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(54) Planographic printing plate precursor and stack thereof

(57) The invention provides a planographic printing plate precursor having at least a photosensitive layer that has sensitivity to laser light and is provided on or above a surface of a support, wherein an average surface roughness (Ra) of a back surface of the support in both of a longitudinal direction and a width direction is 0.15 μm or less. The Ra is preferably from 0.13 μm or less. The support preferably comprises aluminum. A Bekk smoothness of a surface of the planographic printing plate precursor that has sensitivity to laser light is preferably 10,000 seconds or less. The invention further provides a stack having at least a plurality of the planographic printing plate precursors.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a planographic printing plate precursor and a stack thereof. More specifically, it relates to a planographic printing plate precursor that is capable of direct image formation by irradiation of laser, is applicable to high speed processing, and is preferably used as a negative planographic printing plate precursor.

Description of Related Art

[0002] Conventionally, a PS plate having a lipophilic photosensitive resin layer provided on a hydrophilic support has been used widely as a planographic printing plate precursor, and a desired printing plate is obtained by a plate-making method which usually involves masked light exposure (surface light exposure) via a lithographic film and then removing a non-image area by dissolution. In recent years, digitalization techniques which involve electronic processing, accumulation and output of image information with a computer are spreading. A wide variety of new image output systems compatible with these digitalization techniques have come to be used in practice. As a result, there has been demand for computer-to-plate (CTP) techniques for producing a printing plate directly by scanning a highly directional light such as a laser light according to digitalized image information without a lithographic film, and the provision of a planographic printing plate precursor adapted to these techniques has proved a significant technical challenge.

[0003] A planographic printing plate precursorhaving a configuration in which a lipophilic photosensitive resin layer (hereinafter referred to as a "photosensitive layer"), containing a photosensitive composition that can generate active species such as radicals or Brønsted acids by layer exposure is provided on a hydrophilic support, has been proposed as a planographic printing plate precursor configured to be subjected to scanning exposure, and is already commercially available. A negative planographic printing plate precursor can be obtained by laser scanning such a planographic printing plate precursor on the basis of digital information and generating the active species, thus subjecting the photosensitive layer to a physical or a chemical change caused therein by the active species to become insolubilized, and subsequent development processing.

Particularly preferable printing performance can be obtained by a planographic printing plate precursor (such as that described in JP-A No. 10-228109) which is formed by providing, on the hydrophilic support, a photopolymerizable photosensitive layer containing a photopolymerizable initiator exhibiting an excellent photosensitive speed, an ethylenic unsaturated compound capable of addition polymerization, a binder polymer soluble in alkali developer, and a protective layer which has an oxygen blocking property and can be provided as needed to the precursor, since this precursor exhibits excellent productivity, easy developing processability, and good resolution and ink adherence.

[0004] In view of further improving the productivity, that is, to improve plate-making speed, a recording material which uses a photopolymerizable composition composed of a cyanine pigment having a specific structure, an iodonium salt, and an addition polymerizable compound having an ethylenic unsaturated double bond in the photosensitive layer and that does not require a heating process after the imagewise exposure process has been proposed (see, for example, Japanese Patent Application Publication (JP-B) No. 7-103171). However, this printing material has the problem that polymerization is inhibited due to oxygen in the air at the time of a polymerization reaction, causing deterioration in sensitivity and insufficient strength of formed images.

To solve such problems, a method of providing a protective layer containing a water-soluble polymer on a photosensitive layer, or a method of providing a protective layer containing an inorganic layered compound and a water-soluble polymer have been proposed (see, for example, JP-A No. 11-38633). As a result of the presence of such protective layers, polymerization inhibition can be prevented, the curing reaction of the photosensitive layer can be promoted, and the strength of an image portion can be improved.

[0005] On the other hand, reduction of the time required for an exposing process is an important factor to the productivity of the plate-making process of a photopolymerizable planographic printing plate precursor that exhibits simple developing processability.

In the exposing process, a planographic printing plate precursor is typically provided as a stack including ’interleaving sheets’ that serve to prevent adhesion between plates or scratches caused when the relatively soft surface of the protecting layer is contacted with an aluminum support between plates, but the time taken to remove these interleaving sheets in the exposure process has been the cause of inefficiency in the plate-making process. In order to improve the efficiency of the exposure process, it has been necessary to eliminate the interleaving sheet removal process by using a stack that does not have the interleaving sheets interposed between the plates. However, when a stack that does not have the interleaving sheets interposed is used, there are the problems that the surface of the protective layer provided on the photosensitive layer is contacted with a back surface of the aluminum support causing scratches. Thus, further improvement is necessary.

[0006] As described above, there has been a need for a planographic printing plate precursor, which even when plural planographic printing plate precursors are stacked with no interleaf sheets, is excellent in preventing adhesion between planographic printing plate precursors, and capable of suppressing occurrence of scratches on surfaces of printing plates caused by abrasion between a photosensitive layer side surface and a back surface of a support during manufacturing, storage and plate making. However, such a planographic printing plate precursor has not yet been provided.

SUMMARY OF THE INVENTION

[0007] The present invention has been made in view of the circumstances described above.

That is, the invention provides a planographic printing plate precursor and a stack thereof which can reduce scratches generated between a surface of a photosensitive layer or a protective layer and a back surface of an aluminum support even when the planographic printing plate precursor is laminated without interposing an interleaf paper therebetween.

[0008] The inventors found that the problems described above can be solved by controlling a surface roughness of the back surface of the support and thus accomplished the invention.

Namely, a first aspect of the invention is to provide a planographic printing plate precursor comprising a photosensitive layer that has sensitivity to laser light and is provided on or above a surface of a support, wherein an average surface roughness (Ra) of a back surface of the support in both of a longitudinal direction and a width direction is 0.15 μm or less.

A second aspect of the invention is to provide a stack of planographic printing plate precursors comprising a plurality of the planographic printing plate precursors of the first aspect of the invention, wherein each of the planographic printing plate precursors directly contacts with an adjacent planographic printing plate precursor at an uppermost layer thereof and at the back surface of the support.

BRIEF DESCRIPTION OF DRAWINGS

[0009]

Fig. 1 is a perspective view of an embodiment according to the first aspect of the planographic printing plate precursor of the invention.

Fig. 2 is a conceptual view for explaining the longitudinal direction and the width direction of the planographic printing plate precursor.

Fig. 3 is a flowchart showing an example of a process for manufacturing the planographic printing plate precursor of the invention.

Fig. 4 is a schematic diagram showing an example of an apparatus used in a process for manufacturing the planographic printing plate precursor of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The planographic printing plate precursor according to the present invention has at least a photosensitive layer that has sensitivity to laser light and is provided on or above a surface of a support. An average surface roughness (Ra) of a back surface of the support in both of a longitudinal direction and a width direction is 0.15 μm or less.

Details of the support, the back surface of the support and the photosensitive layer are explained hereinafter.

Support

[0011] Conventionally-known hydrophilic supports which can be used for planographic printing plate precursors can be used as the support of the planographic printing plate precursor of the invention without any limitation.

The support is preferably a dimensionally stable plate shape material, and examples thereof include paper, paper laminated with plastic (such as polyethylene, polypropylene, or polystyrene), metal plates (such as those formed of aluminum, zinc, or copper), plastic films ((such as those formed of cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, or polyvinyl acetal) and paper or plastic films having the above-described metal laminated or vapor-deposited thereon. If necessary, the surface of the support may be subjected to an appropriate known physical or chemical treatment for the purpose of imparting hydrophilicity, improving the strength or the like.

[0012] Among these, preferable examples of the support include paper, polyester film, and aluminum plate. In particular, the aluminum plate is more preferable, because it has good dimensional stability, is relatively inexpensive, and can provide a surface having excellent hydrophilicity and strength by being subjected to a surface treatment as needed. Preferable examples of the support further include a composite sheet such as that described in JP-B No. 48-18327, which has a polyethylene terephthalate film and an aluminum sheet bonded thereon.

[0013] The "aluminum plate" is a metal plate that contains at least aluminum as a primary component thereof and exhibits the dimensional stability. The aluminum plate can be selected from: a pure aluminum plate, an alloy plate containing aluminum as a primary component thereof and a trace amount of foreign elemnts; a plastic film laminated or vapor-deposited with aluminum; and a paper laminated or vapor-deposited with aluminum. Hereinafter, the above-described supports containing aluminum or aluminum alloy is referred to as the aluminum support.

Examples of the foreign element which may be contained in the aluminum alloy include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, and titanium. The foreign elemnt content in the alloy is preferably 10 mass% or less. While an aluminum support formed of pure aluminum is particularly preferable in the invention, since it is difficult to produce perfectly pure aluminum in view of the refining technique, the aluminum used in the aluminum support used in the invention may have trace amount of foreign elemnts. The composition of the aluminum plate used in the invention is not specified, and conventionally known aluminum plates in common use can be appropriately used.

The thickness of the aluminum plate used in the invention is approximately in a range of 0.1 to 0.6 mm. The thickness may be appropriately changed depending on a size of a printer, a size of a printing plate, and a user's desire. The aluminum support may be subjected to a support surface treatment described below as needed.

Rear Surface of Support

[0014] The planographic printing plate precursor of the invention is required to have an average surface roughness Ra in a longitudinal direction and a width direction of the back surface of the support of 0.15 μm or less from the viewpoint of reducing scratches generated when the surface of a protective layer is contacted with the back surface of a support. Preferably, Ra is required to be 0.13 μm or less. Here, the average surface roughness (arithmetic average roughness) (Ra) is the value obtained by the equation shown below, expressed in micron units, when a measured length L is extracted from a roughness curve measured by a stylus system in a direction of the center line, and the roughness curve is shown by y = f(x), the center line of the extracted portion being taken as the X-axis and the direction perpendicular thereto being taken as the Y-axis (determination of L and measurement of the average roughness are made according to ISO 4287: 1997).

[0015]

$$Ra = \frac{1}{L}\int_0^L |f(X)|dX$$

[0016]

Fig. 1 is a perspective view according to a first aspect of a planographic printing plate precursor of the invention. The planographic printing plate precursor 10 includes a support 12 and a direct-writing photosensitive layer 14 formed on a surface 12a of the support 12. A back surface 12b of the support 12 may have the same average surface roughness Ra or a different average roughness (Ra) in the longitudinal direction (arrow x in the drawing) and in the width direction (arrow y in the drawing). The average surface roughness in the width direction is denoted by Ral and the average surface roughness in the longitudinal direction is denoted by Ras.

Fig. 2 is a perspective view of the planographic printing plate precursor in a state in which the plate is wound in a roll shape for cutting, so as to further describe the longitudinal direction and the width direction of the planographic printing plate precursor. After the planographic printing plate precursor 10 is manufactured in a web shape through the process described below, typically, the plate is temporarily stored in a state 10' in which the plate is wound in the roll shape shown in Fig. 2 and then cut to a desired length in the longitudinal direction, thereby manufacturing the plate. In the planographic printing plate precursor 10, the back surface 12b of the support 12 may have the same or different average surface roughness (Ra) in the longitudinal direction and the width direction,

Fig. 3 is a flowchart showing an example of a general manufacturing process for making the planographic printing plate precursor 10. The manufacturing process shown in Fig. 3 illustrates an example in which an aluminum alloy plate is used as the support. In addition, for the sake of straightforward explanation, the description of the process is simplified.

Manufacturing method of Planographic printing plate precursor Cleaning treatment of Molten aluminum

[0017] Firstly, a molten aluminum alloy is subjected to a cleaning treatment to remove unnecessary gases such as hydrogen or solid impurities that contaminate the molten aluminum. Examples of the cleaning treatment for removing the unnecessary gas include a flux treatment and a degassing treatment using argon gas, chlorine gas or the like. Examples of the cleaning treatment for removing solid impurities include a filtering treatment using: a so-called rigid media filter (such as a ceramic tube filter or a ceramic foam filter); a filter employing an alumina flake or an alumina ball as a filter medium; or a glass cloth filter. Further, a cleaning treatment, in which the degassing treatment and the filtering treatment are combined, can also be employed.

Casting of Molten Aluminum

[0018] Then, the molten aluminum is subjected to casting. Examples of the casting method include a casting method using a stationary mold (typical examples thereof include a DC casting method) and a casting method using a movable mold (typical examples thereof include a continuous casting method). For example, in the case of a DC casting method, a cast ingot having a predetermined thickness (such as in a range of 300 mm to 800 mm) is manufactured by using a stationary mold. The ingot thus obtained is subjected to a facing treatment and a surface layer is cut to a depth of 1 to 30 mm, and preferably to a depth of 1 to 10 mm in accordance with a normal method, thereby obtaining an aluminum alloy plate having a desired plate thickness. In case of continuous casting, the molten aluminum alloy is inserted between one pair of a twin-belt and passes therebetween so as to continuously obtain an aluminum alloy plate-shaped body having a predetermined plate thickness. The plate-shaped body thus obtained may be subjected to a soaking treatment as needed. When the soaking treatment is performed, the heating treatment is preferably performed at a temperature of from 450 to 620°C for 1 to 48 hours so as not to generate enlarged intermetallic compounds. When the period of the heating treatment is less than one hour, the effect of the soaking treatment may be insufficient.

Hot Rolling Treatment, Cold Rolling Treatment, and Adjustment of Surface Roughness of Rear Surface of Support

[0019] Subsequently, the plate-shaped body is subjected to hot rolling and to cold rolling to form a rolled aluminum alloy plate. The rolling treatment of the plate-shaped body may be performed by inserting the plate-shaped body between a pair of rolls. The starting temperature of the hot rolling is preferably in a range of 350 to 500°C. An intermediate annealing treatment may be performed before or after the cold rolling or in the middle of the cold rolling. The intermediate annealing treatment can be performed under heating conditions of 280 to 600°C in temperature for 2 to 20 hours, and preferably 350 to 500°C for 2 to 10 hours, when a batch type annealing furnace is employed, or under heating conditions of 400 to 600°C in temperature for 360 seconds or less, and preferably 450 to 550°C in temperature for 120 seconds or less, when a continuous annealing furnace is employed. Since it is also possible to make the crystal structure of the aluminum plate fine by heating the aluminum plate at a heating rate of 10°C/sec or more by the use of the continuous annealing furnace, this is preferable. After the hot rolling treatment, the intermediate annealing treatment and the cold rolling treatment may be performed if desired to finally produce an aluminum alloy plate having a thickness of 0.1 to 0.5 mm. When the aluminum alloy plate thus obtained is processed again by the use of a correcting device such as a roller leveler or tension leveler, since the flatness of the aluminum plate is improved, this is preferable. When it is necessary to provide the plate having a predetermined width, the aluminum plate is passed through a slitter line so as to be adjusted to a predetermined width.

[0020] In the cold rolling process, the average surface roughness Ra of the back surface of the aluminum alloy plate can be set to 0.15 μm or less by transferring a pattern of the rolling roll onto the back surface of the aluminum alloy plate,. Alternatively, in the correcting process, the pattern may be transferred onto the back surface of the support by using a roll having a predetermined surface roughness pattern so as to achieve the average surface roughness Ra of the back surface of the aluminum alloy plate of 0.15 μm or less. When the back surface is made to have the predetermined average surface roughness, extra processes for adjusting the surface roughness of the back surface of the support may not be required, so that the process can be simplicated and thus it is preferable. The back surface of the support may be subjected to cold rolling by using a roll having a surface roughness in the rotation direction of the roll which is different from a surface roughness in the direction perpendicular to the rotation direction of the roll so that the support is provided with the back surface having an average surface roughness in the longitudinal direction which is different from that in the width direction.

Surface-Roughening Treatment of Surface of Support

[0021] The surface of the aluminum alloy plate thus having the predetermined average surface roughness on its back surface in the cold rolling process or correcting process (nameyly, the surface on which the photosensitive layer is formed) is then subjected to a surface-roughening treatment. Examples of the surface-roughening treatment include a mechanical surface-roughening treatment, a chemical surface-roughening treatment, and an electrochemical surface-roughening treatment. These treatments may be performed singly or in combination of two or more thereof. For example, after performing the mechanical surface-roughening treatment by using a brush or the like, the electrochemical surface-roughening treatment may be performed. Examples of the mechanical surface-roughening treatment include a ball graining method, a wire graining method, brushing graining method, and a liquid honing method. In addition, for example, mechanical surface-roughening treatments described in JP-A No. 6-135175 and JP-B No. 50-40047 may be employed.

By performing the mechanical surface-roughening treatment, the surface of the aluminum alloy plate can be typically adjusted to have an average surface roughness (Ra) of 0.35 to 1.0 μm. Examples of the chemical surface-roughening treatment include a method in which the aluminum alloy plate is dipped in an alkali solution.

[0022] The electrochemical surface-roughening treatment is advantageous because fine irregularities can be easily formed on the surface of the aluminum alloy plate so that adhesion between the photosensitive layer 14 and the support 12 can be improved. The electrochemical surface-roughening treatment is typically conducted by passing direct current or alternate current on the aluminum alloy plate using acids such as nitric acid or hydrochloric acid as an electrolyte. By performing the electrochemical surface-roughening treatment, it becomes possible to provide craters or honeycomb pits having an average diameter of 0.5 to 20 μm at an area ratio (surface coverage ratio) of 30 to 100% with respect to the area of the surface of the aluminum alloy plate. The pits thus formed serve both to reduce scumming on a non-image area and to improve printing durability of a planographic printing plate formed of the aluminum alloy plate. In the electrochemical treatment, a multiplication between the amount of the current and the current passing time at the time of the electrolysis is set so that shapes of the pits thus formed and the area ratio of the pits can be adjusted.

[0023] An etching treatment using an alkali agent such as caustic soda or caustic potash may be performed onto the surface of the aluminum alloy plate before or after the surface-roughening treatment. When the etching treatment is performed, there may be performed a desmut treatment using acids which removes smut (substances insoluble in alkali), which is remained on the surface of the aluminum plate after the etching treatment. Particularly, when the electrochemical surface-roughening treatment is performed, it is preferable to perform the etching treatment and the desmut treatment before and/or after the surface-roughening treatment.

Anodic oxidation treatment

[0024] After performing the surface-roughening treatment onto the surface of the aluminum alloy plate, it is preferable to additionally perform an anodic oxidation treatment. When, the anodic oxidation treatment is performed, an anodic oxide film can be formed on the surface of the aluminum alloy plate and abrasion resistance can be improved so that it is preferable. The anodic oxide film can be formed by using the aluminum alloy plate as electrodes, dipping the plate in the electrolytic solution, and then applying current thereon. The current can be selected among various kinds of waves of current such as direct current or alternating current depending on purposes. Any electrolytic solution may be used as long as it forms a porous oxide film on the surface of the aluminum alloy plate. In general, a sulfuric acid, a phosphoric acid, an oxalic acid, a chromic acid, or a mixture thereof can be used. The concentration of the electrolyte in the electrolytic solution can be appropriately determined depending on the kinds of the electrolyte. While the conditions such as the concentration of the electrolyte in the electrolytic solution and the time length for electrolysis may vary according to the electrolyte used, it is generally preferable that the concentration of the electrolyte is in a range of about 1 to 80 mass%, the liquid temperature is in a range of about 5 to 70°C, the current density is in a range of about 1 to 60 A/dm^2, the voltage is in a range of about 1 to 100 V, and the electrolysis time is in a range of about 10 seconds to 300 seconds. It is preferable that the amount of the anodic oxide film formed by the anodic oxidation treatment is typically in a range of 1 to 6 g/m^2.

[0025] When the anodic oxidation treatment is performed on the surface of the aluminum alloy plate (the surface on which the photosensitive layer is formed), it is preferable to also perform the anodic oxidation treatment on the back surface thereof. When the anodic oxide film is formed on the back surface, it becomes more difficult for scratches to be formed on the back surface. Thus, scratches on the back surface are prevented from being transferred onto the photosensitive layer when the planographic printing plate precursor is stored in a state in which it is overlapped and wound on a roll. In addition, when the anodic oxide film is formed, the hardness of the back surface of the support is improved. Thus, even when the friction force between the conveying belt and the conveying roll is applied to the back surface, generation of abrasive remnants and the like can be prevented. The anodic oxidation treatment performed on the surface and the back surface of the aluminum alloy plate can be conducted by using, for example, an apparatus as shown in Fig. 4. The apparatus used for the anodic oxidation treatment 20 shown in Fig. 4 includes a power supplying unit 22 and an electrolyte processing vessel 24. In the power supplying unit 22, the electrolytic solution 26 is charged and a power supplying electrode 28 is positioned so as to oppose the surface on which the photosensitive layer is formed on the aluminum alloy plate 30 that will be conveyed thereby. On the other hand, in the electrolyte processing vessel 24, the electrolytic solution 32 is charged and an electrolyte electrode 34 is positioned so as to respectively oppose the surface on which the photosensitive layer is formed and the back surface of the aluminum alloy plate that will be conveyed thereby. The aluminum alloy plate 30 passes the power supplying unit 22 and the electrolyte processing vessel 24 by the use of the conveying roller 36 and the anodic oxide film is formed on the side on which the photosensitive layer is formed and the back surface of the aluminum alloy plate 30.

[0026] The amount of the anodic oxide film formed on the back surface of the aluminum alloy plate is preferably 0.1 g/m^2 or more, and is more preferably 0.5 g/m^2 or more. When the amount of the oxide film is less than 0.1 g/m^2, an effect for improving strength of the back surface may not be obtained. On the other hand, while there are no particular upper limitations, the amount of the anodic oxide film formed on the back surface of the aluminum alloy plate is preferably 4 g/m^2 or less from the viewpoint of the effect for improving the strength and production cost.

[0027] After the anodic oxidation treatment, a sealing treatment may be preformed if desired. The sealing treatment is performed by a method in which the anodic oxidized support is dipped in a hot water or a hot aqueous solution containing an inorganic salt or an organic salt or a method in which the support is exposed to a vapor.

[0028] In addition, after the anodic oxidation treatment is performed, a surface control treatment such as a hydrophilizing treatment may be performed, if desired. Examples of the surface control treatment include a method using an alkali metal silicate (for example, aqueous sodium silicate solution) such as those described in U.S. Patent Nos. 2,714,066, 3,181,461, 3,280,734 and 3,902,734. In this method, the support is dipped in an aqueous sodium silicate solution, or is electrolyzed. Besides the above treatment, methods in which the support is treated with potassium fluorozirconate as disclosed in the publication of JP-B No. 36-22063 and a method in which the support is treated with polyvinylphosphonic acid as disclosed in U.S. Pat. Nos. 3,276,868, 4,153,461 and 4,689,272 are used.

Coating and Drying of Coating Liquid for Photosensitive layer and Cutting

[0029] Next, the photosensitive layer 14 is formed on the support 12, the back surface 12b of which has been roughened with a predetermined average surface roughness and the surface 12a of which has been subjected to the surface-roughening treatment and the anodic oxidation treatment. The photosensitive layer 14 can be formed by coating a coating liquid prepared by dissolving or dispersing each components of the photosensitive layer on the surface 12a of the support 12, and then drying the liquid. Examples of the coating method include bar coater coating, rotation coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, roll coating, and the like. By appropriately repeating the coating process, a photosensitive layer having a multi layered structure can be formed. In addition, a plurality of photosensitive layers may be formed by simultaneous coating.

After the photosensitive layer 14 is formed, the resultant is wound in the roll shape as shown in Fig. 2 and then cut in a desired size.

Photosensitive layer

[0030] The planographic printing plate precursor of the invention has a photosensitive layer which exhibits sensitivity to laser light. The photosensitive layer preferably includes (A) a binder polymer, (B) a compound having an ethylenic unsaturated double bond capable of additional polymerization, (C) a photo- or thermal-polymerization initiator, (D) a sensitizing dye, and (E) other components. Details of these will be described below.

[0031]

(A) Binder polymer

While conventionally-known polymers may be used as the (A) binder polymer used in the photosensitive layer in the invention (hereinafter, appropriately referred to as component (A)') without limitations, a binder polymer having a film property is preferably usd in the invention. Examples of the binder polymer include acryl resins, polyvinyl acetal resins, polyurethane resins, polyurea resins, polyimide resins, polyamide resins, epoxy resins, methacrylic resins, polystyrene resins, novolac phenol resins, polyester resins, synthetic rubbers, natural rubbers and the like. The binder polymer may have a cross-linking property for the purpose of improving the film strength of an image portion to be formed in the photosensitive layer. In order to provide the cross-linking property to the binder polymer, a cross-linking functional group such as the ethylenic unsaturated bond may be introduced in a main chain or a side chain of the polymer. The cross-linking functional group may be introduced to the binder polymer by copolymerization.

[0032] From the viewpoint of alkali solubility, the binder polymer preferably includes an acid group having an acid dissociation constant (pKa) of from 0 to 11 represented by the following Formula (1) in a side chain of the binder polymer.

[0033]

Formula (1) $P\text{-}X\text{-}(A\text{-}H)_m$

[0034] In Formula (1), P represents a main chain skeleton of a polymer. X represents a single bond directly bonded to the main chain skeleton skeleton of the polymer, or a linking selected from the group consisting of a carboxyl acid ester group (-COO-), an amide group (-CONH-), a hydrocarbon group, and an ether group (-O- or -S-).

A-H represents a partial structure that serves as an acid group having an acid dissociation constant (pKa) of from 0 to 11. m denotes an integer of from 1 to 5.

Hereinafter, an acid group having an acid dissociation constant (pKa) of 0 or more to less than 5.5 and an acid group having an acid dissociation constant (pKa) of 5.5 or more to 11 or less will be described.

