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(54) Planographic printing plate precursor

(57) The planographic printing plate precursor of the present invention which has a positive-working recording layer on the support, the recording layer can form an image by illuminating with an infrared-ray, the weight of the recording layer after drying is in the range of about 1.2 g/m^2 to about 1.7 g/m^2, and the areas of portions of a gradient of 15 degrees or more on the surface of the recording layer is about 5% or more of the total recording layer surface area. The recording layer may be a single layer structure or may be a multiple layers structure.

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Description

BACKGROUMD OF THE INVENTION

Field of the Invention

[0001] The present invention relates to an infrared-ray photosensitive planographic printing plate precursor, particularly, to an infrared-ray photosensitive planographic printing plate precursor having excellent printing durability and excellent scratch resistance.

Description of the Related Art

[0002] Development of lasers in recent years has been remarkable, particularly in solid lasers and semiconductor lasers having a light-emitting region in the near-infrared to infrared regions, of which high output and small size lasers have become easily available. Particularly, in the field of planographic printing, these lasers are extremely useful as an exposure light source when a plate is made directly from digital data of computers or the like.

[0003] Positive-working planographic printing plate precursors for direct plate-making using such infrared-ray lasers contain an alkali-soluble resin and an infrared-ray absorbing agent, which absorbs light and generates heat, as essential components. In an unexposed portion (image portion), the infrared-ray absorbing agent acts as a dissolution inhibitor, which substantially reduces solubility of the alkali-soluble resin by interacting with the alkali-soluble resin. On the other hand, in an exposed portion (non-image portion), interaction between the infrared-ray absorbing agent and the alkali-soluble resin is weakened due to the generated heat, and the resin is dissolved in an alkali developer. An image thereby formed.

[0004] In a planographic printing plate precursor having such a positive-working recording layer, generally, the sensitivity for the image formation by the exposure can be improved by reducing the layer thickness of the recording layer. Particularly, in the multi-layered positive-working planographic printing plate precursor having a lower layer containing an alkali-soluble resin and an upper layer containing an alkali-soluble resin and an infrared-ray absorbing agent, that is, having an image forming ability, the upper layer can be extremely thinned in the layer constitution, and thus, a high sensitivity can be obtained by thinning the overall layer thickness of the recording layer.

[0005] However, there has been a problem that in the case of thinning the recording layer, a small change in the surface conditions, which is attributable to contact and the like when plate handling, causes the dissolution of the image portion when developing the plate, resulting in the lowering of printing durability and inking properties.

[0006] Moreover, such a positive-working planographic printing plate precursor had problems such as that the mechanical strength in the formed recording layer due to the interaction of an alkali-soluble resin and a dissolution inhibiting agent such as an infrared-ray absorbing agent was not sufficient, so that when the plate surface was brought into contact strongly with various other members at the time of manufacturing and fabricating, transporting, and handling the printing plate precursor, defects were formed on the plate surface, resulting in formation of image omissions in the image portion after development.

[0007] On the other hand, in various sorts of printing, it is very useful that a planographic printing plate has a high printing durability such that a predetermined number of sheets can be printed without changing the plate until printed matter of the prescribed number of sheets is obtained, so that working efficiency can be improved.

[0008] Although it has been known to increase a coating amount of the recording layer for the purpose of improving the printing durability, the increase in the coating amount causes problems such that the above-mentioned scratch resistance is further lowered, and the sensitivity is also lowered. Furthermore, the reproducibility of small image areas is deteriorated due to the thinness of the small image areas such as thin lines.

[0009] In order to improve the scratch resistance, the technology of adding a particle formation polymer in the recording layer is proposed (see Japanese Patent Application Laid-Open (JP-A) No. 2004-258490). Though the scratch resistance can be improved by this technology, the printing durability is not sufficient in practice. Moreover, to improve the printing durability, an increasing in the coating amount of the recording layer is also exemplified, as mentioned above, but the problem of reduction in the sensitivity accompanied with the increase in the coating amount quantity has not yet been solved.

[0010] As mentioned above, positive-working planographic printing plate precursors for infrared-ray laser exposure in which the sensitivity, the scratch resistance and the printing durability are high and balanced have not yet been developed, and such a development is eagerly awaited.

SUMMARY OF THE INVENTION

[0011] The present invention has been made in view of the above circumstances and provides an infrared-ray photosensitive positive-working planographic printing plate precursor.

[0012] A first aspect of the present invention provides an infrared-ray photosensitive positive-working planographic printing plate precursor, comprising: a support, a positive-working recording layer provided on the support which is capable of forming an image by irradiating with an infrared-ray, and has a coating weight of the layer after drying in the range of about 12 g/m^2 to about 1.7 g/m^2, wherein the area of portions having a gradient of about 15 degrees or more on the surface of the recording layer is about 5% or more of the total surface area of the recording layer.

[0013] A second aspect of the present invention provides an infrared-ray photosensitive positive-working planographic printing plate precursor, comprising: a support, a recording layer formed on the support by laminating a plurality of layers, wherein a recording layer (lower layer) disposed adjacent to the support and a positive-working recording layer (top layer) disposed as the top layer among the plurality of layers contain a water-insoluble and alkali-soluble resin, at least one of the lower layer and the top layer contains an infrared-ray absorbing agent, the total weight of the plurality of layers constituting the recording layer after drying is in a range of about 1.2 g/m^2 to about 1.7 g/m^2, and the area of portions of a gradient of 15 degrees or more on the surface of the top layer is about 5% or more of the total surface layer of the top layer.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The recording layer of the present invention may be a single layer or may be a multiple layers having a laminated structure consisting of a plurality of layers. Here, because the coating amount of the recording layer (in the case of multiple layers, the total coating amounts) is about 1.2 g/m^2 to about 1.7 g/m^2, the balance between the sensitivity and the printing durability becomes good, thinning ofthin lines and the like at the time of development is suppressed, and the reproducibility of the minute area image is improved. Moreover, because the area of portions of a gradient of 15 degrees or more at the top surface of the recording layer is about 5% or more of the total recording surface area, the surface of the recording layer has an appropriate irregularity. When stress is imposed on a smooth surface of a recording layer, continuous flaws tend to arise on the surface of the recording layer. However, in the present invention, because the stress concentration occurs on the projection portions of the surface of the recording layer, even if stress is imposed on the surface of the recording layer, the spread of the flaw caused by the stress is suppressed by the projection portions and the occurrence of such flaws which affect image properties is considered to be effectively prevented.

[0015] Although methods of making the portions of the gradient of 15 degrees or more in the top surface of the recording layer to be 5% or more in the present invention are not especially limited, from the standpoint of the compatibility of the coating amount with the gradient prescribed in the present invention, the following method can be exemplified: a method of making the formation of irregularity by treating the surface of the support and the coating amount of the recording layer to a prescribed range, or a method that a polymer having a long chain alkyl group and a polymer compound which is not mutually insoluble with that the polymer having a long chain alkyl group are dissolved in a coating solvent to form a coating solution, and the solution is coated onto the support and dried, and fine particles are formed by self-aggregation of the polymer having a long chain alkyl group in the recording layer, which forms minute projections comprising the fine particles on the surface of the recording layer.

[0016] The positive-working infrared-ray photosensitive planographic printing plate precursor of the present invention has a positive-working recording layer that can form an image on the support by irradiating with an infrared-ray and that the weight of the recording layer after drying is in the range of about 1.2 g/m^2 to about 1.7 g/m^2, and the area of portions of a gradient of 15 degrees or more on the surface of that recording layer is about 5% or more of the total recording layer surface area.

[0017] Further, as described in the second aspect of the present invention, the recording layer may be not only a single layer but also the multiple layer structure formed by laminating a plurality of layers. In the case that the recording layer is formed of multiple layers, it is needed that the total weight of the plural layers after drying is in the range of about 1.2 g/m^2 to about 1.7 g/m^2, and the area of portions of a gradient of 15 degrees or more on the surface of the uppermost layer is about 5% or more of the total top layer surface area.

[0018] The weight of the recording layer in the infrared-ray photosensitive planographic printing plate precursor of the present invention after drying is in the range of about 1.2 g/m^2 to about 1.7 g/m^2. In the case of a single layer, the coating amount is the coating amount of the recording layer itself and, in the case of the recording layer of the multiple layer structure, the coating amount means the total coating amount of the plural layers.

[0019] As described above, the coating amount of the recording layer of the present invention is needed to be 1.20 g/m^2 to 1.70 g/m^2, preferably 1.30 g/m^2 to 1.60 g/m^2, and more preferably in the range of 1.35 g/m^2 to 1.55 g/m^2.

[0020] The coating amount of the recording layer closely relates to the sensitivity and the printing durability. When the coating amount is less than about 1.2 g/m^2, there is a fear of decrease in the printing durability, and when the coating amount is more than about 1.7 g/m^2, it becomes difficult for the laser beam to reach the interface between the layer and the support, and thus, the reduction of the sensitivity of the recording layer may be caused, and problems such as thinning of thin lines become easy to occur. Accordingly, in the present invention, in light of the both factors, the range of the coating amount for satisfying the printing durability and the sensitivity is prescribed to be about 1.2 g/m^2 to about 1.7 g/m^2.

[0021] In the present invention, the area of portions of a gradient of 15 degrees or more on the surface of the recording layer is about 5% or more.

[0022] When the surface of the recording layer is smooth, if stress is applied to the recording layer to cause flaws, there is no place on which the stress concentrates, and continuous destruction on the surface of the recording layer easily takes place due to the stress. However, when an appropriate irregularity exists on the surface of the recording layer, if stress is applied to the surface of the recording layer having such an irregularity to form flows, it is considered that it is possible that the stress concentrates at the projections on the surface of the recording layer to suppress the occurrence of continuous destruction of the recording layer, and consequently the occurrence of flaws to affect the image quality of the printed matter is suppressed.

[0023] The area of portions of a gradient of 15 degrees or more on the surface of the recording layer is needed to be about 5% or more, preferably the area of portions is about 15% or more, and more preferably the areas portions is about 20% or more. There is especially no upper limit of the area of a gradient of 15 degrees or more, 100%, that is, all area of the surface may be 15 degrees or more in the gradient, but from the standpoint of production applicability and the balance with other characteristics of the recording layer, it is preferable to be in the range of 5 to 80%.

[0024] In the present invention, as the area of the gradient of 15 degrees or more on the top surface of the recording layer, the value measured by the following method is used. <The method for measuring the rate of the gradient of 15 degrees>

[0025] The surface configuration was measured by an atomic force microscope (SPA300/SPI3800N type, manufactured by S11 Nano-Technology Co., Ltd.) and the three dimensional data were found.

[0026] Hereinafter, the concrete procedure will be described. A planographic printing plate precursor was cut out into the size of 1 cm square and the sample was set on the horizontal sample stand on a piezo scanner. A cantilever was approached to the surface of the sample of the recording layer, and the sample was scanned in the XY direction when it reached the region where the atomic force was exerted. At this time, the irregularity of the sample was determined by the piezo displacement in the Z direction.

[0027] The piezo scanner capable of scanning in the X and Y directions by 150 μm and the Z direction by 10 μm was used. The cantilever having a resonance frequency of 200 to 400 kHz and a spring constant of 12 to 103 N/m (AC 160, manufactured by OLYMPUS Corp.) was used and the measurement was carried out in the DFM mode (Dynamic Force Mode). Moreover, small inclinations of the sample were corrected by the least-squares approximation of the obtained three dimensional data and the reference plane was obtained. In obtaining the data, the measurement was carried out with the scanning area of 10 μm; the resolving power of 256 (the number of X data) (256 (the number of Y data), and the scanning frequency of 0.5 Hz.

[0028] Using the obtained three dimensional data (f (x, y)), 3 points adjacent to each other were selected and angles defined by a minute triangle formed in the three points and the reference plane were calculated with respect to all data, and thus the gradient distribution curve was obtained. The ratio of the portions of the gradient of 15 degrees or more was calculated from the gradient distribution curve.

[0029] More specifically, for example, it was confirmed that a recording layer having a mat pattern-like irregularity of about 0.1 μm to 1.0 μm in diameter and about 0.5 μm to 1.0 μm in height exists on the surface satisfies the above-mentioned conditions in the present invention by carrying out the measurement as described herein.

[0030] In the present invention, methods for satisfying the above-mentioned two requirements for physical properties of the recording layer are not especially limited, known methods can be used appropriately. As such a method, for example, the method of blending such a component that can form an irregular shape on the surface in the recording layer can be cited. As such a method, in detail, the method of using a polymer that can form fine particles through the self-aggregation as described in the above-mentioned JP-A No. 2004-258490, the method of blending resin fine particles, which can orient at the surface of the layer, in a coating liquid for the recording layer, and the like can be exemplified.

[0031] Moreover, as other methods, a method in which a predetermined irregularity is formed on the surface of the support by using a known method, and the recording layer is formed by applying a coating solution on the support by selecting the coating amount of the recording layer such that the irregularity on the surface of the support is reflected to the coated surface of the recording layer to some extent, so that the rate of the portions of the gradient of 15 5 degrees or more is made to be 5% or more on the surface of the recording layer, is exemplified.

[0032] As a method for obtaining the recording layer that meets the requirements of the present invention, the method in which fine particles are formed through self-aggregation first, and irregularity is formed on the surface will be described..

[0033] Such a recording layer contains a polymer (a) having a long chain alkyl group and another polymer (b) which is not mutually soluble with the polymer (a), and the recording layer has a property such that in the drying process after the coating solution is coated on a surface of a support, the polymer (a) is phase-separated from the polymer (b) with the removal of the solvent and projections are formed on the top surface through self-aggregation.

[0034] Because the recording layer of the present invention is an infrared-ray photosensitive positive-working recording layer, the recording layer contains an infrared-ray absorbing agent (c) as an essential component other than these polymers. When the recording layer has a multiple layers structure, an infrared-ray absorbing agent (c) may be contained in any one of these plural layers.

[0035] As a method for forming irregularity on the surface with fine particles which orient at the surface, though such a method in which a fine particle dispersion of inorganic particles, metal particles, and organic particles which can form minute projections on the recording layer is added to a coating liquid can be cited, fine particles (minute projections) formed by the above-mentioned method are preferable, because the fine particles have advantageously excellent adhesiveness with a polymer compound which constitutes a matrix.

[0036] The above-mentioned polymer (a) having a long chain alkyl group, preferably contains a vinyl monomer having a carboxyl group in a range of 45 to 99 % by mole, and another polymer (b) is a polymer compound which is not mutually-soluble with the polymer (a), for example, phenolic resins can be cited.

[0037] Although the polymer (a) having a long chain alkyl group is dissolved in a coating solvent together with the other polymer compound (b) in an coating liquid, the polymer (a) has a property that in the drying process after coating, the polymer (a) is phase separated from the other components with the removal of the solvent and projections are formed on the top surface through self-aggregation of the polymer (a).

[0038] In the invention, examples of a factor of controlling a particle diameter and a height of a fine projection consisting of a polymer (a) having a long chain alkyl group present on a recording layer surface include polarity of a polymer (a) having a long chain alkyl group, polarity of a polymer compound to be used jointly, each addition amount, a kind of a coating solvent, other additives contained in a recording layer, and drying condition (temperature, time, humidity, pressure etc.).

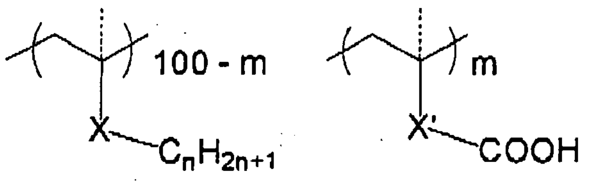
[0039] For example, when a difference in polarity between a polymer (a) having a long chain alkyl group and a polymer (b) which is not mutually-soluble with the polymer (a) to be used together becomes large, a particle diameter of fine projections increases and, by raising a drying temperature to shorten a necessary time for drying, the particle diameter of fine projections becomes small,

[0040] The structural components of the present embodiments will be described in detail hereinafter.

(Polymer having a long chain alkyl group)

[0041] A polymer (a) having a long chain alkyl group used of the invention is indispensable that it contains a vinyl monomer having a carboxyl group at a composition ratio ranging from 45 to 99% by mole% by mole. A long chain alkyl group in the polymer (a) having a long chain alkyl group refers to a carbon number of 6 or more, preferably a carbon number of 12 or more. More specifically, it is preferable that the polymer (a) having a long chain alkyl group is a copolymer of a monomer having a long chain alkyl group and a vinyl monomer having a carboxyl group, and is indispensable that it contains the vinyl monomer having a carboxyl group at a composition ratio ranging from 45 to 99 % by mole.

[0042] In the invention, as the polymer (a) having a long chain alkyl group, for example, it is preferable that the polymer comprises a copolymer represented by the following formula (I).



Formula(1)

[0043] In the formula (I), X and X' each independently represent, a single bond or a divalent linking group. Further, m represents an integer of $45 < m < 99$, preferably an integer of $47 < m < 95$, further preferably an integer of $50 < m < 90$. And, n represents an integer of 6 to 40, more preferably an integer of 12 to 30, further preferably an integer of 14 to 20. A bond represented by a dotted line means that there is a methyl group or hydrogen atom at a tip end thereof.

[0044] Examples of a divalent linking group represented by X or X' in the formula (I) include a straight, branched or cyclic alkylene group of a carbon number of 1 to 20, a straight, branched or cyclic alkenylene group of a carbon number of 2 to 20, an alkynylene group of a carbon number of 2 to 20, an arylene group (monocycle, heterocycle) of a carbon number of 6 to 20, -OC(=O)-, -OC(=O)Ar-, -OC(=O)O-, -OC(=O)OAr-, -C(=O)NR-, -C(=O)NAr-, -S02NR-, -SO2NAr-, -O-(alkyleneoxy, polyalkyleneoxy), -OAr- (aryleneoxy, polyaryleneoxy), -C(=O)O-, -C(=O)O-Ar-, -C(=O)Ar-, -C(=O)-, -SO2O- -SO2OAr-, -OS02-, -OSO2Ar-, -NRSO2-, -NArSO2-, -NRC(=O)-, -NAr-C(=O)-, -NRC(=O)O-, -NArC(=O)O-, -OC(=O)NR-, -OC(=O)NAr-, -NAr-, -NR-, -N+RR'-, -N+RAr-, -N+ArAr'-, -S-, -SAr-, -ArS-, a heterocyclic group (3 to 12-membered monocycle or fused ring containing, for example, at least one of nitrogen, oxygen and sulfur as a hetero atom), -OC(=S)-, -OC(=S)Ar-, -C(=S)O-, -C(=S)OAr-, -C(=S)OAr-, -C(=O)S-, -C(=O)SAr-, -ArC(=O)-, -ArC(=O)NR-, -ArC(=O)NAr-, -ArC(=O)O-, -ArC(=O)S-, -ArC(=S)O-, -ArO-, and -ArNR-. Herein, R and R' each independently represent a hydrogen atom, or a straight or branched, chain-like or cyclic alkyl group, an alkenyl group or an alkynyl group. Ar and Ar' each independently represent an aryl group.

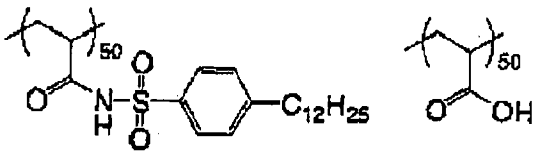
[0045] The linking group may be such that two or more kinds of linking groups listed herein are combined to form a linking group.

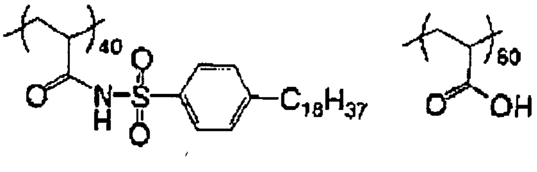
[0046] Among such the linking groups, an arylene group (monocycle, heterocycle) of a carbon number of 6 to 20, -C(=O)NR-, -C(=O)NAr-, -O-(alkyleneoxy, polyalkyleneoxy), -OAr-(aryleneoxy, polyarylencoxy), -C(=O)O-, -C(=O)O-Ar-, -C(=O)-, -C(=O)Ar-, -S-, -SAr-, -ArS-, -ArC(=O)-, -ArC(=O)O-, -ArO-, and -ArNR- are preferable, and an arylene group (monocycle, heterocycle) of a carbon number of 6 to 20, -C(=O)NR-, -C(=O)NAr-, -O-(alkyleneoxy, polyalkyleneoxy), -OAr-(aryleneoxy, polyaryleneoxy), -C(=O)O-, -C(=O)O-Ar-, -SAr-, -ArS-, -ArC(=O)-, -ArC(=O)O-, -ArO-, and -ArNR- are more preferable.

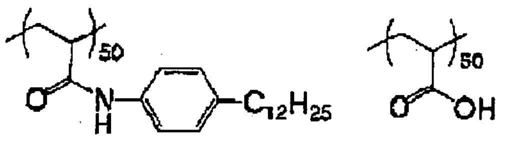
[0047] The linking group may have a substituent, and examples of the substituent include a straight, branched or cyclic alkyl group of a carbon number of 1 to 20, a straight, branched or cyclic alkenyl group of a carbon number of 2 to 20, an alkynyl group of a carbon number of 2 to 20, an aryl group of a carbon number of 6 to 20, an acyloxy group of a carbon number of 1 to 20, an alkoxycarbonyloxy group of a carbon number of 2 to 20, an aryloxycarbonyloxy group of a carbon number of 7 to 20, a carbamoyloxy group of a carbon number of 1 to 20, a carbonamido group of a carbon number of 1 to 20, a sulfonamido group of a carbon number of 1 to 20, a cabamoyl group of a carbon number of 1 to 20, a sulfamoyl group of a carbon number of 0 to 20, an alkoxy group of a carbon number of 1 to 20, an aryloxy group of a carbon number of 6 to 20, an aryloxycarbonyl group of a carbon number of 7 to 20, an alkoxycarbonyl group of a carbon number of 2 to 20, a N-acylsulfamoyl group of a carbon number of 1 to 20, a N-sulfamoylcarbamoyl group of a carbon number of 1 to 20, an alkylsulfonyl group of a carbon number of 1 to 20, an arylsulfonyl group of a carbon number of 6 to 20, an alkoxycarbonylamino group of a carbon number of 2 to 20, an aryloxycarbonylamino group of a carbon number of 7 to 20, an amino group of a carbon number of 0 to 20, an imino group of a carbon number of 1 to 20, an ammonio group of a carbon number of 3 to 20, a carboxyl group, a sulfo group, an oxy group, a mercapto group, an alkylsulfinyl group of a carbon number of 1 to 20, an arylsulfinyl group of a carbon number of 6 to 20, an alkylthio group of a carbon number of 1 to 20, an arylthio group of a carbon number of 6 to 20, an ureido group of a carbon number of 1 to 20, a heterocyclic group of a carbon number of 2 to 20, an acyl group of a carbon number of 1 to 20, a sulfamoylamino group of a carbon number of 0 to 20, a silyl group of a carbon number of 2 to 20, a hydroxyl group, a halogen atom (e.g. fluorine atom, chlorine atom, bromine atom etc.), a cyano group, and a nitro group,

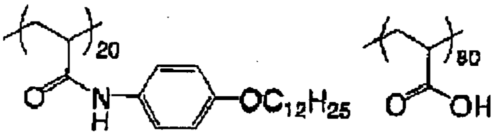
[0048] Such a polymer (a) having a long chain alkyl group is described in detail in the paragraphs of [0016] to [0060] in JP-A No. 2004-258490 that the present inventor proposed previously, and the polymers can be preferably adopted in the present invention.

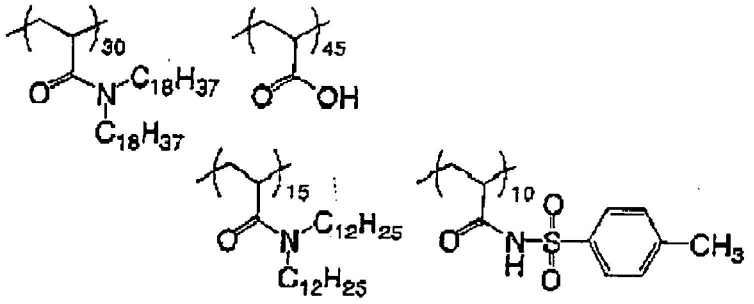
[0049] Examples of (a) a polymer having a long chain alkyl group in the invention are not limited to, but include the following polymers.

