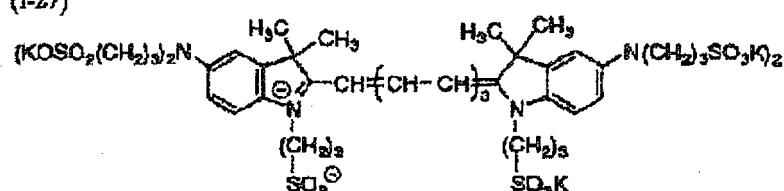
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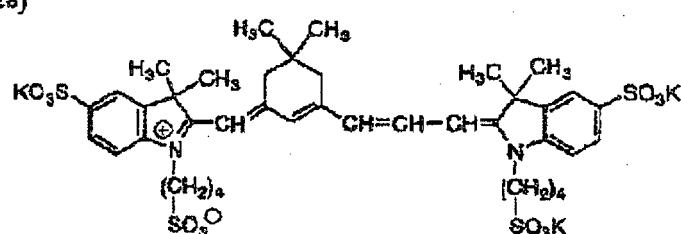
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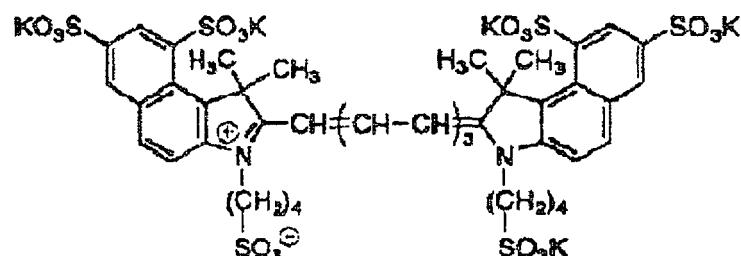
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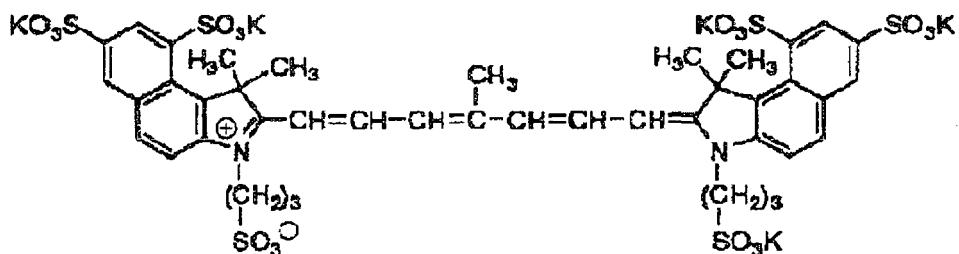
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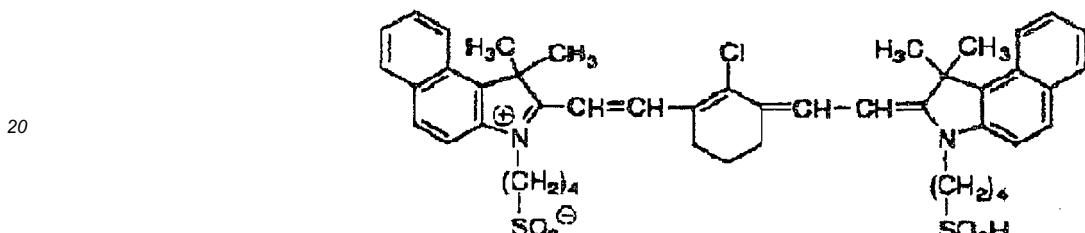


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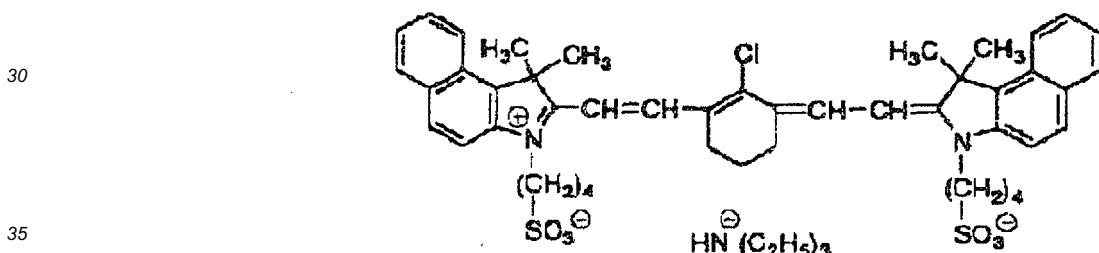
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**[0085]** The amount of the infrared absorbing agent added is preferably in a range from 0.5 to 30 parts by weight, more preferably from 1.0 to 20 parts by weight, most preferably from 2.0 to 10 parts by weight per 100 parts by weight of the total solid content of the image-recording layer.

[Polymerization initiator]

**[0086]** The polymerization initiator for use in the invention is a compound which initiates or accelerates polymerization of the polymerizable compound. The polymerization initiator for use in the invention is preferably a radical polymerizable compound, and includes, for example, known thermal polymerization initiators, compounds containing a bond having small bond dissociation energy and photopolymerization initiators.

**[0087]** The polymerization initiator according to the invention include, for example, (a) an organic halide, (b) a carbonyl compound, (c) an azo compound, (d) an organic peroxide, (e) a metallocene compound, (f) an azido compound, (g) a hexaaryliimidazole compound, (h) an organic borate compound, (i) a disulfone compound, (j) an oxime ester compound and (k) an onium salt compound.

**[0088]** As the organic halide (a), compounds described in Paragraph Nos. [0022] to [0023] of JP-A-2008-195018 are preferred.

**[0089]** As the carbonyl compound (b), compounds described in Paragraph No. [0024] of JP-A-2008-195018 are preferred.

**[0090]** As the azo compound (c), for example, azo compounds described in JP-A-8-108621 are used.

**[0091]** As the organic peroxide (d), for example, compounds described in Paragraph No. [0025] of JP-A-2008-195018 are preferred.

[0092] As the metallocene compound (e), for example, compounds described in Paragraph No. [0026] of JP-A-2008-195 018 are preferred.

[0093] As the azido compound (f), a compound, for example, 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone is exemplified.

[0094] As the hexaarylbimidazole compound (g), for example, compounds described in Paragraph No. [0027] of JP-A-2008-195018 are preferred.

[0095] As the organic borate compound (h), for example, compounds described in Paragraph No. [0028] of JP-A-2008-195018 are preferred.

[0096] As the disulfone compound (i), for example, compounds described in JP-A-61-166544 and JP-A-2002-328465 are exemplified.

[0097] As the oxime ester compound (j), for example, compounds described in Paragraph Nos. [0028] to [0030] of JP-A-2008-195018 are preferred.

[0098] As the onium salt compound (k), onium salts, for example, diazonium salts described in S. I. Schlesinger, Photogr. Sci. Eng., 18, 387 (1974), T. S. Bal et al., Polymer, 21, 423 (1980) and JP-A-5-158230 (corresponding to diazonium of NI3), ammonium salts described in U.S. Patent 4,069,055 and JP-A-4-365049, phosphonium salts described in U.S. Patents 4,069,055 and 4,069,056, iodonium salts described in European Patent 104,143, U. S. Patent Publication No. 2008/0311520, JP-A-2-150848, JP-A-2008-195018 and V. Crivello et al., Macromolecules, 10 (6), 1307 (1977), sulfonium salts described in European Patents 370,693, 233,567, 297,443 and 297,442, U.S. Patents 4,933,377, 4,760,013, 4,734,444 and 2,833,827 and German Patents 2,904,626, 3,604,580 and 3,604,581, selenonium salts described in J. V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 1047 (1979), arsonium salts described in C. S. Wen et al., Teh, Proc. Conf. Rad. Curing ASIA, p. 478, Tokyo, Oct. (1988), and azinium salts described in JP-A-2008-195018 are exemplified.

[0099] Of the polymerization initiators described above, the onium salt is preferred. Of the onium salts, the iodonium salt, sulfonium salt and azinium salt are preferred. Specific examples of these compounds are set forth below, but the invention should not be construed as being limited thereto.