1. Acid group having acid dissociation constant (pKa) of 0 or more to less than 5.5

[0035] The acid group having an acid dissociation constant (pKa) of 0 or more to less than 5.5 that may be contained in the alkali-soluble binder polymer in the invention will be described. Examples of the acid group having an acid dissociation constant (pKa) of 0 or more to less than 5.5 includes a sulfonic acid group, a phosphoric acid group, and a carboxyl group. Specially preferable is a carboxyl group. Specific examples of the carboxyl group-having structure include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, maleic acid, and p-carboxystyrene. Particularly preferable examples thereof include acrylic acid, methacrylic acid, and p-carboxystyrene. One or more of these may be employed herein.

2. Acid group having acid dissociation constant (pKa) of 5.5 or more to 11 or less

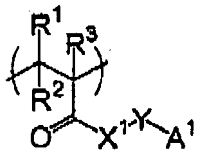
[0036] The acid group having an acid dissociation constant (pKa) of 5.5 or more to 11 or less that may be contained in the alkali-soluble binder polymer in the invention will be described. Its pKa is preferably from 7 to 11, and is more preferably from 8 to 11. Specific examples of the acid group include a phenol group (pKa= 9.99), a 2-methoxyphenol group (pKa = 9.99), a 2-chlorophenol group (pKa = 8.55), a methyl 2-hydroxybenzoate group (pKa = 9.87), a 4-methylphenol group (pKa=10.28), a 1,3-benzenediol group (pKa = 9.20), a 1-naphthol group (pKa = 9.30), a 1,2-benzenediol group (pKa = 9.45), a benzenesulfonamido group (pKa = 10.00), a N-acetylphenylbenxenesulfonamida group (pKa = 6.94), a 4-aminobenzenesulfonamido group (pKa = 10.58), a N-phenyl-4-aminobenzenesulfonamido group (pKa = 6.30), a N-(4-acetylphenyl)-4-aminobenzenesulfonamido group (pKa = 7.61), and an ethyl acetylacetate group (pKa = 10.68). Among these, more preferable are phenol groups which may be substituted on an aromatic group thereof, and benzenesulfonamido groups which may be substituted on an aromatic group thereof.

[0037] The data of the acid dissociation constant pKa of the above-described specific examples are those described in "Ionization Constants of Organic Acids in Aqueous Solution" written by E. P. Serjeant et al. and "Lange's Handbook of Chemistry" written by John A. Dean.

[0038] Preferable exaples of the structural unit that has the specific acid group include those represented by the following Formula (2):

[0039]

Formula (2)



[0040] In Formula (2), X^1 represents O, S or $-NR^4-$.

Y represents a divalent organic group.

A^1 represents the specific acid group.

R^1, R^2, R^3, and R^4 each independently represents a hydrogen atom, a halogen atom, a monovalent organic group, a cyano group, or a nitro group.

[0041] In Formula (2), examples of the monovalent organic group represented by R1, R^2, R^3, or R^4 include a straight chain- branched- or cyclic-alkyl group, an aromatic group, an alkoxy group, an acyl group, an aralkyl group, an alkoxycarbonyl group, and an aryloxy group.

The monovalent organic group may be further substituted. Examples of the substituent that may be introduced into the monovalent organic group include an alkyl group, an aryl group, an alkoxy group, an acyloxy group, a halogen atom, a hydroxyl group, an amino group, a cyano group, and a nitro group.

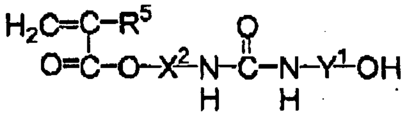
[0042] In Formula (2), examples of the divalent organic group represented by Y include an alkylene group, a phenylene group, and a naphthylene group.

The divalent organic group may be further substituted. Examples of the substituent that may be introduced into the divalent organic group include an alkyl group, an aryl group, an alkoxy group, an acyloxy group, a halogen atom, a hydroxyl group, an amino group, a cyano group, and a nitro group.

[0043] As for the structural unit that has the specific acid group, also prefered are those derived from the monomers represented by the following Formula (3), (6) or (7) and those represented by the following Formula (4), (5) or (8).

[0044]

Formula (3)

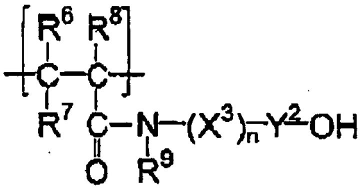


$$H_2C=C(R^5)-C(=O)-O-X^2-NH-C(=O)-NH-Y^1-OH$$

[0045] In Formula (3), R^5 represents a hydrogen atom or an alkyl group.
X^2 represents a divalent linking group.
Y1 represents a divalent aromatic group which may be substituted.
In Formula (3), examples of the divalent linking group represented by X^2 include an alkylene group which may be substituted or a phenylene group which may be substituted.
Examples of the divalent aromatic group represented by Y^1 include a phenylene group which may be substituted or a naphthylene group which may be substituted.

[0046]

Formula (4)

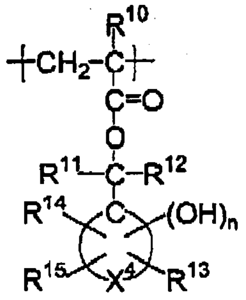


[0047] In Formula (4), R^6 and R7 each independently represents a hydrogen atom, an alkyl group, or a carboxyl group.
R^8 represents a hydrogen atom, a halogen atom, or an alkyl group.
R^9 represents a hydrogen atom, an alkyl group, a phenyl group, or an aralkyl group,
X^3 represents a divalent organic group that links the nitrogen atom to the carbon atom of an aromatic ring in Y^2.
N denotes 0 or 1.
Y^2 represents a phenylene group which may be substituted or a naphthylene group which may be substituted.

[0048] In the structural unit of Formula (4), Y^2 is a phenylene group which may be substituted or a naphthylene group which may be substituted. Variation of the substituent for the group rarely provides a significant influence on the properties of the polymerizable composition of the invention. Therefore, any substituents can be used as the substituent of the structural unit. Specific examples of the substituent include an alkyl group, an alkoxy group, a halogen atom, an acyl group, a hydroxyl group, a carboxyl group, a sulfonic acid group, a cyano group, and a nitro group.

[0049]

Formula (5)



[0050] In Formula (5), R^{10} represents a hydrogen atom, a halogen atom, a cyano group, or an alkyl group.
R^{11} to R^{15} each independently represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, or an aryl

group.

X^4 represents an atomic group necessary for completing a monocyclic- or polycyclic-carbon-cyclic aromatic ring system.

n denotes 1, 2 or 3.

[0051] In the structural unit of Formula (5), R^{10} is preferably a hydrogen atom, a halogen atom, a cyano group, or an alkyl group having 1 to 6 carbon atoms; R^{11} and R^{12} each independently preferably represent a hydrogen atom, or an alkyl group having 1 to 4 carbon atoms; R^{13}, R^{14}, and R^{15} each independently preferably represent a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, or a halogen atom; X^4 is preferably carbon atoms necessary for completing a benzene ring or a naphthalene ring; and n is preferably 1.

[0052] In the structural unit of Formula (5), R^{10} is more preferably a hydrogen atom or a methyl group; R^{11}, R^{12}, and R^{13} are more preferably hydrogen atoms; R^{14} is more preferably a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, or a halogen atom; R^{15} is more preferably a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, an aryl group, or a halogen atom; X^4 is more preferably carbon atoms necessary for completing a benzene ring or a naphthalene ring; and n is more preferably 1.

[0053] When R^{10} in Formula (5) is an alkyl group, it preferably has 1 to 6 carbon atoms, and more preferably has 1 or 2 carbon atoms. Particularly preferably, R^{10} is a hydrogen atom or a methyl group.

In Formula (5), at least one of R^{11} and R^{12} is preferably a hydrogen atom. When at least one of R^{11} and R^{12} is an alkyl group, the alkyl group preferably has 1 to 6 carbon atoms, and more preferably has 1 to 3 carbon atoms.

[0054] In Formula (5), R^{13} is preferably a hydrogen atom. R^{14} is preferably an alkyl group having 1 to 4 carbon atoms, and is more preferably a methyl group. R^{15} is preferably an alkyl group having 1 to 4 carbon atoms, or an aryl group.

In general, the "alkyl group" as referred to herein is meant to indicate a cyclic or open-chain, branched or unbranched, saturated or unsaturated group that may be substituted with a halogen atom or a hydroxyl group and may contain an ether group or a ketone group. Preferably, it is an unbranched alkyl group having 1 to 4 carbon atoms. The aryl group may be a monocyclic or polycyclic, heterocyclic or carbon-cyclic aromatic ring system that may be substituted with an aryl group, an alkoxy group, a hydroxy group or a halogen atom.

[0055] The position of the substituent on the ring X^4 is not specifically limited, and it depends on only the easiness in producing the compounds.

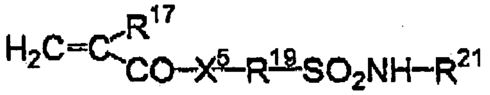
The carbon-cyclic aromatic ring system X^4 may be monocyclic or polycyclic.

Specific examples of the carbon-cyclic ring system include benzenes and naphthalenes.

[0056] The halogen atom in Formula (5) is preferably a chlorine atom, a bromine atom or an iodine atom, and is particularly preferably a chlorine atom.

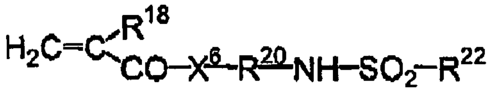
[0057]

Formula (6)



$$H_2C{=}C\begin{smallmatrix}\nearrow R^{17}\\ \searrow CO-X^5-R^{19}-SO_2NH-R^{21}\end{smallmatrix}$$

Formula (7)



$$H_2C{=}C\begin{smallmatrix}\nearrow R^{18}\\ \searrow CO-X^6-R^{20}-NH-SO_2-R^{22}\end{smallmatrix}$$

[0058] In Formulae (6) and (7), X^5 and X^6 each independently represents -O- or $-NR^{16}-$; R^{16} represents a hydrogen atom, or an alkyl group which has 1 to 12 carbon atoms and may be substituted, a cycloalkyl group, an aryl group or an aralkyl group.

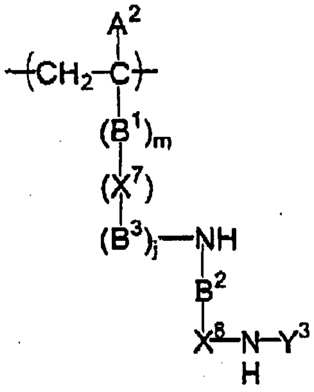
R^{17} and R^{18} each independently represents -H or $-CH_3$; and R^{19} and R^{20} each independently represents an alkylene group which has 1 to 12 carbon atoms and may be substituted, a cycloalkylene group, an arylene group or an aralkylene group.

R^{21} represents -H, or an alkyl group which has 1 to 12 carbon atoms and may be substituted, a cycloalkyl group, an aryl group or an aralkyl group.

R^{22} represents an alkyl group which has 1 to 12 carbon atoms and may be substituted, a cycloalkyl group, an aryl group or an aralkyl group.

[0059]

Formula (8)

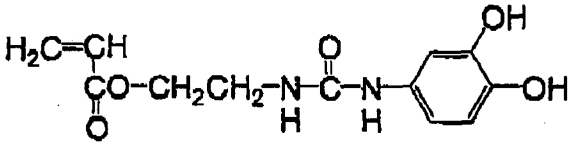


[0060] In Formula (8), A^2 represents a hydrogen atom, a halogen atom, or an alkyl group having 1 to 4 carbon atoms.
B^1 represents a phenylene group, or a substituted phenylene group.
B^2 represents an alkylene group which has 2 to 6 carbon atoms and may be substituted, or a phenylene group which may be substituted.
B^3 represents a divalent organic group.
X^7 and X^8 each independently represents -CO- or $-SO_2-$.
Y^3 represents $-CO-R^{23}$ or $-SO_2-R^{23}$; and R^{23} represents an alkyl group, a substituted alkyl group, an aromatic group, or a substituted aromatic group.
m denotes 0 or 1; and j denotes 0 or 1.

[0061] Specific examples B-1 to B-6, C-1 to C-15, D-1 to D-6, E-1 to E-15, F-1 to F-13, G-1 to G-3, H-1 to H-2, I-1, and J-1 to J-2, which are the comonomers usable as the structural units of any one of the Formulae (2) to (8), are described below, while the invention should not be limited thereto. These comonomers are synthesized according to the methods described in JP-A No. 7-333839, JP-A No. 8-339080, JP-B No. 52-28401, JP-A No. 4-212961, JP-A No. 2-866, and JP-A No. 8-286369.

[0062]

B-1



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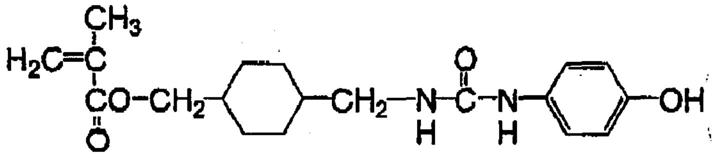

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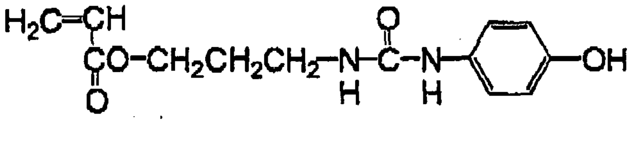

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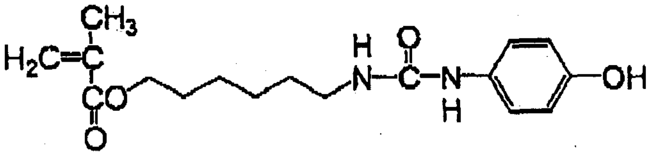

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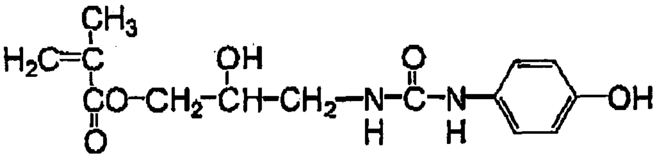

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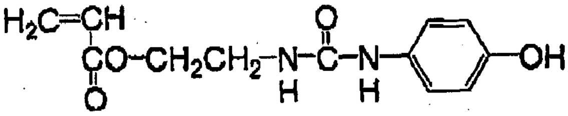
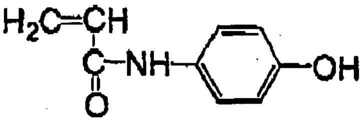


[0063]

C-1



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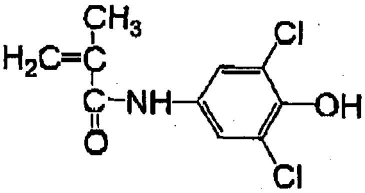

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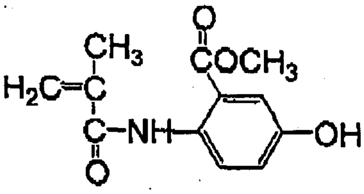

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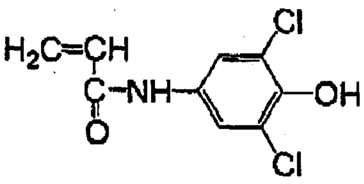

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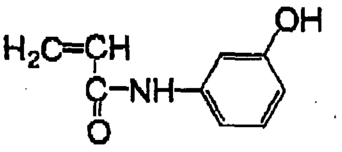

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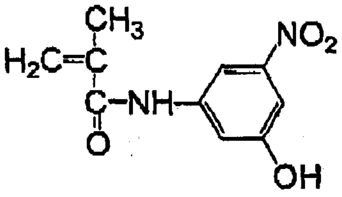

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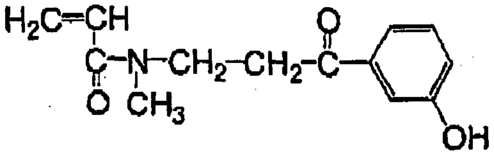

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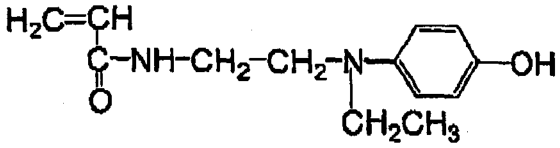

[0064]

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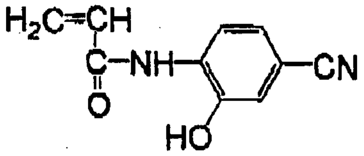

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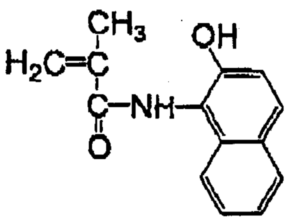

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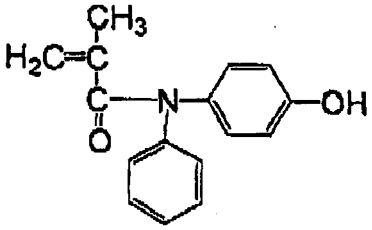

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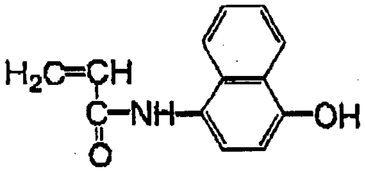

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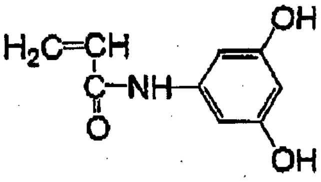

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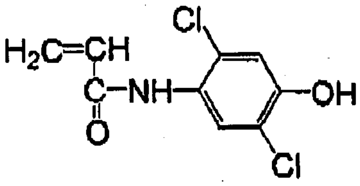

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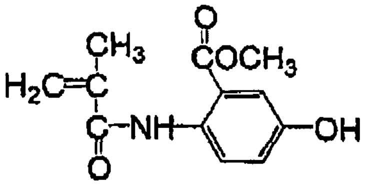
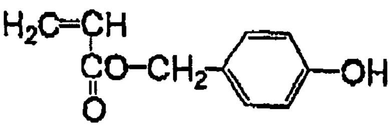


[0065]

D-1



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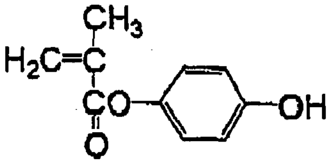

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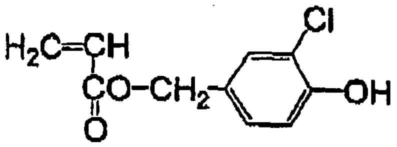

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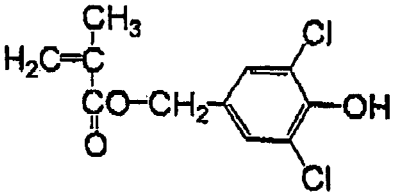

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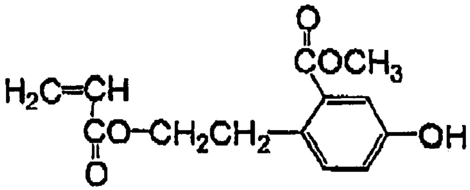

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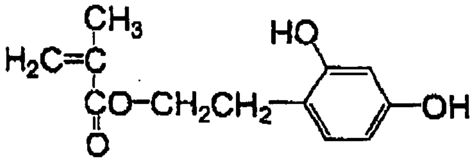

[0066]

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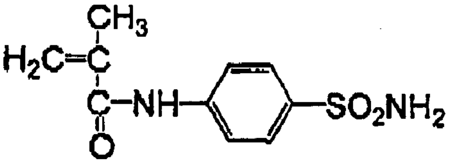

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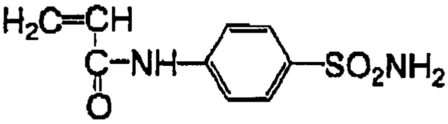

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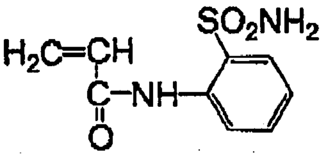

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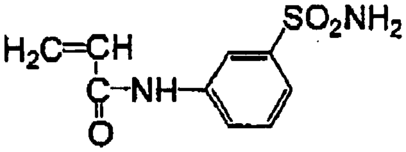

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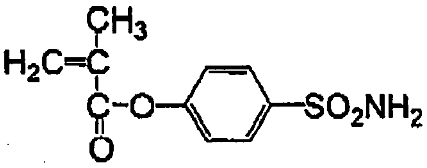

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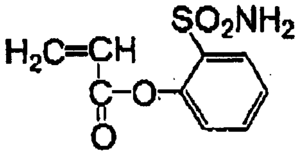

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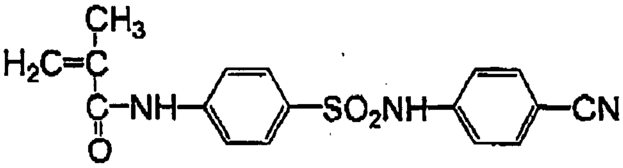

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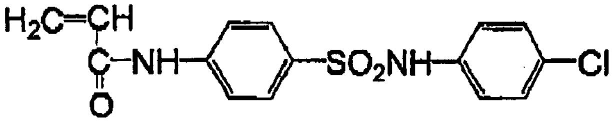

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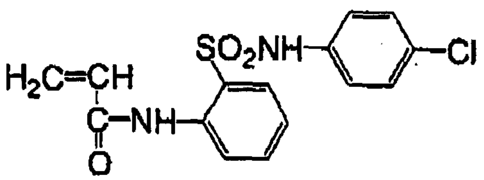

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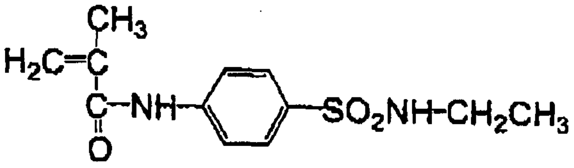

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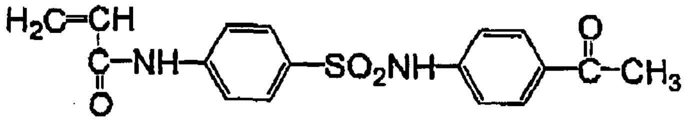

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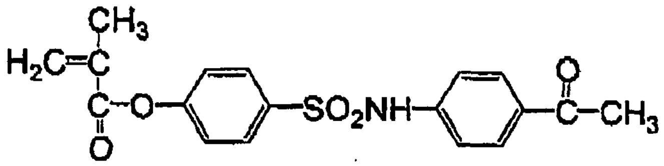

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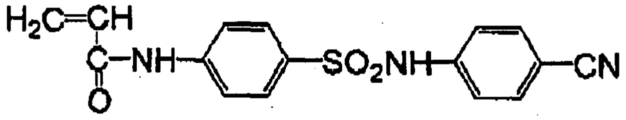

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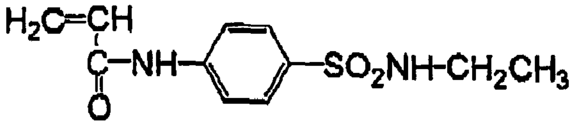

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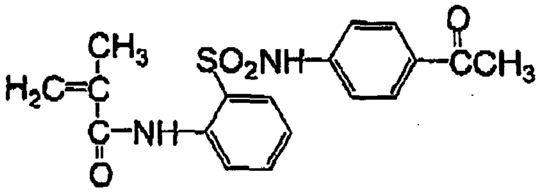

[0068]

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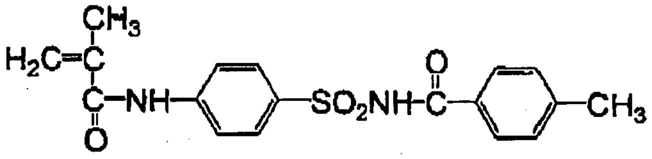

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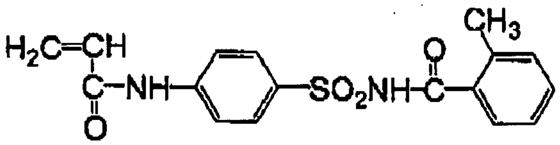

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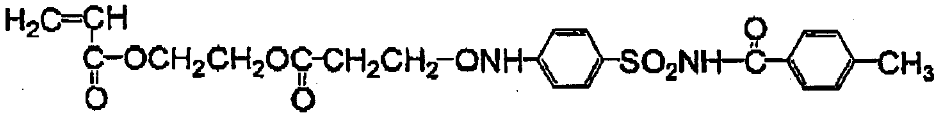

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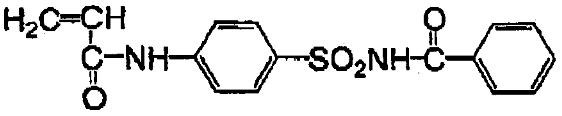

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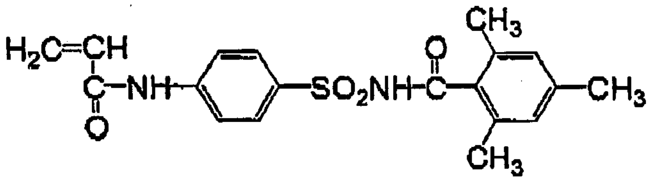

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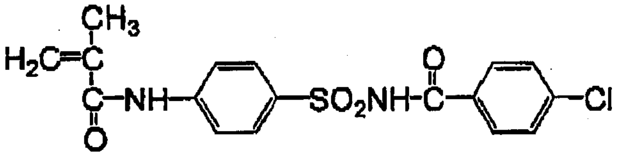

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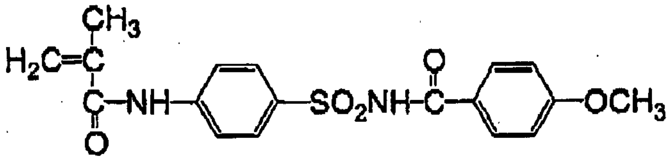