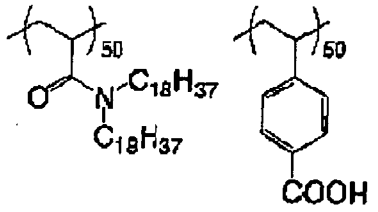


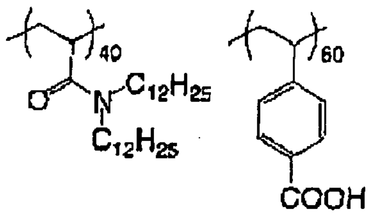


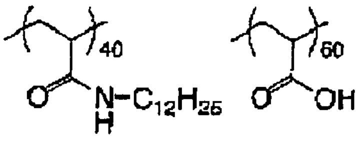


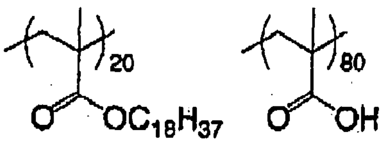


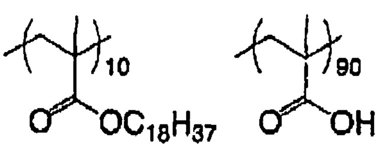


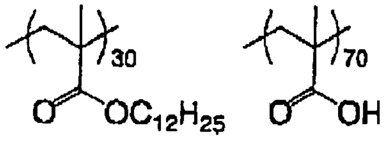


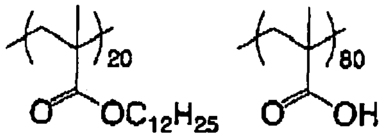


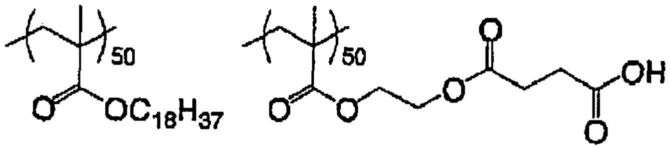


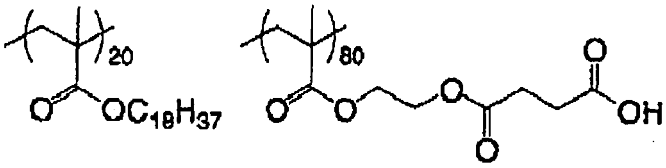


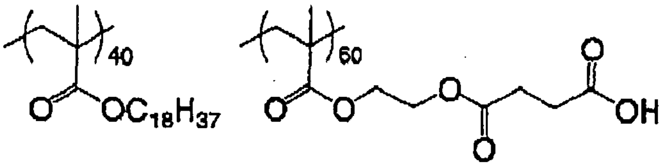


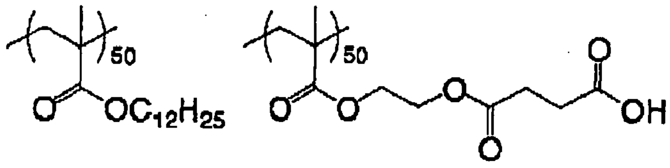


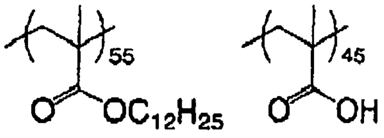


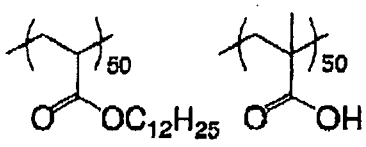


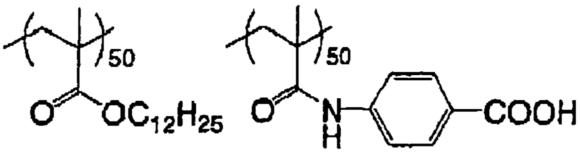


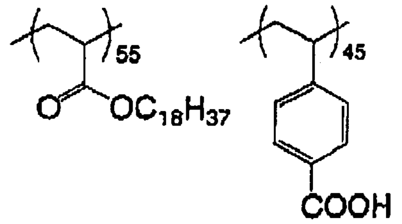


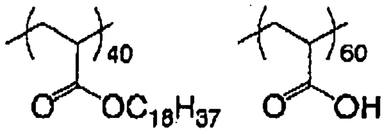


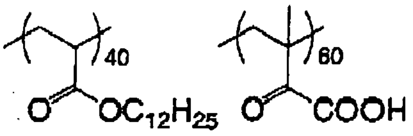


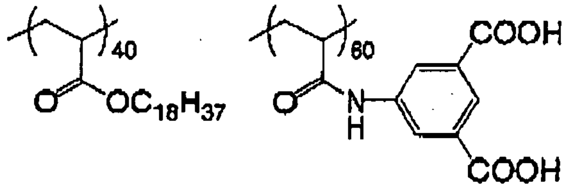


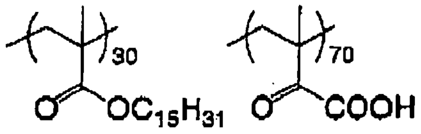


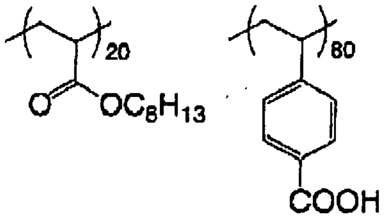


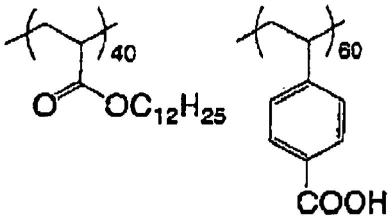


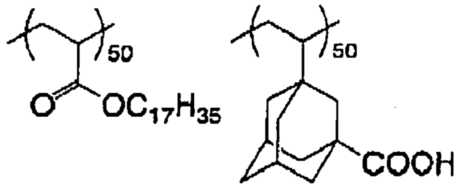


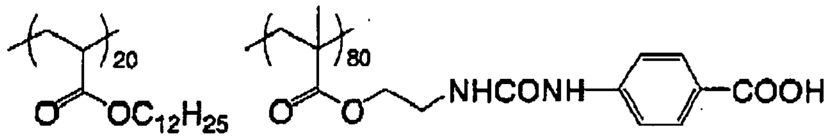


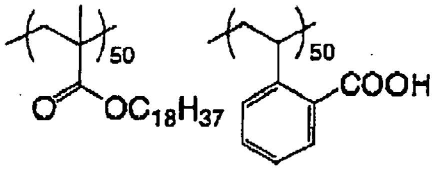


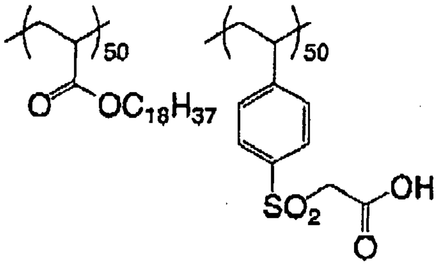


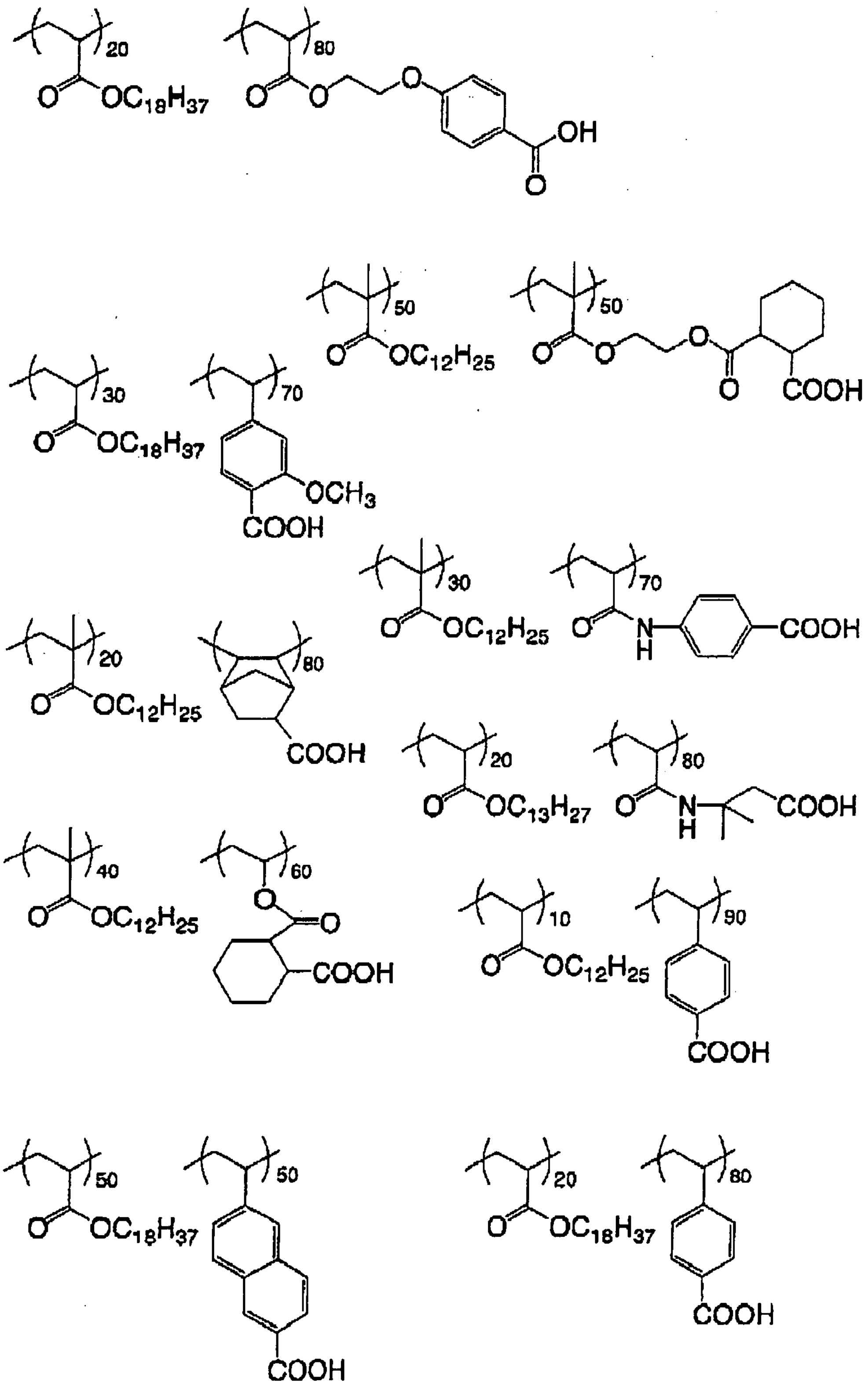


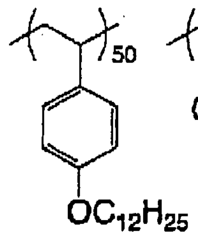








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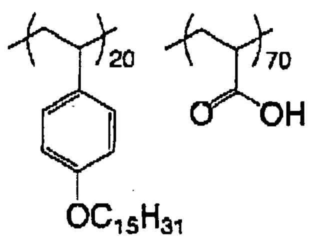
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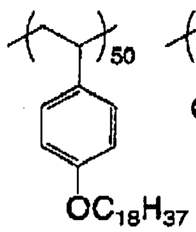
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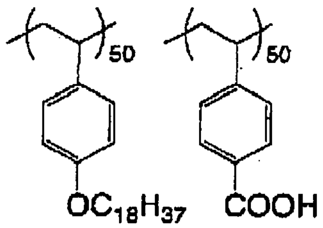
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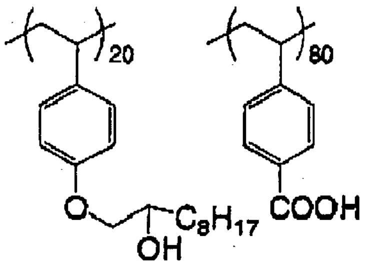
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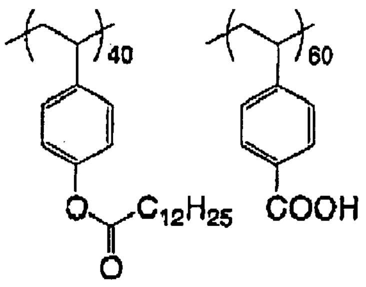
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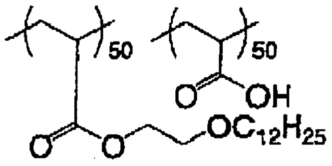
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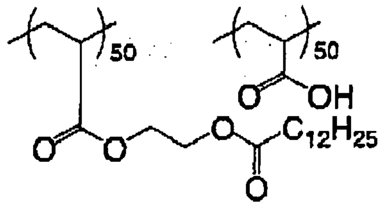
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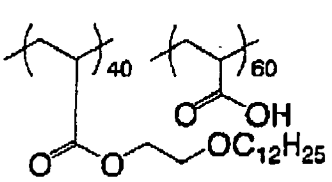
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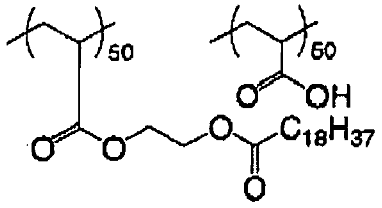
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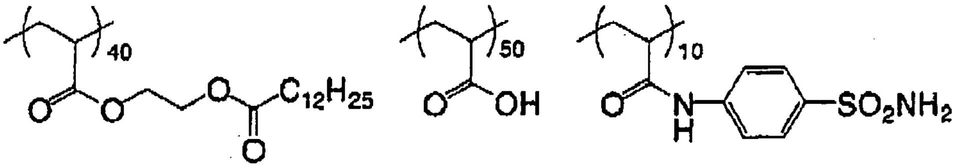

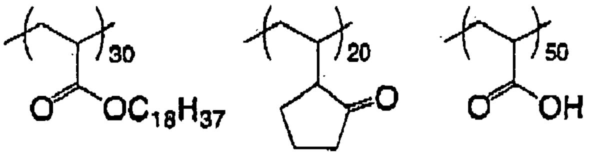

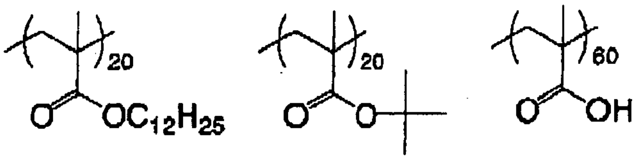

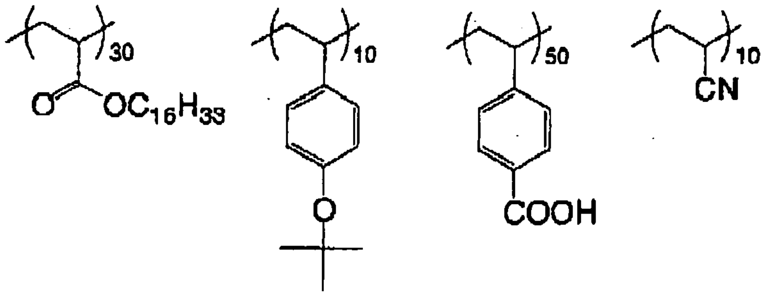

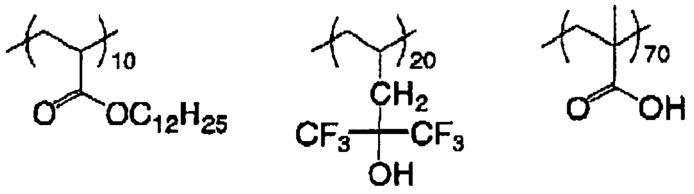

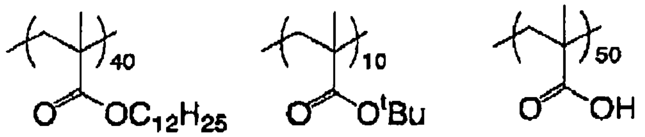

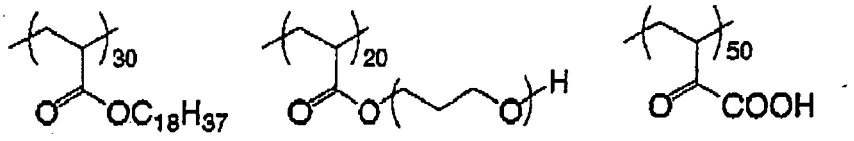
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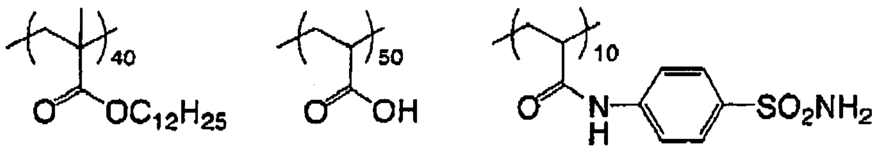
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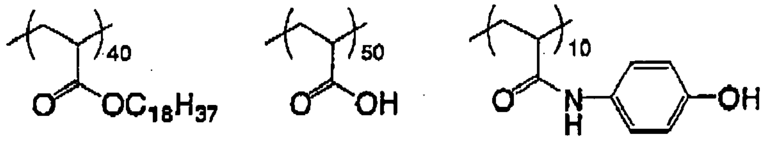
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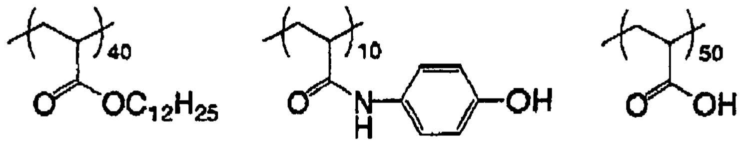
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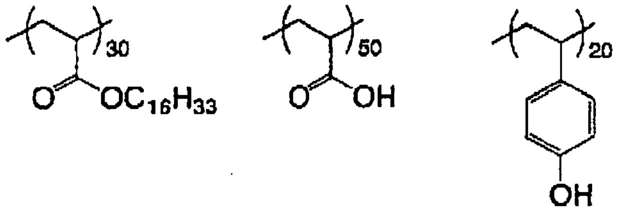
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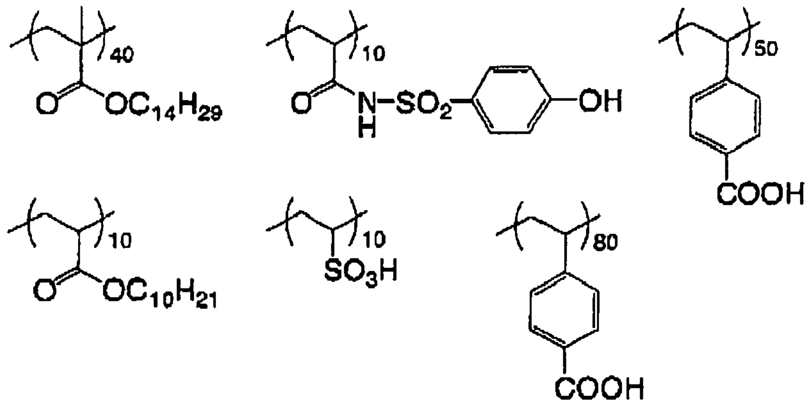
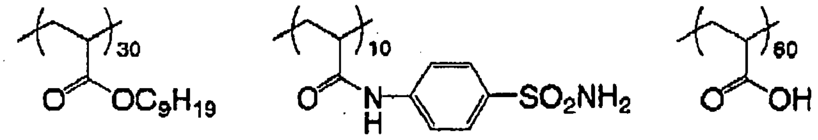
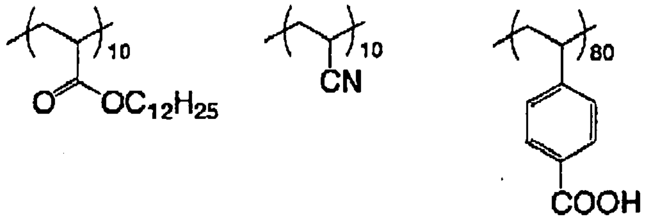
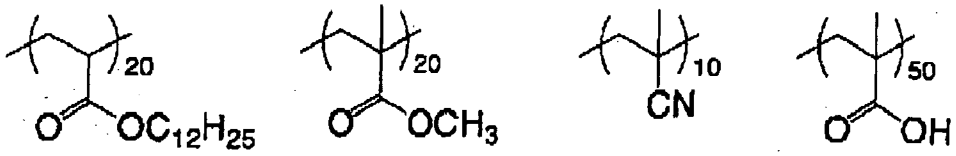
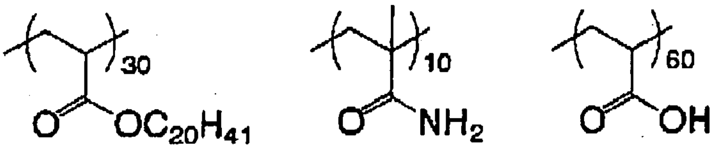
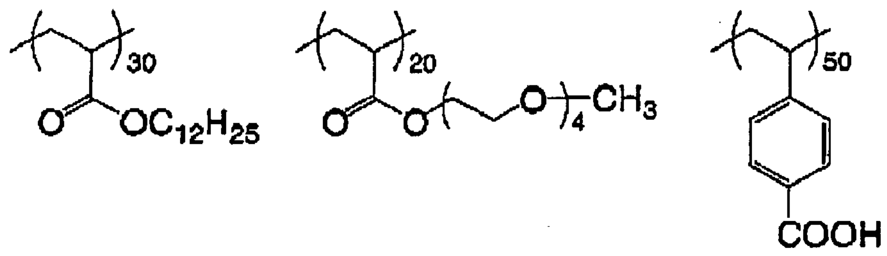


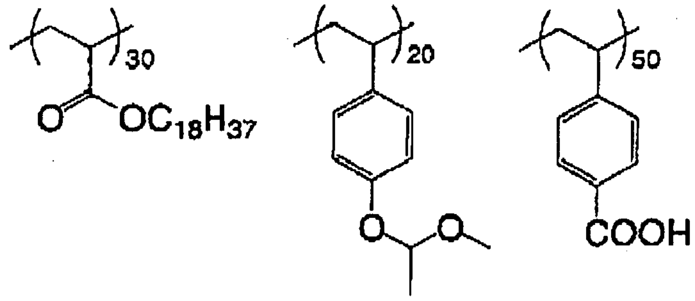


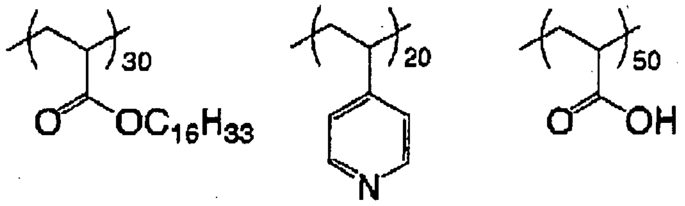


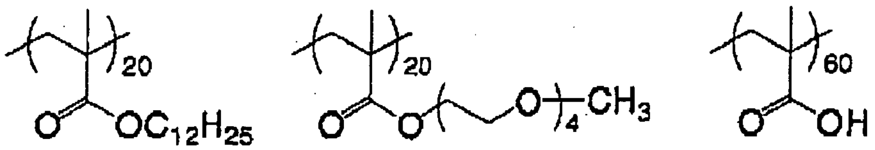












[0050] As a polymer (a) having a long chain alkyl group used in the invention, a polymer having a mass average molecular weight of 5,000 or more, and a number average molecular weight of 1,000 or more is preferably used. Further preferably, a mass average molecular weight in terms of polystyrene is 10,000 to 5,000,000 particularly preferably 10,000 to 2,000,000, further preferably 20,000 to 1,000,000. Such the polymers may be used alone, or two or more kinds may be used in a combination thereof.

[0051] A coating liquid for a recording layer in which the above-mentioned polymer (a) having a long chain alkyl group, the water-insoluble and alkali-soluble polymer [polymer (b)], and components to be used in the positive-working recording layer are mixed is coated on a support to form a recording layer of the present invention. As a result, the phase separation is caused between the polymer (a) having a long chain alkyl group and the polymer compound contained in the components of the recording layer, for example, an alkali-soluble polymer and the like, and the self-aggregation of the polymer (a) having a long chain alkyl group takes place to form minute projections on the surface of the recording layer.

[0052] Here, in order to make the area of the portions of a gradient of 15 degrees or more on the surface of the recording layer about 5% or more, the amount of addition of the polymer (a) having a long chain alkyl group contained in the total solid content of the recording layer is preferably from 0.1 to 30 % by mass, and more preferably from 0.5 to 20 % by mass,

[0053] The positive-working recording layers of the present invention include the type (1)in which a water-insoluble and alkali-soluble resin (hereinafter, occasionally called an alkali-soluble resin) and a substance that interacts with the alkali-soluble resin to suppress the alkali solubility (dissolution inhibitor) are contained, and an image is formed by utilizing an increase in alkali solubility of an exposed area due to release of the interaction by heat during exposure, and the type (2) in which a compound which is changed to be alkali-soluble by the action of an acid and an acid-generating agent which generates an acid with heat are contained, and an image is formed by utilizing an increase in alkali solubility of an exposed area due to the action of an acid generated by heat during exposure.