[0100] Of the iodonium salts, a diphenyliodonium salt is preferred. In particular, a diphenyliodonium salt substituted with an electron donating group, for example, an alkyl group or an alkoxy group is preferred, and an asymmetric diphenyliodonium salt is more preferred. Specific examples of the iodonium salt include diphenyliodonium hexafluorophosphate, 4-methoxyphenyl-4-(2-methylpropyl)phenyliodonium hexafluorophosphate, 4-(2-methylpropyl)phenyl-p-tolyliodonium hexafluorophosphate,

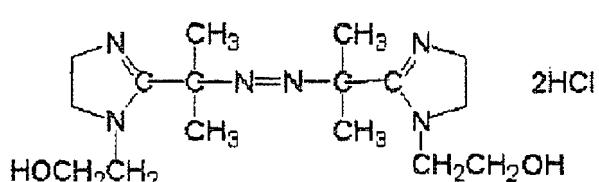
4-hexyloxyphenyl- 2,4,6-trimethoxyphenyliodonium hexafluorophosphate, 4-hexyloxyphenyl-2,4-diethoxyphenyliodonium tetrafluoroborate,

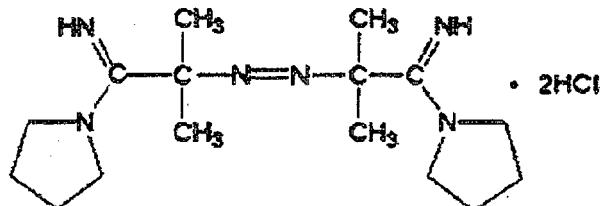
4-octyloxyphenyl-2,4,6-trimethoxyphenyliodonium 1-perfluorobutanesulfonate, 4-octyloxyphenyl-2,4,6-trimethoxyphenyliodonium hexafluorophosphate and bis(4-tert-butylphenyl)iodonium tetraphenylborate.

[0101] Examples of the sulfonium salt include triphenylsulfonium hexafluorophosphate, triphenylsulfonium benzoylformate, bis(4-chlorophenyl)phenylsulfonium benzoylformate, bis(4-chlorophenyl)-4-methylphenylsulfonium tetrafluoroborate, tris(4-chlorophenyl)sulfonium 3,5-bis(methoxycarbonyl)benzenesulfonate and tris(4-chlorophenyl)sulfonium hexafluorophosphate.

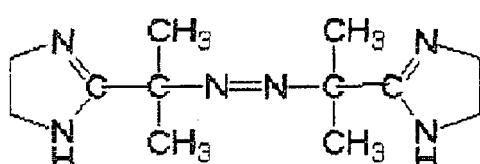
[0102] Examples of the azinium salt include 1-cyclohexylmethoxyypyridinium hexafluorophosphate, 1-cyclohexyloxy-4-phenylpyridinium hexafluorophosphate, 1-ethoxy-4-phenylpyridinium hexafluorophosphate, 1-(2-ethylhexyloxy)-4-phenylpyridinium hexafluorophosphate, 4-chloro-1-cyclohexylmethoxyypyridinium hexafluorophosphate, 1-ethoxy-4-cyanopyridinium hexafluorophosphate, 3,4-dichloro-1-(2-ethylhexyloxy)pyridinium hexafluorophosphate, 1-benzyloxy-4-phenylpyridinium hexafluorophosphate, 1-phenethyloxy-4-phenylpyridinium hexafluorophosphate, 1-(2-ethylhexyloxy)-4-phenylpyridinium p-toluenesulfonate, 1-(2-ethylhexyloxy)-4-phenylpyridinium perfluorobutanesulfonate, 1-(2-ethylhexyloxy)-4-phenylpyridinium bromide and 1-(2-ethylhexyloxy)-4-phenylpyridinium tetrafluoroborate.

[0103] Of the polymerization initiators, water-soluble or water-dispersible polymerization initiators are preferred. Specific examples of water-soluble azo compound are set forth below.

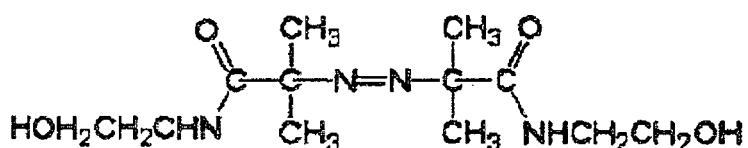




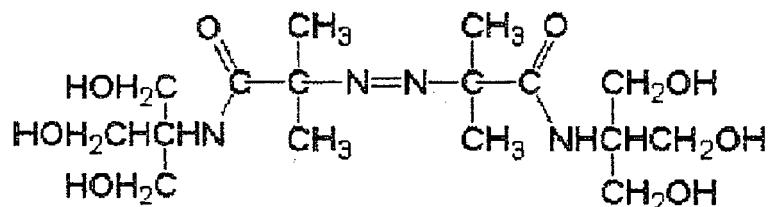
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**[0104]** The polymerization initiator can be added preferably in an amount from 0.1 to 50% by weight, more preferably from 0.5 to 30% by weight, particularly preferably from 0.8 to 20% by weight, based on the total solid content constituting the image-recording layer. In the range described above, good sensitivity and good stain resistance in the non-image area at the time of printing can be achieved.

### [Other components]

**[0105]** The image-recording layer may contain other component, for example, a surfactant, a coloring agent, a development inhibitor, a development accelerator, a low molecular weight polymerizable compound capable of reacting with the crosslinkable group of the thermoplastic polymer fine particle, or a catalyst for increasing curing property or a precursor thereof.

### [Formation of image-recording layer]

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**[0106]** The image-recording layer according to the invention is formed by dispersing or dissolving each of the necessary components described above in a known solvent to prepare a coating solution and coating the solution on a support by a known method, for example, bar coater coating and drying as described, for example, in Paragraph Nos. [0142] to [0143] of JP-A-2008-195018. The coating amount (solid content) of the image-recording layer formed on the support after coating and drying may be varied according to the intended purpose but is in general preferably from 0.3 to 3.0 g/m<sup>2</sup>. In the range described above, good sensitivity and good film property of the image-recording layer can be obtained.

## [Support]

[0107] As the support for use in the lithographic printing plate precursor according to the invention, a known support is used. Particularly, an aluminum plate subjected to roughening treatment and anodizing treatment according to a known method is preferred.

[0108] Also, an enlarging treatment or a sealing treatment of micropores of the anodized film described in JP-A-2001-253181 and JP-A-2001-322365 or a surface hydrophilizing treatment, for example, with an alkali metal silicate as described in U.S. Patents 2,714,066, 3,181,461, 3,280,734 and 3,902,734 or polyvinyl phosphonic acid as described in U.S. Patents 3,276,868, 4,153,461 and 4,689,272 may be appropriately selected and applied to the aluminum plate, if desired.

[0109] The support preferably has a center line average roughness from 0.10 to 1.2  $\mu\text{m}$ .

[0110] The support according to the invention may have a backcoat layer containing an organic polymer compound described in JP-A-5-45885 or an alkoxy compound of silicon described in JP-A-6-35174, provided on the back surface thereof, if desired.

## [Protective layer]

[0111] In the lithographic printing plate precursor according to the invention, a protective layer (overcoat layer) may be provided on the image-recording layer. The protective layer has a function for preventing, for example, occurrence of scratch in the image-recording layer or ablation caused by exposure with a high illuminance laser beam, in addition to the function for restraining an inhibition reaction against the image formation by means of oxygen blocking.

[0112] With respect to the protective layer having such properties, there are described, for example, in U.S. Patent 3,458,311 and JP-B-55-49729. As a polymer having low oxygen permeability for use in the protective layer, any water-soluble polymer and water-insoluble polymer can be appropriately selected to use. The polymers may be used in mixture of two or more thereof, if desired. Specifically, for example, polyvinyl alcohol, a modified polyvinyl alcohol, polyvinyl pyrrolidone, a water-soluble cellulose derivative and poly(meth)acrylonitrile are exemplified.

[0113] As the modified polyvinyl alcohol, an acid-modified polyvinyl alcohol having a carboxyl group or a sulfo group is preferably used. Specifically, modified polyvinyl alcohols described in JP-A-2005-250216 and JP-A-2006-259137 are preferably exemplified.

[0114] It is also preferred for the protective layer to contain an inorganic stratiform compound, for example, natural mica or synthetic mica as described in JP-A-2005-119273 in order to increase the oxygen blocking property.

[0115] Further, the protective layer may contain a known additive, for example, a plasticizer for imparting flexibility, a surfactant for improving a coating property or a fine inorganic particle for controlling a surface slipping property. The oil-sensitizing agent described with respect to the image-recording layer may also be incorporated into the protective layer.

[0116] The protective layer is coated according to a known method. The coating amount of the protective layer is preferably in a range from 0.0 to 10 g/m<sup>2</sup>, more preferably in a range from 0.02 to 3 g/m<sup>2</sup>, most preferably in a range from 0.02 to 1 g/m<sup>2</sup>, in terms of the coating amount after drying.