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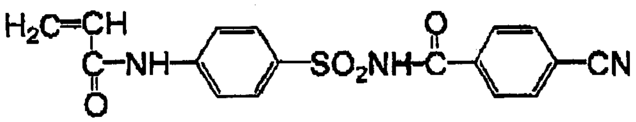
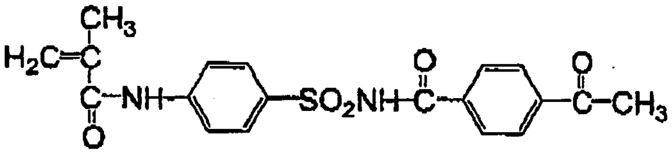


[0069]

F-9



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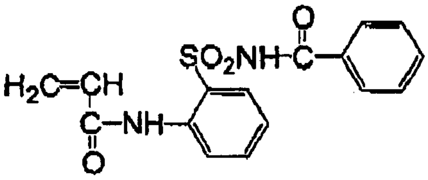

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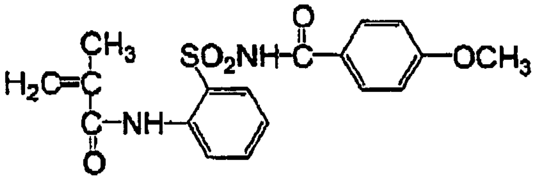

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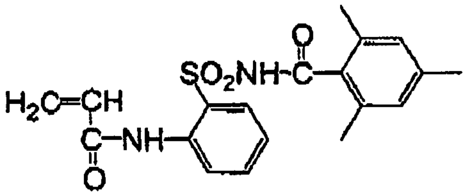

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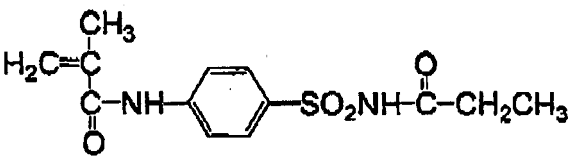
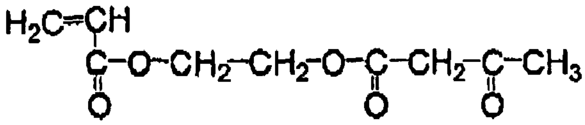


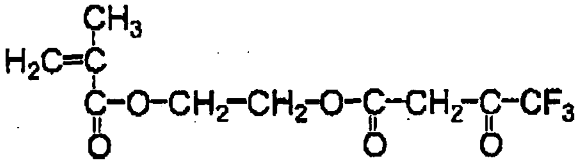
[0070]

G-1



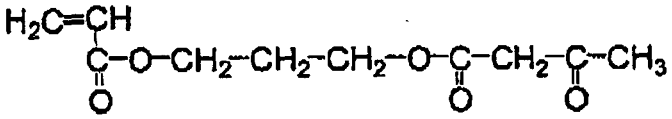
$H_2C{=}CH-C(=O)-O-CH_2-CH_2-O-C(=O)-CH_2-C(=O)-CH_3$

G-2



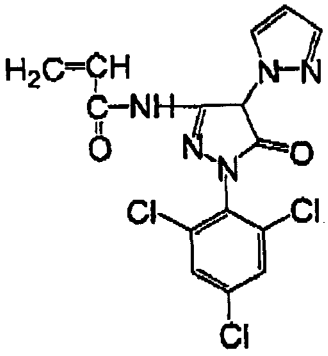
$H_2C{=}C(CH_3)-C(=O)-O-CH_2-CH_2-O-C(=O)-CH_2-C(=O)-CF_3$

G-3

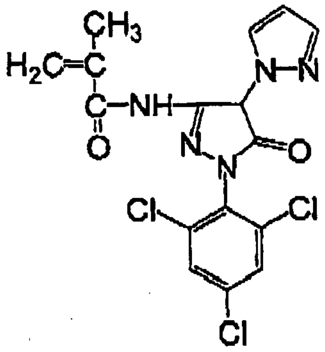


$H_2C{=}CH-C(=O)-O-CH_2-CH_2-CH_2-O-C(=O)-CH_2-C(=O)-CH_3$

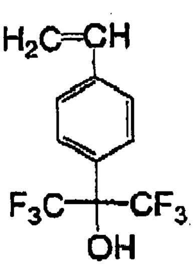
H-1



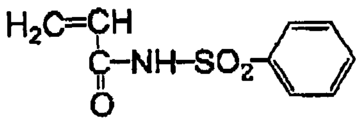
H-2



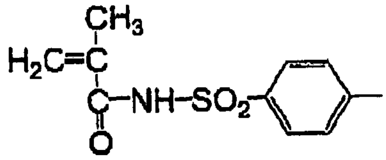
I-1



J-1

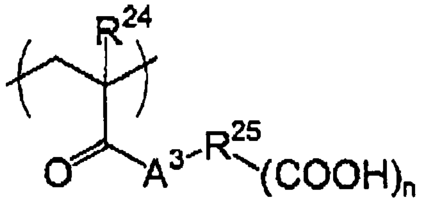


J-2



[0071] The (A) binder polymer is more preferably the one having a carboxylic acid as the acid group, and is further preferably the binder polymer contains a structural unit which has an acid group and is represented by the following Formula (9) . The binder polymer which contains a structural unit which has a carboxyl group at a side chain thereof and is represented by the following Formula (9) is characterized in that no deposition is formed thereby even when the polymer is dissolved in an alkali aqueous solution having a pH of 10 or more and kept at room temperature for 60 days.
[0072]

Formula (9)



[0073] In Formula (9), R^{24} represents a hydrogen atom or a methyl group, and R^{25} represents an (n+1)-valent organic linking group containing an ester group of -O(C=O)-.
A^3 represents an oxygen atom or $-NR^{26}-$; R^{26} represents a hydrogen atom or a monovalent hydrocarbon group having 1 to 10 carbon atoms; and n represents an integer of 1 to 5.

[0074] The means for preventing the deposition over time of the alkali-soluble polymer having a structural unit represented by Formula (9) in aqueous alkali solution is not specifically limited, as long as it may effectively prevent the reduction in the solubility of the polymer owing to the disappearance of the carboxyl group (alkali-soluble group) over time, from the polymer. Example of the means for preventing the deposition over time of the alkali-soluble polymer includes an introduction of an additional functional group capable of changing in aqueous alkali solution to exhibit alkali-solubility; an introduction of an additional functional group having high alkali-solubility and capable of increasing the solubility of the entire of the polymer; and an introduction of a structure which does not function as an alkali-solubilizing group by itself but is capable of increasing the solubility of the polymer (such as a structure having high affinity for aqueous alkali solution).

[0075] Preferable embodiments of the binder polymer used in the invention include (I) one that having, in a side chain of the polymer, a functional group which is represented by Formula (10) and is capable of forming an acid group through hydrolysis with alkali; (II) one that having, in a side chain of the polymer, an acid group which is represented by Formula (1) and has an acid dissociation constant (pKa) of 0 or more to 11 or less; and the like. The embodiment (II) has been described above. The embodiment other than (II) will be described in detail below.

[0076] The functional group capable of forming an acid group through hydrolysis with aqueous alkali solution (developer) having a pH of at least 10 will be described. Preferable examples of the functional group include those represented by the following Formula (10). It is preferable that the binder polymer has the functional group in its side chain.
[0077]

Formula (10) $-Q-X^9$

[0078] In Formula (10), Q represents a linking group that links X^9 to the polymer main chain skeleton.
X^9 represents a protective group hydrolyzable with an aqueous alkali solution having a pH of 10 or more. When the functional group represented by Formula (10) becomes -Q-OH after hydrolysis, the -Q-OH is an acid group having a pKa of 10 or lower.
Q may also be a trivalent or higher valent linking group. In this case, Formula (10) may be represented by the following Formula (10'). In Formula (10'), n denotes an integer selected from 2 to 5.

[0079]

Formula (10') $-Q^1-(X^{10})_n$

[0080] The linking group Q^1 can be specifically selected such that the pKa of $-Q^1$-OH, which is obtained by hydrolysis of the polymer, can be 10 or less, and it is more preferable that Q^1 is selected such that the pKa of-Q^1-OH can be in a range of 3 to 10. Q^1 is preferably a hydrocarbon-type linking group, and examples of such the hydrocarbon group include a straight chain-, branched- or cyclic-alkyl group, and an aromatic group. Among these, Q^1 is selected so that the pKa of the specific functional group after hydrolysis could fall within the above range. In general, an electron-attractive substituent may be introduced into such a divalent or higher valent hydrocarbon group to make the pKa of the specific functional group after hydrolysis fall within the above range.

Preferable examples of the hydrocarbon group for Q^1 include an aromatic group and a cyclo group.

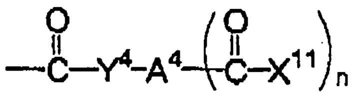
[0081] X^{10} is not particularly limited as long as it may be capable of serving as a protective group until it is removed through hydrolysis with aqueous alkali solution having pH of 10 or more.

Preferable examples of X^{10} include a substituted oxy group, a substituted thio group, and a substituted amino group.

[0082] More preferably, the functional group used in the invention is represented by the following Formula (11):

[0083]

Formula (11)



$$-\overset{O}{\overset{\|}{C}}-Y^4-A^4-\left(\overset{O}{\overset{\|}{C}}-X^{11}\right)_n$$

[0084] In Formula (11), A^4 represents an aromatic group or a cyclo group. Specific examples thereof include an aromatic group, a heterocyclic group, a condensed polycyclic structure or an aliphatic cyclic structure, each of which has about 4 to 50 carbon atoms.

n denotes an integer selected from 1 to 5. In view of the balance between the solubility of the unexposed part of the polymer to alkali and the resistance of the exposed part thereof against alkali development, n is preferably 1 to 3.

[0085] X^{11} represents $-NR^{27}R^{28}$, $-SR^{29}$, or $-OR^{30}$. R^{27} to R^{30} each independently represents a substituent composed of one or more atoms selected from the group consisting of a carbon atom, a hydrogen atom, an oxygen atom, a nitrogen atom, a sulfur atom and a halogen atom. Examples thereof include an alkyl group which may be substituted, and an aryl group which may be substituted.

[0086] Examples of the alkyl group represented by R^{27} to R^{30} include a straight chain, branched or cyclic alkyl group having 1 to 20 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a, hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, a hexadecyl group, an octadecyl group, an eicosyl group, an isopropyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a isopentyl group, a neopentyl group, a 1-methylbutyl group, an isohexyl group, a 2-ethylhexyl group, a 2-methylhexyl group, a cyclohexyl group, a cyclopentyl group and a2-norbomyl group. Among theese, a straight chain alkyl group having 1 to 12 carbon atoms, a branched alkyl group having 3 to 12 carbon atoms and a cyclic alkyl group having 5 to 10 carbon atoms are preferable.

[0087] Examples of the substituent that may be introduced into the alkyl group include a monovalent non-metallic atomic group other than a hydrogen atom. Specific examples thereof include a halogen atom (-F, -Br, -Cl, -I), a hydroxy group, an alkoxy group, an aryloxy group, a mercapto group, an alkylthio group, an arylthio group, an alkyldithio group, an aryldithio group, an amino group, a N-alkylamino group, a N,N-dialkylamino group, a N-arylamino group, a N,N-diarylamino group, a N-alkyl-N-arylamino group, an acyloxy group, a carbamoyloxy group, a N-alkylcarbamoyloxy group, a N-arylcarbamoyloxy group, a N,N-dialkylcarbamoyloxy group, a N,N-diarylcarbamoyloxy group, a N-alkyl-N-arylcarbamoyloxy group, an alkylsulfoxy group, an arylsulfoxy group, an acylthio group, an acylamino group, a N-alkylacylamino group, a N-arylacylamino group, an ureido group, a N'-alkylureido group, a N',N'-dialkylureido group, a N'-arylureido group, a N',N'-diarylureido group, a N'-alkyl-N'-arylureido group, a N-alkylureido group, a N-arylureido group, a N'-alkyl-N-alkylureido group, a N'-alkyl-N-arylurcido group, a N',N'-dialkyl-N-alkylureido group, a N',N'-dialkyl-N-arylureido group, a N'-aryl-N-alkylureido group, a N'-aryl-N-arylureido group, a N',N'-diaryl-N-alkylureido group, a N',N'-diaryl-N-arylureido group, a N'-alkyl-N'-aryl-N-alkylureido group, a N'-alkyl-N'-aryl-N-arylureido group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a N-alkyl-N-alkoxycarbonylamino group, a N-alkyl-N-aryloxycarbonylamino group, a N-aryl-N-alkoxycarbonylamino group, a N-aryl-N-aryloxycarbonylamino group, a formyl group, an acyl group, a carboxy group and a conjugate base group thereof, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, a N-alkylcarbamoyl group, a N,N-dialkylcarbamoyl group, a N-arylcarbamoyl group, a N,N-diarylcarbamoyl group, a N-alkyl-N-arylcarbamoyl group, an alkylsulfinyl group, an arylsulfinyl group, an alkylsulfonyl group, an arylsulfonyl group, a sulfo group (-SO_3H) and a conjugate base group thereof, an alkoxysulfonyl group, an aryloxysulfonyl group, a sulfinamoyl group, a N-alkylsulfinamoyl group, a N,N-dialkylsulfinamoyl group, an N-arylsulfinamoyl group, a N,N-diarylsulfinamoyl group, a N-alkyl-N-arylsulfinamoyl group, a sulfamoyl group, a N-alkylsulfamoyl group, a N,N-dialkylsulfamoyl group, a N-arylsulfamoyl group, a N,N-diarylsulfamoyl group, a N-alkyl-N-arylsulfamoyl group, a N-arylsulfamoyl group and a conjugate base group thereof, an n-alkylsulfonylsulfamoyl group (-SO_2NHSO_2(alkyl)) and a conjugate base group thereof, a N-arylsulfonylsulfamoyl group (-SO_2NHSO_2(aryl)) and a conjugate base group thereof, a N-alkylsulfonylearbamoyl group (-$CONHSO_2$(alkyl)) and a conjugate base group thereof, a N-arylsulfonylcarbamoyl group (-$CONHSO_2$ (aryl)) and a conjugate base group thereof, an alkoxysilyl group (-Si(O-alkyl)$_3$), an aryloxysilyl group (-Si(O-aryl)$_3$), a hydroxysilyl group (-Si(OH)$_3$) and a conjugate base group thereof, a phosphono group (-PO_3H_2) and a conjugate base group thereof, a dialkylphosphono group (-PO_3(alkyl)$_2$), a diarylphosphono group (-PO_3(aryl)$_2$), an alkylarylphosphono group (-PO_3(alkyl)(aryl)), a monoalkylphosphono group (-PO_3H(alkyl)) and a conjugate base group thereof, a monoarylphosphono group (-PO_3H(aryl)) and a conjugate base group thereof, a phosphonoxy group (-OPO_3H_2) and a conjugate base group thereof, a dialkylphosphonoxy group (-OPO3(alkyl)$_2$), a diarylphosphonoxy group (-OPO_3(aryl)$_2$), an alkylarylphosphonoxy group (-OPO_3(alkyl)(aryl)), a monoalkylphosphonoxy group (-OPO_3H(alkyl)) and a conjugate base group thereof, a monoarylphosphonoxy group (-OPO_3H(aryl)) and a conjugate base group thereof, a cyano group, a nitro group, a dialkylboryl group (-B(alkyl)$_2$), a diarylboryl group (-B(aryl)$_2$), an alkylarylboryl group (-B(alkyl)(aryl), a dihydroxyboryl group (-B(OH)$_2$) and a conjugate base group thereof, an alkylhydroxyboryl group (-B(alkyl)(OH)) and a conjugate base group thereof, an arylhydroxyboryl group (-B(aryl)(OH)) and a conjugate base group thereof, an aryl group, an alkenyl group, and an alkynyl group.

[0088] Examples of the aryl group represented by R^{27} to R^{30} include a benzene ring, a condensed ring having two or three benzene rings, and a condensed ring that has a benzene ring and a 5-membered unsaturated ring. Specific examples thereof include a phenyl group, a naphthyl group, an anthryl group, a phenanthryl group, an indenyl group, an acenaphthenyl group and a fluorenyl group. Among these, preferred are a phenyl group and a naphthyl group. Examples of the substituent that may be introduced into the aryl group include those described as the substituent capable of being introduced into the alkyl group or the alkyl group.

[0089] Among these examples of X^{11}, preferable examples of the substituted amino group represented $NR^{27}R^{28}$ include an acylamino group, a N-alkylacylamino group, a N-arylacylamino group, an ureido group, a N'-alkylureido group; a N',N'-dialkylureido group, a N'-arylureido group, a N',N'-diarylureido group, a N'-alkyl-N'-arylureido group, a N-alkylureido group, a N-arylureido group, a N'-alkyl-N-alkylureido group, a N'-alkyl-N-arylureido group, a N',N'-dialkyl-N-alkylureido group, a N',N'-dialkyl-N-arylureido group, a N'-aryl-N-alkylureido group, a N'-aryl-N-arylureido group, a N', N'-diaryl-N-alkylureido group, a N',N'-diaryl-N-arylureido group, a N'-alkyl-N'-aryl-N-alkylureido group, a N'-alkyl-N'-aryl-N-arylureido group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a N-alkyl-N-alkoxycarbonylamino group, a N-alkyl-N-aryloxycarbonylamino group, a N-aryl-N-allcoxycarbonylamino group, and a N-aryl-N-aryloxycarbonylamino group. Specific examples of the alkyl group and the aryl group in these include those described for the alkyl group, the substituted alkyl group, the aryl group and the substituted aryl group described above. Specific examples of the substituent R^{31} in the structure "R^{31}CO-" in the acylamino group, the N-alkylacylamino group or the N-arylacylamino group described include those described for the alkyl group, the substituted alkyl group, the aryl group and the substituted aryl group described above. Among these, more preferable examples thereof include a N-alkylamino group, a N,N-dialkylamino group, a N-arylamino group and an acylamino group. Specific examples of the preferable substituted amino group include a methylamino group, an ethylamino group, a diethylamino group, a morpholino group, a piperidino group, a pyrrolidino group, a phenylamino group, a benzoylamino group, and an acetylamino group.

[0090] Y^4 represents a single bond, -O- or -NR^{32} -. R^{32} represents a hydrogen atom or a hydrocarbon atom. Examples of the hydrocarbon group represented by R^{32} include an alkyl group, an aryl group, an alkenyl group, and an alkynyl group. Specific examples of the alkyl group represented by R^{32} include a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, a octyl group, a nonyl group, a decyl group, an isopropyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, an isopentyl group, a neopentyl group, a 1-methylbutyl group, an isohexyl group, a 2-ethylhexyl group, a 2-methylhexyl group, a cyclohexyl group, a cyclopentyl group, a 1-adamantyl group or a 2-norbornyl group.
Specific examples of the aryl group represented by R^{32} include an aryl group having 1 to 10 carbon atoms, such as a phenyl group, a naphthyl group or an indenyl groups; and a heteroaryl group having one hetero atom selected from a nitrogen atom, an oxygen atom and a sulfur atom and having 1 to 10 carbon atoms, such as a furyl group, a thienyl group, a pyrrolyl group, a pyridyl group or a quinolyl group.
Specific examples of the alkenyl group represented by R^{32} include a straight chain, branched or cyclic alkenyl group having 1 to 10 carbon atoms, such as a vinyl group, a 1-propenyl group, a 1-butenyl group, a 1-methyl-1-propenyl group, a 1-cyclopentenyl group or a 1-cyclohexenyl group.
Specific examples of the alkynyl group represented by R^{32} include those having 1 to 10 carbon atoms, such as ethynyl group, a 1-propynyl group, a 1-butynyl group or a 1-octynyl group.

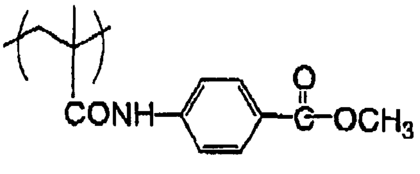
R^{32} may be substituted. Examples of the substituent include those described as the substituent for the alkyl group represented by R^{27} to R^{30}. The number of the carbon atoms constituting R^{32} is 1 to 10 including the number of the carbon atoms of the substituent.

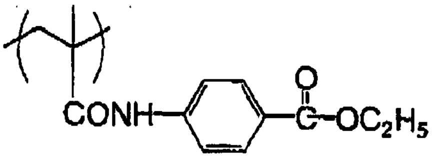
In view of easiness in production of the polymer, Y^4 is preferably an oxygen atom or -NH- .

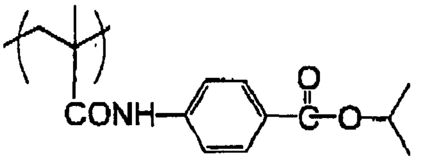
[0091] Examples of the method of introducing the specific functional group into the polymer include a method including copolymerizing a monomer having in its molecule the specific functional group and an unsaturated bond capable of being copolymerized with any other comonomer by any known mode of polymerization. If desired, any other monomer which does not have the specific functional group may be copolymerized therewith. In the invention, the structural unit which is contained in the polymer compound, formed of such monomer and obtained through such copolymerization may be simply referred to as "unit".

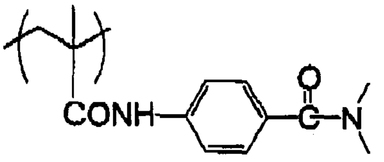
[0092] Specific preferable examples of the units having the functional group are described below, while the invention should not be limited thereto.

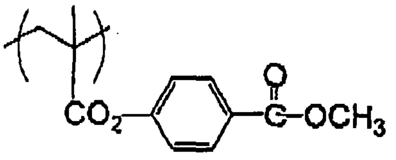
[0093]

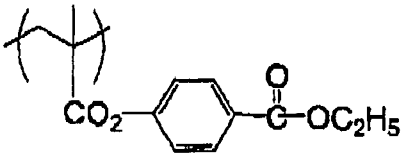


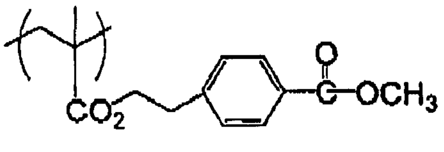


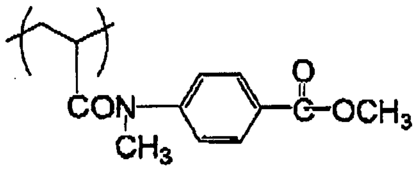


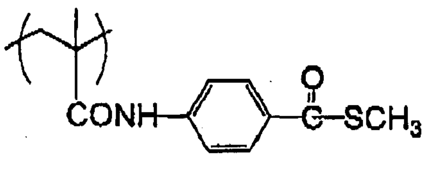


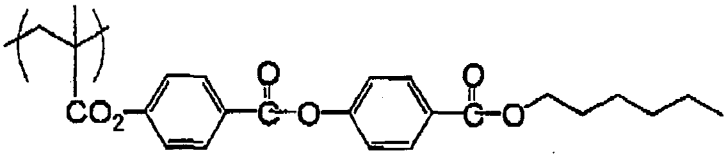


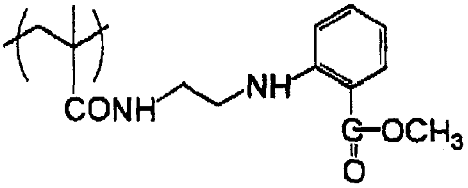


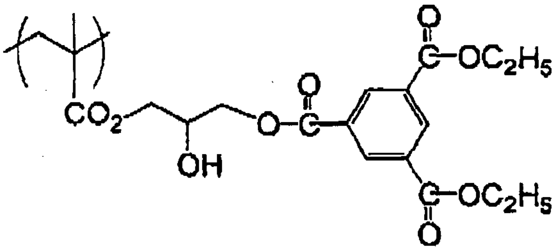


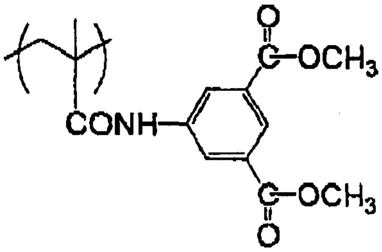




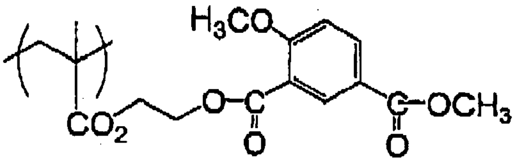


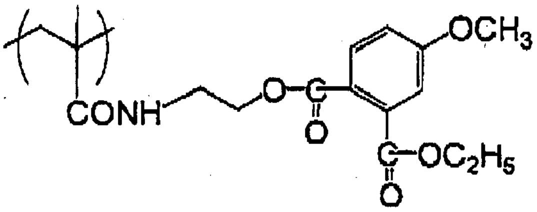


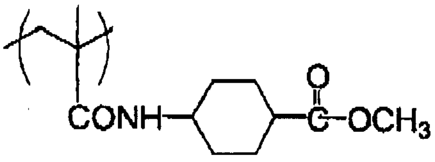


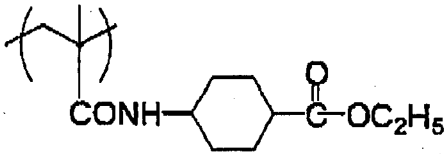


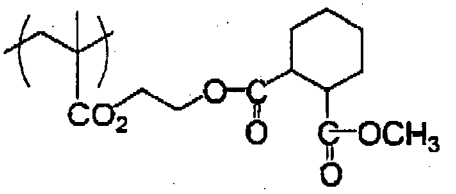
[0094]

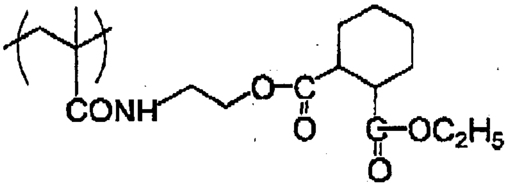


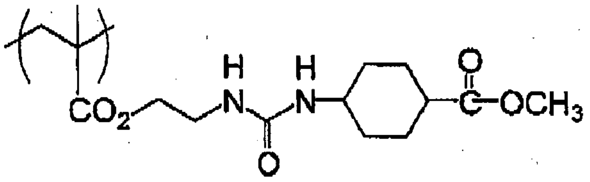


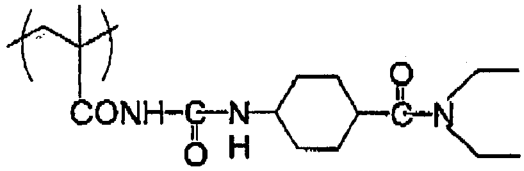


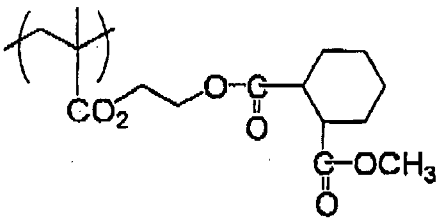


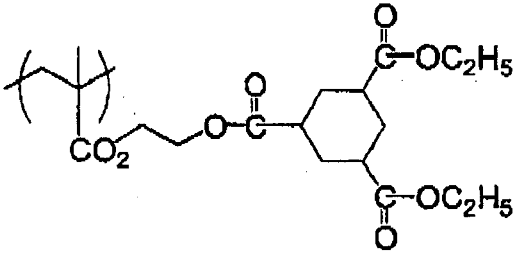












[0095] The binder polymer of the invention may have one or more of the units having the functional group. While the organic high molecular binder polymer in the invention may be a polymer having only the units represented by Formula (9) and the units having the above-described functional group, it is typically formed by further combining with any units of other comonomer described below. While the total content of units having the functional group in the copolymer may be suitably determined depending on the structure of the copolymer and on the design of the photosensitive layer, it is preferably in a range of 1 to 99 mol%, is more preferably in a range of 5 to 90 mol%, and is even more preferably in a range of 10 to 70 mol% relative to the total molar amount of the polymer component.