[0054] The positive-working, planographic printing plate precursors of the above-mentioned (1) include the positive-working planographic printing plate precursors described in U.S. Patent Nos. 3,628,953 and 4,708,925, JP-ANo. 7-285275, WO 97/39,894, JP-A Nos. 11-44956, 11-268512, and 2001-324808 and the like. However, as long as a positive-working planographic printing plate precursor is one in which an image is formed with the above-mentioned principle, any one may be used, and the present invention will not be limited thereto.

[0055] The positive-working planographic printing plate precursors of the above-mentioned (1) to which the image recording material of the present invention is applied have the recording layer containing, specifically, a polymer (a) having a long chain alkyl group, an alkali-soluble resin (b), and an infrared-ray absorbing agent (c) (an agent having an additional function as a dissolution inhibitor is often selected) on a support. Here, an alkali-soluble resin (b) has a function as a polymer compound which is mutually-insoluble with the polymer (a) having a ling chain alkyl group. Moreover, the recording layer may further contain a dissolution inhibitor, and may contain known additives to be added as occasion demands.

<(b) Alkali-soluble resin>

[0056] The aforementioned alkali-soluble resin is a water-insoluble and alkali-soluble resin, and includes homopolymers containing an acid group on a main chain and/or a side chain in a polymer, a copolymer thereof and a mixture thereof. Inter alia, compounds having an acyclic group listed in the following (1) to (6) on a main chain and/or a side chain of a polymer are preferable from the points of the solubility in an alkaline developer, and manifestation of dissolution suppressing ability.

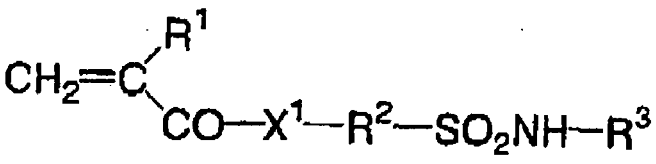
(1) phenol group (-Ar-OH),
(2) sulfonamide group ($-SO_2NH-R$),
(3) active imido group) [$-SO_2NHCOR$, $-SO_2NHSO_2R$, $-CONHSO_2R$]
(4) carboxylic acid group ($-CO_2H$),
(5) sulfonic acid group ($-SO_3H$), and
(6) phosphoric acid group ($-OPO_3H_2$)

[0057] Ar in the above-mentioned groups (1) to (6) represents a divalent aryl linking group optionally having a substituent group and R represents a hydrocarbon group optionally having a hydrogen atom or a substituent group.

[0058] Among the alkali-soluble resins having the acidic group selected from the above-mentioned (1) to (6), an alkali-soluble resin having (1) phenol group, (2) sulfonamide group, (3) active imido group, or (4) carboxylic acid group is preferable, and an alkali-soluble resin having (1) phenol group, (2) sulfonamide group, or (4) carboxylic acid group is more preferable in light of assurance of the sufficient solubility in an alkaline developer, development latitude, and layer strength.

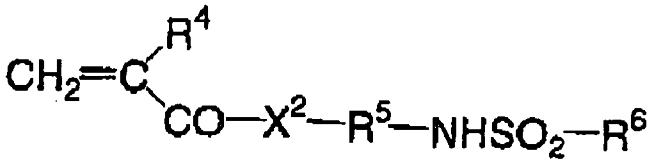
[0059] Examples of a monomer having (1) the phenol group include acrylamide, methacrylamide, acrylic acid ester, methacrylic acid ester, or hydroxystyrene.

[0060] Examples of a monomer having (2) the sulfonamide group include a compound having each one or more of sulfonamide groups of the above structure and polymerizable unsaturated groups in a molecule. Inter alia, a low-molecular compound having an acryloyl group, an aryl group or a vinyloxy group and a sulfonamide group in a molecule is preferable. Examples include compounds represented by the following formulae (i) to (v).



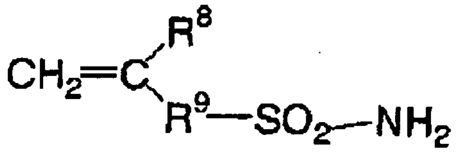
$$CH_2=C(R^1)-CO-X^1-R^2-SO_2NH-R^3$$

(i)



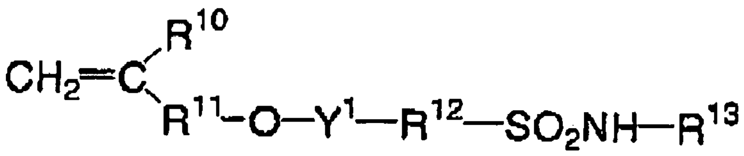
$$CH_2=C\genfrac{}{}{0pt}{}{R^4}{CO-X^2-R^5-NHSO_2-R^6}$$

(ii)



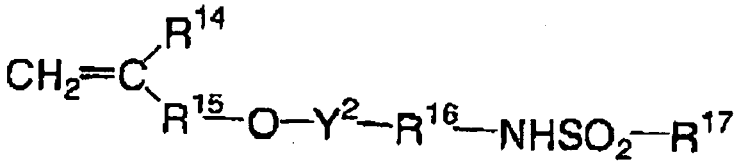
$$CH_2=C\genfrac{}{}{0pt}{}{R^8}{R^9-SO_2-NH_2}$$

(iii)



$$CH_2=C\genfrac{}{}{0pt}{}{R^{10}}{R^{11}-O-Y^1-R^{12}-SO_2NH-R^{13}}$$

(iv)



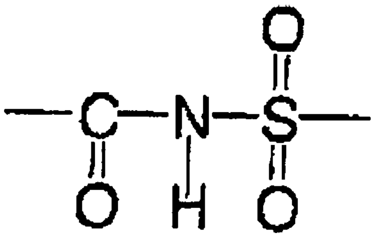
$$CH_2=C\genfrac{}{}{0pt}{}{R^{14}}{R^{15}-O-Y^2-R^{16}-NHSO_2-R^{17}}$$

(v)

[0061] In the formulae (i) to (v), X^1 and X^2 each independently represent -O-or -NR^7-, R^1 and R^4 each independently represent a hydrogen atom or -CH_3. R^2, R^5, R^9, R^{12} and R^{16} each independently represent an alkylene group of a carbon number of 1 to 12 optionally having a substituent, a cycloalkylene group, an arylene group or an aralkylene group. R^3, R^7 and R^{13} each independently represent a hydrogen atom, an alkyl group of a carbon number of 1 to 12 optionally having a substituent, a cycloalkyl group, an aryl group or an aralkyl group. R^6 and R^{17} each independently represent an alkyl group of a carbon number of 1 to 12 optionally having a substituent, a cycloalkyl group, an aryl group, or an aralkyl group. R^8, R^{10} and R^{14} each independently represent a hydrogen atom or -CH_3. R^{11} and R^{15} each independently represent a single bond, or an alkylene group of a carbon number of 1 to 12 optionally having a substituent, a cycloalkylene group, an arylene group or an aralkylene group. Y^1 and Y^2 each independently represent a single bond or -CO-.

[0062] Among compounds represented by the formulae (i) to (v), in the image recording material of the invention, particularly, m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl)methacrylamide, and N-(p-aminosulfonylphenyl)acrylamide can be preferably used.

[0063] Examples of a monomer having (3) the active imido group include a compound having each one or more of active imido groups represented by the above structural formula and polymerizable unsaturated groups in a molecule. Inter alia, a compound having each one or more of unactive imido groups represented by the following structural formula and polymerizable unsaturated groups in a molecule is preferable.



[0064] Specifically, N-(p-toluenesulfonyl) methacrylamide, and N-(p-toluenesulfonyl) acrylamide can be preferably used.

[0065] Examples of a monomer having (4) the sulfonic acid group include a compound having each one or more of sulfonic acid groups and polymerizable unsaturated groups in a molecule.

[0066] Examples of a monomer having (5) the phosphoric acid group include a compound having each one or more of phosphoric acid groups and polymerizable unsaturated groups.

[0067] Among the above hydrophilic monomers, a monomer having (1) a phenol group, (2) a sulfonamide group, or (3) an active imido group is preferable and, particularly, a monomer having (1) a phenol group, or (2) a sulfonamide group is most preferable from a viewpoint of sufficient maintenance of solubility in an alkaline developer, development latitude, and a layer strength.

(Other monomers)

[0068] Further, the water-insoluble and alkali-soluble resin may be a copolymer of the monomer having an acid group with another monomer. The other monomer copolymerizable with the monomer having an acid group includes the following compounds (6) to (16) listed below:

[0069] (6) Acrylic acid esters, and methacrylic acid esters having an aliphatic hydroxyl group such as 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate;

[0070] (7) Acrylate such as methyl acrylate, ethyl acrylate, propyl acrylate, amyl acrylate, benzyl acrylate, 2-chloroethyl acrylate, glycidyl acrylate, N-dimethylaminoethyl acrylate, polyethylene glycol monoacrylate, and polypropylene glycol monoacrylate;

[0071] (8) Methacrylate such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, amyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-chloroethyl methacrylate, glycidyl methacrylate, N-dimethylaminoethyl methacrylate, polyethylene glycol monomethacrylate, and polypropylene glycol monomethacrylate;

[0072] (9) Acrylamide or methacrylamide such as acrylamide, methacrylamide, N-methylolacrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxlethylacrylamide, N-phenylacrylamide, N-nitrophenylacrylamide, and N-ethyl-N-phenylacrylarnide; .,

[0073] (10) Vinyl ethers such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethylvinyl ether, propyl vinyl ether, butyl vinyl ether, and phenyl vinyl ether.

[0074] (11) Vinyl esters such as vinyl acetate, vinyl chloroacetate, vinyl butyrate, and vinyl benzoate;

[0075] (12) Styrenes such as styrene, α-methyl styrene, methylstyrene, and chloromethylstyrene;

[0076] (13) Vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone, and phenyl vinyl ketone.

[0077] (14) Olefins such as ethylene, propylene, isobutylene, butadiene, and isoprene;

[0078] (15) N-vinylpyrrolidone, N-vinylcarbazole, 4-vinylpyridine, acrylonitrile, and methacrylonitrile; and

[0079] (16) Unsaturated imide such as malemide, N-acryloylacrylamide, N-acetylmethacrylamide, N-propionylmethacrylamide, and N-(p-chlorobenzoyl) methacrylamide.

[0080] As the copolymerization methods for the above-mentioned alkali-soluble polymers, the graft copolymerization method, the block copolymerization method, the random copolymerization method and the like that have been known can be used.

[0081] The alkali-soluble resin to be used in the present invention, from the standpoint of the formation of minute projections that is a feature of the present invention, has preferably a mass average molecular weight of 2,000 to 1,000,000, and more preferably 3,000 to 500,000 in terms of polystyrene.

[0082] Moreover, the addition amount of an alkali-soluble resin is preferably 20 to 95% by mass, and more preferably 30 to 90% by mass in the total solid content in the recording layer.

((c) Infrared absorbing agent)

[0083] A recording layer in the invention is required to contain an infrared absorbing agent (c). When the recording layer employs a multilayer structure, the infrared absorbing agent is not required to be included in all layers, and may be included in either of them. As the infrared absorbing agent, a substance which absorbs a light energy irradiating beam, and produces heat can be used without any limitation in an absorption wavelength region, however, from a viewpoint of suitability with an easily available high output laser, preferable examples include an infrared absorbing dye or pigment having absorption maximum in a wavelength of 760 nm to 1200 nm.

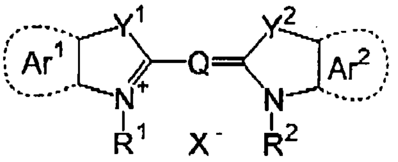
[0084] As the infrared absorbing dye, commercially available dyes, for example, known dyes described in documents such as "DYE HANDBOOK" (edited by Organic Synthetic Chemical Society, published in 1970) may be utilized. Specific examples of the dye include azo dyes, metal complex salt azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocycnine dyes, naphthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, cyanine dyes, squalillium dyes, (thio) pyrylium salts, metal thiolate complexes, indoaniline metal complex dyes, oxonol dyes, diimmonium dyes, aminium dyes, croconium dyes, and intermolecular CT dyes.

[0085] Preferable examples of the dye may include cyanine dyes described in, for example, JP-ANos. 58-125246, 59-84356, 59-202829 and 60-78787, methine dyes described in, for example, JP-ANos. 58-173696, 58-181690 and 58-194595, naphthoquinone dyes described in, for example, JP-A Nos. 58-112793, 58-224793, 59-48187, 59-73996, 60-52940 and 60-63744, squalillium dyes described in, for example, JP-A No. 58-112792 and cyanine dyes described in British Patent No. 434, 875.

[0086] A near-infrared absorbing sensitizer described in U.S. Patent No. 5,156,938 is also preferably used. Substituted arylbenzo(thio)pyrylium salts described in U.S. Patent No. 3,881,924, trimethinethiapyrylium salts described in JP-A No. 57-142645 (U.S. Patent No. 4,327,169), pyrylium type compounds described in JP-A Nos. 58-181051, 58-220143, 59-41363, 59-84248, 59-84249, 59-146063 and 59-14606, cyanine dyes described in JP-A No. 59-216146, pentamethinethiopyrylium salts described in U.S. Patent No. 4,283,475 and pyrylium compounds disclosed in Japanese Patent Application Publication (JP-B) Nos. 05-13514 and 05-19702 are also preferably used.

[0087] Also, other preferable examples of the dye may include near-infrared absorbing dyes described as the formulae (I) and (II) in U.S. Patent No. 4,756,993.

[0088] Particularly preferable examples among these dyes include cyanine dyes, phthalocyanine dyes, oxonol dyes, squarylium dyes, pyrylium salts, thiopyrylium dyes and nickel thiolate complexes. Furthermore, dyes represented by the following formulae (a) to (f) have a high light-to-heat conversion efficiency and are therefore preferable. Particularly cyanine dyes represented by the following formula (a) give a high interaction with an alkali-soluble resin, are also superior in stability and economical when used as the image recording material of the invention and are therefore most preferable.

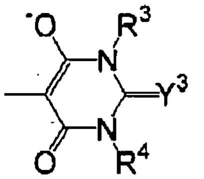


Formula (a)

[0089] In the above-mentioned formula (a), R^1 and R^2 each independently represent an alkyl group having 1 to 12 carbon atoms, and may have a substituent selected from an alkoxy group, an aryl group, an amide group, an alkoxycarbonyl group, a hydroxyl group, a sulfo group, and a carboxy group on the alkyl group. Y^1 and Y^2 independently represent oxygen, sulfur, selenium, a dialkylmethylene group, or CH=CH-, respectively. Ar^1 and Ar^2 each independently represent an aromatic hydrocarbon group, and may have a substituent selected from an alkyl group, an alkoxy group, halogen atoms, and an alkoxycarbonyl group and may be condensed with adjacent consecutive two carbon atoms to make a ring.

[0090] X^- represents a counter ion necessary for neutralizing the charge and not necessarily needed when the dye cationic part has an anionic substituent. Q represents a polymethine group selected from a trimethine group, a pentamethine group, a heptamethine group, a nonamethine group, or an undecamethine group. Among them, a pentamethine group, a heptamethine group or a nonamethine group is preferable in terms of the wavelength suitability and stability to an infrared-ray used for the exposure and it is preferable to have a cyclohexene ring or a cyclopentene ring containing consecutive three methylene groups on either of carbon in terms of the stability.

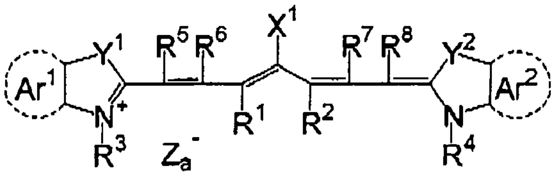
[0091] Q may be substituted with a group selected from an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a dialkylamino group, a diarylamino group, halogen atoms, an alkyl group, an aralkyl group, a cycloalkyl group, an aryl group, an oxy group, an iminium salt group, and substituents shown by the formulas (a-i). Preferable substituents include halogen atoms such as chlorine atom, diarylamino groups such as a diphenylamino group, and arylthio groups such as a phenylthio group.



Formula (a-i)

[0092] In the formulas (a-i), R^3 and R^4 each independently represent a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, or an aryl group having 6 to 10 carbon atoms, and Y^3 represents an oxygen atom or a sulfur atom.

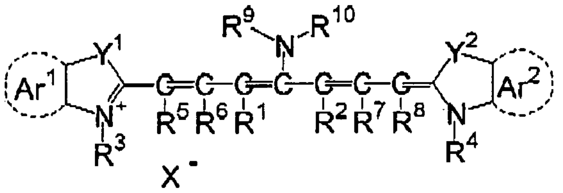
[0093] Among cyanine dyes shown the formula (a), when being exposed to the infrared-ray of 800 to 840 in wavelength, a heptamethine cyanine dye shown by the following formulas (a - 1) to (a - 4) can be cited as particularly preferable one.



Formula (a-1)

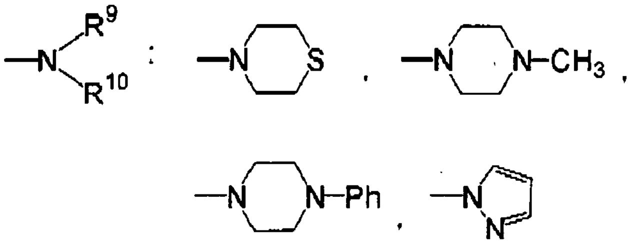
[0094] In the formula (a - 1), X^1 represent a hydrogen atom or a halogen atom. R^1 and R^2 each independently represent a hydrocarbon group having 1 to 12 carbon atoms, From the view point of the preservation stability of the coating liquid for the recording layer, R^1 and R^2 are preferably a hydrocarbon group having 2 or more carbon atoms, and further R^1 and R^2 are particularly preferably bonded each other to form a five-membered ring or a six-membered ring.

[0095] Ar^1 and Ar^2 each represent an aromatic hydrocarbon group that may be the same or different, and may have a substituent. Preferable hydrocarbon groups include a benzene ring and a naphthalene ring. Moreover, preferable substituents include hydrocarbon groups having 12 or less carbon atoms, halogen atoms, an alkoxy groups having 12 or less carbon atoms. Y^1 and Y^2 may be the same or different, and each represent a sulfur atom or a dialkylmethylene group having 12 or less carbon atoms. R^3 and R^4 each represent a hydrocarbon group having 20 or less carbon atoms that may be the same or different, and may have a substituent. Preferable substituents include alkoxy groups having 12 or less carbon atoms, carboxy groups, and sulfo groups. R^5, R^6, R^7, and R^8 may be the same or different, and each represent a hydrogen atom or a hydrocarbon group having 12 or less carbon atoms. In light of easy availability of the raw material, a hydrogen atom is preferable. Moreover, Za^- represents a counter anion necessary for neutralizing the charge, and when either of R^1 to R^8 is substituted with an anionic substituent, Za^- is unnecessary. Preferable Za^-s are, in light of the preservation stability of the coating liquid for the recording layer, a halogen ion, perchlorate ion, tetrafluoroborate ion, hexafluorophosphate ion, and sulfonic acid ion. The perchlorate ion, the tetrafluoroborate ion, the hexafluorophosphate ion, and the sulfonic acid ion are particularly preferable. The heptamethine dye shown by the above-mentioned formula (a - 1) can be suitably used in positive-working image recording materials and particularly, preferably used in so-called interaction releasing positive working photosensitive materials that are combined with an alkali-soluble resin having a phenolic hydroxide group.



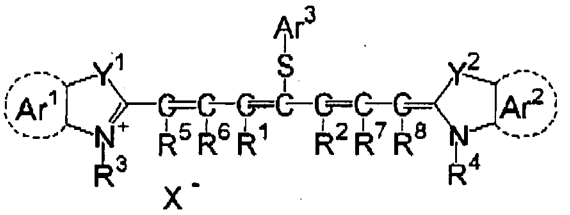
Formula (a-2)

[0096] In the formula (a - 2), R^1 and R^2 each independently represent a hydrogen atom or a hydrocarbon group having 1 to 12 carbon atoms, and R^1 and R^2 may be bonded each other to form ring structure. As a ring to be formed, a five-membered ring and a six-membered ring are preferable, and a five-membered ring is particularly preferable. Ar^1 and Ar^2 each represent an aromatic hydrocarbon group that may be the same or different, and may have a substituent, respectively. Preferable hydrocarbon groups include a benzene ring and a naphthalene ring. Moreover, preferable substituents on that hydrocarbon group include a hydrocarbon group having 12 or less carbon atoms, a halogen atom, an alkoxy group having 12 or less carbon atoms, an alkoxycarbonyl group, an alkylsulfonyl group, and a halogenated alkyl group, and an electron-attracting substituent are particularly preferable. Y^1 and Y^2 may be the same or different, and each represent a sulfur atom or a dialkylmethylene group having 12 or less carbon atoms. R^3 and R^4 each represent a hydrocarbon group having 20 or less carbon atoms that may be the same or different, and may have a substituent, respectively. Preferable substituents include alkoxy groups having 12 or less carbon atoms, carboxy groups, and sulfo groups. R^5, R^6, R^7, and R^8 may be the same or different, and indicate a hydrogen atom or a hydrocarbon group having 12 or less carbon atoms, respectively. In light of easy availability of the raw material, a hydrogen atom is preferable. R^9 and R^{10} may be the same or different, respectively, and represent a hydrogen atom, an aromatic hydrocarbon group having 6 to 10 carbon atoms that may have a substituent, or an alkyl group having 1 to 8 carbon atoms, and R^9 and R^{10} may be bonded each other to form a ring having any of the following structures.



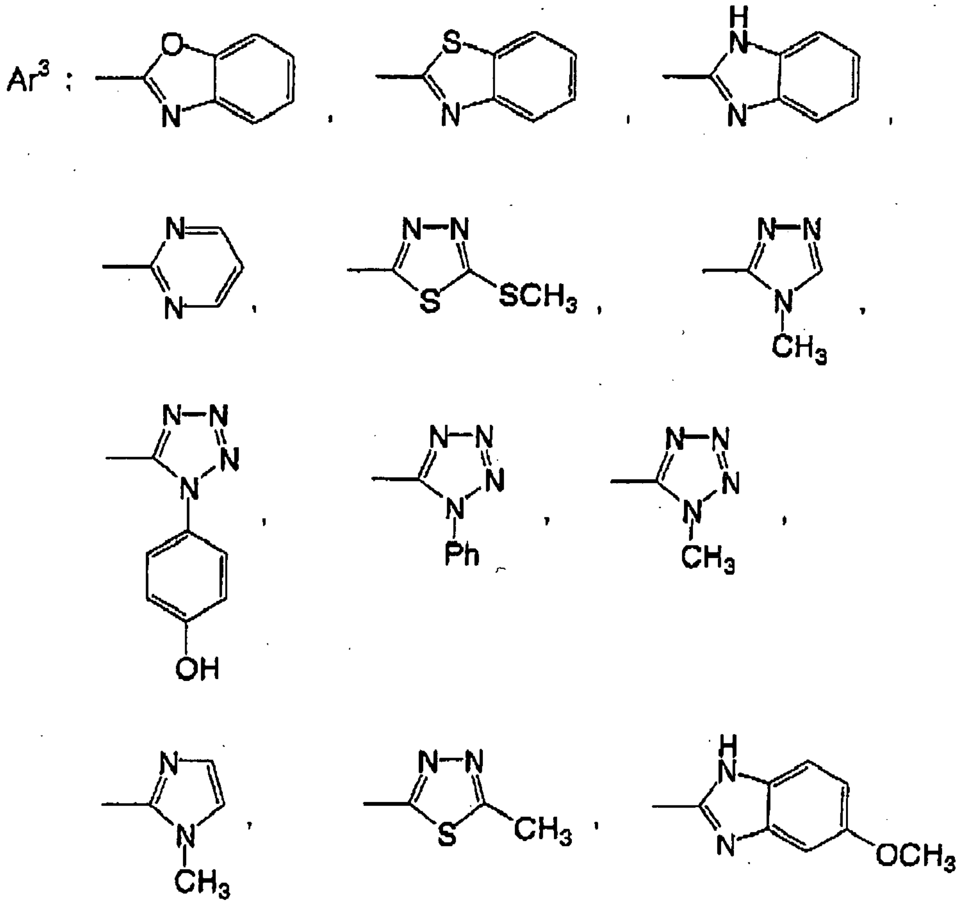
[0097] As for R^9 and R^{10}, among those mentioned above, an aromatic hydrocarbon group such as a phenyl group is most preferable.