## [Plate making method]

[0117] The lithographic printing plate precursor according to the invention is subjected to plate making after image exposure by conducting development processing or development on a printing machine to use in printing.

## &lt;Image exposure&gt;

[0118] The lithographic printing plate precursor is imagewise exposed with laser through a transparent original having a line image, a halftone dot image or the like, or imagewise exposed, for example, by scanning of laser beam based on digital data.

[0119] The wavelength of the exposure light source is preferably from 750 to 1,400 nm. As the light source of 750 to 1,400 nm, a solid laser or semiconductor laser emitting an infrared ray is preferably used. With respect to the infrared laser, the output is preferably 100 mW or more, the exposure time per pixel is preferably within 20 microseconds, and the irradiation energy is preferably from 10 to 300 mJ/cm<sup>2</sup>. Further, in order to shorten the exposure time, it is preferred to use a multibeam laser device. The exposure mechanism may be any of an internal drum system, an external drum system and a flat bed system.

[0120] The image exposure can be conducted in a conventional manner using a plate setter or the like. In the case of on-press development, after mounting the lithographic printing plate precursor on a printing machine, the image exposure may be conducted on the printing machine.

<On-press development>

[0121] According to the on-press development, at least any of oily ink and an aqueous component is supplied on the imagewise exposed lithographic printing plate precursor on a printing machine to remove the image-recording layer in the non-image area, thereby preparing a lithographic printing plate.

[0122] Specifically, when the lithographic printing plate precursor after the image exposure is mounted as it is on a printing machine without undergoing any development processing or the lithographic printing plate precursor is mounted on a printing machine and imagewise exposed on the printing machine and then the oily ink and aqueous component are supplied to conduct printing, at an early stage of the printing in the unexposed area, the uncured image-recording layer is removed by dissolution or dispersion with the oily ink and/or aqueous component supplied to reveal the hydrophilic surface in the area. On the other hand, in the exposed area of the image-recording layer, the image-recording layer cured by the exposure forms the oily ink receptive area having the oleophilic surface. While either the oily ink or aqueous component may be supplied at first on the surface of lithographic printing plate precursor, it is preferred to supply the oily ink at first in view of preventing the aqueous component from contamination with the component of the image-recording layer removed. Thus, the lithographic printing plate precursor is subjected to the on-press development on the printing machine and used as it is for printing a large number of sheets. As the oily ink and aqueous component, conventional printing ink and dampening water for lithographic printing are preferably used, respectively.

<Development with developer having pH from 2 to 11>

[0123] According to a conventional developing process using a highly alkaline developer, a protective layer is removed in a pre-water washing step, the alkali development is conducted, the alkali is removed by washing with water in a post-water washing step, gum solution treatment is conducted and drying is conducted in a drying step. On the contrary, in the case of conducting the development of the lithographic printing plate precursor according to the invention using a developer having pH from 2 to 11, the protective layer and the unexposed area of the image-recording layer are together removed so that the resulting lithographic printing plate can be immediately mounted on a printing machine to perform printing. By incorporating a surfactant and/or a water-soluble polymer of oil-desensitization property into such a developer having pH from 2 to 11, the development and gum solution treatment are conducted at the same time so that the post-water washing step conducted after the alkali development is not particularly necessary and after conducting the development and gum solution treatment with one solution, the drying step can be performed. It is preferred that after the development and gum treatment, the excess developer is removed using a squeeze roller, followed by conducting the drying. Specifically, a considerably simplified processing process (gum development) composed of development and gum treatment with one solution and drying can be conducted.

[0124] The development according to the invention is performed in a conventional manner at liquid temperature ordinarily from 0 to 60°C, preferably from 15 to 40°C, using, for example, a method wherein the imagewise exposed lithographic printing plate precursor is immersed in the developer and rubbed with a brush or a method wherein the developer is sprayed to the imagewise exposed lithographic printing plate precursor and the exposed lithographic printing plate precursor is rubbed with a brush.

[0125] The developer having pH from 2 to 11 is preferably an aqueous solution containing water as a main component (containing 60% by weight or more of water based on weight of the developer). In particular, an aqueous solution containing a surfactant (for example, an anionic, nonionic, cationic or amphoteric surfactant) or an aqueous solution containing a water-soluble polymer is preferred. An aqueous solution containing both the surfactant and the water-soluble polymer is also preferred. The pH of the developer is more preferably from 5 to 10.7, still more preferably from 6 to 10.5, and most preferably from 7.5 to 10.3.

[0126] The anionic surfactant for use in the developer is not particularly limited and includes, for example, fatty acid salts, abietic acid salts, hydroxyalkanesulfonic acid salts, alkanesulfonic acid salts, dialkylsulfosuccinic acid salts, straight-chain alkylbenzenesulfonic acid salts, branched alkylbenzenesulfonic acid salts, alkylphthalenesulfonic acid salts, alkylidiphenylether (di)sulfonic acid salts, alkylphenoxy polyoxyethylene propylsulfonic acid salts, polyoxyethylene alkylsulfophenyl ether salts, N-alkyl-N-oleyltaurine sodium salt, N-alkylsulfosuccinic acid monoamide disodium salts, petroleum sulfonic acid salts, sulfated castor oil, sulfated beef tallow oil, sulfate ester salts of fatty acid alkyl ester, alkyl sulfate ester salts, polyoxyethylene alkyl ether sulfate ester salts, fatty acid monoglyceride sulfate ester salts, polyoxyethylene alkyl phenyl ether sulfate ester salts, polyoxyethylene styryl phenyl ether sulfate ester salts, alkyl phosphate ester salts, polyoxyethylene alkyl ether phosphate ester salts, polyoxyethylene alkyl phenyl ether phosphate ester salts, partially saponified products of styrene-maleic anhydride copolymer, partially saponified products of olefin-maleic anhydride copolymer and naphthalene sulfonate formalin condensates. Of the compounds, alkylbenzenesulfonic acid salts, alkyl-naphthalenesulfonic acid salts and alkylidiphenylether (di)sulfonic acid salts are particularly preferably used.

[0127] The cationic surfactant for use in the developer is not particularly limited and hitherto known cationic surfactants may be used. For example, alkylamine salts, quaternary ammonium salts, alkylimidazolinium salts, polyoxyethylene

alkyl amine salts and polyethylene polyamine derivatives are exemplified.

[0128] The nonionic surfactant for use in the developer is not particularly limited and includes, for example, polyethylene glycol type higher alcohol ethylene oxide adducts, alkylphenol ethylene oxide adducts, alkylnaphthal ethylene oxide adducts, phenol ethylene oxide adducts, naphthol ethylene oxide adducts, fatty acid ethylene oxide adducts, polyhydric alcohol fatty acid ester ethylene oxide adducts, higher alkylamine ethylene oxide adducts, fatty acid amide ethylene oxide adducts, ethylene oxide adducts of fat, polypropylene glycol ethylene oxide adducts, dimethylsiloxane-ethylene oxide block copolymers, dimethylsiloxane-(propylene oxide-ethylene oxide) block copolymers, fatty acid esters of polyhydric alcohol type glycerol, fatty acid esters of pentaerythritol, fatty acid esters of sorbitol and sorbitan, fatty acid esters of sucrose, alkyl ethers of polyhydric alcohols and fatty acid amides of alkanolamines. Of the compounds, those having an aromatic ring and an ethylene oxide chain are preferred, and alkyl-substituted or unsubstituted phenol ethylene oxide adducts and alkyl-substituted or unsubstituted naphthol ethylene oxide adducts are more preferred.

[0129] The amphoteric surfactant for use in the developer is not particularly limited and includes, for instance, amine oxide type, for example, alkylidimethylamine oxide, betaine type, for example, alkyl betaine and amino acid type, for example, sodium salt of alkylamino fatty acid. In particular, an alkylidimethylamine oxide which may have a substituent, an alkyl carboxy betaine which may have a substituent and an alkyl sulfo betaine which may have a substituent are preferably used. Specific examples of the compound are described, for example, in Paragraph Nos. [0255] to [0278] of JP-A-2008-203359 and Paragraph Nos. [0028] to [0052] of JP-A-2008-276166. Specific examples of the more preferable compound include a 2-alkyl-N-carboxymethyl-N-hydroxyethyl imidazolinium betaine, an alkylidiaminoethylglycine hydrochloride, lauryldimethylaminoacetic acid betaine, N-lauric acid amidopropidimethyl betaine and N-lauric acid amidopropyldimethylamine oxide.

[0130] Two or more surfactants may be used in combination. The content of the surfactant in the developer is preferably from 0.01 to 20% by weight, and more preferably from 0.1 to 10% by weight.