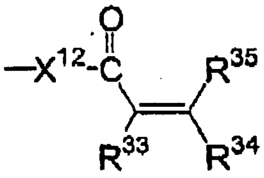
[0096] The binder polymer may contain one or more of the structural units having the specific acid group.

[0097] The content of the acid group having the acid dissociation constant (pKa) of 0 to 11 is preferably in a range of 0.01 to 10.0 mmol, and is more preferably in a range of 0.05 to 7.0 mmol, per 1 g of the organic high molecular polymer of the embodiment (II).

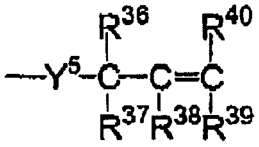
[0098] In a more preferable embodiment, the binder polymer which includes the acid group having pKa of 0 to 11 further has, in a side chain thereof, an ethylenic unsaturated double bond (hereinafter appropriately referred to as a "radical polymerizable group"). Examples of the method of introducing such a radical polymerizable group into the side chain of the organic high molecular binder polymer of the invention include a method of combining units having a radical polymerizable group represented by any of the following Formulae (A) to (E) in addition to the units having the functional group described above. The content of the radical polymerizable group in the organic high molecular polymer (the content of radical polymerizable unsaturated double bond determined through iodine titration) is preferably 0.1 to 10.0 mmol, is more preferably 1.0 to 8.0 mmol, and is most preferably 1.5 to 7.0 mmol, per 1 g of the organic high molecular binder polymer. One or more of these units may be in the organic high molecular binder polymer.

[0099]

Formula (A)

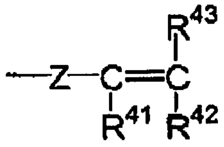


Formula (B)



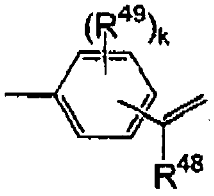
$$-Y^5-\overset{R^{36}}{\underset{R^{37}}{C}}-\underset{R^{38}}{C}=\overset{R^{40}}{\underset{R^{39}}{C}}$$

Formula (C)

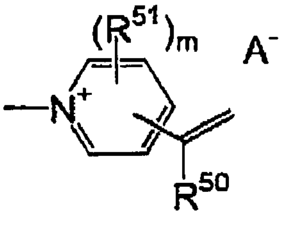


$$-Z-\underset{R^{41}}{C}=\overset{R^{43}}{\underset{R^{42}}{C}}$$

Formula (D)



Formula (E)



[0100] In Formulae (A) to (C), R^{33} to R^{43} each independently represents a hydrogen atom or a monovalent substituent. X^{12} and Y^5 each independently represents an oxygen atom, a sulfur atom, or $-NR^{44}-$.
Z represents an oxygen atom, a sulfur atom, $-NR^{44}-$, or a phenylene group.

[0101] In Formula (A), R^{33} to R^{35} each independently represents a hydrogen atom or a monovalent substituent. R^{33} may be a hydrogen atom, or an organic group such as an alkyl group. Specifically, R^{33} is preferably a hydrogen atom, a methyl group, an methylalkoxy group, or a methyl ester group. R^{34} and R^{35} each independently represents a hydrogen atom, a halogen atom, an amino group, a dialkylamino group, a carboxyl group, an alkoxycarbonyl group, a sulfo group, a nitro group, a cyano group, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylamino group, an arylamino group, an alkylsulfonyl group, or an arylsulfonyl group. Among these, R^{34} and R^{35} each independently represents a hydrogen atom, a carboxyl group, an alkoxycarbonyl group, an alkyl group, or an aryl group.

Each of the substituents represented by R^{33} to R^{35} may have a substituent. Examples of the substituent include a methoxycarbonyl group, an ethoxycarbonyl group, an isopropoxycarbonyl group, a methyl group, an ethyl group, and a phenyl group.

X^{12} represents an oxygen atom, a sulfur atom, or $-N-R^{44}-$. R^{44} may be an alkyl group which may have a substituent.

[0102] In Formula (B), R^{36} to R^{40} each independently represents a hydrogen atom or a monovalent substituent. Examples thereof include a hydrogen atom, a halogen atom, an amino group, a dialkylamino group, a carboxyl group, an alkoxycarbonyl group, a sulfo group, a nitro group, a cyano group, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylamino group, an arylamino group, an alkylsulfonyl group, and an arylsulfonyl group. Preferable examples thereof among these include a hydrogen atom, a carboxyl group, an alkoxycarbonyl group, an alkyl group, and an aryl group.

Each of these groups may have a substituent, and examples of the substituent are the same as those described as the substituent which can be introduced into the substituents represented by R^{33} to R^{35} in Formula (A).

Y^5 represents an oxygen atom, a sulfur atom, or $-N-R^{44}-$. R^{44} is similar to that in Formula (A).

[0103] In Formula (C), R^{41} to R^{43} each independently represents a hydrogen atom or a monovalent substituent. Specific examples thereof include a hydrogen atom, a halogen atom, an amino group, a dialkylamino group, a carboxyl group, an alkoxycarbonyl group, a sulfo group, a nitro group, a cyano group, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylamino group, an arylamino group, an alkylsulfonyl group, and an arylsulfonyl group. Preferable examples thereof among these include a hydrogen atom, a carboxyl group, an alkoxycarbonyl group, an alkyl group, and an aryl group.

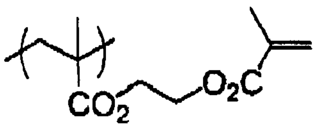
Each of these groups may have a substituent, and examples of the substituent are the same as those described as the substituent which can be introduced into the substituents represented by R^{33} to R^{35} in Formula (A).

Z represents an oxygen atom, a sulfur atom, $-N-R^{44}-$ or a phenylene group. R^{44} is similar to that in Formula (A).

Specific examples 1 to 47, which are preferable examples of the unit having such a radical polymerizable group represented by any one of Formulae (A) to (C), are described below, while the invention should not be limited thereto.

[0104]

1)



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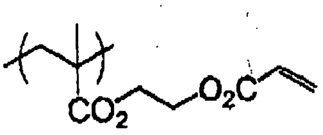

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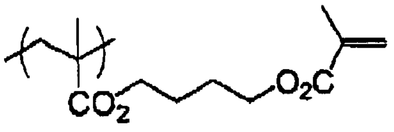

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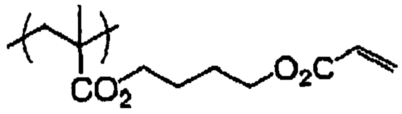

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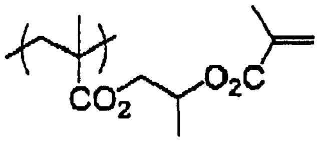

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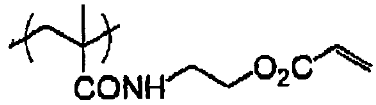

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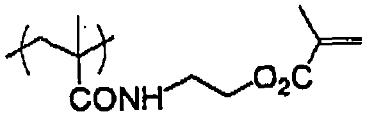

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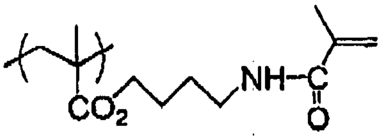

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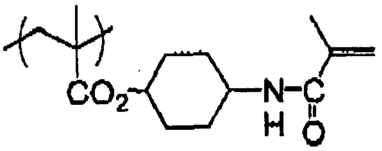

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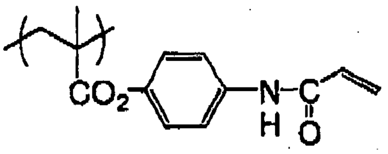

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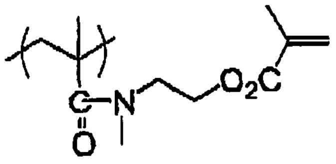

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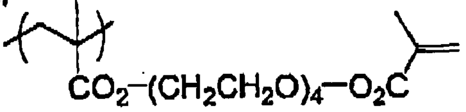

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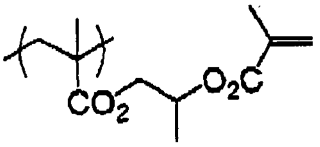

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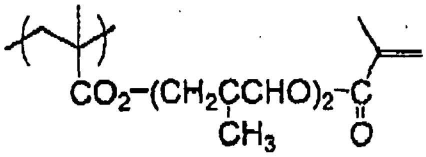

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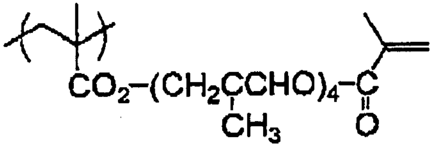

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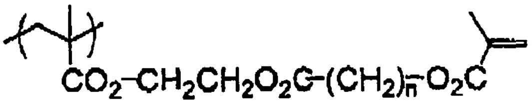

n = 4 or 5

[0105]

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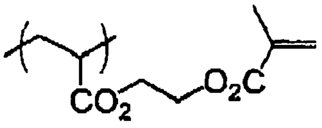

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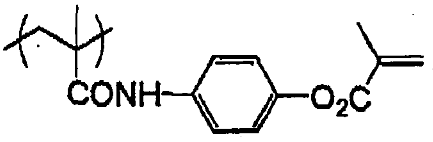

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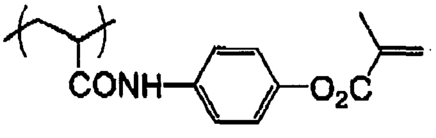

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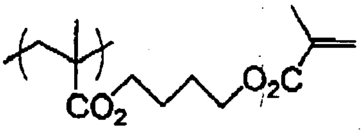

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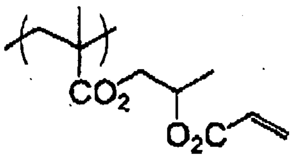

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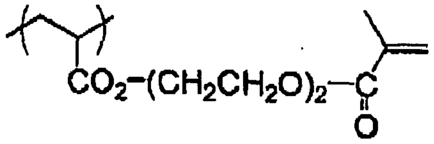

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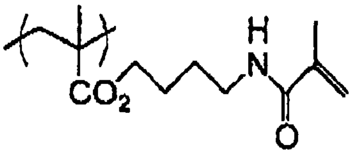

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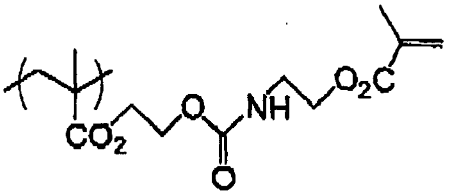

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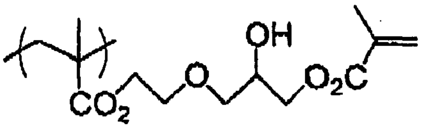

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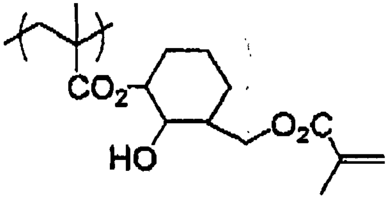

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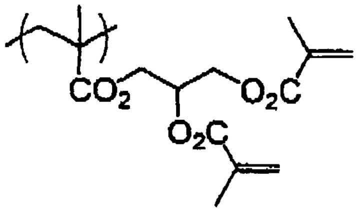

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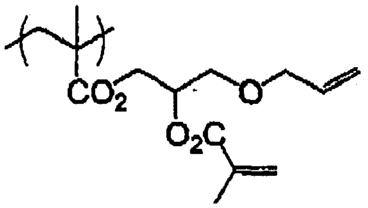

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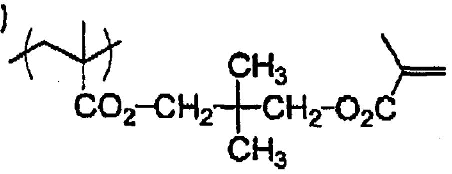

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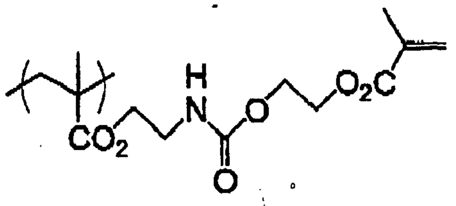

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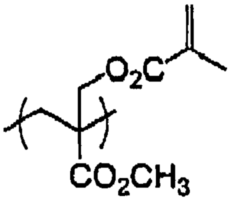

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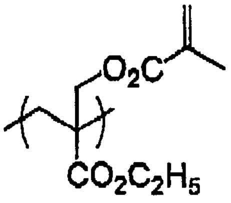

[0106]

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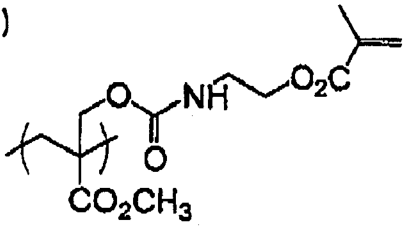

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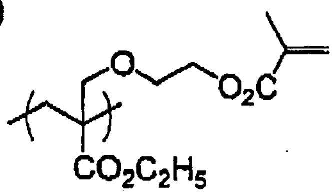

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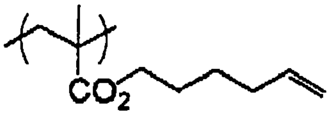

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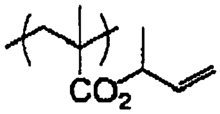

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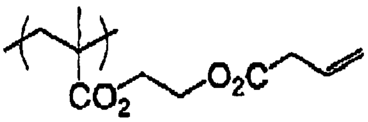

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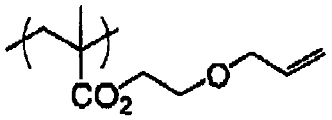

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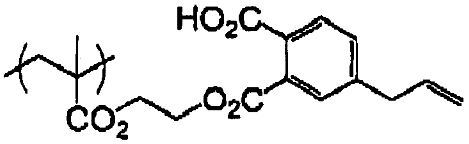

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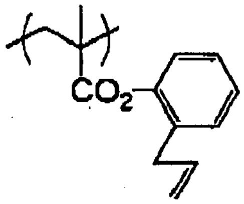

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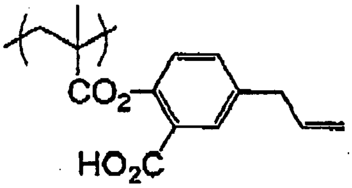

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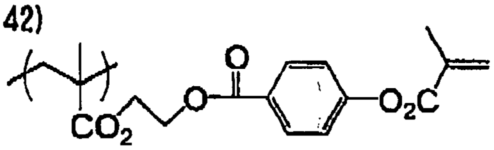

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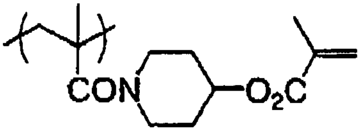

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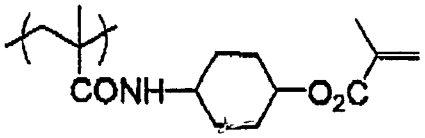

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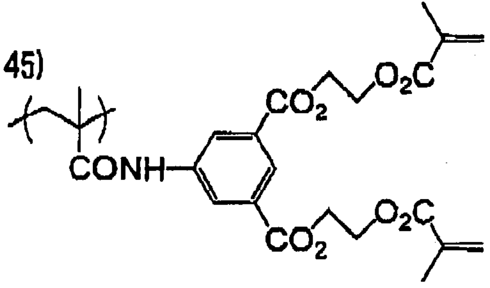

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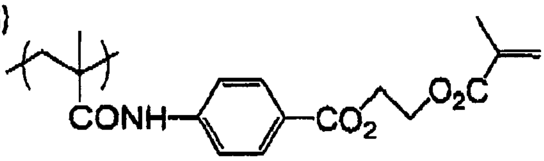

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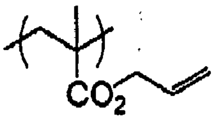
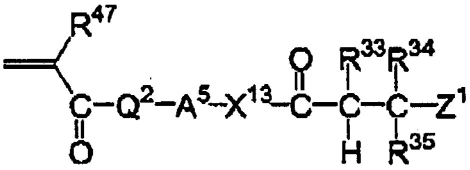


[0107] The polymer which is used in the invention and has a radical polymerizable group represented by Formula (A) may be produced according to at least one of the following synthesis methods (1) and (2).

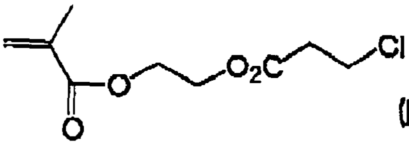
Synthesis method (1)

[0108] At least one radical polymerizable compound of the following Formula (a) is used for polymerization to give a polymer compound, and this is deprotonated by a base to remove Z^1 so as to provide a desired polymer compound.
[0109]

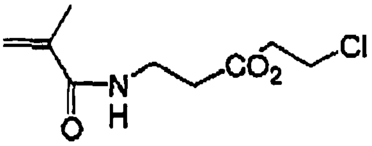
Formula (a)



[0110] In Formula (a), each of R^{33} to R^{35} is similar to each of R^{33} to R^{35} in Formula (A).
X^{13} represents an oxygen atom, a sulfur atom, -NH-, or -NR^{45}- (here, R^{45} represents an alkyl group which may have a substituent).
Z^1 represents an anionic removable group.
Q^2 represents an oxygen atom, -NH-, or -NR^{46}- (here, R^{46} represents an alkyl group which may have a substituent).
R^{47} is a hydrogen atom or an alkyl group which may have a substituent, and preferable examples thereof include a hydrogen atom, a methyl group, a methylalkoxy group, and a methyl ester group.
A^5 represents a divalent organic linking group.
[0111] Examples of the radical polymerizable compound represented by Formula (a) are described below, while the invention should not be limited thereto.
[0112]



(M-1)



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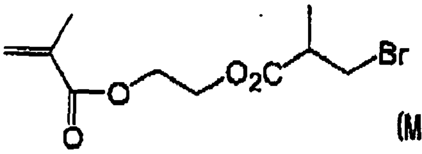
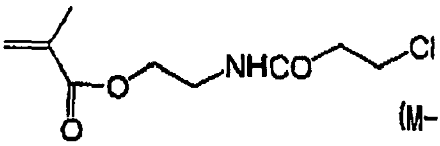
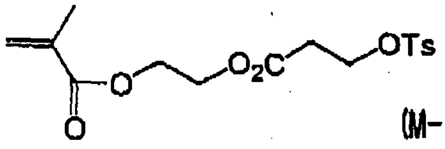


(M-2)



(M-8)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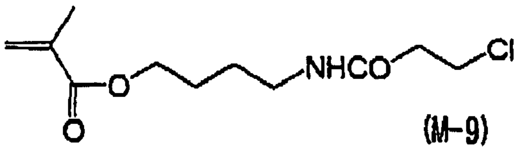
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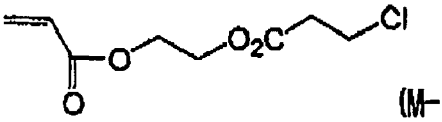
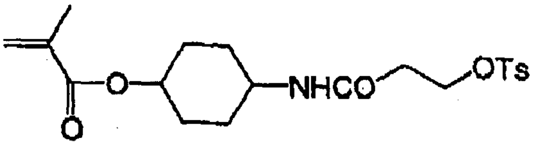

(M-4)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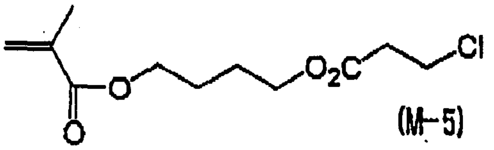
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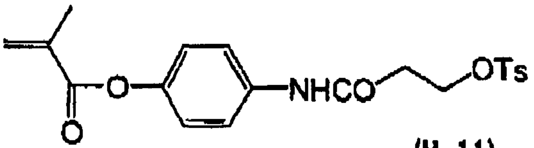
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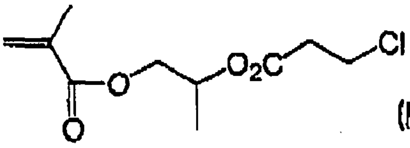
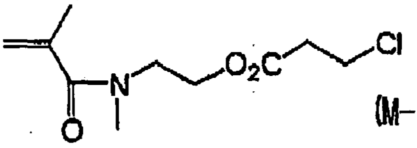

(M-6)


(M-12)

[0113] These radical polymerizable compounds represented by Formula (a) are available as commercial products, or can be readily produced according to the synthesis methods shown in the Synthesis Examples described below.

The unit which has a radical polymerizable group and is represented by Formula (A) can be introduced into the side chain of the organic high molecular binder polymer of the invention by a method including: performing polymerization by using one or more radical polymerizable compounds represented by Formula (a) and other radical polymerizable compound which can be optionally added if desired in accordance with an ordinary radical polymerization process to give a polymer compound; and adding a desired amount of a base in a dropwise manner to the resulted polymer liquid with cooling or heating to cause reaction, in which, if desired, the resultant thereby is further neutralized with acid. Any known method such as suspension polymerization or solution polymerization method can be employed for producing the polymer compound.

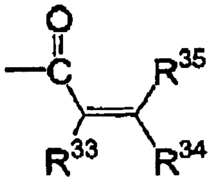
The base used herein may be any of an inorganic compound (inorganic base) and an organic compound (organic base). Preferable examples of the inorganic base include sodium hydroxide, potassium hydroxide, sodium carbonate, sodium hydrogencarbonate, potassium carbonate, and potassium hydrogencarbonate. Preferable examples of the organic base include metal alkoxides such as sodium methoxide, sodium ethoxide, or potassium t-butoxide; and organic amine compounds such as triethylamine, pyridine, or diisopropylethylamine.

Synthesis method (2)

[0114] One or more radical polymerizable compounds having a functional group are polymerized to give a stem polymer compound (a polymer compound which configurates a main chain skeleton of a desired polymer compound), and then a compound having a structure of the following Formula (b) is reacted with the functional group in the side chain of the stem polymer compound to give the desired polymer compound.

[0115]

Formula (b).



[0116] Each of R^{33} to R^{35} in Formula (b) is similar to each of R^{33} to R^{35} in Formula (A).

[0117] Examples of the functional group in the radical polymerizable compound having the functional group to be used for producing the stem polymer compound according to the synthesis method (2) include a hydroxyl group, a carboxyl group, a carboxylic acid halide group, a carboxylic acid anhydride group, an amino group, an alkyl halide group, an isocyanate group, and an epoxy group. Specific examples of the radical polymerizable group having such a functional group include 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 4-hydroxybutyl acrylate, 4-hydroxybutyl methacrylate, acrylic acid, methacrylic acid, acrylic acid chloride, methacrylic acid chloride, methacrylic anhydride, N,N-dimethyl-2-aminoethyl methacrylate, 2-chloroethyl methacrylate, 2-isocyanatoethyl methacrylate, glycidyl acrylate, and glycidyl methacrylate.

The desired polymer compound can be obtained by a method including: performing polymerization by using or more radical polymerizable compounds having such a functional group and other radical polymerizable compound which can be optionally added for copolymerization if desired to give a stem polymer compound; and reacting the stem polymer compound with a compound having the group represented by Formula (b) to give a desired polymer compound. Examples of the compounds having the group represented by Formula (b) may be the same as those described for the examples of the radical polymerizable group having the functional group.

[0118] The polymer used in the invention that has a radical polymerizable group represented by Formula (B) may be produced according to at least one of the following production methods (3) and (4).