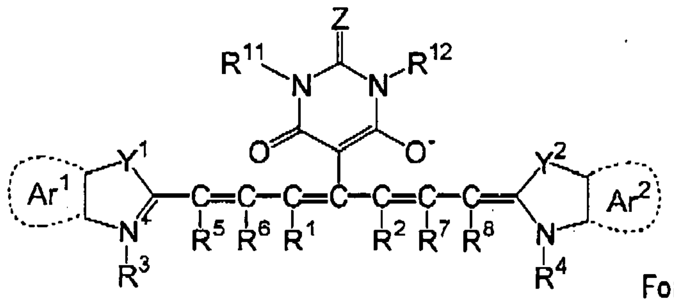
[0098] Moreover, X^- represents a counter anion necessary for neutralizing the charge, which is the same definition as that of Za^- in the above-mentioned formula (a - 1). The heptamethine dye represented by the above-mentioned formula (a - 2) can be suitably used in image recording materials in which an acid such as an onium salt and/or a radical generating agent is used together.



Formula (a-3)

[0099] In the formula (a - 3), R^1 to R^8, Ar^1, Ar^2, Y^1, Y^2, and X^- have the same meaning as those in the above-mentioned formula (a - 2), respectively. Ar^3 represents a monocyclic or polycyclic heterocyclic group that contains an aromatic hydrocarbon group such as a phenyl group and a naphthyl group, and at least one of nitrogen atom, oxygen atom, and sulfur atom. A heterocyclic group selected from the group consisting of thiazole series, benzothiazole series, naphthothiazole series, thianaphtheno-7', 6', 4, 5-thiazole series, oxazole series, benzoxazole series, naphthoxazole series, selenazole series, benzoselenazole series, naththoselenazole series, thiazoline series, 2-quinoline series, 4-quinoline series, 1-isoquinoline series, 3-isoquinoline series, benzimidazole series, 3,3-dialkylbenzoindrenine series, 2-pyridine series, 4-pyridine series, 3,3-dialkylbenzo[e]indole series, tetrazole series, triazole series, pyrimidine series, and thiaziazole series is preferable, and particularly preferable heterocyclic groups include those of the following structures.

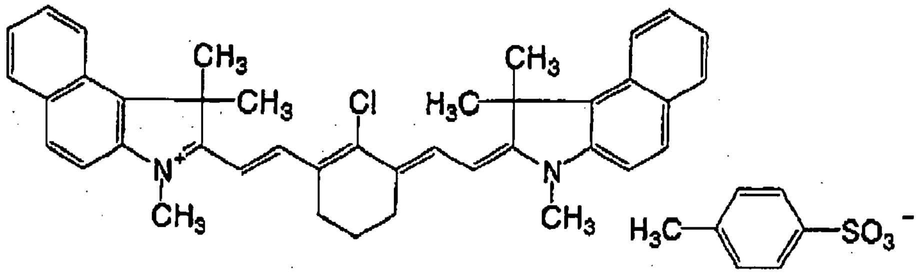


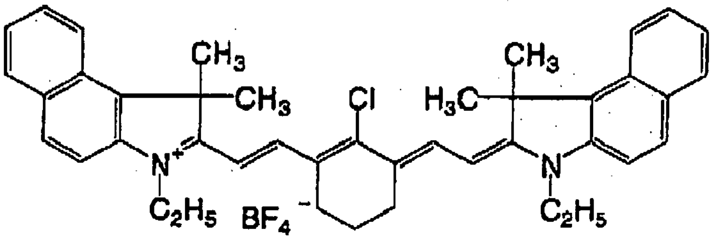


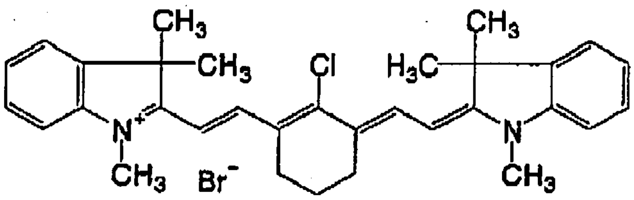
Formula (a-4)

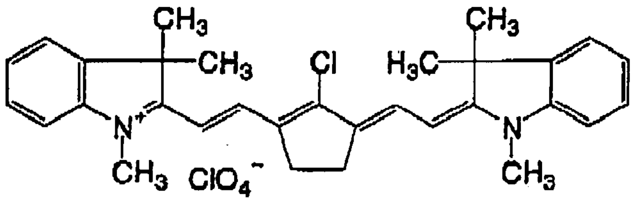
[0100] In the formula (a - 4), R^1 to R^8, Ar^1, Ar^2, Y^1, and Y^2 have the same meaning as those in the above-mentioned formula (a - 2), respectively. R^{11}, and R^{12} may be the same or different, and each represent a hydrogen atom, an aryl group, a cyclohexyl group, or an alkyl group having 1 to 8 carbon atoms. Z represents an oxygen atom or a sulfur atom.

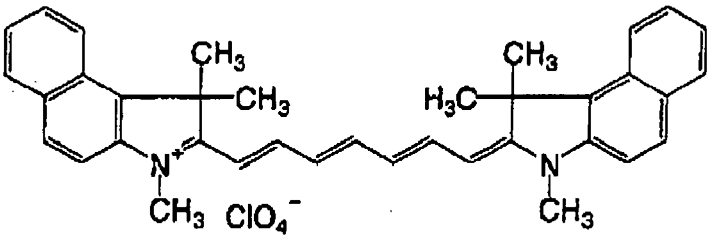
[0101] Specific examples of cyanine dyes that can be suitably used in the present invention and are represented by the formula (a) include those described in the paragraphs of [0017] to [0019] of JP-ANo. 2001-133969, the paragraphs of [0012] to **[0038]** of JP-A No. 2002-40638, and the paragraphs of [0012] to [0023] of JP-A No. 2002-23360 other than those exemplified below.

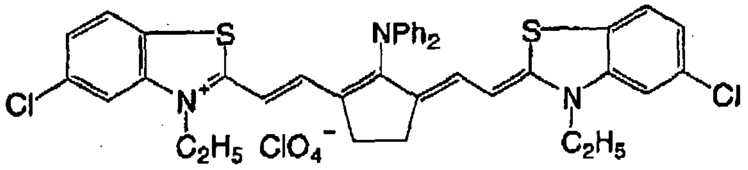








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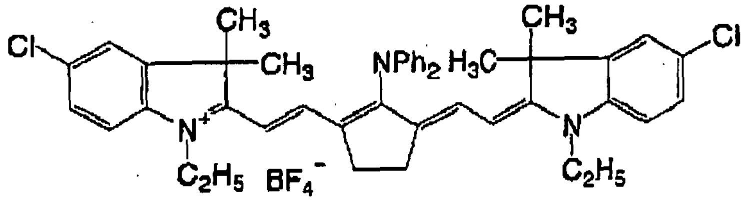
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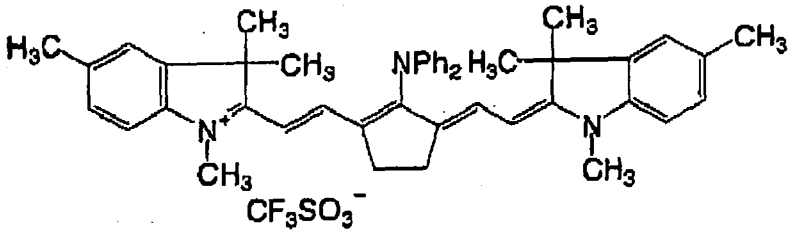
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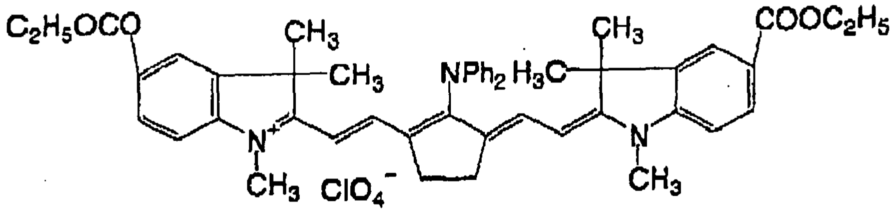
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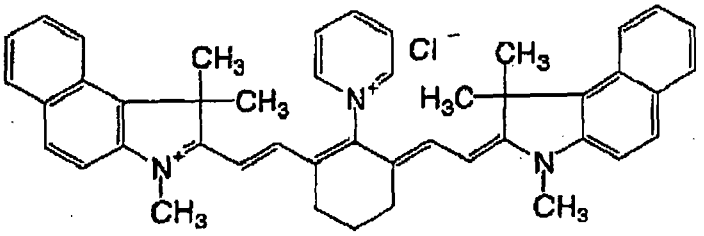
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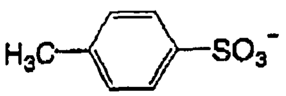

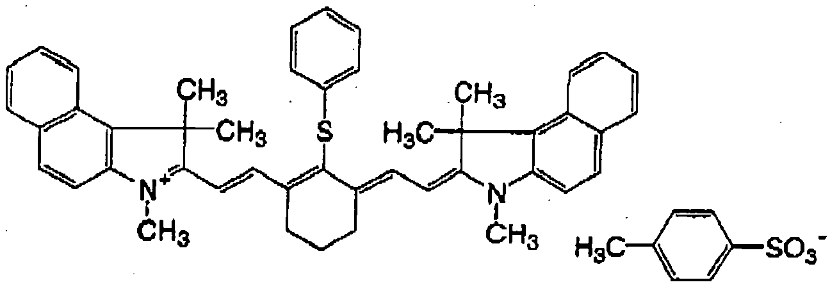

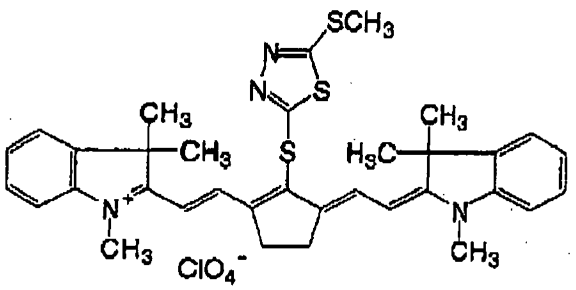

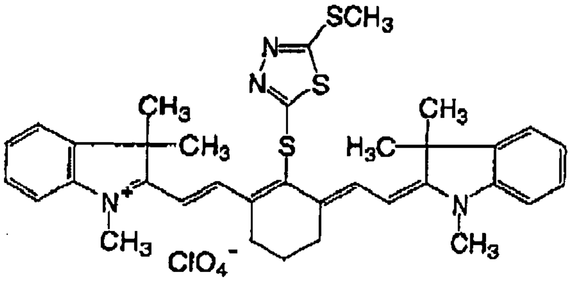

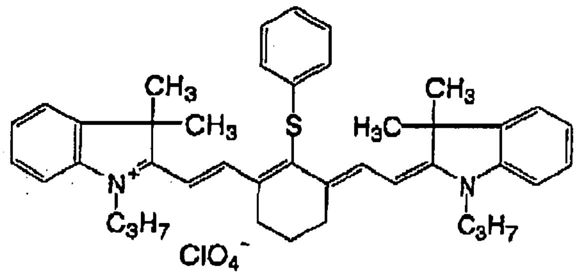

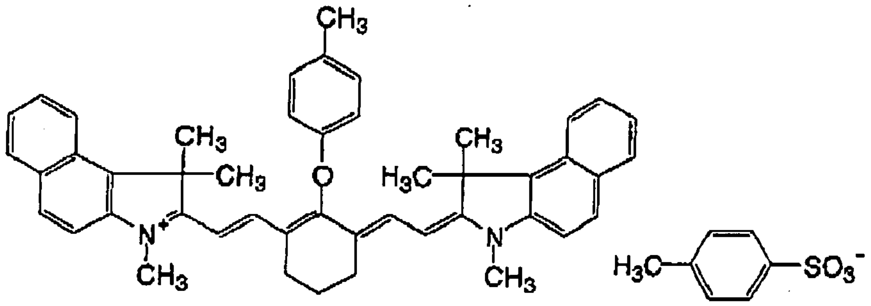

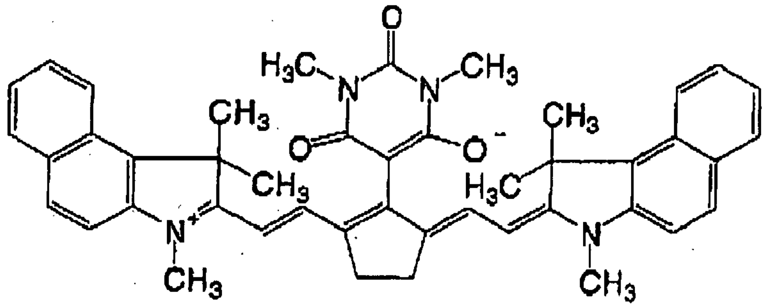

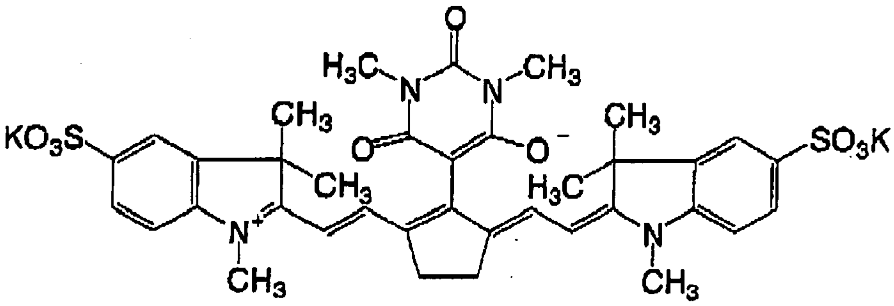

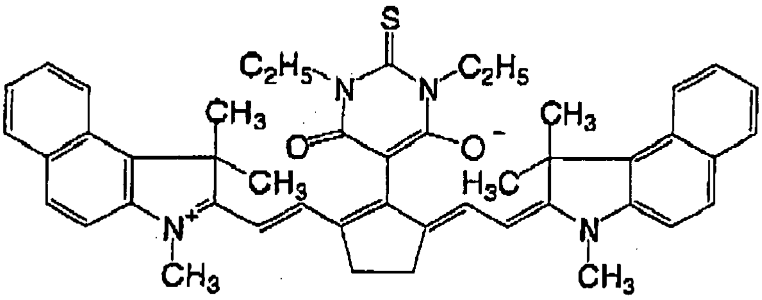

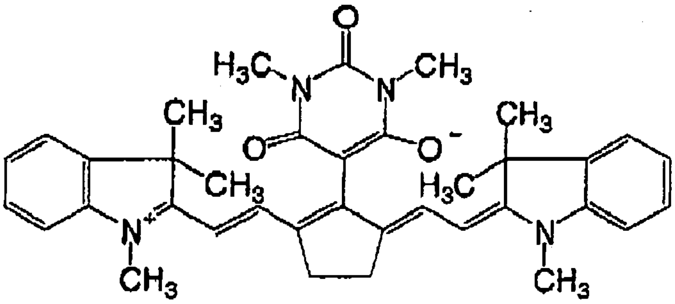

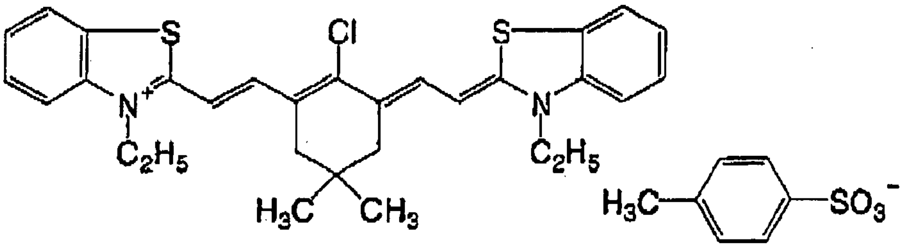

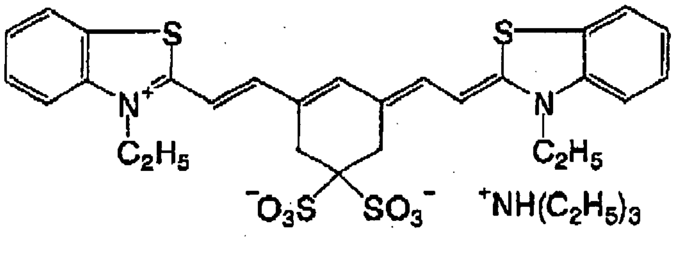

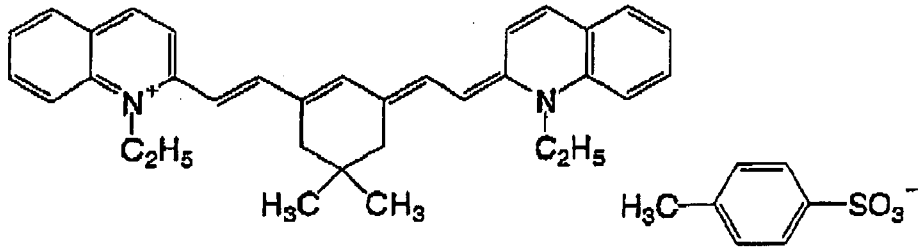
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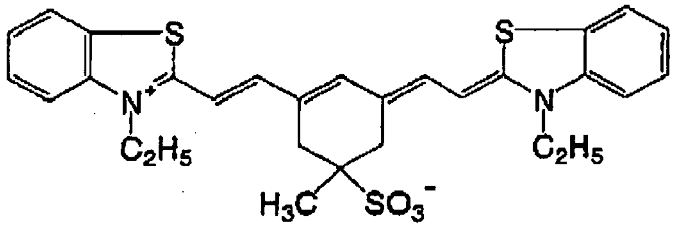
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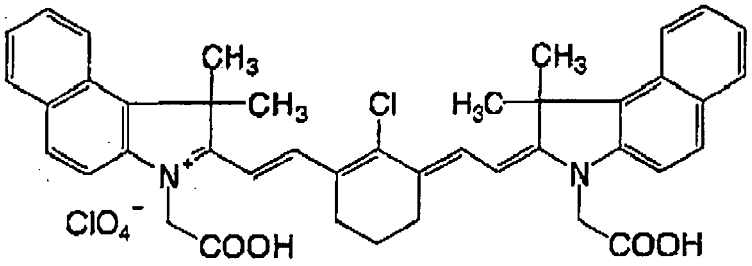
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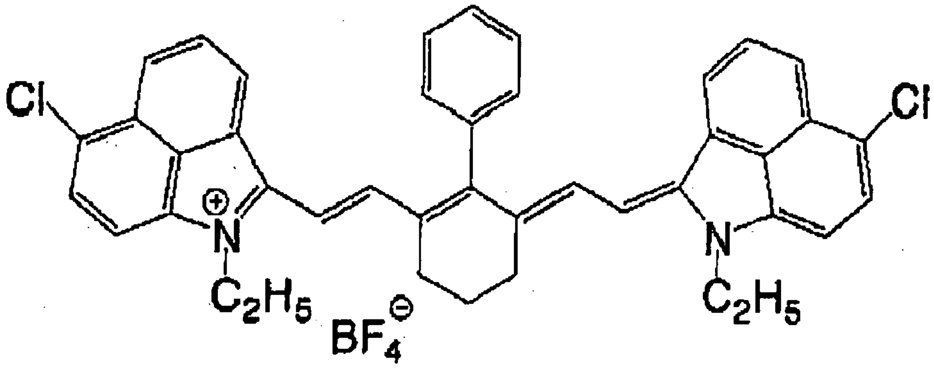
N
COOH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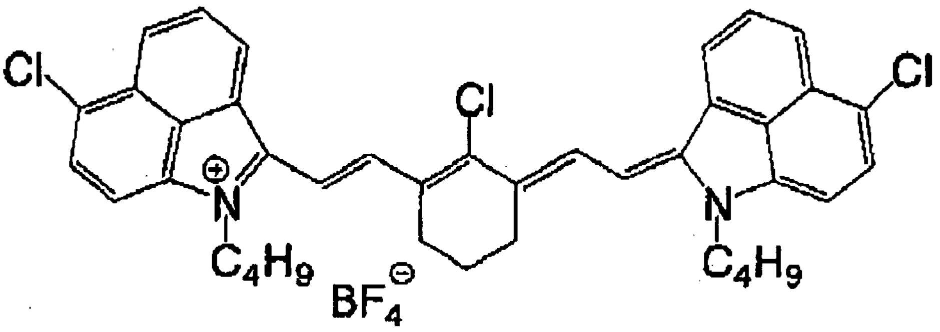
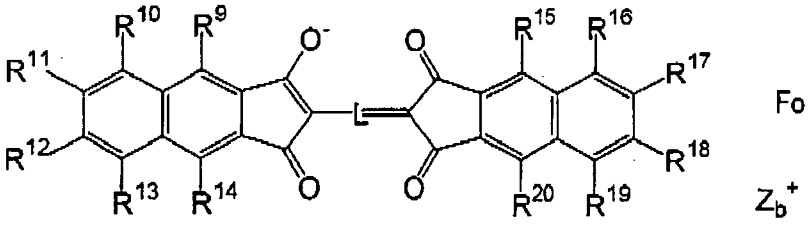




Formula (b)

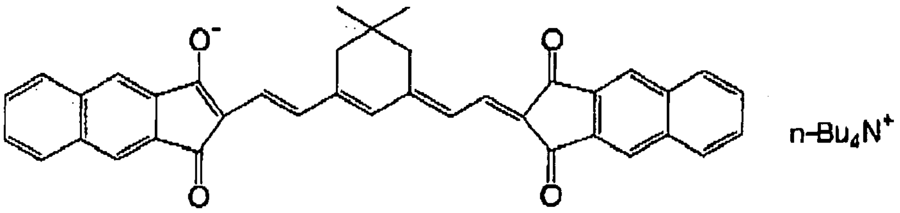
[0102] In the formula (b), L represents a methine chain having 7 or more conjugate carbon atoms, wherein the methine chain may have substituents, which may be combined with each other to form a cyclic structure. Z_b^+ represents a counter cation.

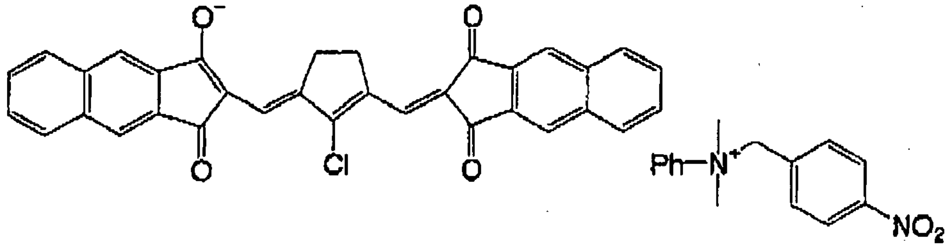
[0103] Preferable examples of the counter cation include ammonium, iodonium, sulfonium, phosphonium, pyridinium and alkali metal cations (Ni’, K’ and Li^+).

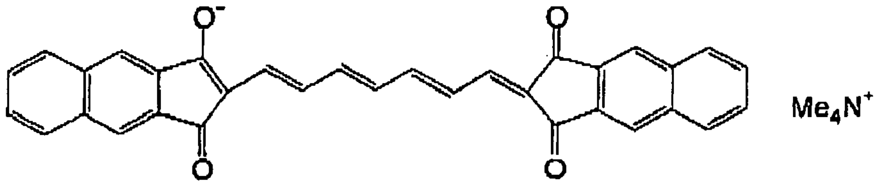
[0104] R^9 to R^{14} and R^{15} to R^{20} each represent a hydrogen atom or a substituent selected from a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl group, an alkynyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group and an oxy group and an amino group or a substituent which is a combination of two or three of these groups and may be combined with each other to form a cyclic structure.

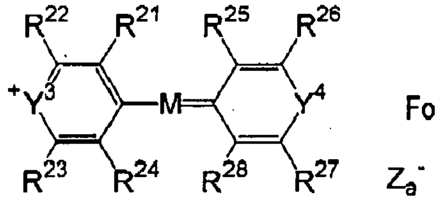
[0105] Among the compounds represented by the formula (b), those represented by the formula (b) in which L represents a methine chain having 7 conjugate carbon atoms and those represented by the formula (b) in which all of R^9 to R^{14} and R^{15} to R^{20} represent a hydrogen atom are preferable from the viewpoint of availability and effect.

[0106] Specific examples of the dye represented by the formula (b) which can be preferably used in the invention may include those exemplified below.