[0131] The water-soluble polymer for use in the developer having pH from 2 to 11 includes, for example, soybean polysaccharide, modified starch, gum arabic, dextrin, a cellulose derivative (for example, carboxymethyl cellulose, carboxyethyl cellulose or methyl cellulose) or a modified product thereof, pllulan, polyvinyl alcohol or a derivative thereof, polyvinyl pyrrolidone, polyacrylamide, an acrylamide copolymer, a vinyl methyl ether/maleic anhydride copolymer, a vinyl acetate/maleic anhydride copolymer and a styrene/maleic anhydride copolymer.

[0132] As the soybean polysaccharide, known soybean polysaccharide can be used. For example, as a commercially available product, SOYAFIVE (trade name, produced by Fuji Oil Co., Ltd.) is available and various grade products can be used. The soybean polysaccharide preferably used is that having viscosity in a range from 10 to 100 mPa/sec in the 10% by weight aqueous solution thereof.

[0133] As the modified starch, known modified starch can be used. The modified starch can be prepared, for example, by a method wherein starch, for example, of corn, potato, tapioca, rice or wheat is decomposed, for example, with an acid or an enzyme to an extent that the number of glucose residue per molecule is from 5 to 30 and then oxypropylene is added thereto in an alkali.

[0134] Two or more water-soluble polymers may be used in combination. The content of the water-soluble polymer in the developer is preferably from 0.1 to 20% by weight, and more preferable from 0.5 to 10% by weight.

[0135] Into the developer having pH from 2 to 11 for use in the invention, a pH buffer agent may further be incorporated.

[0136] As the pH buffer agent used in the invention, a pH buffer agent exhibiting a pH buffer function at pH from 2 to 11 is used without particular restriction. In the invention, a weak alkaline buffer agent is preferably used and includes, for example, (a) a carbonate ion and a hydrogen carbonate ion, (b) a borate ion, (c) a water-soluble amine compound and an ion of the water-soluble amine compound, and combinations thereof. Specifically, for example, (a) a combination of a carbonate ion and a hydrogen carbonate ion, (b) a borate ion, or (c) a combination of a water-soluble amine compound and an ion of the water-soluble amine compound exhibits a pH buffer function in the developer to prevent fluctuation of the pH even when the developer is used for a long period of time. As a result, for example, the deterioration of development property resulting from the fluctuation of pH and the occurrence of development scum are restrained. The combination of a carbonate ion and a hydrogen carbonate ion is particularly preferred.

[0137] In order for a carbonate ion and a hydrogen carbonate ion to be present in the developer, a carbonate and a hydrogen carbonate may be added to the developer or a carbonate ion and a hydrogen carbonate ion may be generated by adding a carbonate or a hydrogen carbonate to the developer and then adjusting the pH. The carbonate or hydrogen carbonate used is not particularly restricted and it is preferably an alkali metal salt thereof. Examples of the alkali metal include lithium, sodium and potassium and sodium is particularly preferable. The alkali metals may be used individually or in combination of two or more thereof.

[0138] When the combination of (a) a carbonate ion and a hydrogen carbonate ion is adopted as the pH buffer agent, the total amount of the carbonate ion and hydrogen carbonate ion is preferably from 0.05 to 5 mole/l, more preferably from 0.1 to 2 mole/l, particularly preferably from 0.2 to 1 mole/l, in the developer.

[0139] The developer may contain an organic solvent. As the organic solvent to be contained, for example, an aliphatic hydrocarbon (e.g., hexane, heptane, ISOPAR E, ISOPAR H, ISOPAR G (produced by Esso Chemical Co., Ltd.)), an

aromatic hydrocarbon (e.g., toluene or xylene), a halogenated hydrocarbon (methylene dichloride, ethylene dichloride, trichlene or monochlorobenzene) or a polar solvent is exemplified. Examples of the polar solvent include an alcohol (e.g., methanol, ethanol, propanol, isopropanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 2-octanol, 2-ethyl-1-hexanol, 1-nonanol, 1-decanol, benzyl alcohol, ethylene glycol monomethyl ether, 2-ethoxyethanol, diethylene glycol monomethyl ether, diethylene glycol monohexyl ether, triethylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monomethyl ether, polyethylene glycol monomethyl ether, polypropylene glycol, tetraethylene glycol, ethylene glycol monobutyl ether, ethylene glycol monobenzyl ether, ethylene glycol monophenyl ether, propylene glycol monophenyl ether, methyl phenyl carbinol, n-amyl alcohol or methylamyl alcohol), a ketone (e.g., acetone, methyl ethyl ketone, ethyl butyl ketone, methyl isobutyl ketone or cyclohexanone), an ester (e.g., ethyl acetate, propyl acetate, butyl acetate, amyl acetate, benzyl acetate, methyl lactate, butyl lactate, ethylene glycol monobutyl acetate, polyethylene glycol monomethyl ether acetate, diethylene glycol acetate, diethyl phthalate or butyl levulinate) and others (e.g., triethyl phosphate, tricresyl phosphate, N-phenylethanolamine, N-phenyldiethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, 4-(2-hydroxyethyl)morpholine, N,N-dimethylacetamide or N-methylpyrrolidone).

[0140] Two or more organic solvents may be used together in the developer.

[0141] Further, when the organic solvent is insoluble in water, it may be employed by being solubilized in water using a surfactant or the like. In the case where the developer contains an organic solvent, the concentration of the organic solvent is desirably less than 40% by weight in view of safety and inflammability.

[0142] The developer having pH from 2 to 11 may contain a preservative, a chelating agent, a defoaming agent, an organic acid, an inorganic acid, an inorganic salt or the like in addition the components described above. Specifically, compounds described in Paragraph Nos. [0266] to [0270] of JP-A-2007-206217 are preferably used.

[0143] The developer described above can be used as a developer and a development replenisher for the exposed lithographic printing plate precursor and it is preferably applied to an automatic processor described hereinafter. In the case of conducting the development processing using an automatic processor, the developer becomes fatigued in accordance with the processing amount, and hence the processing ability may be restored using a replenisher or a fresh developer.

[0144] The development processing using the developer having pH from 2 to 11 according to the invention is preferably performed by an automatic processor equipped with a supplying means for the developer and a rubbing member. An automatic processor using a rotating brush roll as the rubbing member is particularly preferred. Further, the automatic processor is preferably provided with a means for removing the excess developer, for example, a squeeze roller or a drying means, for example, a hot air apparatus, subsequently to the development processing means.

[0145] The lithographic printing plate precursor according to the invention may be subjected to heat treatment in a post heating step (baking process) after the development processing in order to improve printing durability.

[0146] The baking process is conducted at temperature higher than the coagulation temperature of the thermoplastic polymer fine particle, for example, from 100 to 230°C for 5 to 40 minutes. For example, the exposed and developed lithographic printing plate precursor is subjected to baking at temperature of 230°C for 5 minutes, at temperature of 150°C for 10 minutes or at temperature of 120°C for 34 minutes. The baking can be conducted in a conventional hot air oven or by irradiation using a lamp emitting an infrared or ultraviolet spectrum.

## EXAMPLES

[0147] The present invention will be described in more detail with reference to the following examples, but the invention should not be construed as being limited thereto. With respect to the polymer compounds used in the examples, unless otherwise particularly defined, a molecular weight means a weight average molecular weight (Mw) and a ratio of repeating unit is indicated in mole percent.

[Synthesis example of star polymer]

### Synthesis of Star Polymer (P-4)

[0148] Under a nitrogen stream, a mixed solution composed of 283 g of acrylic acid, 2.3 g of pentaerythritol tetrakis(mercaptoacetate), 2.4 g of V-601 (produced by Wako Pure Chemical Industries, Ltd.) and 330 g of 1-methoxy-2-propanol was dropwise added to 330 g of 1-methoxy-2-propanol heated at 80°C over a period of 2 hours and 30 minutes. After the completion of the dropwise addition, the reaction was further continued for 3 hours. A weight average molecular weight (Mw) of the resulting polymer was  $5 \times 10^4$ .