Synthesis method (3)

[0119] Synthesis method (3) includes polymerizing at least one radical polymerizable compound which has an unsaturated group represented by Formula (B) and an ethylenic unsaturated group having addition-polymerizability which is higher than that of the unsaturated group, and other radical polymerizable compound which can be optionally added to give a polymer compound. This method uses a compound having, in one molecule thereof, a plurality of ethylenic unsaturated groups, the addition-polymerizability,of each of which is different from those of others. Examples of such a compound include allyl methacrylate.

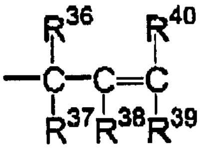
[0120] Examples of the radical polymerizable compound having an unsaturated group represented by Formula (B) and an ethylenic unsaturated group having addition-polymerizability which is higher than that of the unsaturated group of Formula (B) include allyl acrylate, allyl methacrylate, 2-allyloxyethyl acrylate, 2-allyloxyethyl methacrylate, propargyl acrylate, propargyl methacrylate, N-allyl acrylate, N-allyl methacrylate, N,N-diallyl acrylate, N,N-diallylmethacrylamide, allylacrylamide, and allylmethacrylamide.

Synthesis method (4)

[0121] Synthesis method (4) includes: polymerizing at least one radical polymerizable compound having a functional group to give a polymer compound; and reacting the functional group on a side chain of the polymer compound with a compound having a structure represented by the following Formula (c) so as to introduce a group represented by Formula (B) into the polymer compound.

[0122]

Formula (c)



[0123] Each of R^{36} to R^{40} in Formula (c) is similar to each of R^{36} to R^{40} in Formula (A).

[0124] Specific examples of the radical polymerizable compound having the functional group for use in the synthesis method (4) may be the same as those of the radical polymerizable compound having the functional group used in the synthesis method (2).

Examples of the compound having the structure represented by Formula (c) include allyl alcohol, allylamine, diallylamine, 2-allyloxyethyl alcohol, 2-chloro-1-butene, and allyl isocyanate.

[0125] The polymer used in the invention that has a radical polymerizable group represented by Formula (C) may be produced according to any one of the following production methods (5) and (6).

Synthesis method (5)

[0126] Synthesis method (5) includes polymerizing at least one radical polymerizable compound having an unsaturated group represented by Formula (C) and an ethylenic unsaturated group that has addition-polymerizablility that is higher than that of the unsaturated group and other radical polymerizable compound which can be optionally copolymerized therewith to give a polymer compound.

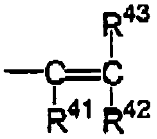
[0127] Examples of the radical polymerizable compound having an ethylenic unsaturated group that has addition-polymerizablility that is higher than that of the unsaturated group represented by Formula (C) include vinyl acrylate, vinyl methacrylate, 2-phenylvinyl acrylate, 2-phenylvinyl methacrylate, 1-propenyl acrylate, 1-propenyl methacrylate, vinylacrylamide, and vinylmethacrylamide.

Synthesis method (6)

[0128] Synthesis method (6) includes: polymerizing at least one radical polymerizable compound having the functional group to give a polymer compound; reacting the functional group on a side chain of the polymer compound with a compound having a structure represented by the following Formula (d) at the functional group in the side chains of the polymer compound to thereby introduce a group of Formula (C) into the polymer compound.

[0129]

Formula (d)



$$-\overset{}{\underset{R^{41}}{C}}=\overset{R^{43}}{\underset{R^{42}}{C}}$$

[0130] Each of R^{41} to R^{43} in Formula (d) is similar to each of R^{41} to R^{43} in Formula (C).

[0131] Specific examples of the radical polymerizable compound having the functional group for use in the synthesis method (6) may be the same as those of the radical polymerizable compound having the functional group used in the synthesis method (2).

Examples of the compound having the structure represented by Formula (d) include 2-hydroxyethyl monovinyl ether, 4-hydroxybutyl monovinyl ether, diethylene glycol monovinyl ether, and 4-chloromethylstyrene.

[0132] Synthesis methods (1) to (6) for the polymer in the invention that has a radical polymerizable group represented by any one of the Formulae (A) to (C) are described above. The specific binder polymer of the invention can be obtained by copolymerizing units represented by Formula (9) with the radical polymerizable compound in a predetermined ratio when the radical polymerizable compound is produced according to any one of the synthesis methods (1) to (6).

[0133] Next, Formulae (D) and (E) will be explained.

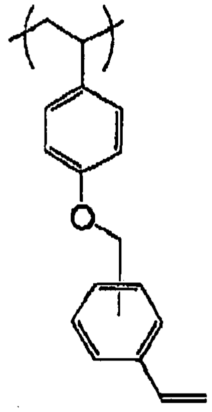
In Formula (D), R^{48} represents a hydrogen atom or a methyl group; R^{49} represents an arbitrary atom or an arbitrary atomic group, each of which may be substituted; and k denotes an integer of 0 to 4. The radical polymerizable group represented by Formula (D) bonds to the polymer backbone via a single bond or via a linking group formed of an atom or an atomic group, and its bonding mode is not specifically limited.

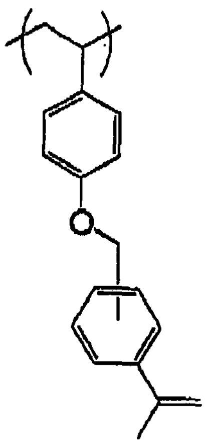
[0134] In Formula (E), R^{50} represents a hydrogen atom or a methyl group; R^{51} represents an arbitrary atom or an arbitrary atomic group, each of which may be substituted; m denotes an integer of 0 to 4; and A^- represents an anion. The pyridinium ring of Formula (E) may be in the form of benzopyridinium having a condensed benzene ring as a substituent thereof, and examples of such embodiment include a quinolinium group and an isoquinolinium group. The radical polymerizable group represented by Formula (E) bonds to a main chain of the polymer via a single bond or via a linking group formed of an atom or an atomic group, and its bonding mode is not specifically limited.

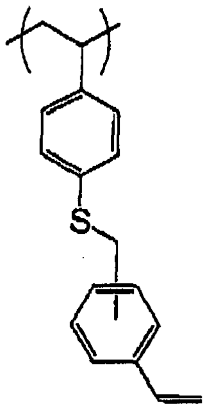
[0135] Preferable examples of the unit (repeating unit) having the radical polymerizable group represented by Formulae

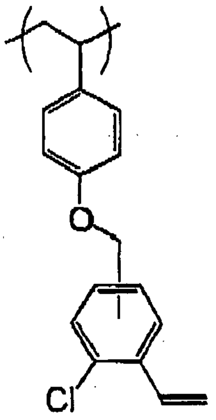
(D) or (E) are described below, while the invention should not be limited thereto.

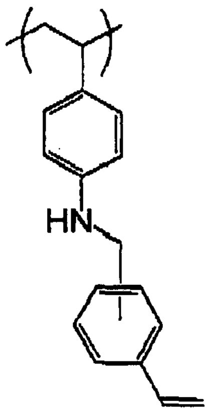
[0136]

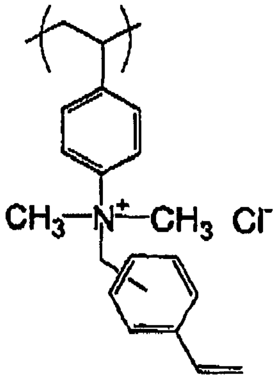


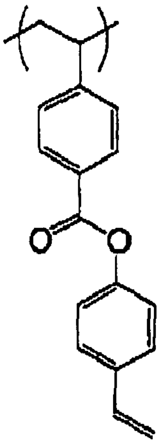


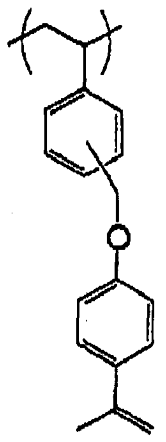


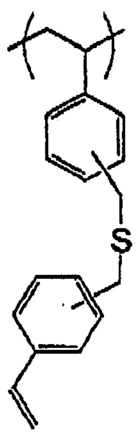












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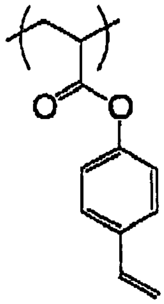

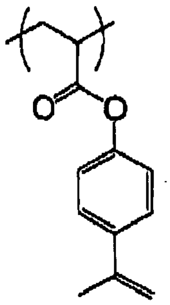

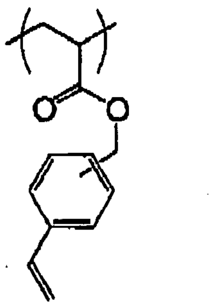

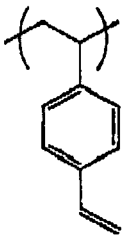

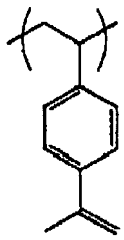

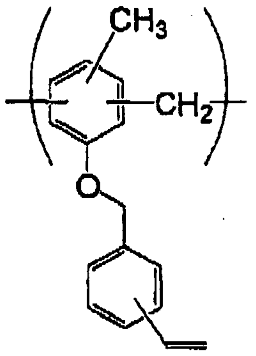

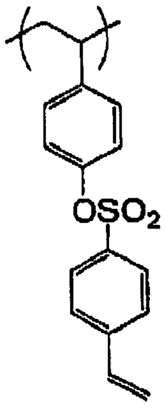

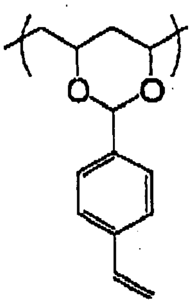

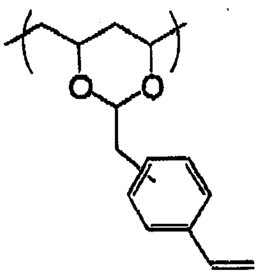

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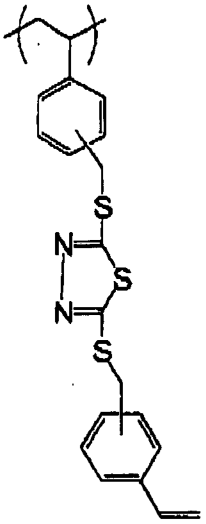
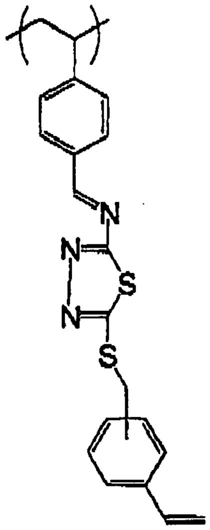
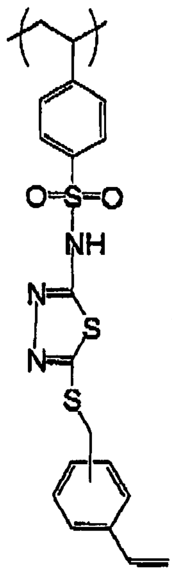
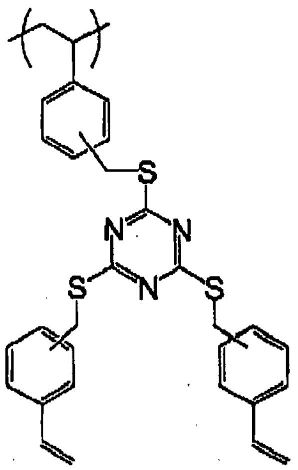
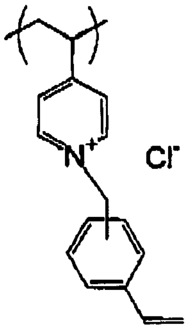
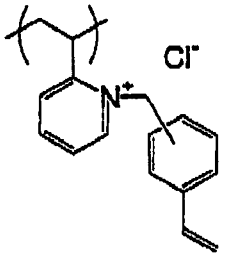
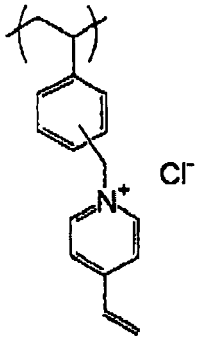
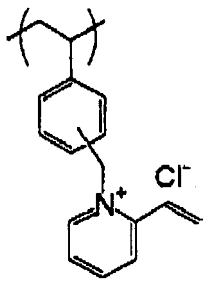




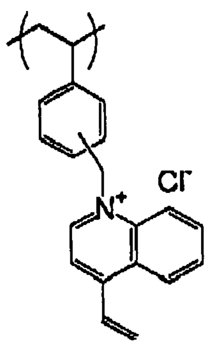



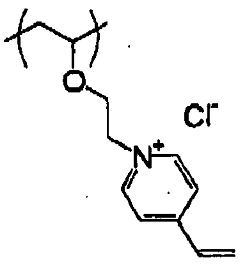


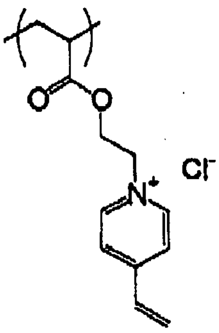
[0139]











[0140] Among the radical polymerizable groups represented by one of Formulae (A) to (E) described above, preferred are those represented by one of Formulae (A) and (B). More preferred are the radical polymerizable groups represented by Formula (A); and most preferred are the radical polymerizable groups represented by Formula (A) in which R^{33} is a hydrogen atom or a methyl group and X^{12} is an oxygen atom or a nitrogen atom.

[0141] In addition to the units having the carboxyl group and the units having the preferable radical polymerizable group, the organic high molecular binder polymer used in the invention may be further copolymerized with any other component such as those described below. Any known radical polymerizable monomers may be used for the comonomer component without limitation. Specific examples thereof include monomers described in Polymer Data Handbook-Primary Edition- (edited by the Polymer Society of Japan, Baifukan, 1986). Either one or a combination of two or more of such comonomers may be used in the invention.

[0142] Particularly preferable examples of the comonomer among these are monomers having a radical polymerizable group described below.

Namely, examples thereof include radical polymerizable compounds selected from acrylic acid esters, methacryllic acid esters, N,N-disubstituted acrylamides, N,N-disubstituted methacrylamides, styrenes, acrylonitriles, and methaerylonitriles.

[0143] Specific examples thereof include: acrylic esters such as alkyl acrylates (in which the alkyl group preferably has 1 to 20 carbon atoms) (for example, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, ethylhexyl acrylate, octyl acrylate, t-octyl acrylate, chloroethyl acrylate, 2,2-dimethylhydroxypropyl acrylate, 5-hydroxypentyl acrylate, trimethylolpropane monoacrylate, pentaerythritol monoacrylate, glycidyl acrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate, and tetrahydrofurfuryl acrylate); aryl acrylates (for example, phenyl acrylate); methacrylic esters such as alkyl methacrylates (in which the alkyl group preferably has 1 to 20 carbon atoms) (for example, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, chlorobenzyl methacrylate, octyl methacrylate, 4-hydroxybutyl methacrylate, 5-hydroxypentyl methacrylate, 2,2-dimethyl-3-hydroxypropyl methacrylate, trimethylolpropane monomethacrylate, pentaerythritol monomethacrylate, glycidyl methacrylate, furfuryl methacrylate, and tetrahydrofurfuryl methacrylate); aryl methacrylates (for example, phenyl methacrylate, cresyl methacrylate, and naphthyl methacrylate); styrenes such as styrene or alkylstyrenes (for example, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, isopropylstyrene, butylstyrene, hexylstyrene, cyclohexylstyrene, decylstyrene, benzylstyrene, chloromethylstyrene, trifluoromethylstyrene, ethoxymethylstyrene, and acetoxymethylstyrene); alkoxystyrenes (for example, methoxystyrene, 4-methoxy-3-methylstyrene, and dimethoxystyrene); halogenostyrenes (for example, chlorostyrene, dichlorostyrene, trichlorostyrene, tetrachlorostyrene, pentachlorostyrene, bromostyrene, dibromostyrene, iodostyrene, fluorostyrene, trifluorostyrene, 2-bromo-4-trifluoromethylstyrene, and 4-fluoro-3-trifluoromethylstyrene); acrylonitrile; and methacrylonitrile.

[0144] Among these radical polymerizable compounds, preferred are acrylic acid esters, methacrylic acid esters and styrenes.

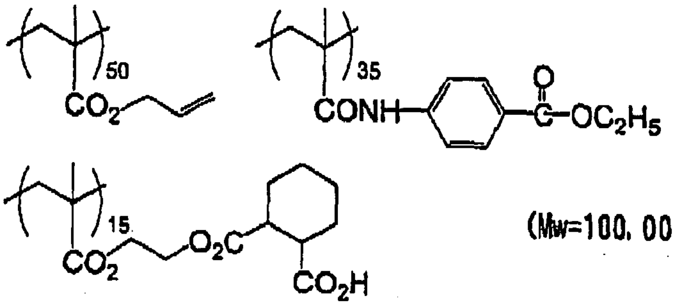
Either one or a combination of two or more of these radical polymerizable compounds may be used in the invention.

[0145] One of the most preferable embodiment of the binder polymer used in the invention is the polymer having the carboxyl group represented by Formula (9) and the specific radical polymerizable group.

[0146] Specific examples of the binder polymer of the invention are described below. Each of (i-1) to (i-46) has the radical polymerizable group, and (ii-1) to (ii-5) do not have such group. The molar ratio of each of the structural units is shown as a suffix. In addition, Mw represents an average molecular weight. It should be remarked that the invention should not be limited to these.

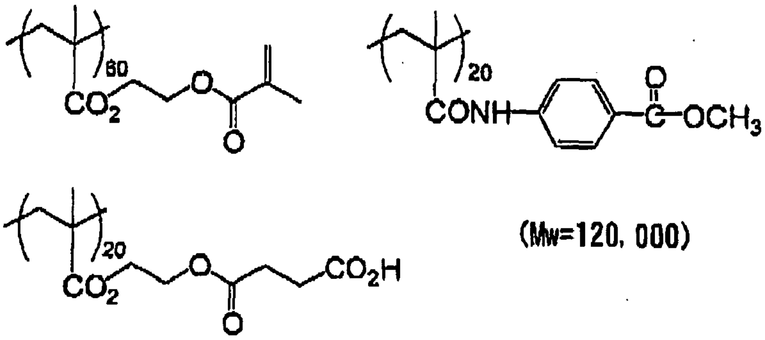
[0147]

(i-1)



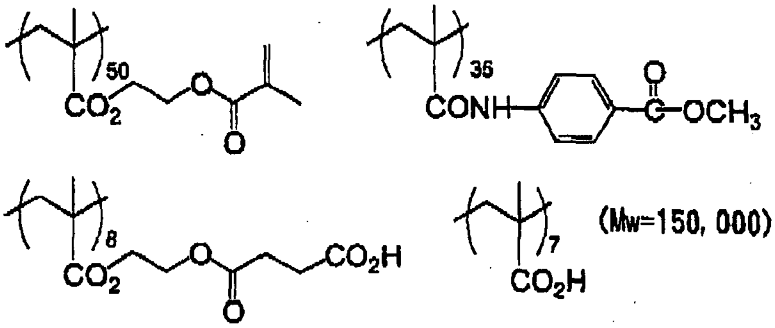
(Mw=100, 000)

(i-2)



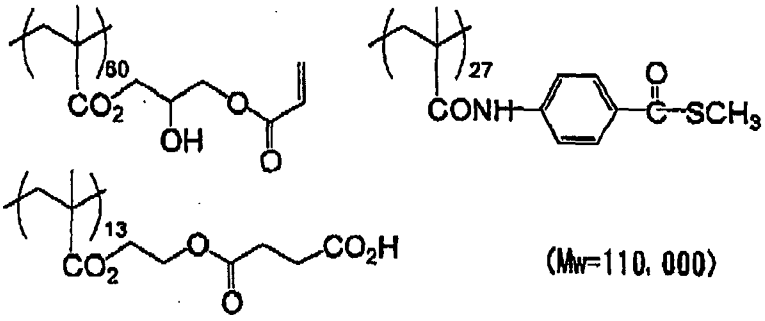
(Mw=120, 000)

(i-3)



(Mw=150, 000)

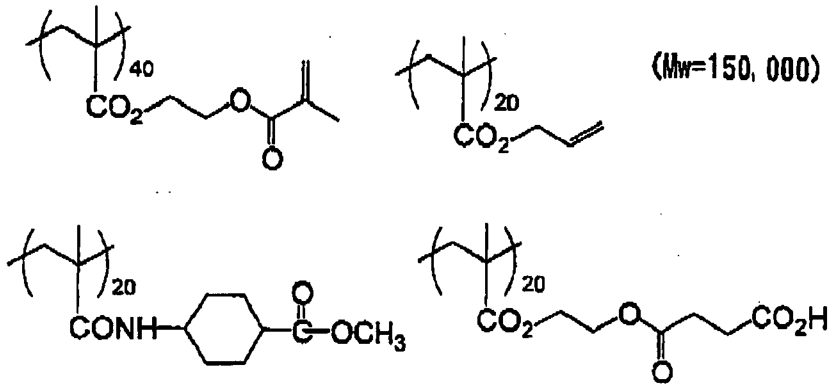
(i-4)



(Mw=110, 000)

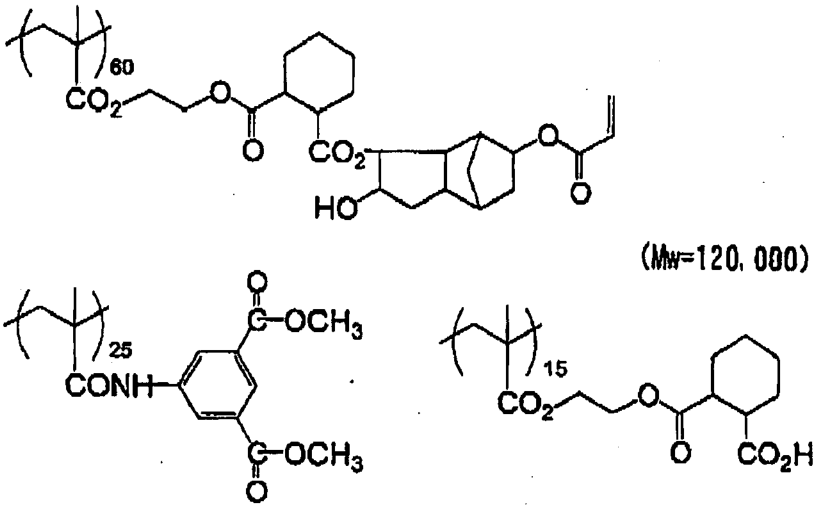
[0148]

(i-5)



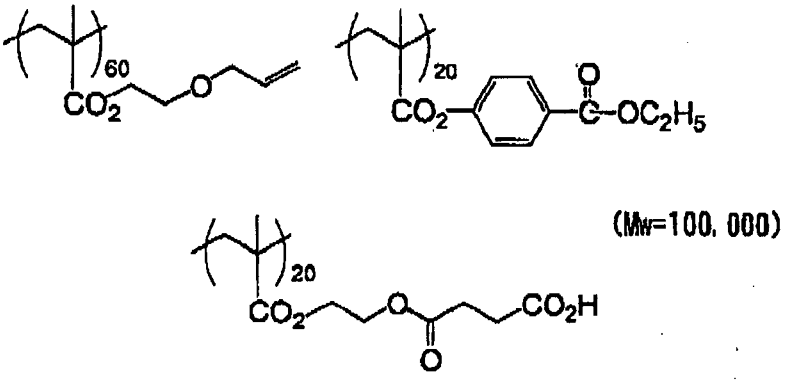
(Mw=150, 000)

(i-6)



(Mw=120, 000)

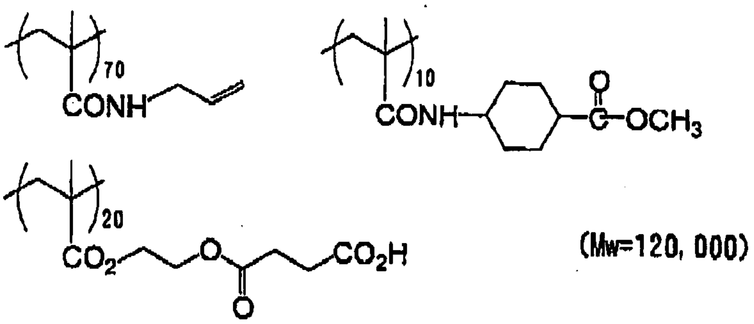
(i-7)



(Mw=100, 000)

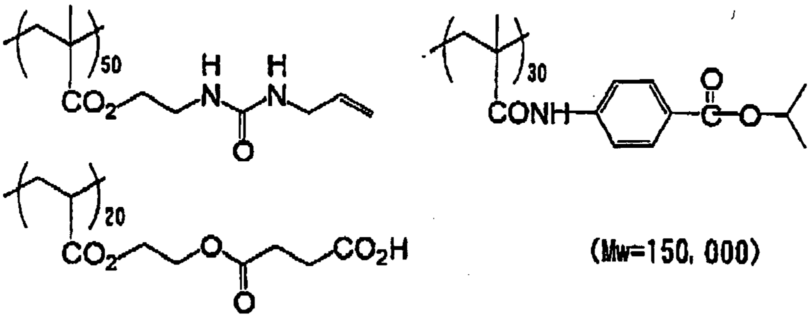
[0149]

(i-8)