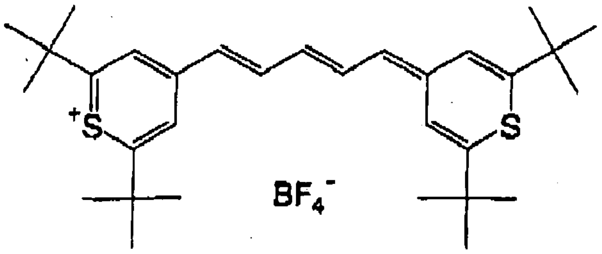


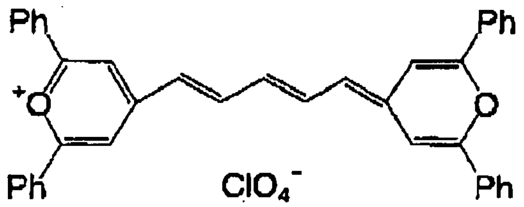


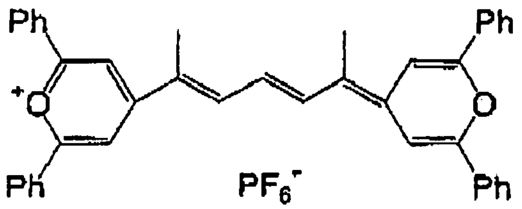
Formula (c)

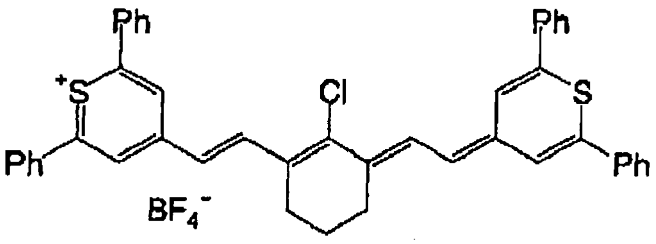
[0107] In the formula (c), Y^3 and Y^4 respectively represent an oxygen atom, a sulfur atom, a selenium atom or a tellurium atom. M represents a methine chain having 5 or more conjugate carbon atoms. R^{21} to R^{24} and R^{25} to R^{28}, which may be the same or different, respectively represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl group, an alkynyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group, an oxy group or an amino group. Also, Z_3^- in the formula represents an anion and has the same meaning as Z_a^- in the formula (a).

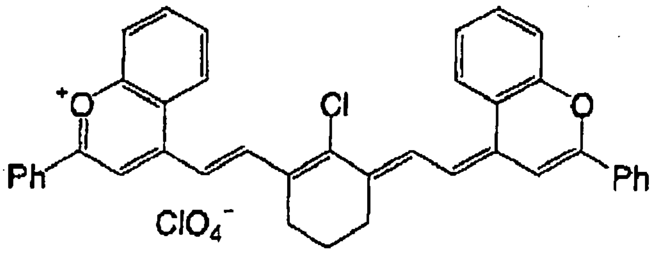
[0108] Specific examples of the dye represented by the formula (c) which can be preferably used in the invention may include those exemplified below.

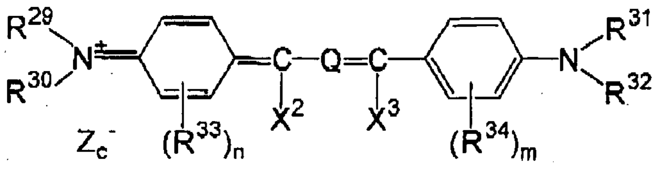












Formula(d)

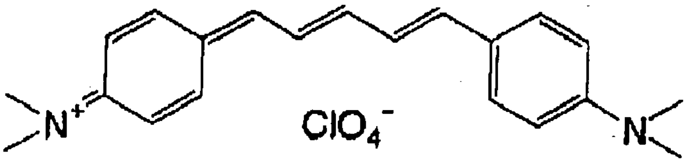
[0109] In the formula (d), R^{29} to R^{32} each independently represent a hydrogen atom, an alkyl group or an aryl group.

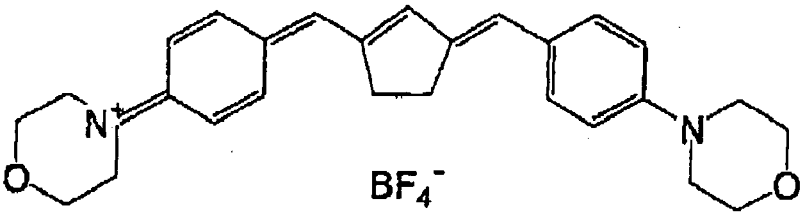
R^{33} and R^{34} each independently represent an alkyl group, a substituted oxy group or a halogen atom, n and m each independently represent an integer from 0 to 4. R^{29} and R^{30} or R^{31} and R^{32} may be combined with each other to form a ring. Further, R^{29} and/or R^{30} and R^{33} or R^{31} and/or R^{32} and R^{34} may be combined with each other to form a ring. Moreover, when R^{33} or R^{34} is present in the plural, R^{33}s or R^{34}s may be combined among them to form a ring.

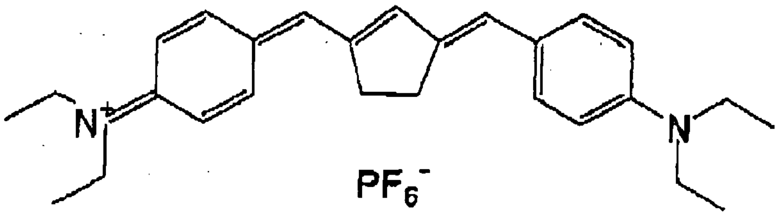
[0110] X^2 and X^3 each independently represent a hydrogen atom, an alkyl group or an aryl group.

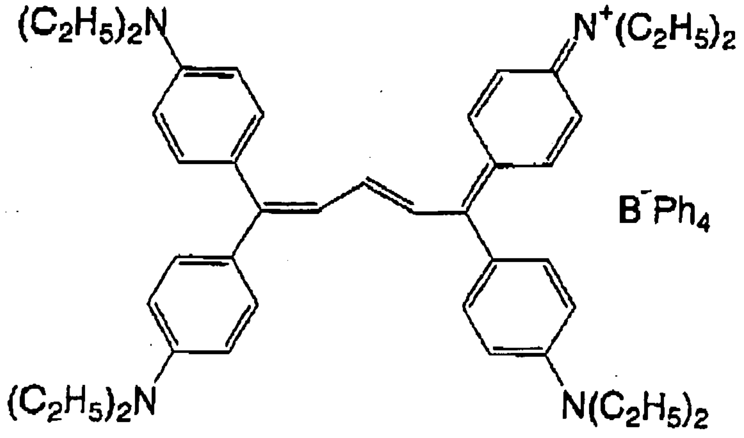
[0111] Q represents a trimethine group or a pentamethine group which may have a substituent and may form a cyclic structure in combination with a divalent organic group. Z_c^- represents a counter anion and has the same meaning as Z_a^- in the above formula (a-1),

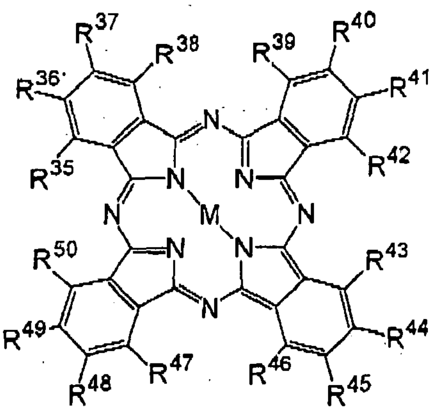
[0112] Specific examples of the dye represented by the formula (d) which can be preferably used in the invention may include those exemplified below.







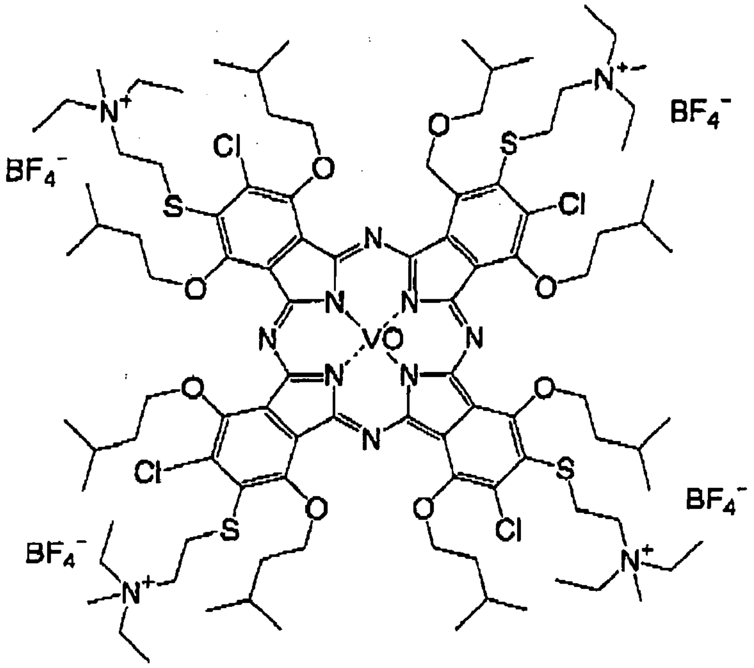




Formula (e)

[0113] In the formula (e), R^{35} to R^{50} respectively represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl group, an alkynyl group, a hydroxyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group, an oxy group, an amino group or an onium salt structure which may have a substituent.
M represents two hydrogen atoms or a metal atom, a halo-metal group or an oxy metal group. Examples of the metal atoms contained therein include the IA, IIA, IIIB or IVB group atoms in the periodic chart, transition metals of the first, second and third periods and lanthanoid elements. Among these materials, copper, nickel, magnesium, iron, zinc, tin, cobalt, aluminum, titanium and vanadium are preferable, and vanadium, nickel, zinc, tin are particularly preferable. These metals may bond to an oxygen atom, halogen atom or the like in order to keep the valence suitable.

[0114] Specific examples of the dye represented by the formula (e) which can be preferably used in the invention may include those exemplified below.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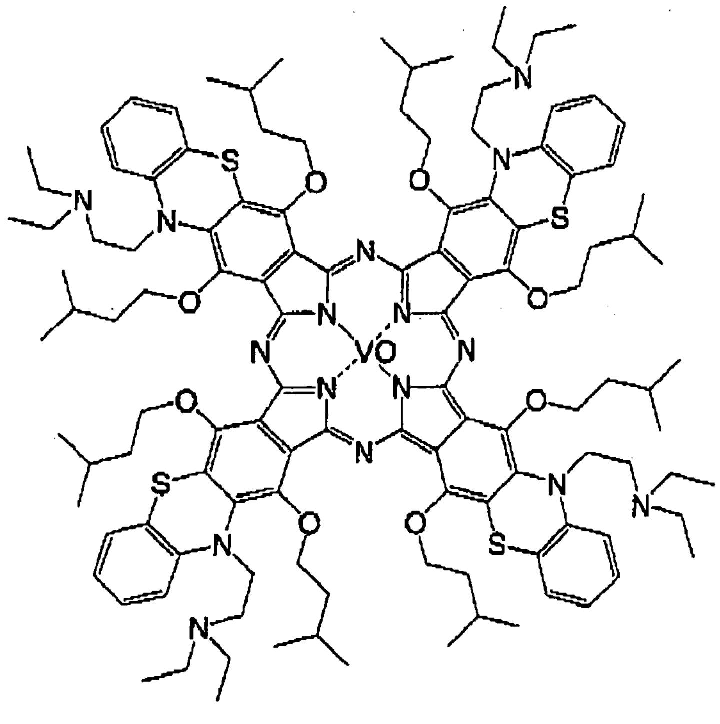
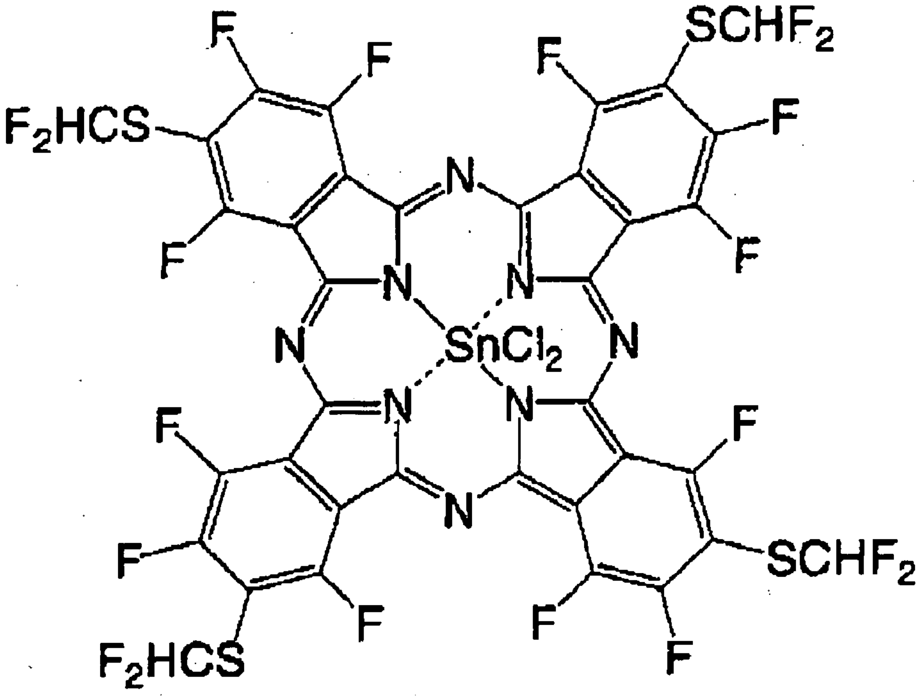
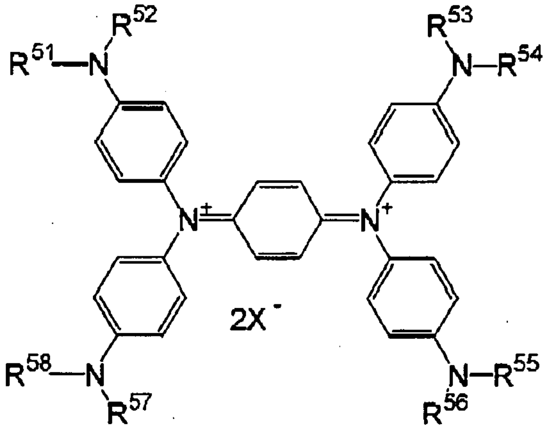
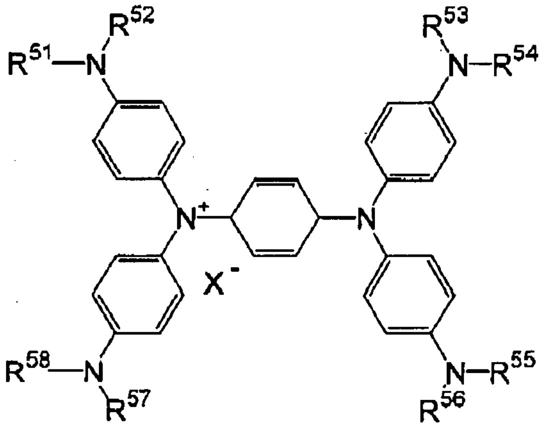
BF4-
BF4-
BF4-
VO


VO



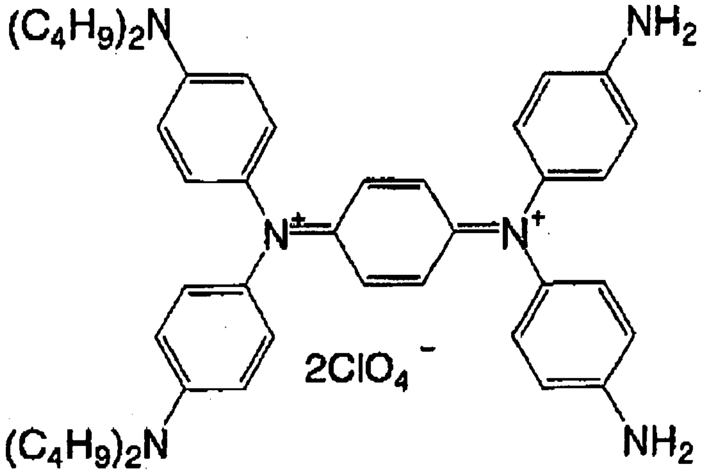

Formula(f-1)

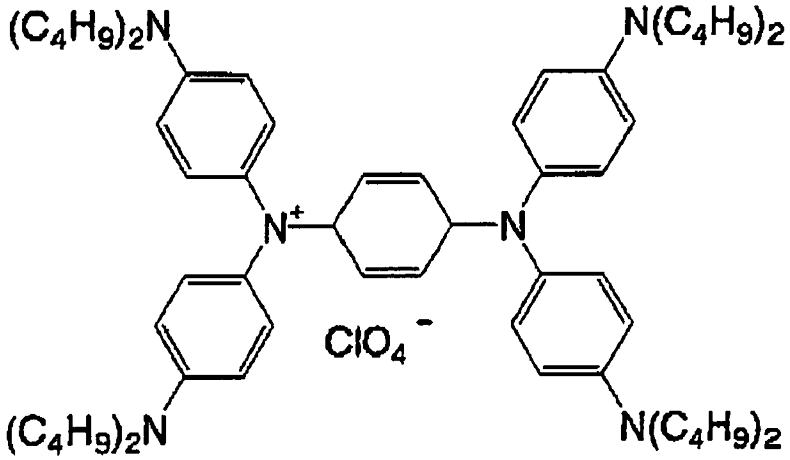


Formula (f-2)

[0115] In the above-mentioned formulas (f- 1) and (f- 2), R^{51} to R^{58} each independently represent a hydrogen atom, or an alkyl group and an aryl group that may have a substituents. X^- has the same meaning as that in the above-mentioned formula (a - 2).

[0116] Concrete examples of dyes that can be suitably used in the present invention and are shown by the formula (f- 1) and (f- 2) include those exemplified below.





[0117] As an infrared-ray absorbing agent (c) other than the above-mentioned matter, the following ones can be suitably used: dyes having plural chromophores that are described in JP-A No. 2001-242613, coloring matters that a chromophore is connected to a polymer compound by a covalent bond, and that are described in JP-A No. 2002-97384 and U.S. Patent No. 6,124,425, anionic dyes described in U.S. Patent No. 6,248,893, dyes having a surface orientation group that are described in JP-A No. 2001-347765, and others.

[0118] Examples of the pigment to be used as the infrared absorber (c) in the invention include commercially available pigments and pigments described in Color Index (C.I.) Handbook, "Latest Pigment Handbook" (edited by Japanese Pigment Technological Society, published in 1977), "Latest Pigment Applied Technology" (CMC Publishing Co., Ltd., published in 1986) and "Printing Ink Technology" CMC Publishing Co., Ltd., published in 1984).

[0119] Examples of these pigments include black pigments, yellow pigments, orange pigments, brown pigments, red pigments, violet pigments, blue pigments, green pigments, fluorescent pigments, metal powder pigments and polymer binder dyes. Specifically, insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyanine type pigments, anthraquinone type pigments, perylene and perinone type pigments, thioindigo type pigments, quinacridone type pigments, dioxazine type pigments, isoindolinone type pigments, quinophthalone type pigments, dyeing lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments, carbon black and the like may be used. Among these pigments, carbon black is preferable.

[0120] These pigments may be used either without any surface treatment or with surface treatment. As the surface treating method, it is considered to use, for example, a method in which the surface is coated with a resin or wax, a method in which a surfactant is adhered to the surface of a pigment or a method in which a reactive material (e.g., a silane coupling agent, epoxy compound and polyisocyanate) is bonded to the surface of a pigment. The above surface treating methods are described in "Nature and Application of Metal Soaps" (Saiwai Shobo), "Printing Ink Technology" CMC Publishing Co., Ltd., published in 1984) and "Latest Pigment Applied Technology" (CMC Publishing Co., Ltd., published in 1986).

[0121] Particle diameter of the dye is preferably in the range of 0.01 to 10 μm, more preferably 0.05 to 1 μm, particularly preferably 0.1 to 1 μm. The particle diameter of the dye less than 0.1 μm is not preferable in light of stability of dispersed substances in the coating liquid for the recording layer; and the particle diameter exceeding 10 μm is not preferable in light of uniformity of the recording layer.

[0122] As a method of dispersing the pigment, known dispersing technologies used for the production of ink and toners may be used. Examples of a dispersing machine include a ultrasonic dispersing machine, sand mill, attritor, pearl mill, super mill, ball mill, impeller, disperser, KD mill, colloid mill, dynatron, three-roll mill and pressure kneader. The details of these machines are described in "Latest Pigment Applied Technology" (CMC Publishing Co., Ltd., published in 1986).

[0123] These pigments or dyes are 0.01 to 50% by mass, preferably 0.1 to 10% by mass relative to a total solid matter constituting a recording layer. A dye can be added particularly preferably at a ratio of 0.5 to 10% by mass, and a pigment can be added at a ratio of particularly preferably 0.1 to 10% by mass. When an addition amount of a pigment or a dye is less than 0,01% by mass, there is a tendency that sensitivity is reduced and, when a pigment or dye is blended at an amount exceeding 50% by mass, there is a fear that as a blending amount is increased, uniformity of a recording layer, and durability of a recording layer are not desirably influenced.

[0124] Moreover, a dye or a pigment to be used may be a single compound or a mixture of two or more compounds. In order to use an exposure apparatus which emits lights having a plurality of wavelengths, dyes or pigments which absorb lights having different wavelengths are also preferably used together.

<(d) Dissolution inhibitor>

[0125] A dissolution inhibitor can be used in the recording layer of the positive-working planographic printing plate precursor (1) above. When such a material similar to the cyanine dye which has an interaction with an alkali-soluble resin to exhibit dissolution inhibitory action is used as an infrared-ray absorbing agent (c), a dissolution inhibitor (d) is not always needed, but when the infrared-ray absorbing agent (c) not having such a function is used, the dissolution inhibitor (d) may become an important component. As dissolution inhibitors (d) that can be used in the present invention, compounds that are thermally decomposable and in the state of not being decomposed, can control the dissolution of the image area in the developer are preferable. Onium salts, o-quinone diazide compounds, aromatic sulfone compounds, aromatic sulfonate compounds, and the like are preferable. Onium salts include diazonium salts, ammonium salts, phosphonium salts, iodonium salts, sulfonium salts, selenium salts, and arsonium salts.

[0126] The addition amount of these dissolution inhibitors is preferably from 0.5 to 40% by mass in the total solid content in the recording layer, and more preferably from 1 to 30% by mass.

[0127] Further, known additives to be added in the recording layer of the planographic printing plate precursor (1) above as occasion demands will be described later.

[0128] The positive-working planographic printing plate precursor (2) above include positive-working planographic printing plate precursors described in JP-A Nos. 9-171254, 10-55067, 10-87733, 10-268507, and the like. However, as long as a positive-working planographic printing plate precursor is one in which an image is formed in accordance with the above-mentioned principle, any one may be used, and is not limited to these precursors.

[0129] The positive-working planographic printing plate precursor (2) in the above, in which the image recording material of the present invention is applied, , specifically, has, on a support, a recording layer containing a polymer (a) having a long chain alkyl group, an infrared-ray absorbing agent (c), and a compound that can generates an acid by irradiating with actinic light (an acid-generating agent).

<Compound decomposable with acid>

[0130] The above compounds decomposable with acids include compounds having a C-O-C bond as described in JP-A Nos. 48-89603, 51-120714, 53-133429, 55-12995, 55-126236, and 56-17345, compounds having a Si-O-C bond as described in JP-ANos. 60-37549 and 60-121446, and other compound decomposable with acids as described in JP-A Nos. 60-3625 and 60-10247. Further, the following compounds can also be used: compounds having a Si-N bond as described in JP-A No. 62-222246, carbonates as described in JP-ANo. 62-251743, orthocarbonates as described in JP-ANo. 62-209451, orthotitanates described in JP-A No, 62-280841, orthosilicates as described in JP-A No. 62-280842, acetals, ketals and orthocarboxylates as described in JP-ANos. 63-010153, 9-171254, 10-55067, 10-111564, 10-87733, 10-153853, 10-228102, 10-268507, 10-282648, and 10-282670, and EP-0884547 A1, and compounds having a C-S bond as described in JP-A No. 62-244038.

[0131] Among them, compounds having a C-O-C bond, compounds having a Si-O-C bond, orthocarbonates, acetals, ketals, and silyl ethers are preferable. Moreover, polymer compounds which have a repeated acetal moiety or ketal moiety in the main chain and the solubility is increased due to generated acid in the developer are preferably used.

[0132] The compounds decomposable with acids to be used in the present invention, from the standpoint of the formation of minute projections that is a feature of the present invention, has, in terms of polystyrene, a mass average molecular weight of preferably 2,000 to 1,000,000, and more preferably 3,000 to 500,000.