### Synthesis of Star Polymer (P-16)

[0149] Under a nitrogen stream, a mixed solution composed of 144 g of acrylic acid, 2.3 g of pentaerythritol tetrakis(rner-

5 captoacetate), 2.4 g of V-601 (produced by Wako Pure Chemical Industries, Ltd.) and 100 g of 1-methoxy-2-propanol was dropwise added to 200 g of 1-methoxy-2-propanol heated at 80°C over a period of 2 hours and 30 minutes. After tie completion of the dropwise addition, 0.143 g of V-601 was added to the reaction mixture and the temperature was raised to 90°C to continue the reaction for 2 hours. After the reaction, the mixture was cooled to 50°C and a mixed  
10 solution composed of 0.971 g of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxide free radical, 28.4 g of glycidyl methacrylate and 13.6 g of 1-methoxy-2-propanol was added thereto, followed by stirring for 5 minutes. The temperature of reaction mixture was raised to 90°C and after stirring for 10 minutes, 2.21 g of tetraethylammonium bromide was added thereto. The tetraethylammonium bromide attached to the wall of the reaction vessel was washed with 30.47 g of 1-methoxy-2-propanol. After stirring at 90°C for 18 hours, 1-methoxy-2-propanol was further added to dilute the reaction mixture so as to have a solid content concentration of 24.5%. A weight average molecular weight of the solution of Star Polymer (P-16) represented by the structural formula shown above measured by GPC was  $8.0 \times 10^4$ .

Examples 1 to 16 and Comparative Examples 1 to 3

15 [Preparation of Lithographic printing plate precursors (1) to (19)]

(1) Preparation of Support

20 [0150] An aluminum plate (material: JIS A 1050) having a thickness of 0.3 mm was subjected to a degreasing treatment at 50°C for 30 seconds using an aqueous 10% by weight sodium aluminate solution in order to remove rolling oil on the surface thereof and then neutralization and desmut treatment at 50°C for 30 seconds using an aqueous 30% by weight sulfuric acid solution.

25 [0151] Next, the aluminum plate was subjected to a so-called graining treatment in which the surface of support was roughened in order to improve adhesion property between the support and the image-recording layer and to impart water retentivity in the non-image area. Specifically, an aqueous solution containing 1% by weight of nitric acid and 0.5% by weight of aluminum nitrate was maintained at 45°C and the aluminum plate was run in the solution to conduct electrolytic graining by providing anode side electric amount of 240C/dm<sup>2</sup> with alternating wave of current density of 20A/dm<sup>2</sup> and a duty ratio of 1:1 from an indirect electric supplying cell. Then, an etching treatment was conducted in an aqueous 10% by weight sodium aluminate solution at 50°C for 30 seconds and neutralization and desmut treatment were conducted at 50°C for 30 seconds using an aqueous 30% by weight sulfuric acid solution.

30 [0152] Further, an oxide film was formed on the support by anodic oxidization in order to improve abrasion resistance, chemical resistance and water retentivity. As the electrolyte, an aqueous 20% by weight sulfuric acid solution was used and the aluminum web was transported in the electrolyte to conduct electrolytic treatment with direct current of 14A/dm<sup>2</sup> from an indirect electric supplying cell to form an anodic oxide film of 2.5 g/m<sup>2</sup>.

35 [0153] Thereafter, a silicate treatment was conducted in order to ensure hydrophilicity in the non-image area of a lithographic printing plate. Specifically, the aluminum web was transported in an aqueous 1.5% by weight sodium silicate No.3 solution while maintaining at 70°C so as to have the contact time of the aluminum web of 15 seconds, followed by washing with water. The amount of Si adhered was 10 mg/m<sup>2</sup>. The center line surface roughness (Ra) of the support thus-prepared was 0.25  $\mu$ m.

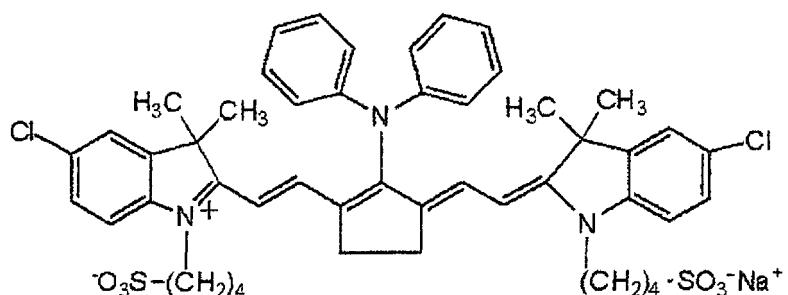
40 (2) Formation of image-recording layer

45 [0154] Coating solution (1) or (2) for image-recording layer shown below was coated as shown in Table 2 on the support described above using a bar and dried by an oven to from an image-recording layer having a dry coating amount of 0.6 g/m<sup>2</sup>, thereby preparing Lithographic printing plate precursors (1) to (19), respectively.

<Coating solution (1) for image-recording layer>

[0155]

Aqueous dispersion of polymer fine particle shown in Table 2	12.5 g (in terms of solid content)
Infrared absorbing dye (3) having structure shown below	1.0 g
Polymer compound represented by formula (1) shown in Table 2	2.0 g
Disodium 1,5-naphthalenedisulfonate	0.1 g
Pure water	10.0 g

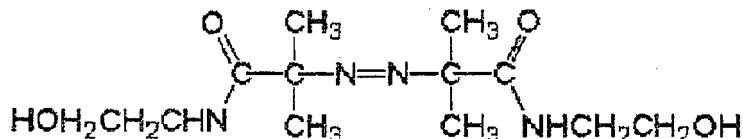


Infrared absorbing dye (3)

15 <Coating solution (2) for image-recording layer>

[0156]

20	Aqueous dispersion of polymer fine particle shown in Table 2	12.5 g (in terms of solid content)
	Infrared absorbing dye (3) having structure shown above	1.0 g
	Polymer compound represented by formula (1) shown in Table 2	2.0 g
	Water-soluble azo compound shown below	0.5 g
	Disodium 1,5-naphthalenedisulfonate	0.1 g
25	Pure water	10.0 g



35 Water-soluble azo compound

(Preparation of Aqueous dispersion of polymer fine particle (1))

40 [0157] A stirrer, a thermometer, a dropping funnel, a nitrogen inlet tube and a reflux condenser were attached to a 1,000 ml four-neck flask and while carrying out deoxygenation by introduction of nitrogen gas, 350 ml of distilled water was charged therein and heated until the internal temperature reached 80°C. To the flask was added 1.5 g of sodium dodecylsulfate as a dispersing agent, then was added 0.45 g of ammonium persulfate as an initiator, and thereafter was dropwise added 45.0 g of styrene through the dropping funnel over a period of about one hour. After the completion of the dropwise addition, the mixture was continued to react as it was for 5 hours, followed by removing the unreacted monomers by steam distillation. The mixture was cooled, adjusted the pH to 6 with aqueous ammonia and finally added pure water thereto so as to have the nonvolatile content of 15% by weight to obtain Aqueous dispersion of fine polymer particle (1). The particle size distribution of the fine polymer particle had the maximum value at the particle size of 60 nm.

45 [0158] The particle size distribution was determined by taking an electron microphotograph of the fine polymer particle, measuring particle sizes of 5,000 fine particles in total on the photograph, and dividing a range from the largest value of the particle size measured to 0 on a logarithmic scale into 50 parts to obtain occurrence frequency of each particle size by plotting. With respect to the aspherical particle, a particle size of a spherical particle having a particle area equivalent to the particle area of the aspherical particle on the photograph was defined as the particle size.

(Preparation of Polymer fine particle (2) having thermo-reactive functional group)

55 [0159] In a reaction vessel, 7.5 g of allyl methacrylate, 7.5 g of butyl methacrylate and 200 ml of an aqueous solution of polyoxyethylene nonylphenol (concentration:  $9.84 \times 10^{-3}$  mol/l) were placed and while stirring at 250 rpm, the air in the system was replaced by nitrogen gas. The solution was controlled at 25°C and then 10 ml of an aqueous solution

of ammonium salt of cerium (IV) (concentration:  $0.984 \times 10^{-3}$  mol/l) was added thereto. At this time, an aqueous solution of ammonium nitrate (concentration:  $58.8 \times 10^{-3}$  mol/l) was also added and pH of the reaction solution was adjusted to 1.3 to 1.4, followed by stirring for 8 hours. The resulting solution had the solid content concentration of 9.5% by weight and the average particle size of 0.4  $\mu\text{m}$ . (Preparation of Polymer fine particle (3) having thermo-reactive functional group)

5 [0160] In a reaction vessel, 7.5 g of glycidyl methacrylate, 7.5 g of butyl methacrylate and 200 l of an aqueous solution of polyoxyethylene nonylphenol (concentration:  $9.84 \times 10^{-3}$  mol/l) were placed and while stirring at 250 rpm, the air in the system was replaced by nitrogen gas. The solution was controlled at 25°C and then 10 ml of an aqueous solution of ammonium salt of cerium (IV) (concentration:  $0.984 \times 10^{-3}$  mol/l) was added thereto. At this time, an aqueous solution of ammonium nitrate (concentration:  $58.8 \times 10^{-3}$  mol/l) was also added and pH of the reaction solution was adjusted to 10 1.3 to 1.4, followed by stirring for 8 hours. The resulting solution had the solid content concentration of 9.5% by weight and the average particle size of 0.4  $\mu\text{m}$ .