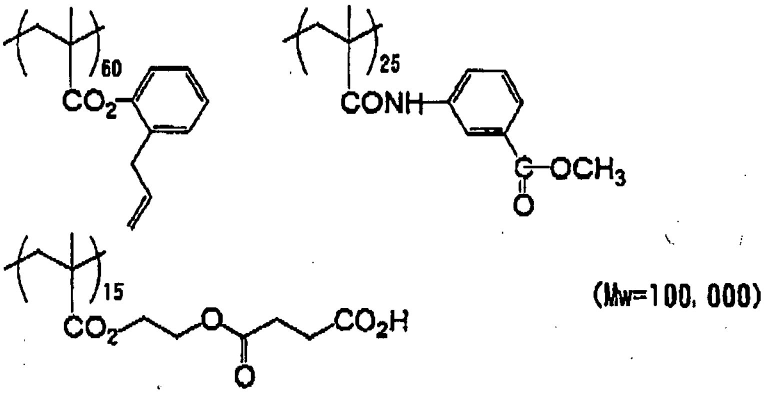
(Mw=120, 000)

(i-9)



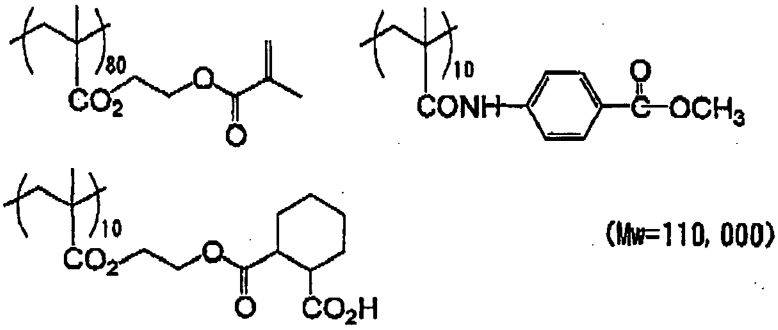
(Mw=150, 000)

(i-10)



(Mw=100, 000)

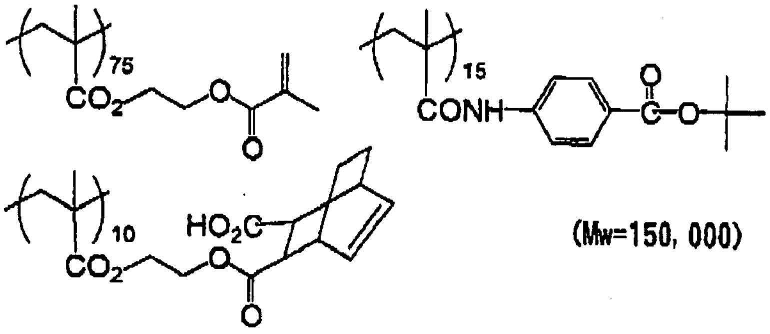
(i-11)



(Mw=110, 000)

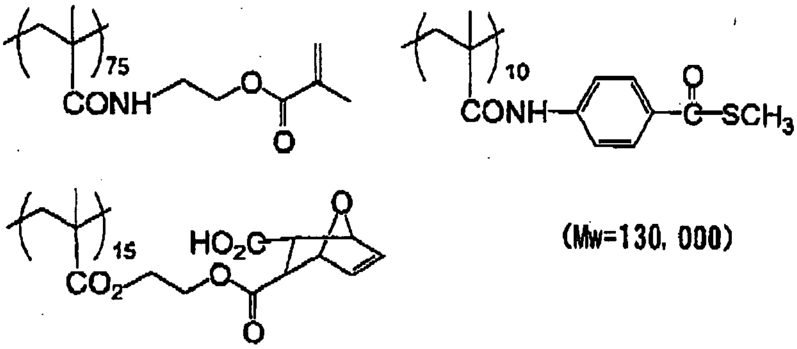
[0150]

(i-12)



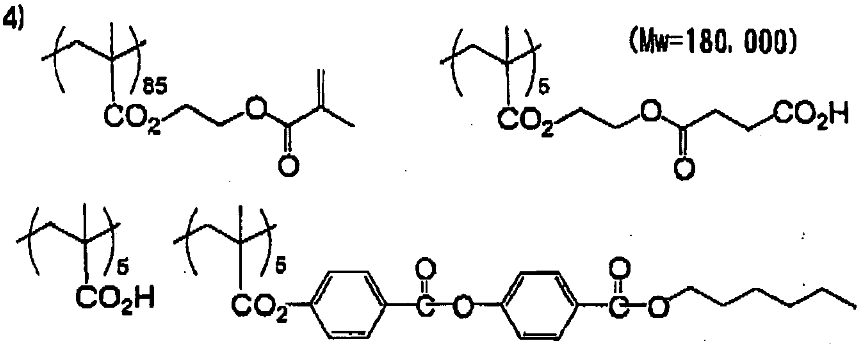
(Mw=150, 000)

(i-13)



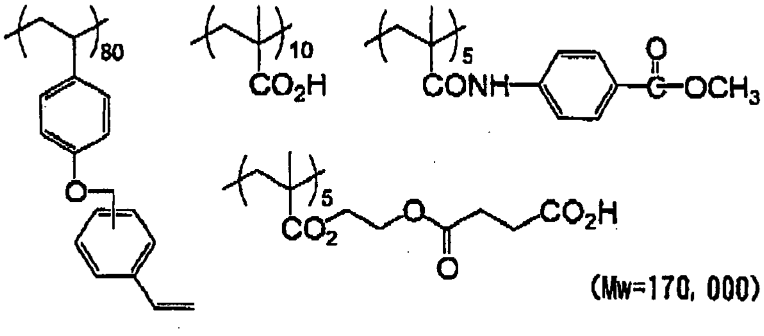
(Mw=130, 000)

(i-14)



(Mw=180, 000)

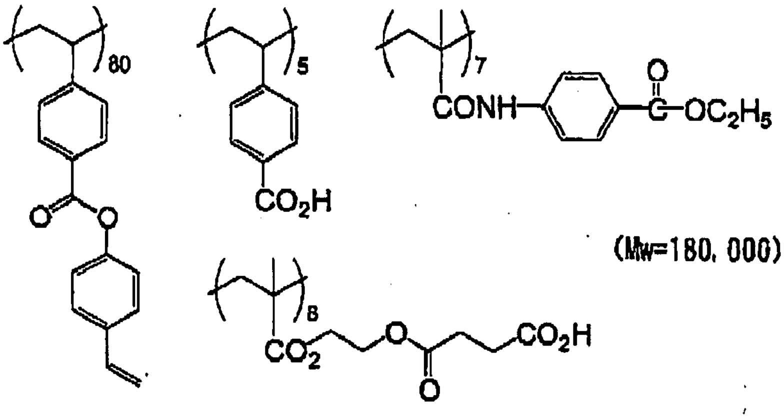
(i-15)



(Mw=170, 000)

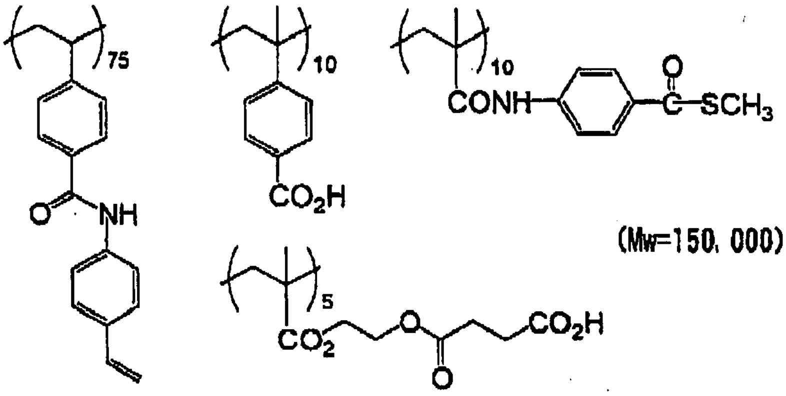
[0151]

(i-16)



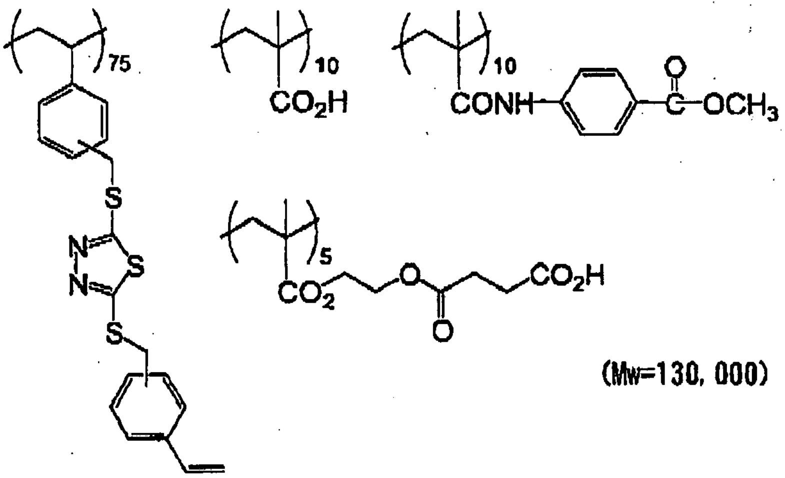
(Mw=180, 000)

(i-17)



(Mw=150, 000)

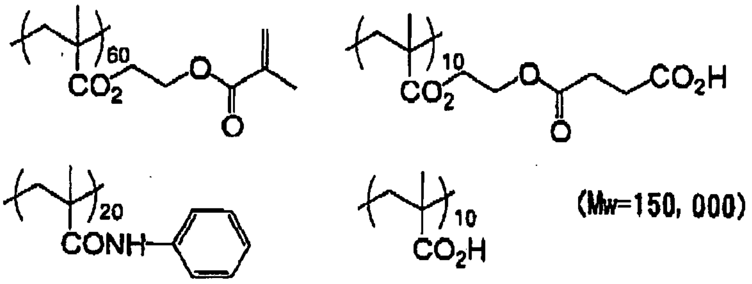
(i-18)



(Mw=130, 000)

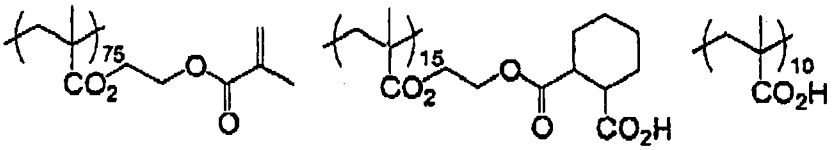
[0152]

(i-19)



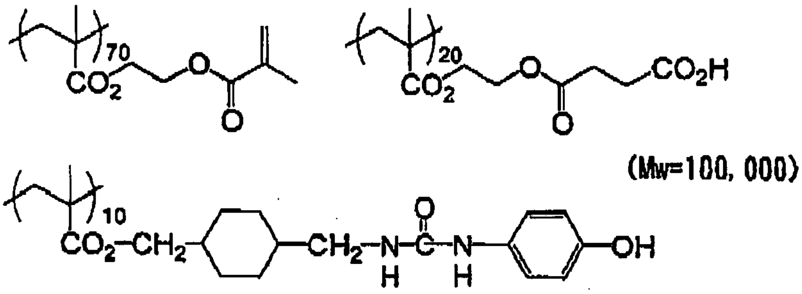
(Mw=150, 000)

(i-20)



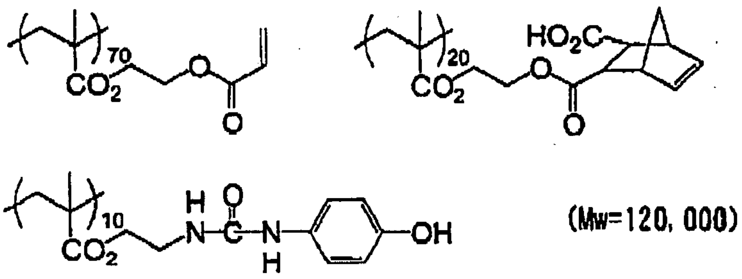
(Mw=120, 000)

(i-21)



(Mw=100, 000)

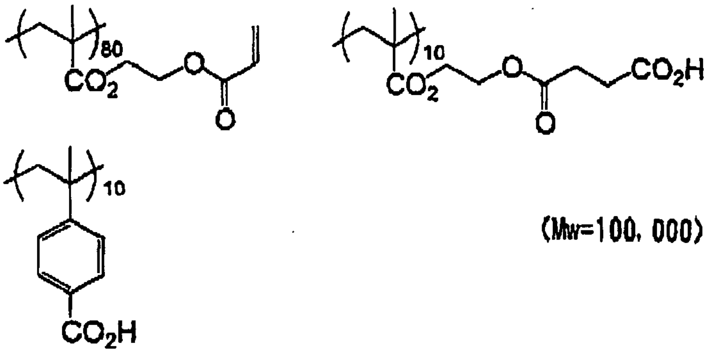
(i-22)



(Mw=120, 000)

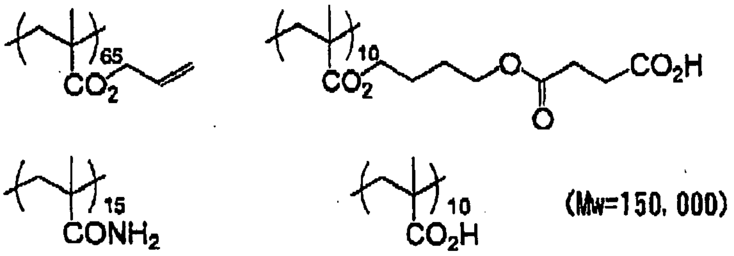
[0153]

(i-23)



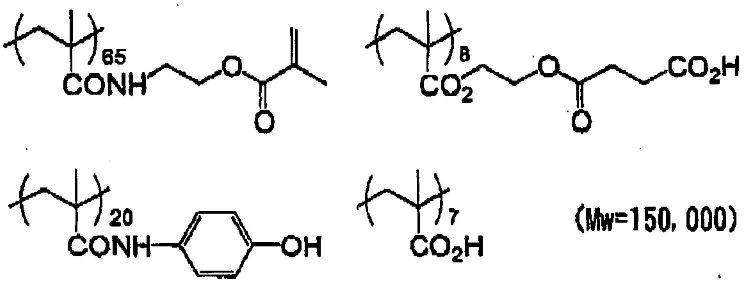
(Mw=100, 000)

(i-24)



(Mw=150, 000)

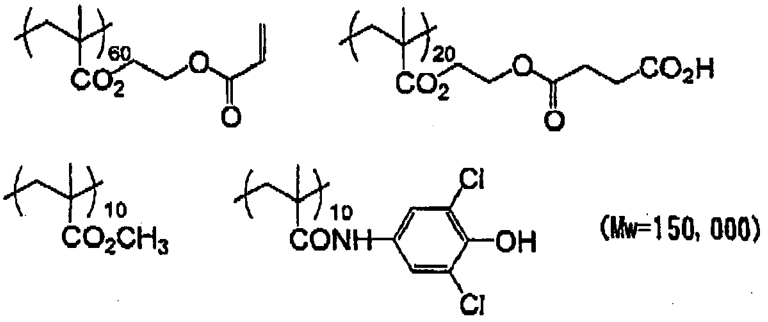
(i-25)



(Mw=150, 000)

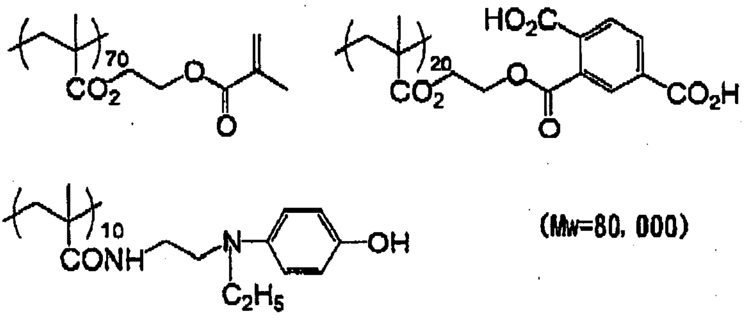
[0154]

(i-26)



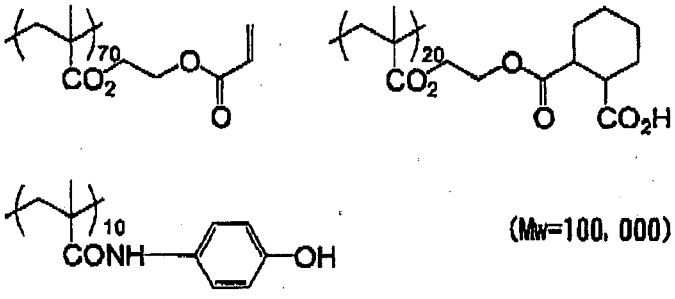
(Mw=150, 000)

(i-27)



(Mw=80, 000)

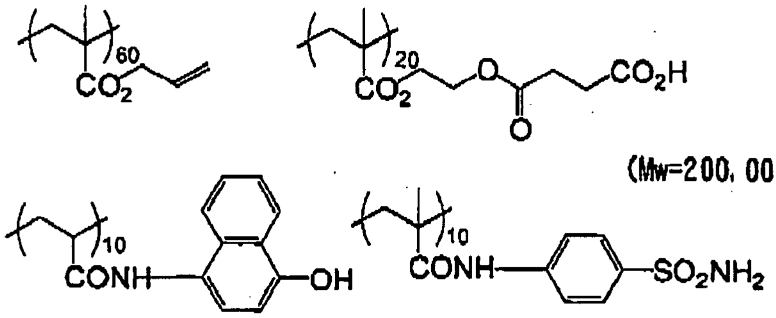
(i-28)



(Mw=100, 000)

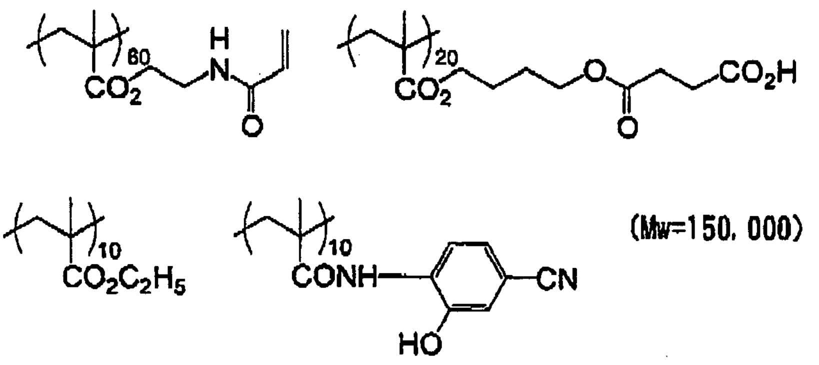
[0155]

(i-29)



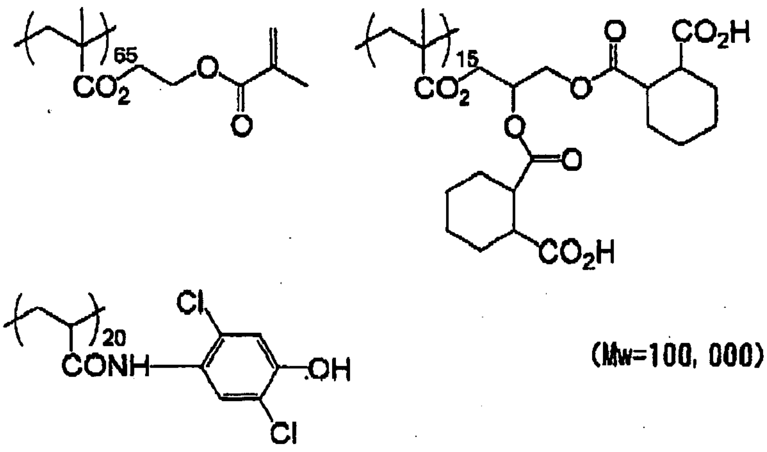
(Mw=200, 000)

(i-30)



(Mw=150, 000)

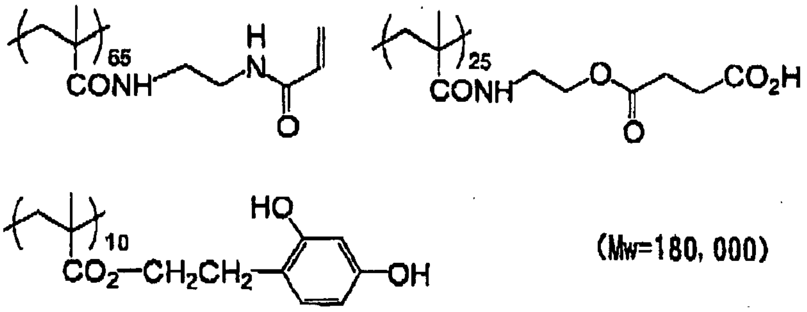
(i-31)



(Mw=100, 000)

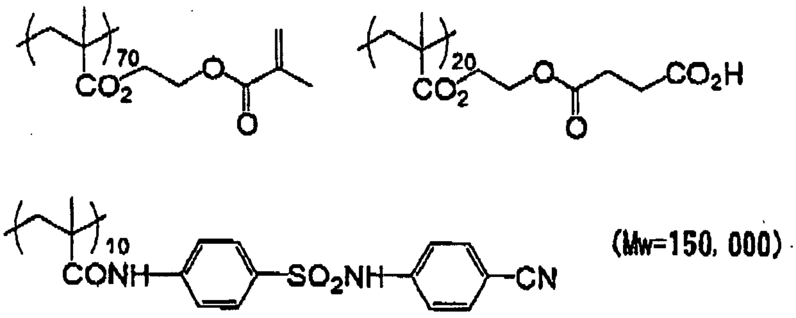
[0156]

(i-32)



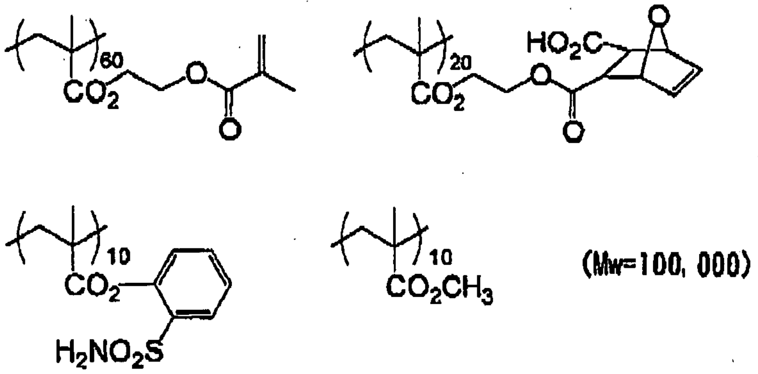
(Mw=180, 000)

(i-33)



(Mw=150, 000)

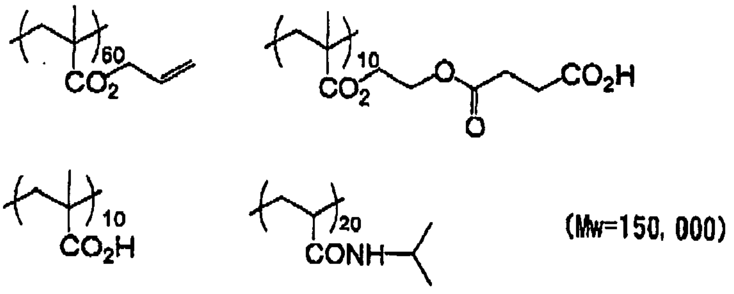
(i-34)



(Mw=100, 000)

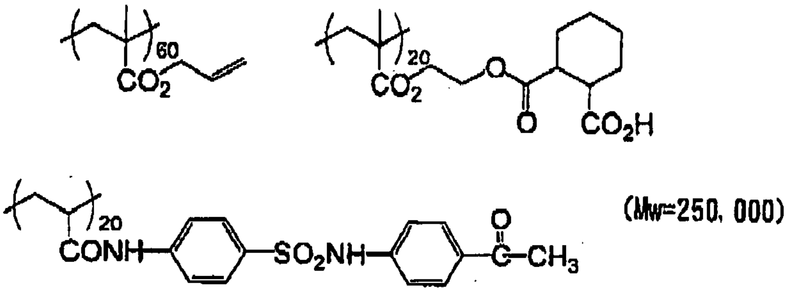
[0157]

(i-35)



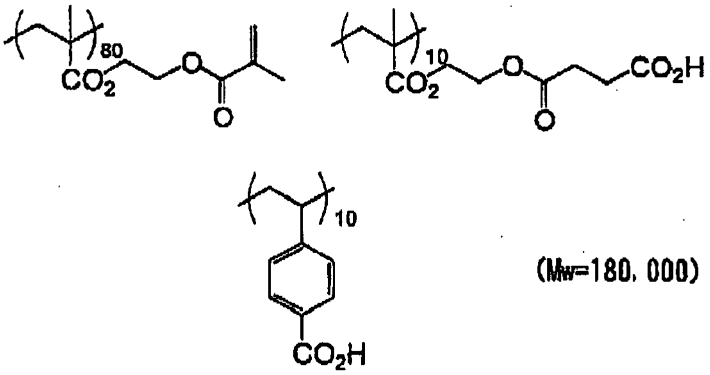
(Mw=150, 000)

(i-36)



(Mw=250, 000)

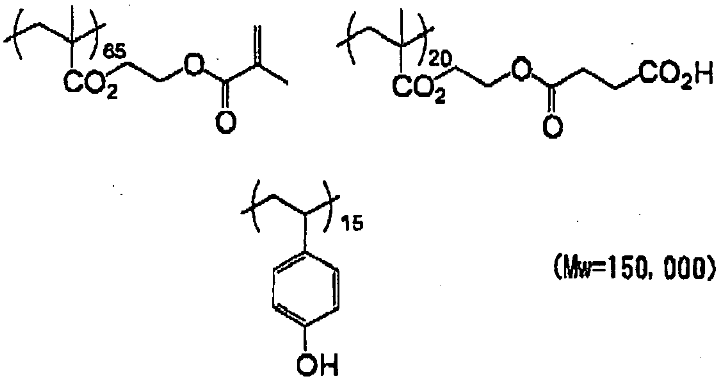
(i-37)