[0133] Moreover, the addition amount of a compound decomposable with acid is preferably from 0.5 to 80% by mass, and more preferably from 1 to 70% by mass in the total solid content in the recording layer.

<Acid-generating agent>

[0134] Acid-generating agents that can be used together with the above compound decomposable with acid include onium salts such as iodonium salts, sulfonium salts, phosphonium salts, and diazonium salts. Specifically, compounds as described in U.S. Patent No. 4,708,925 and JP-A No. 7-20629 can be cited. More specifically, iodonium salts, sulfonium salts and diazonium salts having a sulfonic acid ion as a counter ion are preferable. As diazonium salts, diazonium compounds as described in U.S. Patent No. 3,867,147, diazonium compounds as described in the specification of U.S.

Patent No. 2,632,703, and diazo resins as described in JP-ANas. 1-102456 and 1-102457 are also preferable. Further, benzylsulfonates as described in U.S. Patent Nos. 5,135,838 and 5,200,544 are also preferable. Furthermore, active sulfonic esters and disulfonyl compounds as described in JP-A Nos. 2-100054, 2-100055, and 9-197671 are also preferable. In addition, S-triazines substituted with a halogenated alkyl group as described in JP-A No. 7-271029 are also preferable.

[0135] The addition amount of these acid-generating agents is preferably from 0.5 to 40% by mass in the total solid content in the recording layer, and more preferably from 1 to 30% by mass.

<Additives>

[0136] In the positive-working recording layer, known additives can be used together as occasion demands in the range where the effect of the present invention is not impaired.

(Development accelerator)

[0137] In the positive-working recording layer in the present invention, cyclic acid anhydrides, phenols and organic acids can be added further as occasion demands, for increasing the sensitivity. Moreover, a printout agent for obtaining a visible image immediately after exposure, a dye as a coloring agent for an image, and other fillers can be added.

[0138] As described in the specification of U.S. Patent No. 4,113,128. cyclic acid anhydrides include phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endoxy-Δ4-tetrahydrophthalic anhydride, tetrachlorphthalic anhydride, maleic anhydride, chlormaleic anhydride, (-phenylmaleic anhydride, succinic anhydride, and pyromellitic anhydride. Phenols include bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,3,4-trihydroxybenzophenone, 4-hydroxybenzophenone, 2,4,4'-trihydroxybenzophenone, 4,4',4"-trihydroxy-triphenylmethane, and 4, 4', 3", 4"-tetrahydroxy-3,5,3', 5'-tetramethyltriphenylmethane.

[0139] Organic acids include sulfonic acids, sulfinic acids, alkyl sulfuric acids, phosphonic acids, phosphinic acids; phosphates, and carboxylic acids as described in JP-A Nos. 60-88942 and 2-96755, and the like. Specifically, p-toluenesulfonic acid, dodecylbenzcnesulfonic acid, p-toluenesulfinic acid, ethylsulfuric acid, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluic acid, 3,4-dimethoxybenzoic acid, phthalic acid, terephthalic acid, 1,4-cyclohexene-2,2-dicarboxylic acid, erucic acid, lauric acid, n-undecanoic acid, ascorbic acid, and the like can be citedexemplified,

[0140] The ratio that content of the above-mentioned cyclic acid anhydrides, phenols, and organic acids account for in the image recording material is preferably 0.05 to 15% by mass, and more preferably 0.1 to 5% by mass.

(Printout agent)

[0141] In the recording layer of the positive-working planographic printing plate precursor concerned in the present invention, as a printout agent for obtaining a visible image just immediately after exposure, a combination of a photosensitive compound that releases an acid by exposure with an organic dye that forms a salt with the acid to change a color tone can be added.

[0142] The photosensitive compound that releases an acid by exposure include, for example, o-naphthoquinonediazide-4-sulfonic acid halogenide as described in JP-A No. 50-36209, trihalomethyl-2-pyrone and trihalomethyl-s-triazine as described in JP-A No. 53-36223, various o-naphthoquinonediazide compounds as described in JP-A No.55-62444, 2-trihalomethyl-5-aryl-1,3,4-oxadiazole compounds as described in JP-A No. 55-77742, and diazonium salts.

[0143] These compounds can be used separately or in a mixture. The addition amount of these compounds is preferably in the range of 0.3 to 15% by mass relative to the total solid content in the image recording material.

(Color-changing dye with acid)

[0144] In the recording layer of the positive-working planographic printing plate precursor in the present invention, at least one kind or more of organic dyes that change their color tone by interacting with a photolytic product of a compound which photolyzes to generate an acid material can be added.

[0145] As such an organic dye, a dye of diphenylmethane series, triarylmethane series, thiazine series, oxazine series, phenazine series, xanthene series, anthraquinone series, iminonaphthoquinone series, and azomethine series can be used. Specifically, the following dyes are listed.

[0146] Brilliant green, eosin, ethyl violet, erythrocin B, methyl green, crystal violet, basic fuchsin, phenolphthalein, 1,3-diphenyltriazine, alizarin red S, thymolphthalein, methyl violet 2B, quinaldine red, rose bengal, thymolsulfophthalein, xylenol blue, methyl orange, orange IV, diphenylthiocarbazone, 2,7-dichlorofluorescein, paramethyl red, congo red, benzopurpurin 4B, α-naphthyl red, Nile blue 2B, Nile blue A, phenacethalline, methyl violet, malachite green, parafuchsin, oil blue # 603 [manufactured by Orient Chemical Co., Ltd.], oil pink #312 [manufactured by Orient Chemical Co., Ltd.], oil red 5B [manufactured by Orient Chemical Co., Ltd.], oil scarlet # 308 [manufactured by Orient Chemical Co., Ltd.], oil red OG [manufactured by Orient Chemical Co., Ltd.], oil red RR [manufactured by Orient Chemical Co., Ltd.], oil green # 502 [manufactured by Orient Chemical Co., Ltd.], spiron red BEH special [manufactured by Hodogaya Chemical Co., Ltd.], victoria pure blue BOH [manufactured by Hodogaya Chemical Co., Ltd.], patent pure blue [manufactured by Sumitomo Mikuni Kagaku Kogyo Co., Ltd.], sudan blue II [manufactured by BASF Corp.], m-cresol purple, cresol red, rhodamine B, rhodamine 6G, first acid violet R, sulforhodamine B, auramine, 4-p-diethylaminophenyliminonaphthoquinone, 2-carboxyanilino-4-p-diethylaminophenyliminonaphthoquinone, 2-carbostearylamino-4-p-dihydroxyethyl-aminophenyliminonaphthaquinone, p-methoxybenzoyl-p'-diethylamino-o'-methylphenyliminoacetanilide, cyano-p-diethylaminophenyliminoacetanilide, 1-phenyl-3-methyl-4-p-diethylaminophenylimino-5-pyrazolone, 1(((naphthyl-4-p-diethylaminophenylimino-5-pyrazolone, and the like.

[0147] Particularly preferable organic dyes are triarylmethane-based dyes, the triarylmethanebased dyes contain a sulfonic acid compound as a counter ion as described in JP-A No. 62-2932471 and Japanese Patent No. 2969021 are especially useful.

[0148] These dyes can be used singly or as a mixture. The addition amount of these dyes is preferablyfrom 0.3 to 15% by mass to the total mass of the image recording material. As occasion demands, these dyes can be used together with other dyes and pigments, the amount used is 70% by mass or less to the total mass of the dyes and pigments, and preferably 50% by mass or less.

(Inking property enhancing agent)

[0149] In the recording layer of the positive-working planographic printing plate precursor in the present invention, various kinds of resins having a hydrophobic group for enhancing the inking property on the image, for example, octyl phenol (formaldehyde resin, t-butyl phenol(formaldehyde resin, t-butyl phenol (benzaldehyde resin, rosin modified novolac resin, and o-naphthoquinoneazide sulfonates of these modified novolac resins, and the like; plasticizers for improving the flexibility of a coated layer, for example, dibutyl phthalate, butyl glycolate, tricresyl phosphate, dioctyl adipate, and the like, various kinds of additives can be added according to various purposes. The addition amount of these additives is preferably in a range of 0.01 to 30% by mass relative to the total solid content in the image recording material.

(Development inhibitor)

[0150] In the recording layer of the positive-working planographic printing plate precursor in the present invention, as a development inhibiting agent for extending the latitude of development, nonionic surface-active agents as described in JP-A Nos. 62-251740 and 4-68355,and amphoteric surface-active agents as described in JP-A Nos. 59-121044 and 4-13149 can be added. Specific examples of the nonionic surface-active agents include sorbitan tristearate, sorbitan monopalmitate, sorbitan triolate, stearic acid monoglyceride, polyoxyethylene sorbitan monooleate, and polyoxyethylene nonylphnyl ether, and concrete examples of the amphoteric surface-active agents include alkyldi (aminoethyl)glycine, alkylpolyaminoethylglycine hydrochloride, Amogen K (trade name, manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd., N-tetradecyl-N,N-betaine type), 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazoliniumbetaine, and REBON 15 (trade name, manufactured by Sanyo Chemical Industries, Ltd., alkylimidazorine series).

[0151] The content of the above nonionic surface-active agent and amphoteric surface-active agent is preferably 0.05 to 15% by mass, and more preferably 0.1 to 5% by mass in the total solid content in the image recording material.

(Agent for improving the coated surface quality)

[0152] In the recording layer of the positive-working planographic printing plate precursor in the present invention, as an agent for improving the coated surface quality in order to improve the quality of the coated surface, a surface-active agent, for example, a fluorine-based surfactant as described in JP-A Nos. 62-170950 and 2002-72474 can be added. The preferable addition amount is 0.001 to 1.0% by mass in the total solid content in the image recording material, and further preferably 0.005 to 0.5% by mass.

(Yellow dye)

[0153] In the recording layer of the positive-working planographic printing plate precursor in the present invention, yellow dyes, preferably yellow dyes in which the absorbance at 417 nm is 70% or more relative to that at 436 nm can be added.

[Method for forming the recording layer]

[0154] As to the recording layer of the planographic printing plate precursor of the present invention, in the case of the above-mentioned first aspect, a polymer (a) having a long chain alkyl group, (b) a polymer compound which is mutually insoluble with the polymer (a) having a long chain alkyl group (an alkali-soluble resin), and an infrared-ray absorbing agent (c) are dissolved in a coating solvent to prepare an coating liquid for the recording layer. Thereafter, the coating liquid is coated on a suitable support and dried. Thus, the recording layer can be manufactured.

[0155] Further, in this drying process, the phase separation take place between the polymer (a) having a long chain alkyl group and the polymer compound (b) in the coating liquid for the recording layer as the solvent is removed and the self-aggregation of the polymer (a) having a long chain alkyl group consequently occurs to form fine particles, so that fine particles form minute projections on the surface. For this reason, from the standpoint of forming the desired minute projections, the coating solvent and the drying conditions are selected.

<Coating solvent>

[0156] As a coating solvent used for dissolving components of the recording layer and coating the coating liquid in the present invention, although any of known solvents commonly used can be used, it is necessary to select a solvent which can dissolve both of the above polymer (a) having a long chain alkyl group and the other polymer compound which is mutually insoluble with the polymer (a).. However, the solvent is sufficient when both of the polymers can be uniformly dissolved under a certain condition and the solubility of the polymers in the solvent may be different from each other..

[0157] A solvent having a boiling point in the range of 40°C to 200°C, and particularly in the range of 60°C to 160°C is preferably selected because such a solvent is advantageous when the layer is dried.

[0158] As such solvents, the following solvents are suitably used singly or in combination: for example, alcohols such as methyl alcohol, ethyl alcohol, n- or iso-propyl alcohol, n- or iso-butyl alcohol, and diacetone alcohol, ketones such as acetone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, methyl amyl ketone, methyl hexyl ketone, diethyl ketone, diisobutyl ketone, cyclohexanone, methylcyclohexanone, and acetylacetone, hydrocarbons such as benzene, toluene, xylene, cyclohexne, and methoxybenzene, acetates such as ethyl acetate, n- or iso-propyl acetate, n- or iso-butyl acetate, ethyl butyl acetate, and hexyl acetate, halogenides such as methylene dichloride, ethylene dichloride, and monochlorobenzene, and ethers such as isopropyl ether, n-butyl ether, dioxane, dimethyl dioxane, and tetrahydrofuranpolyhydric alcohols and their derivatives such as ethylene glycol, methyl cellosolve, methyl cellosolve acetate, ethyl cellosolve, diethyl cellosolve, cellosolve acetate, butyl cellosolve, butyl cellosolve acetate, methoxy methoxy ethanol, diethylene glycol monomethyl ether, diethylene glycol dimethyl ether, diethylene glycol methyl ethyl ether, diethylene glycol diethyl ether, propylene glycol, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether, propylene glycol monoethyl ether acetate, propylene glycol monobutyl ether, and 3-methyl-3-methoxybutanol, special solvents such as dimethyl sulfoxide, and N,N-dimethylformamide, and the like.

[0159] The concentration of the solid content in the coating liquid for the recording layer is suitably 2 to 50% by mass.

[0160] Further, because first the coating liquid for the recording layer is prepared by dissolving the above-mentioned components in the image recording material in the coating solvent, and thereafter, the coating liquid is applied on the support and dried to prepare the recording layer in the present invention, particularly from the standpoint of the solubility of the polymer (a) having a long chain alkyl group, methyl ethyl ketone, 1-methoxy-2-propanol and the like are preferably used as a coating solvent.

<Coating method>

[0161] As the method for coating the above-mentioned coating liquid for the recording layer, for example, the methods of roll coating, dip coating, air knife coating, gravure coating, gravure offset coating, hopper coating, blade coating, wire doctor coating, spray coating and the like are used.

<Drying method>

[0162] Drying of the coating liquid for the recording layer applied onto the support is generally carried out by heated air. Heating temperature is generally in the range of 30 °C to 200 °C, especially in the range of 40 °C to 140 °C. The temperature for drying, not only a method of keeping the temperature at constant during drying but a method of increasing the temperature stepwise can be practiced. Moreover, a good result may be obtained by eliminating moisture from the air for drying. It is suitable to supply heated air to the coated surface at a rate of 0.1 m/sec. to 30 m/sec., especially 0.5 m/sec. to 20 m/sec.

[0163] Because these drying conditions affect the size of minute projections to be formed, for example, the drying conditions are selected such that when relatively large projections are to be formed, the drying temperature is lowered, and when small projections are to be formed, the drying temperature is raised.

[0164] In the present invention, it is necessary to coat the coating liquid for the recording layer so that the mass of the recording layer after drying becomes in the range of about 1.2 g/m2 to about 1,7 g/m2. In this case, large projections tend to be formed as the coating amount becomes large. In light of this tendency, an optimum coating amount is selected.

<Support>

[0165] As to a support for the planographic printing plate precursor in the present invention, as long as a plate-like support is dimensionally stable, the support can be used especially without any limitation. Such supports include paper, plastics (for example, polyethylene, polypropylene, polystyrene, or the like) laminated paper, metal plates, for example, of aluminum (including aluminum alloys), zinc, iron, copper and the like, plastics films such as, for example, diacetyl cellulose, triacetyl cellulose, propionyl cellulose, butyl cellulose, acetyl butyl cellulose, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, and polyvinyl acetal, paper or plastics films on which any of metals as mentioned above is laminated or deposited, but particularly, aluminum plates are preferable. Aluminum plates include a pure aluminum plate and aluminum alloy plates. Various types of aluminum alloys can be used, for example, alloys of aluminum and metals such as silicon, copper, manganese, magnesium, chromium, zinc, lead, bismuth, and nickel are used. These compositions contain other impurities in a negligible amount in addition to a certain amount of iron and titanium.

[0166] The support is subjected to surface treatment as occasion demands. The support surface of the planographic printing plate precursor of the present invention is preferably subjected to a hydrophilic treatment. When the support has a surface made of a metal, particularly aluminum, a surface treatment such as graining, an immersion treatment of the support into the aqueous solution of sodium silicate, potassium fluorozirconate, phosphate and the like, or anodizing is preferably conducted. Further, an aluminum plate that is subjected to the immersion treatment into the aqueous solution of sodium silicate after graining as described in the specification of U.S. Patent No. 2,714,066, and an aluminum plate that is subjected to the immersion treatment into the aqueous solution of alkali metal silicate after anodizing as described in the specification of U.S. Patent No. 3,181,461 are also suitably used.

[0167] The above anodizing is carried out by immersing an aluminum plate in an aqueous electrolytic solutions or non-aqueous electrolytic solution containing an inorganic acid such as phosphoric acid, chromic acid, sulfuric acid, and boric acid, or an organic acid such as oxalic acid and sulfamic acid, or their derivatives, singly or in combination thereof, and an electric current is allowed to pass the aluminum plate as the anode. Further, silicate electrodeposition as described in the specification of U.S. Patent No. 3,658,662 is also effective. These hydrophilic treatments are conducted not only for making the surface of the support hydrophilic but for preventing a harmful reaction with the recording layer provided on the support and for improving the adhesiveness of the support with the recording layer.

[0168] Prior to graining of the aluminum plate, a pretreatment of the surface may be conducted to remove a rolling-mill lubricant on the surface as occasion demands and to obtain a clean aluminum surface. Solvents such as trichlene, surfactant and the like are used for the former. A method of using alkali etching agents such as sodium hydroxide and potassium hydroxide is widely used for the latter.

[0169] As the graining method, any of mechanical methods, chemical methods and electrochemical methods is useful. The mechanical methods include the ball polishing method, the blast polishing method, and the brush polishing method in which a plate is rubbed by a nylon brush with slurry in which an abrasive such as pumice stone is dispersed in water. As the chemical methods, a method of immersing a plate in a saturated aqueous solution of an aluminum salt of a mineral acid as described in JP-A No. 54-31187 is suitable. As the electrochemical methods, a method of conducting alternating-current electrolysis in an acidic electrolytic solution such as hydrochloric acid, nitric acid, or their combination is preferable. Among such surface roughening methods, the surface roughening method of combining the mechanical roughening and electrochemical roughening as described in JP-A No. 55-137993 is preferable because the adhesive strength of a sensitizing image to the support is high. Graining according to the methods mentioned above is preferably conducted so that the surface roughness at the center line on the surface of the aluminum plate (Ra) becomes in the range of 0.35 μ to 1.0 μm. An aluminum plate thus subjected to graining is washed with water and chemically etched as occasion demands.

[0170] An etching treatment liquid is generally selected from an aqueous solution of a base or acid for dissolving aluminum. In this case, the treatment liquid must be such one so as not to form a coated layer different from aluminum derived from the component of the etching liquid on the etched surface. As preferable etching agents, basic substances such as sodium hydroxide, potassium hydroxide, trisodium phosphate, disodium phosphate, tripotassium phosphate, and dipotassium phosphate, acidic substances such as sulfuric acid, persulfuric acid, phosphoric acid, hydrochloric acid, and their salts can be exemplified. However, salts of metals having a lower ionization tendency than aluminum, for example, zinc, chromium, cobalt, nickel, copper and the like are not preferable because they form unnecessary coating on the etched surface. These etching agents are most preferably used so that the concentration used and the temperature setting are adjusted so as to make the velocity of dissolution of aluminum or its alloy used to be 0.3 to 40 g/m^2 per 1 minute of immersion time. The velocity of dissolution is justifiable even if being over or below the above-mentioned range.

[0171] Etching is carried out by immersing the aluminum plate into the above-mentioned etching liquid or applying the etching liquid on the aluminum plate and the aluminum plate is preferably treated such that the etching amount is in the range of 0.5 to 10 g/m^2. As the above-mentioned etching agent, the use of an aqueous base solution is desirable because of its property of a high etching rate. In this case, because smuts are formed, a desmutting treatment is usually carried out. As an acid used in the desmutting treatment, nitric acid, sulfuric acid, phosphoric acid, chromic acid, hydrofluoric acid, fluoroboric acid, and the like are used. An etched aluminum plate is washed with water and anodized as occasion demands. Anodizing can be conducted by any of the known methods in the art.

[0172] Specifically, an anodized coating can be formed on the surface of the aluminum support by allowing to pass a direct current or an alternating current to aluminum in the aqueous solution or nonaqueous solution of any one or a combination of two kinds or more of sulfuric acid, phosphoric acid, chromic acid, oxalic acid, sulfamic acid, benzenesulfonic acid, and the like.

[0173] Though the treating conditions for anodizing vary with an electrolytic solution to be used and cannot generally be determined, generally the following conditions are suitable: the concentration of an electrolytic solution is 1 to 80% by mass, liquid temperature is 5 to 70(C, current density is 0.5 to 60 A/dm2, voltage is 1 to 100 V, electrolysis time is 30 seconds to 50 minutes. Among these anodizing treatment methods, particularly, the method of anodizing at a high current density in sulfuric acid as described in the specification of British Patent No. 1,412,768 and the method of anodizing using an electrolytic bath of phosphoric acid as described in the specification of U.S. Patent No. 3,511,661 are preferable. An aluminum plate that has been roughened and further anodized as mentioned above may be subjected to hydrophilic treatment as occasion demands. Preferable examples of the methods include the method of treating with a metal silicate, for example, an aqueous sodium silicate solution disclosed in U.S, Patent Nos. 2,714,066 and 3,181,461, or the method of treating with potassium fluorozirconate as disclosed in Japanese Patent Application Publication (JP-B) No. 36-22063, and the method oftreating with polyvinyl phosphonic acid disclosed in the specification of U.S. Patent No. 4,153,461.

[0174] Further, as the second method for preparing the planographic printing plate precursor having the area of portions having a gradient of 15 degrees or more on the uppermost surface of the recording layer is about 5% or more, the method in which an coating amount is selected such that an irregularity is formed on the surface of the support under a prescribed condition and the irregularity is reflected to the configuration of the top surface of the recording layer.

[0175] In order to make the portions having the gradient of 1degrees or more at the top surface of the recording layer being at a rate of 5% or more, more specifically, a method for selecting conditions for treating the support surface so that Ra of the support surface becomes 0.35 ((m) or more, and the coating amount of the recording layer is made to be 1.20 g/m2 to 1.70 g/m2 can be exemplified. Further, Ra in the present invention uses values measured in accordance with JIS B0601 (1994) (ISO 4287).

<Organic undercoat layer>

[0176] In the planographic printing plate precursor, providing an organic undercoat layer before preparing the recording layer by applying the coating liquid is preferable for reducing residual layer in non-image area of the recording layer. Organic compound used in such a undercoat layer is selected from, for example, carboxymethyl cellulose, dextrin, gum arabic, phosphonic acids having an amino group such as 2-aminoethylsulfonic acid, organic phosphonic acids such as phenylphosphnic acid which may have a substituent, naphthylphosphonic acid, alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid, and ethylenediphosphonic acid, organic phosphoric acids such as phenylphosphoric acid which may have a substituent, naphthylphosphoric acid, alkylphosphoric acid, and glycerophosphoric acid, organic phosphinic acids such as phenylphosphinic acid which may have a substituent, naphthylphosphinic acid, alkylphosphinic acid, and glycerophosphinic acid, amino acids such as glycine and (-alanine, and amine hydrochlorides having a hydroxyl group such as triethanolamine hydrochloride, but they may be used in a mixture of two or more kinds.

[0177] Moreover, it is also preferable that the organic undercoat layer contains a compound having an onium group. Compounds having an onium group are described in detail in JP-A Nos. 2000-10292 and 2000-108538.

[0178] Further, at least one compound selected from the group of polymer compounds having a structural unit represented by poly (p-viny) benzoic acid) and the like in the molecule can be used. In more detail, the compound includes a copolymer of p-vinyl benzoic acid and vinylbenzyl triethylammonium salt, a copolymer of p-vinyl benzoic acid and vinylbenzyl trimethylammonium chloride, and the like.

[0179] This organic undercoat layer can be provided by the following method. That is, one method is performed in such a manner that a solution in which the above organic compound is dissolved in water or an organic solvent such as methanol, ethanol, and methyl ethyl ketone, or a mixed solvent thereof is applied onto an aluminum plate and dried. The other method is performed in such a manner that an aluminum plate is immersed in a solution in which the above-mentioned organic compound is dissolved in water or an organic solvent such as methanol, ethanol, and methyl ethyl ketone, or a mixed solvent thereof, and is allowed to adsorb the compound, and thereafter, the aluminum plate is washed with water and dried to obtain an organic undercoat layer. In the former method, the above organic compound solution having a concentration of 0.005 to 10% by mass can be coated by various methods. For example, any of a bar coater coating, rotating coating, spray coating, and curtain coating can be used. And, in the latter method, the concentration of the solution is 0.01 to 20% by mass and preferably 0,05 to 5% by mass, the immersion temperature is 20 to 90(C and preferably 25 to 50 °C, and the immersion time is 0.1 seconds to 20 minutes and preferably 2 seconds to 1 minute.