[Evaluation of Lithographic printing plate precursor]

15 (1) On-press development property

[0161] Each of the lithographic printing plate precursors thus-obtained was exposed by LUXEL PLATESETTER T-6000III equipped with an infrared semiconductor laser, produced by FUJIFILM Corp. under the conditions of a rotational number of an external drum of 1,000 rpm, laser output of 70% and resolution of 2,400 dpi. The exposed image contained 20 a solid image and a 50% halftone dot chart of a 20  $\mu\text{m}$ -dot FM screen.

[0162] The exposed lithographic printing plate precursor was mounted without undergoing development processing on a plate cylinder of a printing machine (LITHRONE 26, produced by Komori Corp.). Using dampening water (ECOLITY-2 (produced by FUJIFILM Corp.)/tap water = 2198 (volume ratio)) and VALUES-G (N) Black Ink (produced by DIC Corp.), the dampening water and ink were supplied according to the standard automatic printing start method of LITHRONE 26 25 to conduct printing on 100 sheets of TOKUBISHI art paper (76.5 kg) at a printing speed of 10,000 sheets per hour.

[0163] A number of the printing papers required until the on-press development of the unexposed area of the image-recording layer on the printing machine was completed to reach a state where the ink was not transferred to the printing paper in the non-image area was measured to evaluate the on-press development property. The results obtained are shown in Table 2.

30 (2) Printing durability

[0164] After performing the evaluation for the on-press development property described above, the printing was continued. As the increase in a number of printed materials, the image-recording layer was gradually abraded to cause 35 decrease in the ink density on the printed material. A number of printed materials wherein a value obtained by measuring a halftone dot area rate of the 50% halftone dot of FM screen on the printed materials using a Gretag densitometer decreased by 5% from the value measured on the 100<sup>th</sup> paper of the printing was determined to evaluate the printing durability. The results obtained are shown in Table 2.

40 TABLE 2: Examples 1 to 16 and Comparative Examples 1 to 3

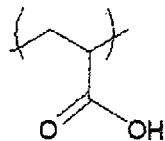
45	Lithographic Printing Plate Precursor	Coating Solution for Image- recording Layer	Polymer Fine Particle	Star Polymer or Comparative Polymer	Evaluation Result of Printing	
					Printing Durability (x $10^4$ sheets)	On-press Development Property (sheets)
	Example 1	(1)	(1)	(1)	P-1	3.0
	Example 2	(2)	(1)	(1)	P-2	3.0
50	Example 3	(3)	(1)	(1)	P-3	3.0
	Example 4	(4)	(1)	(1)	P-4	3.0
	Example 5	(5)	(1)	(1)	P-5	3.0
55	Example 6	(6)	(1)	(1)	P-6	3.0
	Example 7	(7)	(1)	(1)	P-7	2.9
	Example 8	(8)	(1)	(1)	P-8	2.8
						18

(continued)

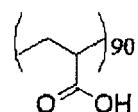
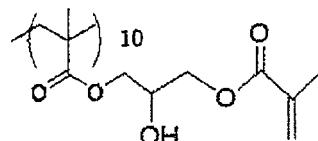
5	Lithographic Printing Plate Precursor	Coating Solution for Image- recording Layer	Polymer Fine Particle	Star Polymer or Comparative Polymer	Evaluation Result of Printing	
					10	On-press Development Property (sheets)
Example 9	(9)	(1)	(1)	P-19	3.0	22
Example 10	(10)	(1)	(1)	P-27	3.0	22
Example 11	(11)	(1)	(2)	P-4	3.2	21
Example 12	(12)	(1)	(2)	P-16	3.5	20
Example 13	(13)	(1)	(3)	P-8	2.8	18
Example 14	(14)	(1)	(3)	P-4	3.5	18
Example 15	(15)	(2)	(2)	P-4	3.5	22
Example 16	(16)	(2)	(2)	P-16	4.0	21
Comparative Example 1	(17)	(1)	(1)	R-1	2.5	30
Comparative Example 2	(18)	(1)	(2)	R-2	2.5	30
Comparative Example 3	(19)	(1)	(3)	R-1	2.5	30

[0165] Straight-chain polymer for comparison

R - 1

Mw:  $2.6 \times 10^4$ 

R - 2

Mw:  $4.6 \times 10^4$ Examples 17 to 32 and Comparative Examples 4 to 6

[0166] The lithographic printing plate precursor prepared as above was exposed and subjected to development processing to conduct plate making and then printing was performed.

(1) Exposure, Development and Printing

[0167] Each of the lithographic printing plate precursors was subjected to image exposure by Violet semiconductor laser plate setter Vx9600 (having InGaN semiconductor laser (emission wavelength:  $405 \text{ nm} \pm 10 \text{ nm}$ /output: 30 mW)) produced by FUJIFILM Electronic Imaging Ltd. (FFEI). The image drawing was performed at resolution of 2,438 dpi using FM screen TAFFETA 20, produced by FUJIFILM Corp.) in a plate surface exposure amount of  $0.05 \text{ mJ/cm}^2$  so as to have a halftone dot area rate of 50%.[0168] The exposed lithographic printing plate precursor was subjected to preheating at  $100^\circ\text{C}$  for 30 seconds and then subjected to development processing in an automatic development processor having a structure as shown in Fig. 2 using a developer 1 having the composition shown below.

[0169] The automatic development processor comprises a developing unit 6 for developing a lithographic printing plate precursor (hereinafter, also referred to as a "PS plate") 4 and a drying unit 10 for drying the developed PS plate 4. An insertion slot is formed in a side plate of the automatic development processor (on the left side in Fig. 1) and the PS plate 4 inserted through the insertion slot is transported into the developing unit 6 by canting-in rollers 16 provided inside the side plate of the automatic development processor. In a developing tank 20 of the developing unit 6, transport rollers 22, a brush roller 24 and squeeze rollers 26 are provided in order from the upstream side in the transporting direction and backup rollers 28 are disposed in appropriate positions therebetween. The PS plate 4 is immersed in the developer while being transported by the transport rollers 22 and the protective layer and the unexposed area of the image-recording layer of PS plate 4 were removed by rotation of the brush roller 24 to conduct development processing.

5 The PS plate 4 subjected to the development processing is transported into the drying unit 10 by the squeeze rollers (carrying-out rollers) 26.

[0170] In the drying unit 10, a guide roller 36 and a pair of skewer rollers 38 are disposed in order from the upstream side in the transporting direction. In the drying unit 10, drying means, for example, hot air supply means or heat generating means (not shown) is also provided. A discharge slot is provided in the drying unit 10 and the PS plate 4 dried by the drying means is discharged through the discharge slot, whereby the processing of PS plate by the automatic development processor is completed. The automatic development processor used in the examples had one brush roller having an outer diameter of 50 mm and being implanted with fiber of polybutylene terephthalate (bristle diameter: 200  $\mu\text{m}$ , bristle length: 17 mm), and the brush roller was rotated at 200 rpm (peripheral velocity at the tip of brush: 0.52 m/sec) in the same direction as the transporting direction of the lithographic printing plate precursor. The temperature of the developer was 30°C. The transportation of the lithographic printing plate precursor was conducted at transporting speed of 82 cm/min (the transporting speed was varied in the evaluation of development property). After the development processing, the lithographic printing plate was dried in the drying unit. The drying temperature was 80°C.

[0171] The lithographic printing plate obtained was mounted on a printing machine (SOR-M., produced by Heidelberg) and printing was performed at a printing speed of 6,000 sheets per hour using dampening water (EU-3 (etching solution, produced by FUJIFILM Corp.)/water/isopropyl alcohol = 1/89/10 (by volume ratio)) and TRANS-G (N) Black Ink (produced by DIC Corp.).

(Developer)

[0172] The compositions of Developer 1 used in the examples and comparative examples are shown in Table 3 below. In the developer. NEWCOL B13 is polyoxyethylene  $\beta$ -naphthyl ether (average number of oxyethylene: n=13, produced by Nippon Nyukazai Co., Ltd.) and gum arabic used has a weight average molecular weight (Mw) of  $20 \times 10^4$ .