(Mw=180, 000)

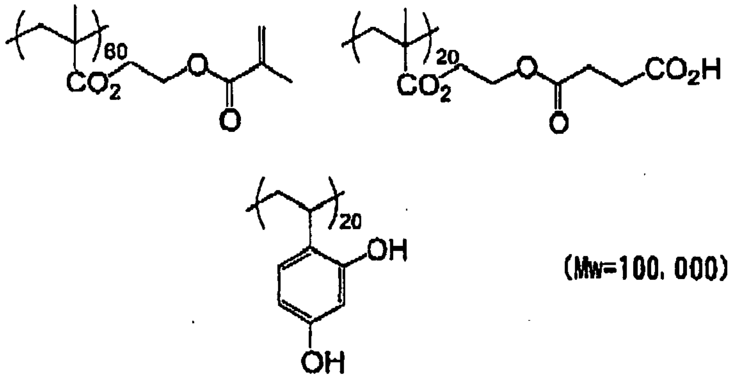
[0158]

(i-38)



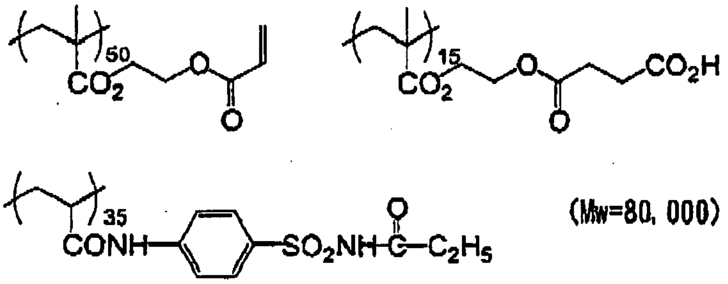
(Mw=150, 000)

(i-39)



(Mw=100, 000)

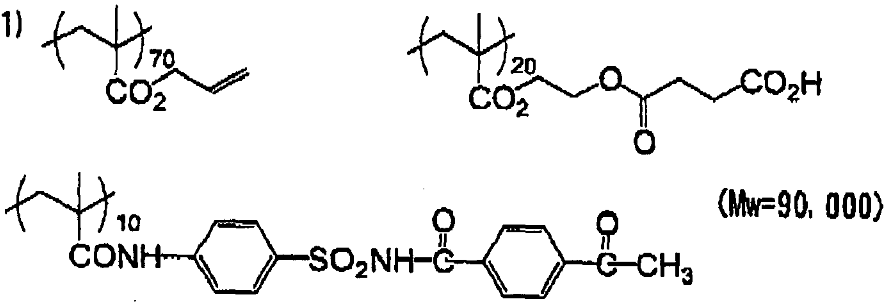
(i-40)



(Mw=80, 000)

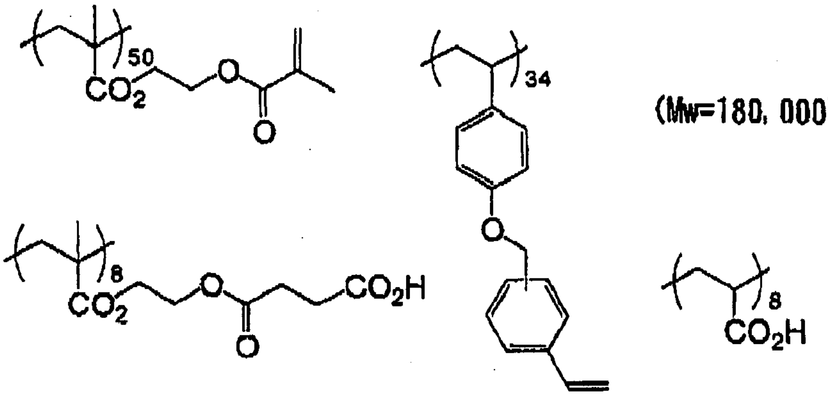
[0159]

(i-41)



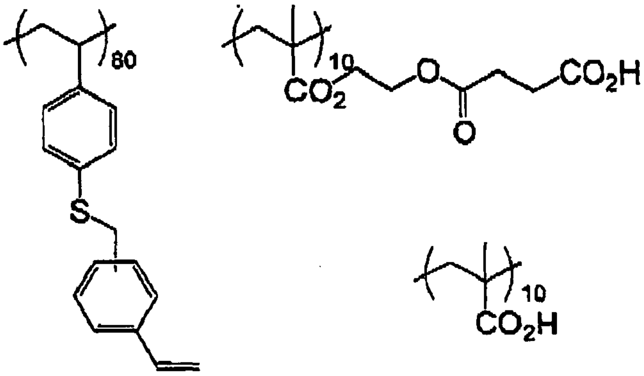
(Mw=90, 000)

(i-42)



(Mw=180, 000)

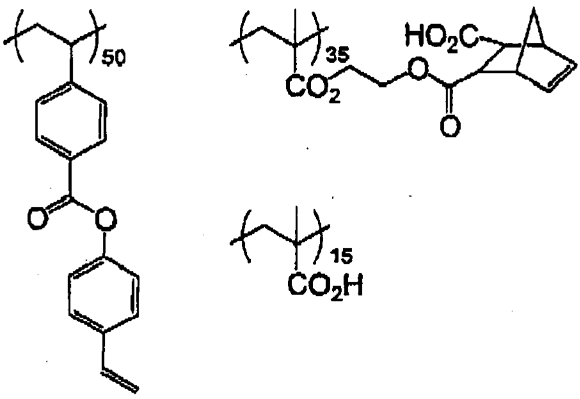
(i-43)



(Mw=150, 000)

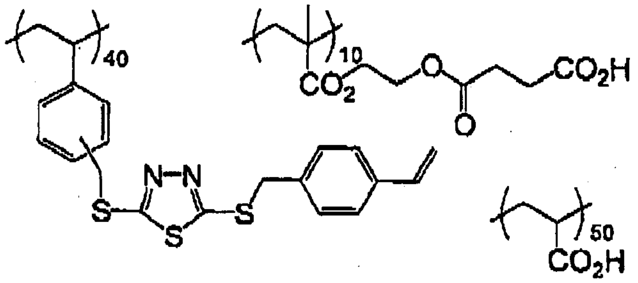
[0160]

(i-44)



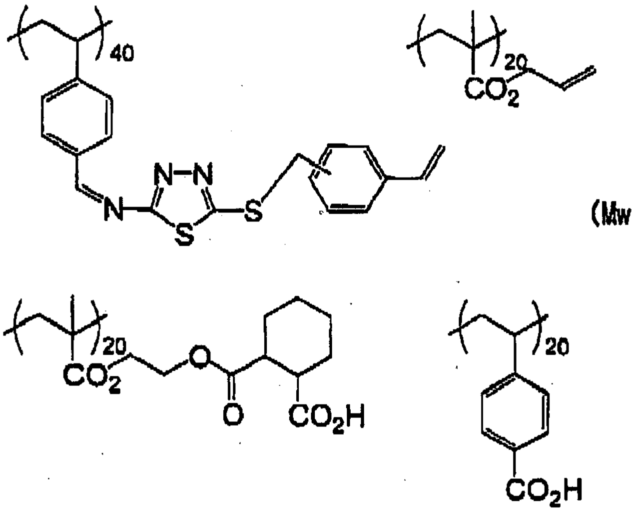
(Mw=100, 000)

(i-45)



(Mw=90, 000)

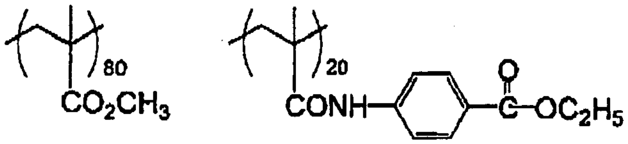
(i-46)



(Mw=120, 000)

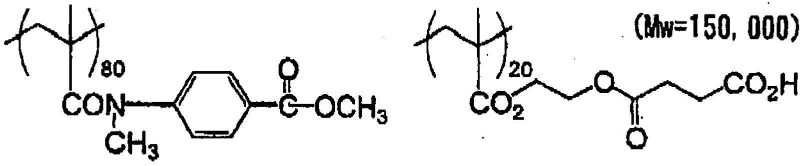
[0161]

(i i-1)



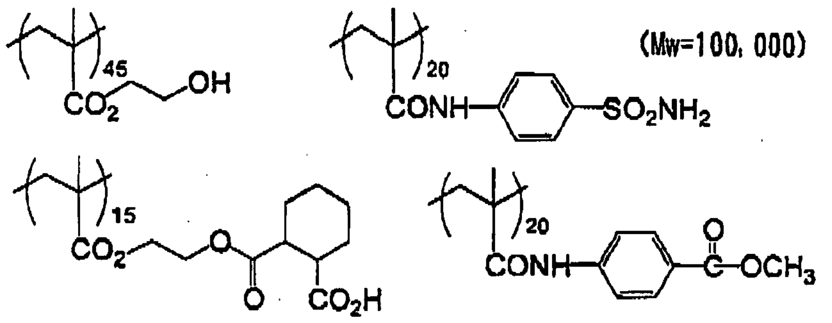
(Mw=100, 000)

(i i-2)

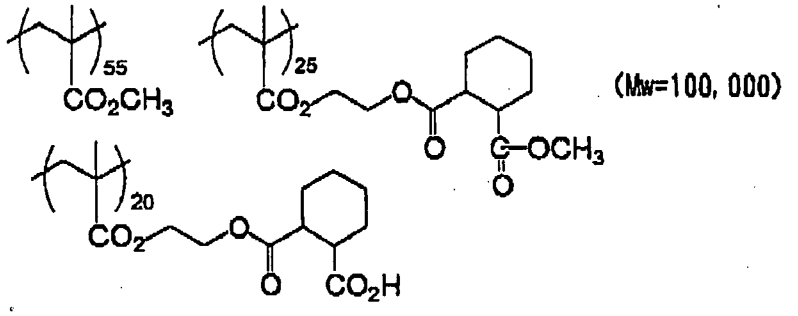


(Mw=150, 000)

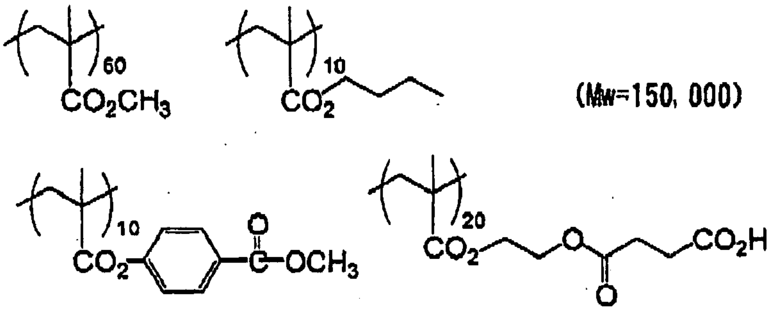
(ii-3)



(ii-4)



(ii-5)



[0162] For example, when the binder polymer is used as a component of a photosensitive layer of the planographic printing plate precursor of the invention, the molecular weight of the polymer may be suitably determined from the viewpoint of the image-formability of the precursors and the printing durability of a printing plate formed from the precursor. In general, when the molecular weight of the polymer increases, the printing durability will be increased, but the image-formability may be decreased. In contrast, when the molecular weight of the polymer is decreased, the image-formability will be increased, but the printing durability may be decreased. The molecular weight of the organic high molecular polymer is preferably in a range of 400 to 6,000,000, and is more preferably in a range of 900 to 600,000 in terms of the weight-average molecular weight.
The content of the binder polymer of the invention may be preferably 20 to 80 mass%, and is more preferably 30 to 70 mass%, relative to the total weight of the total solid content constituting the photosensitive layer from the viewpoint of the printing durability and the image formability.

(B) Compound having Ethylenic unsaturated bond ,

[0163] The (B) compound having addition polymerizable ethylenic unsaturated bond for use in the invention (hereinafter suitably referred to as a "(B) component") is an addition polymerizable compound having at least one ethylenic unsaturated double bond, and is selected from compounds having at least one ethylenic unsaturated bond, and is preferably selected from compounds having two or more ethylenic unsaturated bonds. The compound group is widely known in the industrial field of the art, and any one belonging thereto may be used in the invention with no specific limitation. For example, the compound may have one selected from various chemical morphologies of monomers, prepolymers (that is, dimers, trimers and oligomers), their mixtures and copolymers. Examples of the monomers and their copolymers include unsaturated carboxylic acids (for example, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, and maleic acid) and their esters and amides. Preferable examples thereof include esters of unsaturated carboxylic acids and aliphatic polyvalent alcohols, and amides of unsaturated carboxylic acids and aliphatic polyvalent amines. Preferable examples thereof further include: addition-reaction products of an unsaturated carboxylic acid ester or amide having a nucleophilic substituent such as a hydroxyl group, an amino grouor a mercapto group and a monofunctional or polyfunctional isocyanate or an epoxides; and dehydrating condensation products of an unsaturated carboxylic acid ester or amide having a nucleophilic substituent such as a hydroxyl group, an amino grouor a mercapto group and monofunctional or polyfunctional carboxylic acids. Preferable examples thereof further include: addition-reaction products of an unsaturated carboxylate or amide having an electrophilic substituent such as an isocyanate group or an epoxy group and a monofunctional or polyfunctional alcohol, amine or thiol; and substitution-reaction products of an unsaturated carboxylate or amide having a removable substituent such as a halogen or a tosyloxy group and a monofunctional or polyfunctional alcohol, amine or thiol. Preferable examples thereof further include compounds formed by using unsaturated phosphonic acids, styrenes or vinyl ethers in place of the unsaturated carboxylic acids.

[0164] Specific examples of monomer, which is the ester of an aliphatic polyvalent alcohol compound and an unsaturated carboxylic acid, include acrylic esters such as ethylene glycol diacrylate, triethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol diacrylate, propylene glycol diacrylate, neopentylglycol diacrylate, trimethylolpropane triacrylate, trimethylolpropane tri(acryloyloxypropyl)ether, trimethylolethane triacrylate, hexanediol diacrylate, 1,4-cyclohexanediol diacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol diacrylate, dipentaerythritol hexaacrylate, sorbitol triacrylate, sorbitol tetraacrylate, sorbitol pentaacrylate, sorbitol hexaacrylate, tri(acryloyloxyethyl)isocyanurate, polyester acrylate oligomers, or the like;

[0165] methacrylic esters such as tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, neopentylglycol dimethacrylate, trimethylolpropane trimethacrylate, trimethylolethane trimethacrylate, ethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, hexanediol dimethacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol dimethacrylate, dipentaerythritol hexamethacrylate, sorbitol trimethacrylate, sorbitol tetramethacrylate, bis[p-(3-methacryloxy-2-hydroxypropoxy) phenyl] dimethyl methane, bis-[p-(methacryloxyethoxy)phenyl] dimethyl methane, or the like;

[0166] itaconate esters such as ethylene glycol diitaconate, propylene glycol diitaconate, 1,3-butanediol diitaconate, 1,4-butanediol diitaconate, tetramethylene glycol diitaconate, pentaerythritol diitaconate, sorbitol tetraitaconate, or the like;

[0167] crotonate esters such as ethylene glycol dicrotonate, tetramethylene glycol dicrotonate, pentaerythritol dicrotonate, sorbitol tetradicrotonate, or the like;

[0168] isocrotonate esters such as ethylene glycol diisocrotonate, pentaerythritol diisocrotonate, sorbitol tetraisocrotonate, or the like; and

[0169] maleate esters such as ethylene glycol dimalate, triethylene glycol dimalate, pentaerythritol dimalate, sorbitol tetramalate, or the like.

[0170] Examples of other esters preferably used include the aliphatic alcohol esters described in JP-B No. 46-27926, JP-B No. 51-47334, JP-A No. 57-196231; the aromatic skeleton-containing esters described in JP-A No. 59-5240, JP-A No. 59-5241, JP-A No; 2-226149; the amino group-containing esters described in JP-A No. 1-165613; and the like.

[0171] Specific examples of the amide monomer consisting of an aliphatic polyvalent amine compound and an unsaturated carboxylic acid include methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, 1,6-hexamethylene bis-methacrylamide, diethylenetriamine trisacrylamide, xylylene bisacrylamide, xylylene bismethacrylamide, and the like.

[0172] Examples of other preferable amide monomers include the monomers having a cyclohexylene structure described in JP-B No. 54-21726.

[0173] Urethane addition-polymerizable compounds produced in addition reaction between an isocyanate and a hydroxyl group are also preferable, and specific examples thereof include the vinyl urethane compounds containing two or more polymerizable vinyl groups in the molecule, which are produced by addition of a polyisocyanate compound having two or more isocyanate groups in the molecule and a hydroxyl group-containing vinyl monomer represented by the following Formula (i), described in JP-B No. 48-41708.

[0174]

$$CH_2=C(R^{51})COOCH_2CH(R^{52})OH \qquad \text{Formula (i)}$$

[0175] In Formula (i), each of R^{51} and R^{52} represents H or CH_3.

[0176] Also preferable are the urethane acrylates described in JP-A No. 51-37193 and JP-B Nos. 2-32293 and 2-16765; and the urethane compounds having an ethylene oxide skeleton described in JP-B Nos. 58-49860, 56-17654, 62-39417, and 62-39418.

[0177] In addition, utilization of addition-polymerizable compounds having an amino structure or a sulfide structure in the molecule described in JP-A No. 63-277653, JP-A No. 63-260909, or JP-A No. 1-105238 may provide a photopolymerizable compound having excellent applicability in high-speed sensitization.

[0178] Other preferable examples thereof include polyfunctional acrylates and methacrylates such as the polyester acrylates and epoxyacrylates obtained in reaction of an epoxy resin with acrylic acid or methacrylic acid described in JP-A No. 48-64183, and JP-B Nos. 49-43191 or 52-30490. Still another examples thereof include the particular unsaturated compounds described in JP-B Nos. 46-43946,1-40337, or 1-40336, the vinylphosphonic acid compounds described in JP-A No. 2-25493, and the like. In addition, the structures containing a perfluoroalkyl group described in JP-A No. 61-22048 are used preferably in some cases. Further, the photo-curing monomers and oligomers described in J. Adhesion Soc. Jpn. Vol. 20, No. 7, pp. 300 - 308 (1984) can be also preferably used.

[0179] The details of a compound (B) such as its structure, the mode using thereof (namely, whether it is used singly or in a combination of two or more of them), the amount thereof to be used or the like may be determined in any desired manner depending on the performance design of the final polymerizable composition of the invention. For example, when the component (B) of the invention is used in the photosensitive layer of negative planographic printing plate precursor, then the compound (B) may be selected from the following viewpoints. As to the photosensitivity speed, the content of unsaturated group of the compound per molecule is preferably larger. In many cases, bifunctional or more polyfunctional compounds are preferable. For increasing the strength of the image area, that is the cured film containing portion, trifunctional or more polyfunctional compounds are preferable. Further, compounds that is different in point of the number of the functional groups therein and of the type of the polymerizable group therein (for example, acrylates, methacrylates, styrene compounds, vinyl ether compounds) may be combined to thereby control both the photosensitivity of the compound and the mechanical strength of the processed materials. Compounds having a large molecular weight and compounds having a high degree of hydrophobicity are excelent in the photosensitivity and the film strength, however are often unfavorable since their developability is not good and they may form depositions in developer. In addition, the compatibility of the component with other components (for example, the binder polymer such as the components (A), a photo- or thermal-polymerization initiator such as component (C), dye) in the image-recording layer of negative image-recording materials and the dispersibility thereof in those components are also important factors in selecting and using the addition polymerizable compound for the component (B). For example, using low-purity compounds or combining two or more different types of compounds may improve the compatibility of the compounds with such other components.

[0180] When the polymerizable composition of the invention is applied to the protective layer of the planographic printing plate precursor, the polymerizable composition may employ a specific configuration for the purpose of improving adhesiveness to the support of the planographic printing plate precursor and to the protective layer described below. The higher the content of the component (B) in the photosensitive layer, the better from the point of sensitivity. However, an excessively higher content may cause problems such as unfavorable phase separation, which may cause problems in production due to the adhesiveness of the photosensitive layer (e.g., production defects due to transfer or adhesion of photosensitive layer components), precipitation in the developing solution and the like. From these viewpoints, the ratio of the content of the component (B) is preferably 5 to 80 % by mass, and is more preferably 25 to 75 % by mass, with respect to the total content of non-volatile components in the photosensitive layer. The component (B) may be used singly or in combination of two or more thereof. In addition, the component (B) may be suitably determined depending on the suitable structure, blending ratio, and content from the viewpoint of the degree of polymerization inhibition by oxygen, the resolution, the fogging resistance, the refractivity change, and the surface adhesiveness. The component (B) may also be used in the layer configurations and coating methods of the undercoat layer described below in accordance with occasion.

(C) Photo-polymerization Initiator and Thermal-polymerization Initiator

[0181] As the photopolymerization initiator for use in the invention, known photopolymerization initiators disclosed in patents or literatures, and the combination of two or more kinds ofphotopolymerization initiators (photopolymerization initiation system) can be suitably selected in consideration of the wavelength of the light source to be used.

[0182] In the case where a blue semiconductor laser, an Ar laser, a second harmonic of an infrared semiconductor laser or an SHG-YAG laser is used as a light source, various kinds of photopolymerization initiators (photopolymerization systems) have been proposed. Examples thereof include a certain kind of a photoreducing dye, for example, Rose Bengal, eosin or erythrocin disclosed in U.S. Pat. No. 2,850,445, a system of a combination of a dye and an initiator, for example, a complex initiating system of a dye and an amine (JP-B No. 44-20189), a combination system of hexaarylbiimidazole, a radical generator and a dye (JP-B No. 45-37377), a system of hexaarylbiimidazole and p-dialkylaminobenzylidene ketone (JP-B No. 47-2528 and JP-A No. 54-155292), a system of a cyclic cis-α-dicarbonyl compound and a dye (JP-A No. 48-84183), a system of a cyclic triazine and a merocyanine dye (JP-A No. 54-151024), a system of 3-ketocoumarin and an activator (JP-A No. 52-112681 and JP-A No. 58-15503), a system of biimidazole, a styrene derivative and thiol (JP.-A No. 59-140203), a system of an organic peroxide and a dye (JP-A No. 59-1504, JP-A No. 59-140203, JP-A No. 59-189340, JP-A No. 62-174203, JP-B No. 62-1641 and U.S. Pat. No. 4,766,055), a system of a dye and an active halogen compound (JP-A No. 63-1718105, JP-A No. 63-258903 and JP-A No. 3-264771), a system of a dye and a borate compound (JP-A No. 62-143044, JP-A No. 62-150242, JP-A No. 64-13140, JP-A No. 64-13141, JP-A No. 64-13142, JP-A No. 64-13143, JP-A No. 64-13144, JP-A No. 64-17048, JP-A No. 1-229003, JP-A No. 1-298348 and JP-A No. 1-138204), a system of a dye having a rhodanine ring and a radical generator (JP-A No. 2-179643 and JP-A No. 2-244050), a system of titanocene and a 3-ketocoumarin dye (JP-A No. 63-221110), a system of combining titanocene, a xanthene dye and an addition polymerizable ethylenic unsaturated compound containing an amino group or a urethane group (JP-A No. 4-221958 and JP-A No. 4-219756), a system of titanocene and a specific merocyanine dye (JP-A No. 6-295061), and a system of titanocene and a dye having a benzopyran ring (JP-A No. 8-334897).

[0183] The particularly preferable photopolymerization initiator (system) according in the invention includes at least one titanocene compound. Titanocene compounds for use in the invention are not particularly limited, and any compound can be used as long as it can generate active radicals when irradiated with light in the coexistence with other sensitizing dye. For example, known compounds disclosed in JP-A No. 59-152396, JP-A No. 61-151197, JP-A No. 63-41483, JP-A No. 63-41484, JP-A No. 2-249, JP-A No, 2-291, JP-A No. 3-27393, JP-A No. 3-12403 or JP-A No. 6-41170 can be arbitrarily used.

[0184] Specific examples of the titanocene compounds include di-cyclopentadienyl-Ti-di-chloride, di-cyclopentadienyl-Ti-bis phenyl, di-cyclopentadienyl-Ti-bis2,3,4,5,6-pentafluorophen-1-yl (hereinafter sometimes referred as "T-1"), di-cyclopentadienyl-Ti-bis2,3,5,6-tetrafluorophen-1-yl, di-cyclopentadienyl-Ti-bis2,4,6-trifluorophen-1-yl, di-cyclopentadienyl-Ti-bis2,6-difluorophenl-yl, di-cyclopentadienyl-Ti-bis2,4-difluorophen-1-yl, di-methyl cyclopentadienyl-Ti-bis2,3,4,5,6-pentafluorophen-l-yl, di-methyl cyclopentadienyl-Ti-bis2,3,5,6-tetrafluorophen-1-yl, di-methyl eyclopentadienyl-Ti-bis2,4-difluorophenl-yl, bis(cyclopentadienyl)-bis(2,6-difluoro-3-(pyl-1-yl)phenyl)titanium (hereinafter sometimes referred as "T-2") and the like.

[0185] The titanocene compounds may be further chemically modified in various ways for improvement in the properties of the photosensitive layer. Examples of the modifications include binding with a radical-generating unit of a sensitizer, an addition-polymerizable unsaturated compound, or the like, introduction of a hydrophilic unit, introduction of a substituent group for improvement in compatibility or prevention of crystal precipitation, introduction of a substituent group for improvement in adhesiveness, polymerization, and the like.