[0180] The pH value of the solution used for the above methods is controlled with basic substances such as ammonia, triethylamine, and potassium hydroxide, and acidic substances such as hydrochloric acid and phosphoric acid, and the solution can be used in the range of 1 to 12 in pH. Moreover, a yellow dye can be added in the solution to improve the tone reproducibility of the photosensitive planographic printing plate. Further, a compound represented by the following formula can be added.

$$(HO)_x - R - (COOH)_y \quad \text{Formula}$$

[0181] Here, in the above-mentioned formula, R represents an arylene group having 14 or less carbon atoms that may have a substituent, x and y each independently represent an integer of 1 to 3, respectively. Concrete examples of the compounds represented by the above formula include 3-hydroxybenzoic acid, 4-hydroxybcnzoic acid, salicylic acid, 1-hydroxy-2-naphthoic acid, 2-hydroxy-l-naphthoic acid, 2-hydroxy-3-naphthoic acid, 2, 4-dihydroxybenzoic acid, and 10-hydroxy-9-anthracenecarboxylic acid. The coated amount of the organic undercoat layer after drying is preferably 1 to 100 mg/m2 and preferable to be 2 to 70 mg/m2. When the above coated amount is less than 2 mg/m2, a sufficient printing durability cannot be obtained. And, when the above coated amount exceeds 100 mg/m2, a sufficient printing durability cannot also be obtained.

<Back coating layer>

[0182] a back coat layer is provided on the back of the support, if necessary. As the back coat layer, the back coat layer containing a metal oxide obtained by hydrolysis and polycondensation of an organic polymer compounds as described in JP-A No. 5-45885 and organic or inorganic metal compounds as described in JP-A No. 6-35174 is preferably used. Among these back coat layers, alkoxy compounds of silicon such as $Si(OCH_3)_4$, $Si(OC_2H_5)_4$, $Si(OC_3H_7)_4$, and $Si(OC_4H_9)_4$ are particularly preferable because they are easily available at a low price and the coat layers of metal oxides obtained therefrom have an excellent developer resistance.

<Plate-making and printing>

[0183] In the planographic printing plate precursor of the invention, an image is formed by heat. Specifically, direct image-wise recording with a thermal recording head, scanning light exposure with infrared-ray laser, high illuminance flash exposure such as xenon discharge lamp, and infrared-ray lamp exposure are used, and exposure with a solid high output infrared-ray laser such as a semiconductor laser and YAG laser which radiates infrared-ray having a wavelength of 700 to 1200 nm is suitable.

[0184] The exposed planographic printing plate precursor is developed and subjected to a post-treatment with a finisher and protective gum, to from a printing plate.

[0185] Moreover, as processing agents used in the developing processing and post-treatment, any one properly selected from known processing agents can be used. Suitable developers have a pH value in the range of 9.0 to 14.0, and preferably in the range of 12.0 to 13.5. Aqueous alkali solutions which have been known can be used for the developer. Among the above-mentioned aqueous alkali solution, particularly suitable developers include an aqueous solution having a pH value of 12 or more, which has been known as a so-called "Silicate developer", which contains an alkali silicate as a base, or contains a mixture in which a silicon compound is mixed in a base to prepare an alkali silicate, and a so-called "silicate-free developer" which does not contain alkali silicate, but contains nonreducing sugar (an organic compound having buffer action) and a base, and which is described in JP-A No. 8-305039.

[0186] The plate burning treatment of the planographic printing plate of the present invention is preferably carried out by a known method in which a plate burning is performed using a counter-etching liquid and a plate burning processor.

[0187] The planographic printing plate obtained through such processings is placed on an offset press and the like, and used for printing a large number of sheets.

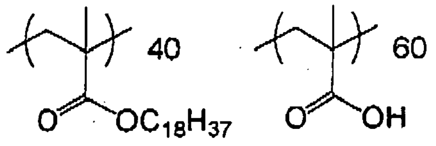
EXAMPLES

[0188] Hereinafter, the present invention will be described in detail with examples, but the present invention should not be limited by these examples.

[Synthesis Example 1: synthesis of (a) polymer having a long chain alkyl group A]

[0189] 59 g of 1-methoxy-2-propanol was placed into a 1000 ml three-neck flask equipped with a condenser and a stirrer, and this was heated to 80°C. Under a nitrogen stream, a solution containing 42.0 g of stearyl n-methacrylate, 16.0 a of methacrylic acid, 0.714 g of polymerization initiator V-601 (manufactured by Wako Pure Chemical Industries, Ltd.), and 59 g of 1-methoxy-2-propanol was added dropwise over two and a half hours. Further, the mixture was reacted at 80°C for 2 hours. The reaction mixture was cooled to room temperature, and the reaction solution was poured into 1000 ml of water. After decantation, this was washed with methanol, and the resulting liquid product was dried under reduced pressure to obtain 73.5 g of the (a) polymer having a long chain alkyl group A shown below. The mass average molecular weight was measured by a gel permeation chromatography method (GPC) using polystyrene as the standard substance and, as a result, it was 66,000.

Polymer A having a long chain alkyl group



Mass average molecular 66,000

(Preparation of support)

[0190] Using an aluminum alloy containing Si: 0.06% by mass, Fe: 0.30 % by mass, Cu: 0.005 % by mass, Mn: 0.001 % by mass, Mg: 0.001 % by mass, Zn; 0.001 % by mass, and Ti: 0.03 % by mass, and the remainder A1 and unavoidable impurities, a molten metal was prepared, molten metal treatment and filtration were performed, and an ingot having a thickness of 500 mm and a width of 1200 mm was prepared by a DC casting method. About 10 mm of the surface was cut off with a scalping machine, this was soaked at 550 °C for about 5 hours and then, when the temperature had fallen to 400 °C, a rolled plate having a thickness of 2.7 mm was prepared using a hot rolling machine. Further, heat treatment was performed at 500 °C using a continuous annealing machine, and this was finished to a thickness of 0.24 mm by cold rolling to obtain an aluminum plate of JIS 1050 material. This aluminum plate was processed to a width of 1030 mm, and was subjected to the surface treatment shown below.

(a) Mechanical surface-roughening treatment

[0191] Mechanical surface roughening treatment was carried out by a rotating roller type nylon brush by supplying a suspension of an abrasive agent (silica sand) having a specific gravity of 1.12 and water as an abrasive slurry solution to the surface of the aluminum plate. The average particle size of the abrasive agent was 8 μm and the maximum particle size was 50 μm. The material of the nylon brush was 6-10 nylon with a hair length of 50 mm and a hair diameter of 0.3 mm, The nylon brush was produced by implanting hairs densely in holes formed in a stainless cylinder having a diameter of 300 mm. Three rotary brushes were employed. The distance between two supporting rollers (diameter: 200 mm) under the brush was 300 mm. The brush roller was pressed to the aluminum plate until the load was increased to a load higher by 7 kW than that before it was pressed to the aluminum plate. The rotation direction of the brush was the same as the direction of the movement of the aluminum plate. The rotation speed of the brush was 200 rpm.

(b) Alkali etching treatment

[0192] The obtained aluminum plate was etched by spraying an aqueous NaOH solution (concentration: 26% by mass, aluminum ion concentration of 6.5% by mass) at 70 °C to etch 6 g/m2 of the aluminum plate, followed by washing with water by spraying.

(c) Desmutting treatment

[0193] Desmutting treatment was carried out by spraying an aqueous 1% by mass nitric acid solution (containing 0.5 % by mass of aluminum ion) at 30 °C, followed by washing with water by spraying. As the aqueous nitric acid solution, a waste solution obtained from the step of electrochemical surface roughening treatment by applying A.C. current in an aqueous nitric acid solution was used.

(d) Electrochemical surface roughening treatment

[0194] Electrochemical surface roughening treatment was carried out continuously using an A.C. voltage of 60 Hz. The electrolytic solution was an aqueous solution containing 10.5 g/L of nitric acid (including 5 g/L of aluminum ions) and 0.007% by mass of ammonium ions at 50 °C. The A.C. power source had the waveform in which the time TP required for current value to reach a peak from 0 was 0.8 msec and the duty ratio was 1 : 1, and trapezoidal rectangular wave A.C. current was used to carry out electrochemical surface roughening treatment using a carbon electrode as a counter electrode. Ferrite was used as an auxiliary anode. The electrolytic bath employed was a radial cell type.
[0195] The current density was 30 A/dm^2 as a peak current, and the quantity of electricity was 220 C/dm^2 as the total quantity of electricity when the aluminum plate was an anode. 5 % of the current flowing from the power source was branched to the auxiliary electrode. Thereafter, the aluminum plate was washed with water by spraying.

(e) Alkali etching treatment

[0196] Etching treatment was carried out by spraying a solution containing 26% by mass of caustic soda and 6.5% by mass of aluminum ions to the aluminum plate at 32°C to etch 0.25 g/cm^2 of the aluminum plate to remove the smut component primarily containing aluminum hydroxide generated when performing the foregoing electrochemical surface roughening treatment using A.C. current, and also to etch the edge part of the pits produced to thereby round the edge part. Thereafter, the aluminum plate was washed with water by spraying.

(f) Desmutting treatment

[0197] Desmutting treatment was carried out by spraying an aqueous 15 % by mass nitric acid solution (including 4.5% by mass of aluminum ions) at 30 °C, followed by washing with water by spraying. As the aqueous nitric acid solution used in the desmutting treatment, a waste solution obtained in the step of electrochemical surface roughening treatment by applying A.C. current in an aqueous nitric acid solution was used.
[0198] Electrochemical surface roughening treatment was continuously carried out by applying an A.C. voltage of 60 Hz. In this case, the electrolytic solution was an aqueous solution containing 2.5 g/L of hydrochloric acid (including 5 g/L of aluminum ions) at 35 °C. The A.C. power source had a rectangular waveform and a carbon electrode was used as a counter electrode to carry out electrochemical surface roughening treatment. Ferrite was used as an auxiliary anode. The electrolytic bath employed was a radial cell type.
[0199] The current density was 25 A/dm^2 as a peak current and the quantity of electricity was 50 C/dm^2 as the total quantity of electricity when the aluminum plate was an anode.
[0200] Thereafter, the aluminum plate was washed with water by spraying.

(h) Alkali etching treatment

[0201] Etching treatment was carried out by spraying a solution containing 26% by mass of caustic soda and 6.5% by mass of aluminum ions to the aluminum plate at 32 °C to etch 0.10 g/cm^2 of the aluminum plate to remove the smut component primarily containing aluminum hydroxide generated when performing the foregoing electrochemical surface roughening treatment using A.C. current, and also to etch the edge part of the pits produced to thereby round the edge part. Thereafter, the aluminum plate was washed with water by spraying.

(i) Desmutting treatment

[0202] Desmutting treatment was carried out by spraying an aqueous solution containing 25 % by mass sulfuric acid solution (including 0.5% by mass of aluminum ions) at 60 °C, followed by washing with water by spraying.

(j) Anodization treatment

[0203] Sulfuric acid was used as the electrolytic solution. The electrolytic solution contained 170 g/L of sulfuric acid (including 0.5% by mass of aluminum ions) at 38 °C. Thereafter, the aluminum plate was washed with water by spraying.
[0204] The current densities were respectively about 30 A/dm2. The final anodized coating amount was 2.7 g/m2.

(k) Alkali metal silicate treatment

[0205] Alkali metal silicate treatment (silicate treatment) was carried out by immersing the above-mentioned aluminum support obtained by anodization treatment in an aqueous solution containing 1% by mass of No. 3 sodium silicate at 30

°C for 10 seconds, followed by washing with water by spraying. The amount of silicate adhering to the support was 3.5 mg/m^2.

<Support A>

[0206] Each of the aforementioned processes (a) to (k) were sequentially performed, and an etching amount in process (e) was adjusted to 3.4 g/m^2 to prepare a support A.

<Support B>

[0207] Each of the processes for manufacturing a support A were sequentially performed, except that process (a) was omitted, to prepare a support B.

<Support C>

[0208] Each of the processes for manufacturing a support A were sequentially performed, except that processes (a), (d), (e) and (f) were omitted, and the sum of the quantity of electricity in process (g) was adjusted to 450 C/dm^2, to prepare a support C.

[Positive-working planographic printing plate precursor]

[0209] On the supports A, B, and C obtained as mentioned above, subsequently, undercoat layers were prepared according to the following.

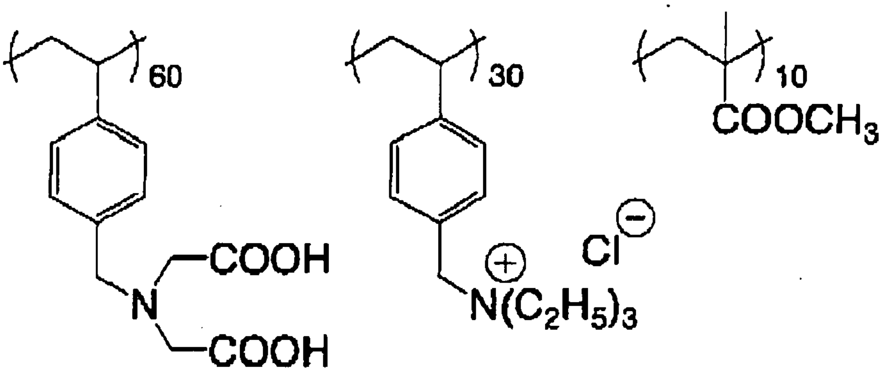
(Formation of organic undercoat layer)

[0210] On the aluminum supports A to C that were obtained by the above-mentioned processes after the alkali metal silicate treatment was performed, an organic undercoat coating liquid having the following composition was applied and dried at 80 °C for 15 seconds. The coated amount after drying was 18 mg/m^2.

<Coating of organic undercoat coating liquid>

[0211]

-The following polymer compound (the weight average molecular weight; 50,000)	0.3 g
- Methanol	100g



[Example 1]

[0212] A recording layer was formed on the base plate in which an organic undercoat layer was prepared on the support B obtained as described above, according to the following method.

<Formation of recording layer>

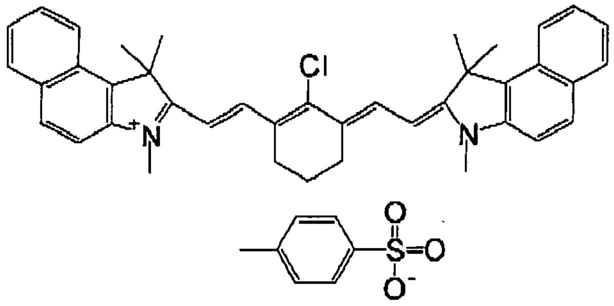
[0213] The following coating liquid 1 for forming a recording layer was coated by using a bar coater and dried at 130 °C for 50 seconds in PERFECT OVEN PH 200 manufactured by TABAI Corp. to prepare a recording layer having a coated amount after drying of 1.3 g/m^2. Thereafter, the following coating liquid 2 for forming a recording layer was coated by using a bar coater and dried at 130 °C for 60 seconds in PERFECT OVEN PH 200 manufactured by TABAI Corp. to prepare a recording layer with the amount coated after drying of 0.26 g/m^2. Thus, the infrared-ray photosensitive planographic printing plate precursor of Example 1 was obtained.

[0214]

(Recording layer forming coating solution 1)

-N-(4-nimnosulfonylphenyl) methacrylamide/ acrylonitrile/methyl methacrylate copolymer	1.9 g
-36/34/30 % by mass; weight average molecular weight 50000, acid value 2.65)	
-m/p cresol novolak	0.3 g
-m/p=6/4, weight average molecular weight 4500, containing 0.8 % by mass of unreacted cresol)	
-Cyanine dye B (following structure)	0.13 g
-4, 4'-Bishydroxyphenylsulfone	0.13 g
-Tetrahydrophthalic acid anhydride	0.19 g
-p-toluenesulfonic acid	0.008 g
-3-Methoxy-4-diazodiphenylamine hexafluorophosphate	0.032 g
-Ethyl Violet in which a counter ion was changed to 6-hydroxy-2-naphthalenesulfonic acid ion	0.078 g
-Fluorine-based surfactant	0.2 g
-Megaface F780, manufactured by Dainippon Ink and Chemicals, Incorporated, with 30% methyl ethyl ketone)	
-Methyl ethyl ketone	16.0 g
-1-Methoxy-2-propanol	8.0 g
y-butyrolactone	8.0 g

Cyanine Dye A



[0215]

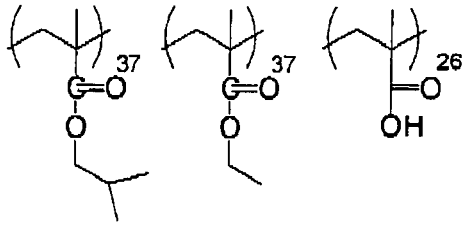
- Recording layer forming coating solution 2)

-Phenol/m/p cresol novolak	0.27 g
-phenol/m/p=5/3/2, mass average molecular weight 5000, containing 0.8 % by mass of unreacted cresol)	
-Acryl-based resin C (following structure)	0.042 g
-Cyanine dye B (above structure)	0.019 g

(continued)

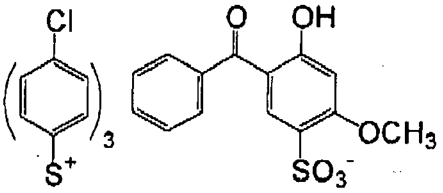
-Polymer having a long chain alkyl group A	0.042 g
-Sulfonium salt compound D (following structure)	0.065 g
-Ammonium compound (following structure)	0.004 g
-Fluorine-based surfactant	0.02 g
-Megaface F780, manufactured by Dainippon Ink and Chemicals, Incorporated, with 30% methyl ethyl ketone)	
-Fluorine-based surfactant E (following structure) (methyl ethyl ketone 60 %)	0.032 g
-Methyl ethyl ketone	13.0 g
-1-Methoxy-2-propanol	7.0 g

Acryl-based resin B

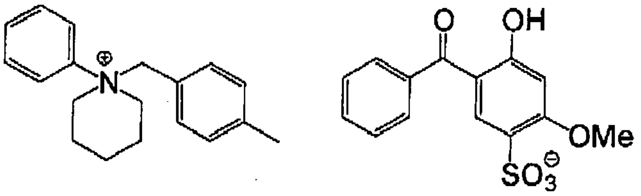


Molecular weight 50,000

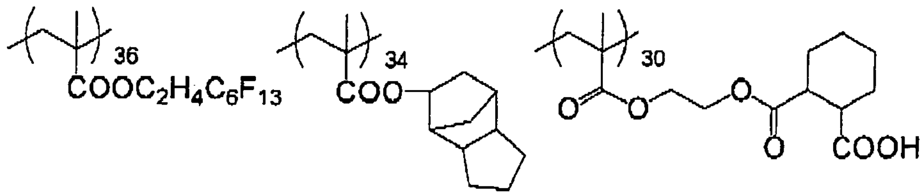
Sulfonium compound C



Ammonium compound D



Fluorine-based surfactant E



Molecular weight 16,000

[Example 2]

[0216] The infrared-ray photosensitive planographic printing plate precursor of Example 2 was obtained by the same method as Example 1, except that the coated amount after drying was made to be 0.99 g/m^2 by changing the wet coated amount by using a bar coater which is different from the bar coater used for coating the coating liquid 1 for forming the recording layer of Example 1 was applied.

[Example 3]

[0217] The infrared-ray photosensitive planographic printing plate precursor of Example 3 was obtained by the same method as Example 1, except that the amount coated after drying was made to be 1.44 g/m^2 by changing the wet coated amount by using a bar coater which is different from the bar coater used for coating the coating liquid 1 for forming the recording layer of Example 1 was applied.

[Example 4]

[0218] The infrared-ray photosensitive planographic printing plate precursor of Example 4 was obtained by the same method as Example 1, except that the support B used in Example 1 was changed to the support A.

[Example 5]

[0219] The infrared-ray photosensitive planographic printing plate precursor of Example 5 was obtained by the same method as Example 1, except that the support B used in Example 1 was changed to the support C.

[Example 6]

[0220] After an organic undercoat layer and a recording layer using the recording layer forming liquid 1 were prepared on the surface of the above-mentioned support A in the same method as Example 1, the following coating liquid 3 for forming a recording layer in place of the above-mentioned coating liquid 2 for forming a recording layer was applied with a bar coater and dried at 130°C for 60 seconds in PERFECT OVEN PH 200 manufactured by TABAI Corp. to prepare a recording layer (the top layer) having a coated amount of 0.26 g/m^2 after drying, so that the infrared-ray photosensitive planographic printing plate precursor of Example 6 was obtained.

[0221]

(Coating liquid 3 for forming a recording layer)

- Phenol/m/p cresol novolac (Plienol/m/p = 5/3/2, mass average molecular weight 5000, containing 0.8% by mass of unreacted cresol)	0.27 g
- Acryl-based resin B (above structure)	0.042 g
- Cyanine dye A (above structure)	0.019 g
- Sulfonium salt compound C (above structure)	0.065 g
- Ammonium compound D (above structure)	0.004 g
- Fluorine-based surfactant	0.02 g

(continued)

(Megafac F780, manufactured by Dainippon Ink and Chemicals, containing 30% methyl ethyl ketone)	
- Fluorine-based surfactant E (above structure) (methyl ethyl ketone 60%)	0.032 g
- Methyl ethyl ketone	13.0 g
- 1-Methoxy-2-propanol	7.0 g

[Example 7]

[0222] After the organic undercoat layer and a recording layer using the recording layer forming liquid 1 were prepared on the surface of the above-mentioned support C in the same method as Example 1, the above-mentioned coating liquid 3 for forming a recording layer was applied with a bar coater and dried at 130°C for 60 seconds in PERFECT OVEN PH 200 manufactured by TABAI Corp. to prepare a recording layer having a coated amount of 0.26 g/m^2 after drying, so that the infrared-ray photosensitive planographic printing plate precursor of Example 7 was obtained.

[Example 8]

[0223] The infrared-ray photosensitive planographic printing plate precursor of Example 8 was obtained by the same method as Example 6, except that the coated amount of the coating liquid 1 for forming a recording layer in Example 6 was changed to 1.44 g/m^2.

[Comparative example 1]

[0224] The infrared-ray photosensitive planographic printing plate precursor of Comparative example 1 was obtained by the same method as Example 1, except that the amount applied of the coating liquid 1 for forming a recording layer in Example 1 was changed to be 0.75 g/m^2.

[Comparative example 2]

[0225] The infrared-ray photosensitive planographic printing plate precursor of Comparative example 2 was obtained by the same method as Example 1, except that the amount applied of the coating liquid I for forming a recording layer in Example 1 was changed to be 1.75 g/m^2.

[Comparative example 3]

[0226] The infrared-ray photosensitive planographic printing plate precursor of Comparative example 3 was obtained by the same method as Example 1, except that the coating liquid 2 for forming a recording layer in Example 1 was changed to the coating liquid 3 for forming a recording layer.

[Example 9]

[0227] The above-mentioned organic undercoat layer was prepared on the above-mentioned support B, and then the following coating liquid 4 for forming a recording layer was coated by using a bar coater and dried at 140(C for 50 seconds in PERFECT OVEN PH 200 manufactured by TABAI Corp. to prepare a recording layer with having a coated amount of 1.56 g/m2 after drying, so that the infrared-ray photosensitive planographic printing plate precursor of Example 9 was obtained.

[0228] (Coating liquid 4 for forming a recording layer)

- Polymer having a long chain alkyl group A	0.09 g
- Novolac resin	0.90 g
(m/p-cresol (6/4), mass average molecular weight 7000 containing 0.5%by mass of unreacted cresol)	
- Ethyl methacrylate/isobutyl methacrylate/Methacrylic acid copolymer (35/35/30% by mole)	0.10 g
- Cyanine dye (above structure)	0.10 g
- Phthalic anhydride	0.05 g
- p-toluenesulfonic acid	0.002 g

(continued)

- Ethyl violet in which a counter ion was changed to 6-hydroxy-(-naphthalenesulfonic acid ion	0.02 g
- Fluorine-based surfactant (F-167 PF, manufactured by Dainippon Ink and Chemicals, containing 20% methyl ethyl ketone)	0.015 g
- Fluorine-based surfactant (MCF-312, manufactured by Dainippon Ink and Chemicals, containing 30% methyl ethyl ketone)	0.035 g
- Methyl ethyl ketone	1.2 g

[Example 10]

[0229] The infrared-ray photosensitive planographic printing plate precursor of Example 10 was obtained by the same method as Example 9, except that the coated amount after drying was made to be 1.25 g/m2 by changing the wet coated amount by using a bar coater which is different from the bar coater used for coating the coating liquid 4 for forming a recording layer of Example 9 was coated.