TABLE 3: Developer 1 (pH: 9.8)

35	0.2 M Aqueous boric acid solution	25.00 parts by weight
40	0.2 M Aqueous sodium chloride solution	25.00 parts by weight
45	0.1M Aqueous sodium hydroxide solution	40.60 parts by weight
50	Water	9.40 parts by weight
	NEWCOL B13 (produced by Nippon Nyukazai Co., Ltd.)	5.00 parts by weight
	Gum arabic	2.50 parts by weight
	Hydroxy-alkylated starch (PENON JE66, produced by Nippon Starch Chemical Co., Ltd.)	7.00 parts by weight

## (2) Evaluation

[0173] Development property and printing durability were evaluated in the following manner. The results obtained are shown in Table 4.

5

<Development property>

10

[0174] With the lithographic printing plates obtained by performing the development while varying the transporting speed, cyan density of the non-image area was measured by a Macbeth densitometer (produced by Gretag Macbeth Co., Ltd.). The transporting speed at which the cyan density of the non-image area became equivalent to cyan density of the aluminum support was determined and at the transporting speed, a time period from when the top of the lithographic printing plate precursor was immersed in the developer to when the top of the lithographic printing plate precursor came out from the developer was regarded as a developing time to evaluate the development property.

15

<Printing durability>

20

[0175] After performing the evaluation for the development property described above, the printing was continued. As the increase in a number of printed materials, the image-recording layer was gradually abraded to cause decrease in the ink density on the printed materials. A number of printed materials wherein a value obtained by measuring a halftone dot area rate of the 50% halftone dot of FM screen on the printed material using a Gretag densitometer decreased by 5% from the value measured on the 100<sup>th</sup> paper of the printing was determined to evaluate the printing durability. The results obtained are shown in Table 4.

TABLE 4: Examples 17 to 32 and Comparative Examples 4 to 6

25

	Lithographic Printing Plate Precursor	Coating Solution for Image-recording Layer	Polymer Fine Particle	Star Polymer or Comparative Polymer	Evaluation Result of Printing	
					Printing Durability (x 10 <sup>4</sup> sheets)	Development Property (sec)
30	Example 17	(1)	(1)	(1)	P-1	2.8
35	Example 18	(2)	(1)	(1)	P-2	2.8
40	Example 19	(3)	(1)	(1)	P-3	2.8
45	Example 20	(4)	(1)	(1)	P-4	2.8
50	Example 21	(5)	(1)	(1)	P-5	2.8
55	Example 22	(6)	(1)	(1)	P-6	2.8
	Example 23	(7)	(1)	(1)	P-7	2.7
	Example 24	(8)	(1)	(1)	P-8	2.6
	Example 25	(9)	(1)	(1)	P-19	2.8
	Example 26	(10)	(1)	(1)	P-27	2.8
	Example 27	(11)	(1)	(2)	P-4	3.0
	Example 28	(12)	(1)	(2)	P-16	3.3
	Example 29	(13)	(1)	(3)	P-8	2.6
	Example 30	(14)	(1)	(3)	P-4	3.3
	Example 31	(15)	(2)	(2)	P-4	3.5
	Example 32	(16)	(2)	(2)	P-16	4.0
	Comparative Example 4	(17)	(1)	(1)	R-1	2.3
	Comparative Example 5	(18)	(1)	(2)	R-2	33

(continued)

5	Lithographic Printing Plate Precursor	Coating Solution for Image- recording Layer	Polymer Fine Particle	Star Polymer or Comparative Polymer	Evaluation Result of Printing		
					Printing Durability (x 10 <sup>4</sup> sheets)	Development Property (sec)	
10	Comparative Example 6	(19)	(1)	(3)	R-1	2.3	33

Examples 33 to 39

15 [0176] Each of Lithographic printing plate precursors (4) and (11) to (16) was exposed and development as described above and then heated in an oven at 130°C for 2 minutes. The printing durability was evaluated under the same conditions as in Example 17 and the results shown in Table 5 were obtained.

TABLE 5: Examples 33 to 39

	Lithographic Printing Pilate Precursor	Printing Durability (x 10 <sup>4</sup> sheets)
20	Example 33 (4)	3.3
	Example 34 (11)	3.8
25	Example 35 (12)	4.5
	Example 36 (13)	3.0
	Example 37 (14)	4.5
	Example 38 (15)	5.0
30	Example 39 (16)	6.0

**Claims**

1. A lithographic printing plate precursor comprising: an image-recording layer containing a thermoplastic polymer fine particle, an infrared absorbing agent and a polymer compound; and a support having a hydrophilic surface, wherein the polymer compound has a star-like shape in which a main chain is branched to three or more branches and the branched main chains have a hydrophilic group in a side chain of the branched main chain.
2. The lithographic printing plate precursor as claimed in Claim 1, wherein the hydrophilic group is at least one of a carboxyl group or a salt thereof, a sulfo group or a salt thereof and a polyethylene oxy group.
3. The lithographic printing plate precursor as claimed in Claim 1 or 2, wherein the thermoplastic polymer fme particle has a crosslinkable group.
- 45 4. The lithographic printing plate precursor as claimed in Claim 3, wherein the polymer compound having the star-like shape has, in a side chain of the branched main chain, a group capable of reacting with the crosslinkable group of the thermoplastic polymer fine particle.
5. The lithographic printing plate precursor as claimed in Claim 4, wherein both the crosslinkable group of the thermoplastic polymer fine particle and the group capable of reacting with the crosslinkable group of the thermoplastic polymer fine particle are ethylenically unsaturated groups.
6. The lithographic printing plate precursor as claimed in any one of Claims 1 to 5, wherein the image-recording layer contains a polymerization initiator.
- 55 7. The lithographic printing plate precursor as claimed in any one of Claims 1 to 6, wherein the image-recording layer is capable of being removed with at least any of printing ink and dampening water.

## 8. A lithographic printing method comprising:

either mounting the lithographic printing plate precursor as claimed in Claim 7 on a printing machine and exposing imagewise the mounted lithographic printing plate precursor with laser or exposing imagewise the lithographic printing plate precursor as claimed in Claim 7 with laser and mounting the exposed lithographic printing plate precursor on a printing machine; and  
 supplying at least one of printing ink and dampening water onto the exposed lithographic printing plate precursor to remove an unexposed area of the image-recording layer.

## 10 9. A plate making method of a lithographic printing plate comprising:

exposing imagewise the lithographic printing plate precursor as claimed in any one of Claims 1 to 6 with laser; and developing the exposed lithographic printing plate precursor with an aqueous solution having pH of from 2 to 12.

## 15 10. The plate making method of a lithographic printing plate as claimed in Claim 9, which further comprises, after the developing, subjecting the lithographic printing plate precursor to a heat treatment.

**Patentansprüche**

1. Lithografiedruckplattenvorläufer, umfassend: eine Bildaufzeichnungsschicht, die einen Feinpartikel eines thermoplastischen Polymers, einen Infrarotabsorber und eine Polymerverbindung enthält; und einen Träger, der eine hydrophile Oberfläche aufweist, worin die Polymerverbindung eine sternartige Form aufweist, worin eine Hauptkette in drei oder mehr Verzweigungen verzweigt ist und die verzweigten Hauptketten eine hydrophile Gruppe in einer Seitenkette der verzweigten Hauptkette aufweisen.
2. Lithografiedruckplattenvorläufer gemäß Anspruch 1, worin die hydrophile Gruppe mindestens eine von einer Carboxylgruppe oder einem Salz hiervon, einer Sulfogruppe oder einem Salz hiervon und einer Polyethylenoxygruppe ist.
3. Lithografiedruckplattenvorläufer gemäß Anspruch 1 oder 2, worin der Feinpartikel eines thermoplastischen Polymers eine vernetzbare Gruppe aufweist.
4. Lithografiedruckplattenvorläufer gemäß Anspruch 3, worin die Polymerverbindung mit der sternartigen Form in einer Seitenkette der verzweigten Hauptkette eine Gruppe aufweist, die in der Lage ist, mit der vernetzbaren Gruppe des Feinpartikels des thermoplastischen Polymers zu reagieren.
5. Lithografiedruckplattenvorläufer gemäß Anspruch 4, worin sowohl die vernetzbare Gruppe des Feinpartikels des thermoplastischen Polymers als auch die Gruppe, die in der Lage ist, mit der vernetzbaren Gruppe des Feinpartikels des thermoplastischen Polymers zu reagieren, ethylenisch ungesättigte Gruppen sind.
6. Lithografiedruckplattenvorläufer gemäß irgendeinem der Ansprüche 1 bis 5, worin die Bildaufzeichnungsschicht einen Polymerisationsinitiator enthält.
- 45 7. Lithografiedruckplattenvorläufer gemäß irgendeinem der Ansprüche 1 bis 6, worin die Bildaufzeichnungsschicht durch zumindest eines von Drucktinte und Anfeuchtwasser entfernt werden kann.
8. Lithografisches Druckverfahren, umfassend:
- 50 entweder Montieren des Lithografiedruckplattenvorläufers gemäß Anspruch 7 auf einer Druckmaschine und bildweises Belichten des montierten Lithografiedruckplattenvorläufers mit Laser, oder bildweises Belichten des Lithografiedruckplattenvorläufers gemäß Anspruch 7 mit Laser und Montieren des belichteten Lithografiedruckplattenvorläufers auf einer Druckmaschine; und  
 Zuführen von zumindest einem von Drucktinte und Anfeuchtwasser zu dem belichteten Lithografiedruckplattenvorläufer, um einen nichtbelichteten Bereich der Bildaufzeichnungsschicht zu entfernen.
- 55 9. Plattenherstellungsverfahren für eine Lithografiedruckplatte, umfassend:

bildweises Belichten des Lithografiedruckplattenvorläufers gemäß irgendeinem der Ansprüche 1 bis 6 mit Laser; und  
 Entwickeln des belichteten Lithografiedruckplattenvorläufers mit einer wässrigen Lösung, die einen pH-Wert von 2 bis 12 aufweist.