[Example 11]

[0230] The infrared-ray photosensitive planographic printing plate precursor of Example 11 was obtained by the same method as Example 9, except that the amount coated after drying was made to be 1.70 g/m2 by changing the wet coated amount by using a bar coater which is different from the bar coater used for coating the coating liquid 4 for forming a recording layer of Example 9 was coated.

[Example 12]

[0231] The infrared-ray photosensitive planographic printing plate precursor of Example 12 was obtained by the same method as Example 9, except that the support B used in Example 9 was changed to the support A.

[Example 13]

[0232] The infrared-ray photosensitive planographic printing plate precursor of Example 13 was obtained by the same method as Example 9, except that the support B used in Example 9 was changed to the support C.

[Example 14]

[0233] The above-mentioned organic undercoat layer was prepared on the above-mentioned support A, and then the following coating liquid 5 for forming a recording layer was coated by using a bar coater and dried at 140 °C for 60 seconds in **PERFECT OVEN** PH 200 manufactured by TABAI Corp. to prepare a recording layer having a coated amount of 1.56 g/m^2 after drying, and the infrared-ray photosensitive planographic printing plate precursor of Example 14 was obtained.

[0234]

(Coating liquid 5 for forming a recording layer)

- Novolac resin (m/p-cresol (6/4), mass average molecular weight 7000, containing 0.5% by mass of unreacted cresol)	0.90 g
- Ethyl methacrylate/isobutyl methacrylate/Methacrylic acid copolymer (35/35/30% by mole)	0.10 g
- Cyanine dye (above structure)	0.10 g
- Phthalic anhydride	0.002 g
- Ethyl violet in which a counter ion was changed to 6-hydroxy-(-naphthalenesulfonic acid ion	0.02 g
- Fluorine-based surfactant (F-167 PF, manufactured by Dainippon Ink and Chemicals, containing 20% methyl ethyl ketone)	0.015 g
- Fluorine-based surfactant (MCF-312. manufactured by Dainippon Ink and Chemicals, containing 30% methyl ethyl ketone)	0.035 g
- Methyl ethyl ketone	1.2 g

[Example 15]

[0235] The above-mentioned organic undercoat layer was prepared on the above-mentioned support C, and then the coating liquid 5 for forming a recording layer was coated by using a bar coater and dried at 140°C for 60 seconds in PERFECT OVEN PH 200 manufactured by TABAI Corp. to prepare a recording layer with the amount coated after drying of 1.56 g/m^2, so that the infrared-ray photosensitive planographic printing plate precursor ofExample 15 was obtained.

[Example 16]

[0236] The infrared-ray photosensitive planographic printing plate precursor of Example 16 was obtained by the same method as Example 14, except that the amount applied of the coating liquid 1 for forming a recording layer in Example 14 was changed to 1.70 g/m^2.

[Comparative example 4]

[0237] The infrared-ray photosensitive planographic printing plate precursor of Comparative example 4 was obtained by the same method as Example 8, except that the amount applied of the coating liquid 4 for forming a recording layer in Example 8 was changed to 1.01 g/m^2.

[Comparative example 5]

[0238] The infrared-ray photosensitive planographic printing plate precursor of Comparative example 5 was obtained by the same method as Example 8, except that the amount applied of the coating liquid 4 for forming a recording layer in Example 8 was changed to 2.01 g/m^2.

[Comparative example 6]

[0239] The infrared-ray photosensitive planographic printing plate precursor of Comparative example 6 was obtained by the same method as Example 8, except that the coating liquid 4 for forming a recording layer in Example 8 was changed to the coating liquid 5 for forming a recording layer.

[Evaluation of Examples 1 to 14 and Comparative examples 1 to 6]

[0240] 1. Measurements of the ratio of portions of the gradient of 15 degrees or more
The surface configuration of the obtained planographic printing plate precursor was measured by an atomic force microscope (SPA300/SPI3800N type, manufactured by SII Nano-Technology Co., Ltd.) and three dimensional data were found.

[0241] Hereinafter, the concrete procedure will be described. A planographic printing plate precursor was cut out into the size of 1 cm square and the sample was set on the horizontal sample stand on a piezo scanner. The cantilever was approached to the surface of the sample of the recording layer, and the sample was scanned in the XY direction when it reached the region where the atomic force was exerted. At this time, the irregularity of the sample was determined by the piezo displacement in the Z direction.

[0242] The piezo scanner capable of scanning in the X and Y directions by 150 μm and the Z direction by 10 μm was used. The cantilever having a resonance frequency of 200 to 400 kHz and a spring constant of 12 to 103 N/m (AC 160, manufactured by OLYMPUS Corp.) was used and the measurement was carried out in the DFM mode (Dynamic Force Mode). Moreover, small inclinations of the sample were corrected by the least-squares approximation of the obtained three dimensional data and the reference plane was obtained. In obtaining the data, the measurement was carried out with the scanning area of 10 μm, the resolving power of 256 (the number of X data) (256 (the number of Y data), and the scanning frequency of 0.5 Hz.

[0243] Using the obtained three dimensional data (f (x, y)), 3 points adjacent to each other were selected and angles defined by a minute triangle formed in the three points and the reference plane were calculated with respect to all data, and thus the gradient distribution curve was obtained. The ratio of the portions of the gradient of 15 degrees or more was calculated from the gradient distribution curve. These values are represented by a15 and listed in Tables 1 and 2.

2. Evaluation of scratch resistance

[0244] The obtained planographic printing plate precursor was put on a scratch tester manufactured by HEIDON Corp. and the surface of the recording layer was scratched with the sapphire stylus (the tip end diameter of 1.0 mm) on which a load was applied. Thereafter, the printing plate precursor was development-processed in the developer of DT-2 manufactured by Fuji Photo Film Co., Ltd. and Finisher FG-1 (that diluted with 1:1) manufactured by Fuji Photo Film Co., Ltd. in an automatic processor LP-940H manufactured by Fuji Photo Film Co., Ltd., at the developing temperature of 32°C for 12 seconds. At this time, the conductivity of the developer was 43 mS/cm. The planographic printing plate after development was visually inspected and the maximum load (in grams) where no omission of the image due to the scratching was regarded as the value of scratch resistance. It is evaluated that the larger this value is, the higher the scratch resistance is. The results are shown in the following Tables 1 and 2.

3. Evaluation of sensitivity

[0245] The obtained planographic printing plate precursor was power-exposed by TrendSetter3244 VFS manufactured by Creo Co., Ltd. while changing exposure energy at a drum rotating speed of 150 rpm. After that, the precursor was treated under the same development treating conditions as that in the above-mentioned scratch resistance evaluation. The planographic printing plate after the development was visually inspected and an exposing light amount at which a non-image area could be developed was measured, and the value was regarded as the sensitivity. It is evaluated that the smaller this value is, the higher the sensitivity is. The results are shown in the following Tables 1 and 2.

4. Evaluation of printing durability

[0246] The obtained planographic printing plate precursor, was image-wisely exposed by TrendSetter3244 VFS manufactured by Creo Co., Ltd at a beam intensity of 9.0 W and at a drum rotation speed of 150 rpm. Thereafter the precursor was development processed under the same development processing conditions as that in the above scratch resistance evaluation. Printing was carried out by the use of the development processed planographic printing plate using a printing machine, Rislon 226 manufactured by Komori Corporation. At that time, the number of sheets having enough printed ink density was visually inspected and the value was assumed as the printing durability. It is evaluated that the larger this value is, the more excellent the scratch resistance is. The results are shown in the following Tables 1 and 2.

[0247]

[Table 1]

	Support		Amount of photosensitive layer applied (g/m^2) (Coating liquid)			a15 (%)	Scratch resistance (g)	Sensitivity (W)	Printing durability (Ten thousand sheets)
	Kind	Ra (μm)	Lower layer	Upper layer	Total				
Example 1	B	025	1.3 (Coating liquid 1)	0.26 (Coating liquid 2)	1.56	23	10	5	10
Example 2	B	025	0.99 (Coating liquid 1)	0.26 (Coating liquid 2)	1.25	23	10	4.5	9
Example 3	B	025	1.44 (Coating liquid 1)	0.26 (Coating liquid 2)	1.70	23	10	5.5	11
Example 4	A	0,50	1.3 (Coating liquid 1)	0.26 (Coating liquid 2)	1.56	23	10	5	10
Example 5	C	0.45	1.3 (Coating liquid 1)	0.26 (Coating liquid 2)	1.56	23	10	5	10
Example 6	A	0.50	1.3 (Coating liquid 1)	0.26 (Coating liquid 3)	1.56	15	8	5	10

(continued)

	Support		Amount of photosensitive layer applied (g/m^2) (Coating liquid)			a15 (%)	Scratch resistance (g)	Sensitivity (W)	Printing durability (Ten thousand sheets)
	Kind	Ra (μm)	Lower layer	Upper layer	Total				
Example 7	C	0.45	1.3 (Coating liquid 1)	0,26 (Coating liquid 3)	1.56	15	8	5	10
Examples 8	A	0.50	1.44 (Coating liquid 1)	0.26 (Coating liquid 3)	1.70	6	6	5.5	10
Comparative Example 1	B	0.25	0.75 (Coating liquid 1)	0.26 (Coating liquid 2)	1.01	23	10	4.5	6.0
Comparative Example 2	B	0.25	1.75 (Coating liquid 1)	0.26 (Coating liquid 2)	2.01	23	10	7	12
Comparative Example 3	B	0.25	1.3 (Coating liquid 1)	0.26 (Coating liquid 3)	1.56	1	1	5	10

[0248]

[Table 2]

	Support		Photosensitive layer		a15 (%)	Scratch resistance (g)	Sensitivity (W)	Printing durability (Ten thousand sheets)
	Kind	Ra (μm)	Coating liquid	Amount applied (g/m2)				
Example 9	B	0.25	(Coating liquid 4)	1.56	22	9	5.5	9
Example 10	B	0.25	(Coating liquid 4)	1.25	22	9	5	8
Example 11	B	0.25	(Coating liquid 4)	1.70	22	9	6	10
Example 12	A	0.50	(Coating liquid 4)	1.56	22	9	5.5	9
Example 13	C	0.45	(Coating liquid 4)	1.56	22	9	5.5	9
Example 14	A	0.50	(Coating liquid 5)	1.56	15	7	5.5	9
Example 15	C	0.45	(Coating liquid 5)	1.56	15	7	5.5	9
Example 16	A	0.50	(Coating liquid 5)	1.70	6	6	6	10
Comparative Example 4	B	0.25	(Coating liquid 5)	1.01	3.0	9	5	5.0

(continued)

	Support		Photosensitive layer		a15	Scratch resistance (g)	Sensitivity (W)	Printing durability (Ten thousand sheets)
	Kind	Ra (μm)	Coating liquid	Amount applied (g/m2)	(%)			
Comparative Example 5	B	0.25	(Coating liquid 5)	2.01	3.0	9	7.5	11
Comparative Example 6	B	0.25	(Coating liquid 5)	1.56	1	1	5.5	9

[0249] From the results in Table 1 ands 2, it has been found that the planographic printing plate precursor of the present invention, exhibit an excellent scratch resistance, sensitivity, and printing durability, even if the surface treatment conditions for the support and the prescription of the recording layer are changed. Moreover, from Examples 1 to 8 and Examples 9 to 16, it has become clear that the present invention exerts excellent effects even if the recording layer is formed of a single layer similar to the effects of the recording layer formed of multiple layers.

[0250] The present invention includes the following embodiments 1 to 13:

(1). An infrared-ray photosensitive positive-working planographic printing plate precursor, comprising a support, a positive-working recording layer provided on the support which is capable of forming an image by irradiating with an infrared-ray, and has a coating weight of the layer after drying in the range of about 1.2 g/m^2 to about 1.7 g/m^2, wherein the area of portions having a gradient of about 15 degrees or more on the surface of the recording layer is about 5% or more of the total surface area of the recording layer.

(2). The infrared-ray photosensitive positive-working planographic printing plate precursor of the above (1), wherein the recording layer contains a polymer (a) having a long chain alkyl group and a polymer (b) not mutually soluble with the polymer (a) having a long chain alkyl group.

(3). The infrared-ray photosensitive positive-working planographic printing plate precursor of the above (2), wherein the polymer (a) having a long chain alkyl group is a copolymer of a monomer having an alkyl group having 6 or more carbon atoms and a vinyl monomer having a carboxyl group.

(4). The infrared-ray photosensitive positive-working planographic printing plate precursor of the above (3), wherein the mass average molecular weight of the polymer (a) having a long chain alkyl group is about 5000 or more and the number average molecular weight is about 1000 or more.

(5). The infrared-ray photosensitive positive-working planographic printing plate precursor of the above (4), wherein the vinyl monomer having a carboxyl group is contained in the composition range of about 45 to about 99% by mole with respect to the polymer (a) having a long chain alkyl group.

(6). The infrared-ray photosensitive positive-working planographic printing plate precursor of the above (5), wherein the polymer (b) not mutually soluble with the polymer (a) having a long chain alkyl group is a resin which is water-insoluble and alkali-soluble.

(7). The infrared-ray photosensitive positive-working planographic printing plate precursor of above (6), wherein the recording layer further contains an infrared-ray absorbing agent (c).

(8). An infrared-ray photosensitive positive-working planographic printing plate precursor, comprising: a support, a recording layer formed on the support by laminating a plurality of layers, wherein a recording layer (lower layer) disposed adjacent to the support and a positive-working recording layer (top layer) disposed as the top layer among the plurality of layers contain a water-insoluble and alkali-soluble resin, at least one of the lower layer and the top layer contains an infrared-ray absorbing agent, the total weight of the plurality of layers constituting the recording layer after drying is in a range of about 1.2 g/m^2 to about 1,7 g/m^2, and the area of portions of a gradient of 15 degrees or more on the surface of the top layer is about 5% or more of the total surface layer of the top layer.

(9). The infrared-ray photosensitive positive-working planographic printing plate precursor of the above (8), wherein the recording layer contains a polymer (a) having a long chain alkyl group and a polymer (b) not mutually soluble with the polymer (a) having a long chain alkyl group.

(10). The infrared-ray photosensitive positive-working planographic printing plate precursor of the above (9), wherein the polymer (a) having a long chain alkyl group is a copolymer of a monomer having an alkyl group having 6 or more carbon atoms and a vinyl monomer having a carboxyl group.

(11). The infrared-ray photosensitive positive-working planographic printing plate precursor of the above (10), wherein the mass average molecular weight of the polymer (a) having a long chain alkyl group is about 5000 or more and the number average molecular weight is about 1000 or more.

(12). The infrared-ray photosensitive positive-working planographic printing plate precursor of the above (11), wherein the vinyl monomer having a carboxyl group is contained in the composition range of 45 to 99% by mole with respect to the polymer (a) having a long chain alkyl group.

(13). The infrared-ray photosensitive positive-working planographic printing plate precursor of the above (I2), wherein the polymer (b) not mutually soluble with the polymer (a) having a long chain alkyl group is a resin which is water-insoluble and alkali-soluble.

[0251] The present invention can provide an infrared-ray photosensitive positive-working planographic printing plate precursor capable of recording with a high sensitivity, and the sensitivity, scratch resistance, and printing durability are balanced at a high level, and the reproducibility of a minute area image such as thin lines is excellent. According to the planographic printing plate precursor of the present invention, the scratch resistance in the manufacturing and fabricating processes, and the plate making process becomes a level of substantially no problem.

Claims

1. An infrared-ray photosensitive positive-working planographic printing plate precursor, comprising: a support, a positive-working recording layer provided on the support which is capable of forming an image by irradiating with an infrared-ray, and has a coating weight of the layer after drying in the range of about 1.2 g/m^2 to about 1.7 g/m^2, wherein the area of portions having a gradient of about 15 degrees or more on the surface of the recording layer is about 5% or more of the total surface area of the recording layer.

2. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 1, wherein the recording layer contains a polymer (a) having a long chain alkyl group and a polymer (b) not mutually soluble with the polymer (a) having a long chain alkyl group.

3. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 2, wherein the polymer (a) having a long chain alkyl group is a copolymer of a monomer having an alkyl group having 6 or more carbon atoms and a vinyl monomer having a carboxyl group.

4. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 3, wherein the mass average molecular weight of the polymer (a) having a long chain alkyl group is about 5000 or more and the number average molecular weight is about 1000 or more.

5. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 4, wherein the vinyl monomer having a carboxyl group is contained in the composition range of about 45 to about 99% by mole with respect to the polymer (a) having a long chain alkyl group.

6. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 5, wherein the polymer (b) not mutually soluble with the polymer (a) having a long chain alkyl group is a resin which is water-insoluble and alkali-soluble.

7. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 6, wherein the recording layer further contains an infrared-ray absorbing agent (c).

8. An infrared-ray photosensitive positive-working planographic printing plate precursor, comprising: a support, a recording layer formed on the support by laminating a plurality of layers, wherein a recording layer (lower layer) disposed adjacent to the support and a positive-working recording layer (top layer) disposed as the top layer among the plurality of layers contain a water-insoluble and alkali-soluble resin, at least one of the lower layer and the top layer contains an infrared-ray absorbing agent, the total weight of the plurality of layers constituting the recording layer after drying is in a range of about 1.2 g/m^2 to about 1.7 g/m^2, and the area of portions of a gradient of 15 degrees or more on the surface of the top layer is about 5% or more of the total surface layer of the top layer.

9. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 8, wherein the recording layer contains a polymer (a) having a long chain alkyl group and a polymer (b) not mutually soluble with the polymer (a) having a long chain alkyl group.

10. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 9, wherein the polymer

(a) having a long chain alkyl group is a copolymer of a monomer having an alkyl group having 6 or more carbon atoms and a vinyl monomer having a carboxyl group.

11. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 10, wherein the mass average molecular weight of the polymer (a) having a long chain alkyl group is about 5000 or more and the number average molecular weight is about 1000 or more.

12. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 11, wherein the vinyl monomer having a carboxyl group is contained in the composition range of 45 to 99% by mole with respect to the polymer (a) having a long chain alkyl group.

13. The infrared-ray photosensitive positive-working planographic printing plate precursor of claim 12, wherein the polymer (b) not mutually soluble with the polymer (a) having a long chain alkyl group is a resin which is water-insoluble and alkali-soluble.

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EUROPEAN SEARCH REPORT

Application Number
EP 06 00 7901

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	EP 1 378 348 A (FUJI PHOTO FILM CO., LTD) 7 January 2004 (2004-01-07) * paragraphs [0026] - [0031] * * paragraph [0032] * * examples 2,3 * -----	1-13	INV. B41C1/10
A	EP 1 334 823 A (FUJI PHOTO FILM CO., LTD) 13 August 2003 (2003-08-13) * paragraph [0010] * * paragraph [0028] * * paragraph [0039] * * paragraph [0101] * * examples 1,2 * -----	1-13	
A	EP 1 270 258 A (FUJI PHOTO FILM CO., LTD) 2 January 2003 (2003-01-02) * paragraphs [0186], [0187] * * paragraph [0247] * -----	1-13	
			TECHNICAL FIELDS SEARCHED (IPC)
			B41C

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	15 August 2006	Martins Lopes, L

CATEGORY OF CITED DOCUMENTS

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....
& : member of the same patent family, corresponding document

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EP 06 00 7901

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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15-08-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1378348 A	07-01-2004	CN 1470939 A US 2004131966 A1	28-01-2004 08-07-2004
EP 1334823 A	13-08-2003	US 2003207203 A1	06-11-2003
EP 1270258 A	02-01-2003	CN 1394171 A WO 0234544 A1 US 2003145748 A1	29-01-2003 02-05-2002 07-08-2003

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2004258490 A **[0009] [0030] [0048]**
- US 3628953 A **[0054]**
- US 4708925 A **[0054] [0134]**
- JP 7285275 A **[0054]**
- WO 9739894 A **[0054]**
- JP 11044956 A **[0054]**
- JP 11268512 A **[0054]**
- JP 2001324808 A **[0054]**
- JP 58125246 A **[0085]**
- JP 59084356 A **[0085]**
- JP 59202829 A **[0085]**
- JP 60078787 A **[0085]**
- JP 58173696 A **[0085]**
- JP 58181690 A **[0085]**
- JP 58194595 A **[0085]**
- JP 58112793 A **[0085]**
- JP 58224793 A **[0085]**
- JP 59048187 A **[0085]**
- JP 59073996 A **[0085]**
- JP 60052940 A **[0085]**
- JP 60063744 A **[0085]**
- JP 58112792 A **[0085]**
- GB 434875 A **[0085]**
- US 5156938 A **[0086]**
- US 3881924 A **[0086]**
- JP 57142645 A **[0086]**
- US 4327169 A **[0086]**
- JP 58181051 A **[0086]**
- JP 58220143 A **[0086]**
- JP 59041363 A **[0086]**
- JP 59084248 A **[0086]**
- JP 59084249 A **[0086]**
- JP 59146063 A **[0086]**
- JP 59014606 A **[0086]**
- JP 59216146 A **[0086]**
- US 4283475 A **[0086]**
- JP 5013514 B **[0086]**
- JP 5019702 B **[0086]**
- US 4756993 A **[0087]**
- JP 2001133969 A **[0101]**
- JP 2002040638 A **[0101]**
- JP 2002023360 A **[0101]**
- JP 2001242613 A **[0117]**
- JP 2002097384 A **[0117]**
- US 6124425 A **[0117]**
- US 6248893 B **[0117]**
- JP 2001347765 A **[0117]**
- JP 9171254 A **[0128] [0130]**
- JP 10055067 A **[0128] [0130]**
- JP 10087733 A **[0128] [0130]**
- JP 10268507 A **[0128] [0130]**
- JP 48089603 A **[0130]**
- JP 51120714 A **[0130]**
- JP 53133429 A **[0130]**
- JP 55012995 A **[0130]**
- JP 55126236 A **[0130]**
- JP 56017345 A **[0130]**
- JP 60037549 A **[0130]**
- JP 60121446 A **[0130]**
- JP 60003625 A **[0130]**
- JP 60010247 A **[0130]**
- JP 62222246 A **[0130]**
- JP 62251743 A **[0130]**
- JP 62209451 A **[0130]**
- JP 62280841 A **[0130]**
- JP 62280842 A **[0130]**
- JP 63010153 A **[0130]**
- JP 10111564 A **[0130]**
- JP 10153853 A **[0130]**
- JP 10228102 A **[0130]**
- JP 10282648 A **[0130]**
- JP 10282670 A **[0130]**
- EP 0884547 A1 **[0130]**
- JP 62244038 A **[0130]**
- JP 7020629 A **[0134]**
- US 3867147 A **[0134]**
- US 2632703 A **[0134]**
- JP 1102456 A **[0134]**
- JP 1102457 A **[0134]**
- US 5135838 A **[0134]**
- US 5200544 A **[0134]**
- JP 2100054 A **[0134]**
- JP 2100055 A **[0134]**
- JP 9197671 A **[0134]**
- JP 7271029 A **[0134]**
- US 4113128 A **[0138]**
- JP 60088942 A **[0139]**
- JP 2096755 A **[0139]**
- JP 50036209 A **[0142]**
- JP 53036223 A **[0142]**
- JP 55062444 A **[0142]**
- JP 55077742 A **[0142]**
- JP 622932471 A **[0147]**
- JP 2969021 B **[0147]**
- JP 62251740 A **[0150]**
- JP 4068355 A **[0150]**
- JP 59121044 A **[0150]**
- JP 4013149 A **[0150]**

- JP 62170950 A **[0152]**
- JP 2002072474 A **[0152]**
- US 2714066 A **[0166] [0173]**
- US 3181461 A **[0166] [0173]**
- US 3658662 A **[0167]**
- JP 54031187 A **[0169]**
- JP 55137993 A **[0169]**
- GB 1412768 A **[0173]**
- US 3511661 A **[0173]**
- JP 3622063 B **[0173]**
- US 4153461 A **[0173]**
- JP 2000010292 A **[0177]**
- JP 2000108538 A **[0177]**
- JP 5045885 A **[0182]**
- JP 6035174 A **[0182]**
- JP 8305039 A **[0185]**

Non-patent literature cited in the description

- DYE HANDBOOK. 1970 **[0084]**
- Color Index (C.I.) Handbook. Latest Pigment Handbook. Japanese Pigment Technological Society, 1977 **[0118]**
- Latest Pigment Applied Technology. CMC Publishing Co., Ltd, 1986 **[0118] [0120] [0122]**
- Printing Ink Technology. CMC Publishing Co., Ltd, 1984 **[0118]**
- Nature and Application of Metal Soaps. Printing Ink Technology. CMC Publishing Co., Ltd, 1984 **[0120]**