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10. Plattenherstellungsverfahren für eine Lithografiedruckplatte gemäß Anspruch 9, welches ferner nach dem Entwickeln das Unterziehen des Lithografiedruckplattenvorläufers unter eine Wärmebehandlung umfasst.

10 **Revendications**

1. Précurseur de plaque d'impression lithographique comprenant : une couche d'enregistrement d'image contenant une particule fine de polymère thermoplastique, un agent absorbant de l'infrarouge et un composé polymère ; et un support ayant une surface hydrophile, dans lequel le composé polymère a une forme semblable à une étoile dans laquelle une chaîne principale est ramifiée en trois branches ou plus et les chaînes principales ramifiées ont un groupe hydrophile dans une chaîne latérale de la chaise principale ramifiée.

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2. Précurseur de plaque d'impression lithographique selon dans la revendication 1, dans lequel le groupe hydrophile est au moins un d'un groupe carboxyle ou d'un sel de celui-ci, d'un groupe sulfo ou d'un sel de celui-ci et d'un groupe oxy polyéthylène.

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3. Précurseur de plaque d'impression lithographique selon la revendication 1 ou 2, dans lequel la particule fine de polymère thermoplastique a un groupe réticulable.

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4. Précurseur de plaque d'impression lithographique selon la revendication 3, dans lequel le composé polymère ayant la forme semblable à une étoile a, dans une chaîne latérale de la chaîne principale ramifiée, un groupe capable de réagir avec le groupe réticulable de la particule fine de polymère thermoplastique.

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5. Précurseur de plaque d'impression lithographique selon la revendication 4, dans lequel tant le groupe réticulable de la particule fine de polymère thermoplastique que le groupe capable de réagir avec le groupe pouvant être réticulé de la particule fine de polymère thermoplastique sont des groupes éthyléniquement non saturés.

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6. Précurseur de plaque d'impression lithographique selon l'une quelconque des revendications 1 à 5, dans lequel la couche d'enregistrement d'image contient un initiateur de polymérisation.

7. Précurseur de plaque d'impression lithographique selon l'une quelconque des revendications 1 à 6, dans lequel la couche d'enregistrement d'image est capable d'être enlevée par au moins n'importe laquelle d'une encre d'impression et d'une eau de mouillage.

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8. Procédé d'impression lithographique comprenant les étapes consistant à :

soit monter le précurseur de plaque d'impression lithographique selon la revendication 7 sur une machine d'impression et exposer image par image le précurseur de plaque d'impression lithographique monté avec laser soit l'exposition image par image le précurseur de plaque d'impression lithographique selon la revendication 7 avec laser et monter le précurseur de plaque d'impression lithographique exposé sur une machine d'impression ; et

fournir au moins une d'une encre d'impression et d'une eau de mouillage sur le précurseur de plaque d'impression lithographique exposé pour enlever une zone non exposée de la couche d'enregistrement d'image.

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9. Procédé de fabrication de plaque d'une plaque d'impression lithographique comprenant les étapes consistant à :

exposer image par image le précurseur de plaque d'impression lithographique selon l'une quelconque des revendications 1 à 6 avec laser ; et

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développer le précurseur de plaque d'impression lithographique exposé avec une solution aqueuse ayant un pH de 2 à 12.

10. Procédé de fabrication de plaque d'une plaque d'impression lithographique selon la revendication 9, qui comprend en outre, après le développement, l'étape consistant à soumettre le précurseur de plaque d'impression lithographique

à un traitement thermique.

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FIG. 1

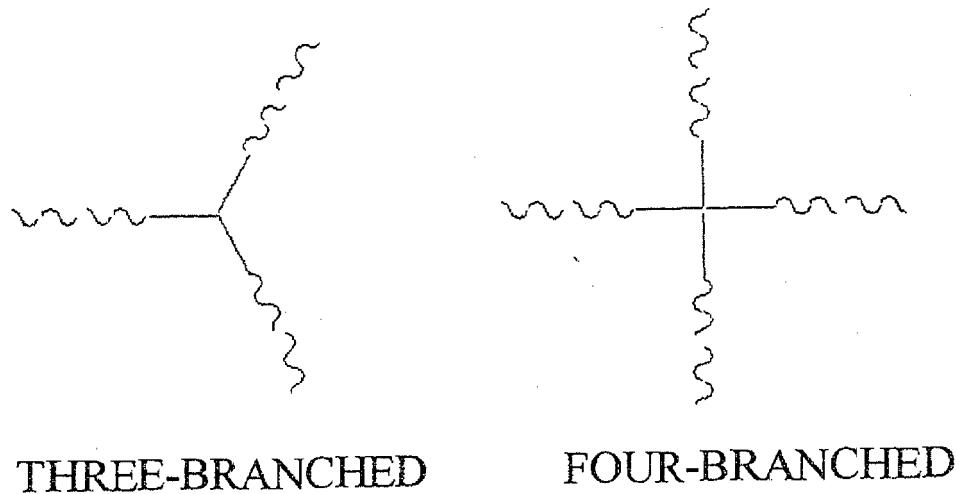
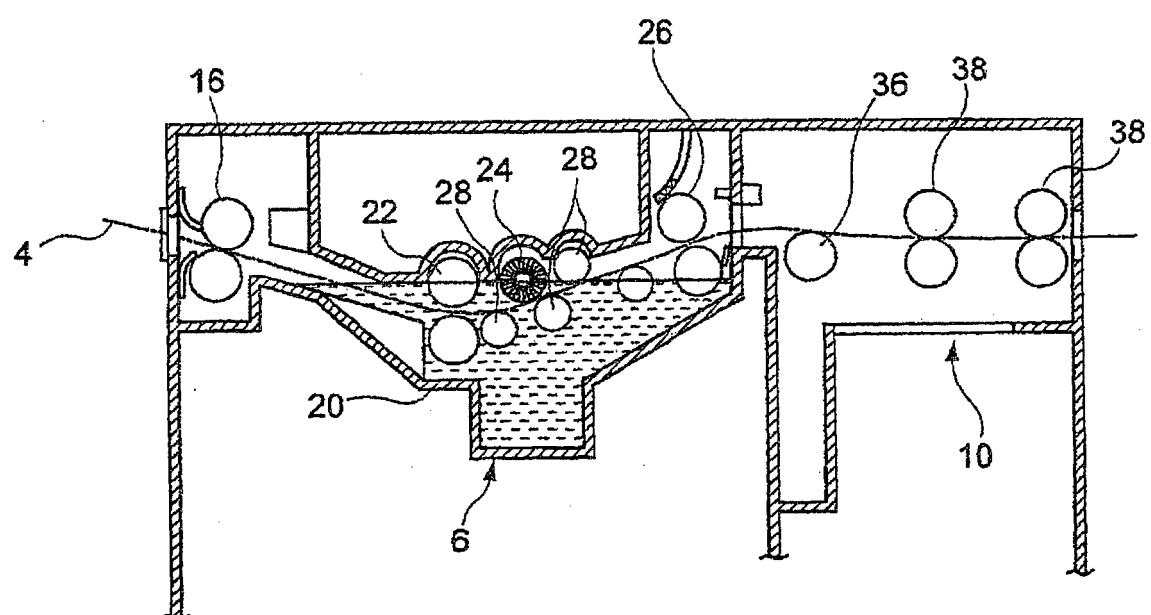


FIG. 2



## REFERENCES CITED IN THE DESCRIPTION

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