[0186] Similarly to the addition polymerizable compounds described above, these titanocene compounds can also be suitably selected according to the designs of the performances of the polymerizable composition or the planographic printing plate precursor employing the polymerizable composition. For example, when it is employed in the photosensitive layer of the planographic printing plate precursor, the compatibility with a photosensitive layer can be increased by using two or more titanocene compounds in combination. In general, it is preferable to use a large amount of photopolymerization initiator such as titanocene compounds from the viewpoint of photosensitivity. The amount of the photopolymerization initiator such as titanocene compounds for obtaining sufficient photosensitivity is typically in a range of 0.5 to 80 parts by weight, and is preferably in a range of 1 to 50 parts by weight, with respect to 100 parts by weight of the nonvolatile components. The typical and preferable ranges of the amount are applicable for both in the case where it is used in the polymerizable composition and in the case where it is used in the photosensitive layer of the planographic printing plate precursor. On the other hand, when the use of a photosensitive layer under a yellow lamp or a white lamp is taken into consideration, the use amount of the titanocene compounds is preferably small from the viewpoint of prevention of fogging due to light having a wavelength in the vicinity of 500 nm. Even if the amount of the titanocene compounds is reduced to 6 parts by weight or less, further reduced to 1.9 parts by weight or less, and still further reduced to 1.4 parts by weight or less with respect to 100 parts by weight of the nonvolatile components, sufficient photosensitivity can be obtained by using in combination with other sensitizing dyes.

[0187] Examples of the thermal polymerization initiator for initiating and progressing of polymerization of the component (B) used in the invention include a thermal decomposable radical generator which is decomposed by heat to generate radical. Such radical generator is used in combination with the infrared absorbing dye described below so that the infrared absorbing dye generates heat when being exposed to infrared laser and the radical is generated by the thus generated heat. Recoding can be performed by utilizing the combination of these components.

Examples of the radical generator include an onium salt, a triazine compound having a trihalomethyl group, a peroxide, an azo polymerization initiator, an azide compound, quinone diazide, an oxime ester compound, and a triaryl monoalkylborate compound. Among them, an onium salt and an oxime ester compound are preferable because of high sensitivity. Hereinafter, specific examples of the onium salt which can be appropriately used as the polymerization initiator in the invention will be described. Preferable examples of the onium salt include an iodonium salt, a diazonium salt, a sulfonium salt, and the like. Although These onium salts work as radical polymerization initiators in the invention rather than work as acid generators. Preferable examples of the onium salts for use in the invention include those represented by the following Formulae (F) to (H).

[0188]

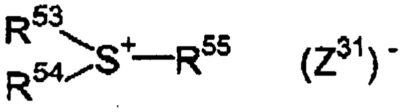
Formula (F)

$$Ar^{11}\text{—}I^{+}\text{—}Ar^{12} \qquad (Z^{11})^{-}$$

Formula (G)

$$Ar^{21}\text{—}N^{+}\equiv N \qquad (Z^{21})^{-}$$

Formula (H)



$$\begin{matrix}R^{53}\searrow \\ R^{54}\nearrow\end{matrix} S^{+}\text{—}R^{55} \qquad (Z^{31})^{-}$$

[0189] In Formula (F), r^{11} and Ar^{12} each independently represents an aryl group having 20 or less carbon atoms which may have one or more substituents. Preferable examples of the substituents of the aryl group include a halogen atom, a nitro group, an alkyl group having 12 or less carbon atoms, an alkoxy group having 12 or less carbon atoms, and an aryloxy group having 12 or less carbon atoms.

$(Z^{11})^-$ represents a counter ion selected from the group consisting of a halogen ion, a perchlorate ion, a tetrafluoroborate ion, a hexafluorophosphate ion, and a sulfonate ion and is preferably a perchlorate ion, a hexafluorophosphate ion, or an aryl sulfonate ion.

[0190] In Formula (G), Ar^{21} represents an aryl group having 20 or less carbon atoms which may have one or more substituents. Preferable examples of the substituent group include a halogen atom, a nitro group, an alkyl group having 12 or less carbon atoms, an alkoxy group having 12 or less carbon atoms, an aryloxy group having 12 or less carbon atoms, an alkylamino groups having 12 or less carbon atoms, a dialkylamino group having 12 or less carbon atoms, an arylamino group having 12 or less carbon atoms, and a diarylamino group having 12 or less carbon atoms.

$(Z^{21})^-$ represents a counter ion which is similar to $(Z^{11})^-$ in Formula (F).

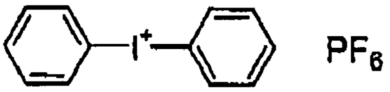
[0191] In Formula (H), R^{53}, R^{54} and R^{55} each independently represents a hydrocarbon group having 20 or less carbon atoms which may have one or more substituents. Preferable examples of the substituent include a halogen atom, a nitro group, an alkyl group having 12 or less carbon atoms, an alkoxy group having 12 or less carbon atoms, and an aryloxy group having 12 or less carbon atoms.

(Z^{31})- represents a counter ion which is similar to (Z^{11})- in Formula (F).

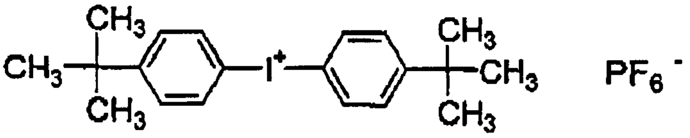
[0192] Specific examples of the onium salt preferably used in the invention include those described in JP-A No. 2001-133969. Following are the specific examples of the onium salt represented by Formula (F) ([OI-1] to [OI-10]), the specific examples of the onium salt represented by Formula (G) ([ON-1] to [ON-5]) and the specific examples of the onium salt represented by Formula (H) ([OS-1] to [OS-7]), which can be preferably used in the invention, while the invention is not limited thereby.

[0193]

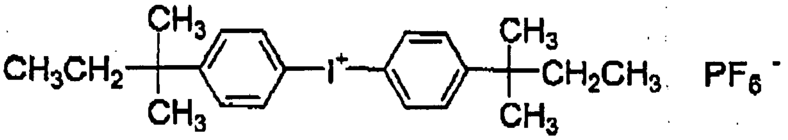
[OI- 1]



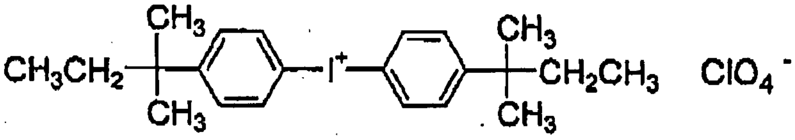
[OI- 2]



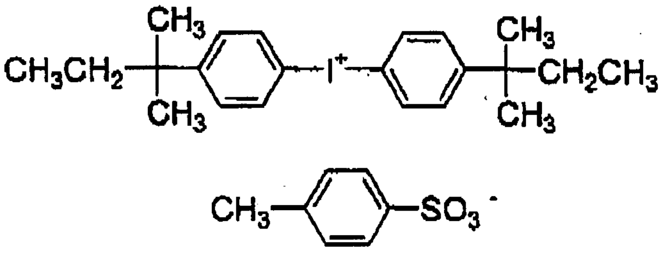
[OI- 3]



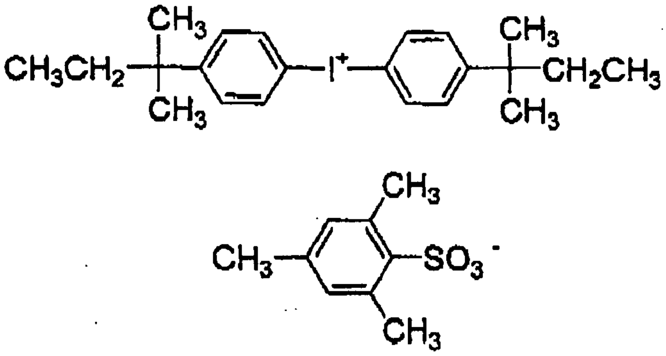
[OI- 4]



[OI- 5]

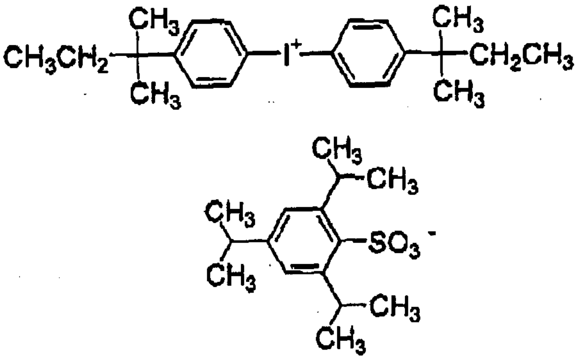


[OI- 6]



[0194]

[01- 7]



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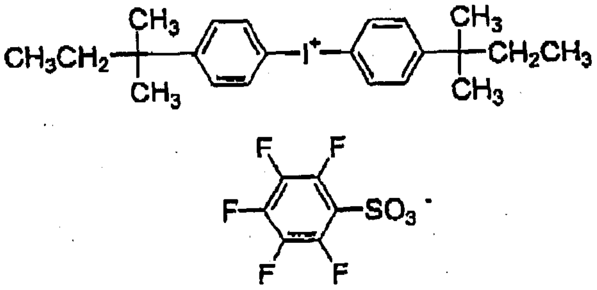
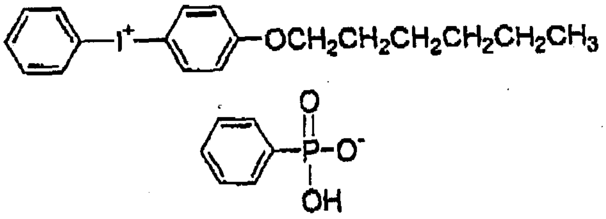
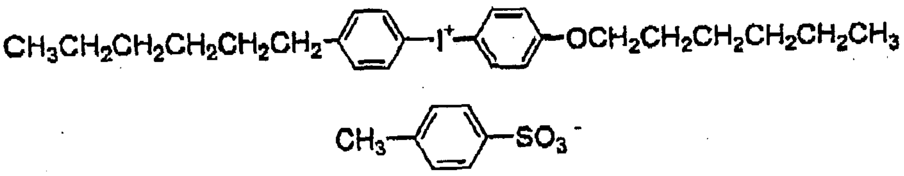


[01- 9]

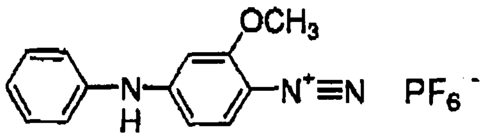


[01- 10]



[0195]

[ON- 1]



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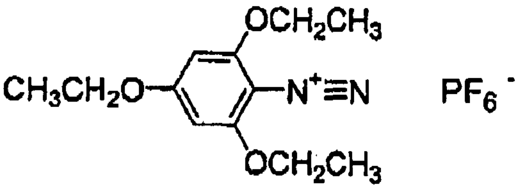

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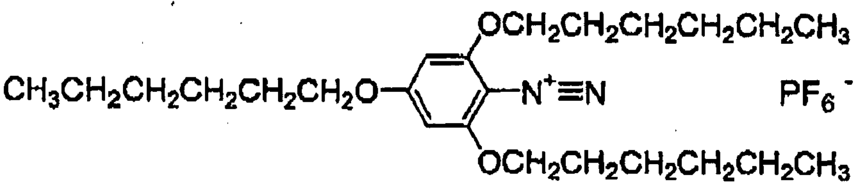
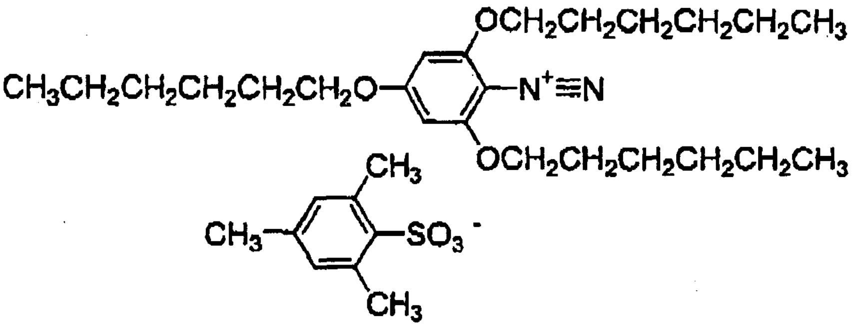
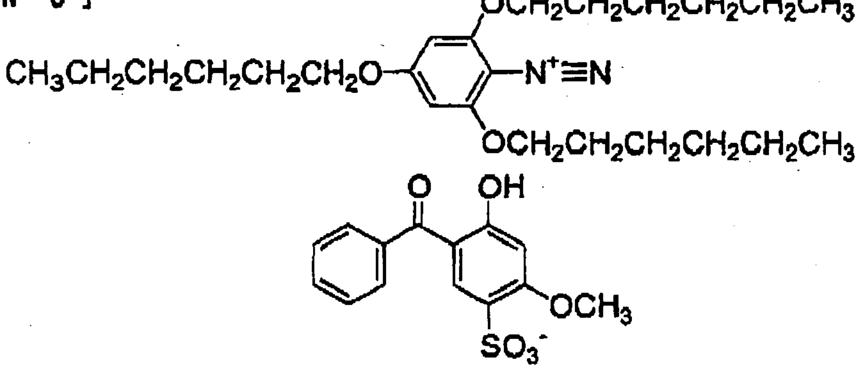


[ON- 4]

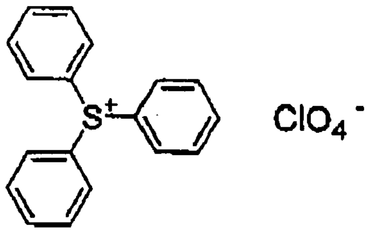


[ON- 5]

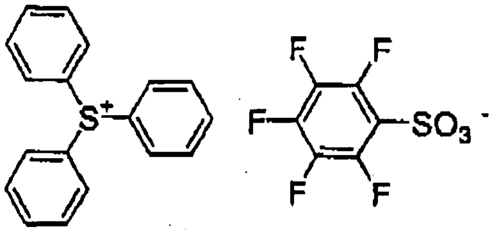


[0196]

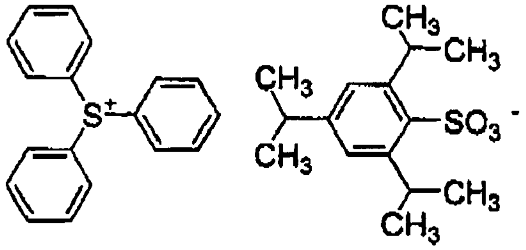
[OS-1]



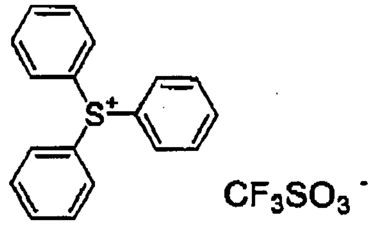
[OS-2]



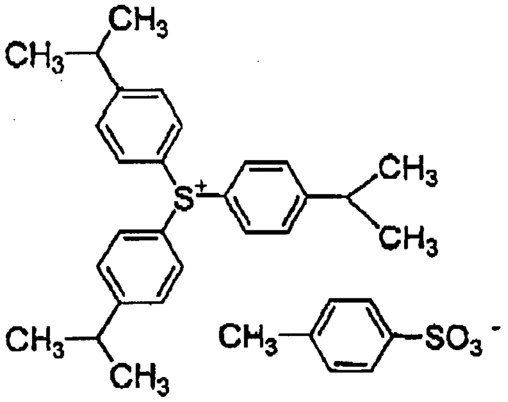
[OS-3]



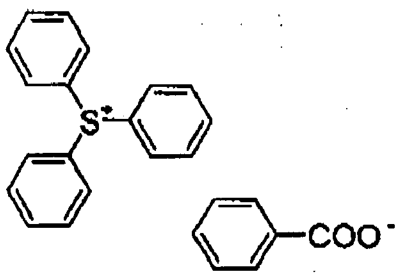
[OS-4]



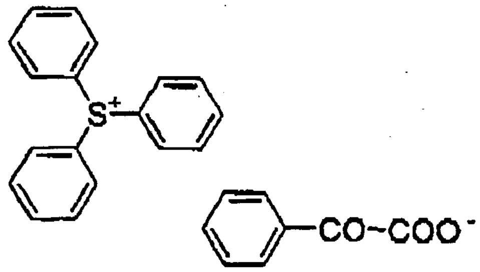
[OS-5]



[OS-6]



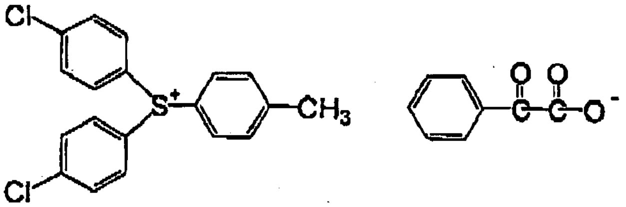
[OS-7]

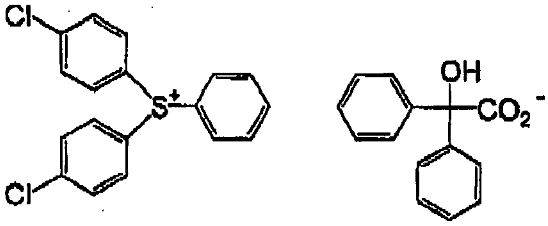


[0197] The polymerization initiator for use in the invention preferably has a maximum absorption wavelength of 400 nm or less, more preferably 360 nm or less. This setting of the absorption wavelength into the ultraviolet ray range enables to process the planographic printing plate precursor under white light.

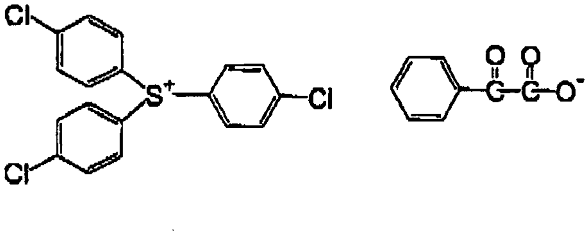
[0198] Preferable examples of the additional polymerization initiator further include specific aromatic sulfonium salts disclosed in JP-A Nos, 2002-148790, 2002-148790, 2001-343742 and 2002-006482, and representative compounds thereof are shown below. Representative compounds among the preferable additional polymerization initiator which can be used in the invention are also exemplified in the followings.

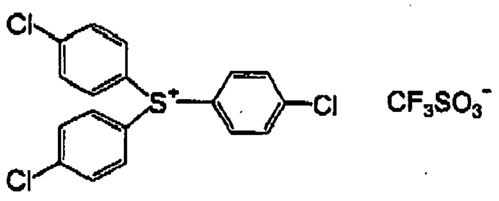
[0199]

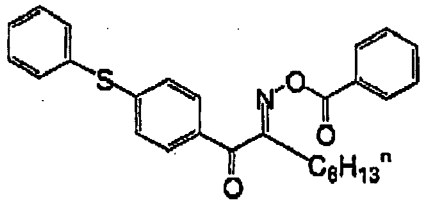


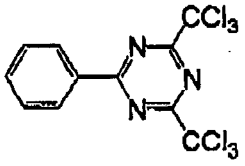


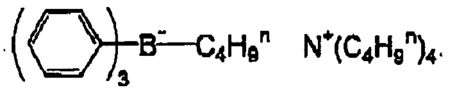
[0200]







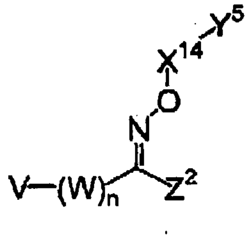




[0201] Oxime ester compounds which can be appropriately used as the polymerization initiator in the invention will be described. Preferable examples of oxime ester compounds for use herein are represented by the following Formula (I):

[0202]

Formula (I)



[0203] In Formula (I), X^{14} represents a carbonyl group, a sulfone group, or a sulfoxide group; Y^5 represents a cyclic or straight chain alkyl, alkenyl or alkynyl group having 1 to 12 carbon atoms, an aryl group having 6 to 18 carbon atoms, or a heterocyclic group. The scope of the "aryl group" includes aromatic hydrocarbon compounds such as a benzene ring, a naphthalene ring, an anthracene ring, a phenanthrene ring, a pyrene group, or a triphenylene group. The scope of the "heterocyclic group" includes aromatic compounds having at least one hetero atom selected from nitrogen, sulfur and oxygen atoms in the cyclic structure thereof, and examples thereof include a pyrrole group, a furan group, a thiophene group, a selenophene group, a pyrazole group, an imidazole group, a triazole group, a tetrazole group, an oxazole group, a thiazole group, an indole group, a benzofuran group, a benzimidazole group, a benzoxazole group, a benzothiazole group, a pyridine group, a pyrimidine group, a pyrazine group, a triazine group, a quinoline group, a carbazole group, an acridine group, a phenoxazine group, and a phenothiazine group.

The substituents represented by Y^5 may be further substituted with one or more compounds having any of a halogen atom, a hydroxyl group, a nitrile group, a nitro group, a carboxyl group, an aldehyde group, an alkyl group, a thiol group, an aryl group, an alkenyl group, an alkynyl group, an ether group, an ester group, an urea group, an amino group, an amido group, a sulfido group, a disulfido group, a sulfoxide group, a sulfo group, a sulfone group, a hydrazine group, a carbonyl group, an imino group, a halogen atom, a hydroxyl group, a nitrile group, a nitro group, a carboxyl group, a carbonyl group, an urethane group, an alkyl group, a thiol group, an aryl group, a phosphoroso group, a phospho group, and a carbonyl-ether group.

[0204] In Formula (I), Z^2 has the same scope as that of Y^5, or represents a nitrile group, a halogen atom, a hydrogen atom or an amino group. These compounds represented by Z^2 may be further substituted with one or more compounds having any of a halogen atom, a hydroxyl group, a nitrile group, a nitro group, a carboxyl group, an aldehyde group, an alkyl group, a thiol group, an aryl group, an alkenyl group, an alkynyl group, an ether group, an ester group, an urea group, an amino group, an amido group, a sulfido group, a disulfido group, a sulfoxide group, a sulfo group, a sulfone group, a hydrazine group, a carbonyl group, an imino group, a halogen atom, a hydroxyl group, a nitrile group, a nitro group, a carboxyl group, a carbonyl group, an urethane group, an alkyl group, a thiol group, an aryl group, a phosphoroso group, a phospho group, and a carbonyl-ether group.

[0205] In Formula (I), W represents a divalent organic group. Examples thereof include a methylene group, a carbonyl group, a sulfoxide group, a sulfone group, and an imino group. The methylene group and the imino group may be substituted with one or more compounds having any of an alkyl group, an aryl group, an ester group, a nitrite group, a carbonyl-ether group, a sulfo group, a sulfo-ether group, and an ether group.

n denotes an integer of 0 or 1.

[0206] In Formula (I), V represents a cyclic or straight chain alkyl, alkenyl or alkynyl group having 1 to 12 carbon atoms, an aryl group having 6 to 18 carbon atoms, an alkoxy group having 6 to 18 carbon atoms, or an aryloxy group having 6 to 18 carbon atoms. The scope of the "aryl group" includes: aromatic hydrocarbon compounds such as a benzene ring, a naphthalene ring, an anthracene ring, a phenanthrene ring, a pyrene group, or a triphenylene group; and hetero atom-containing aromatic compounds such as a pyrrole group, a furan group, a thiophene group, a selenophene group, a pyrazole group, an imidazole group, a triazole group, a tetrazole group, an oxazole group, a thiazole group, an indole group, a benzofuran group, a benzimidazole group, a benzoxazole group, a benzothiazole group, a pyridine group, a pyrimidine group, a pyrazine group, a triazine group, a quinoline group, a carbazole group, an acridine group, a phenoxazine group, or a phenothiazine group. These compounds represented by V may be further substituted with one or more compounds having any of a halogen atom, a hydroxyl group, a nitrile group, a nitro group, a carboxyl group, an aldehyde group, an alkyl group, a thiol group, an aryl group, an alkenyl group, an alkynyl group, an ether group, an ester group, an urea group, an amino group, an amido group, a sulfido group, a disulfido group, a sulfoxide group, a sulfo group, a sulfone group, a hydrazine group, a carbonyl group, an imino group, a halogen atom, a hydroxyl group, a nitrile group, a nitro group, a carboxyl group, a carbonyl group, an urethane group, an alkyl group, a thiol group, an aryl group, a phosphoroso group, a phospho group, and a carbonyl-ether group.

V and Z may be bonded to each other to form a ring.

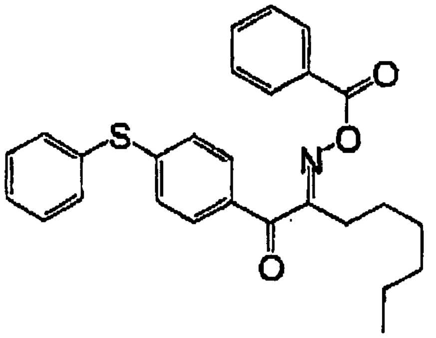
[0207] In the oxime ester compounds represented by Formula (I), it is preferable that X^{14} is a carbonyl group, Y^5 is an aryl or benzoyl group, Z is an alkyl or aryl group, W is a carbonyl group, and V is an aryl group in view of the sensitivity of the compounds. More preferably, the aryl group of V has a thioether substituent.

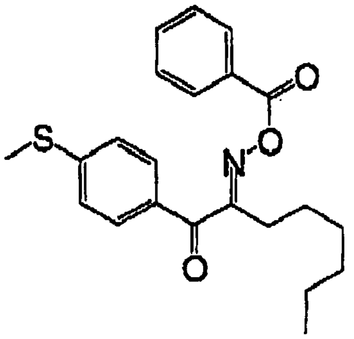
The N-O bond in Formula (I) may be either in an E-form or in a Z-form.

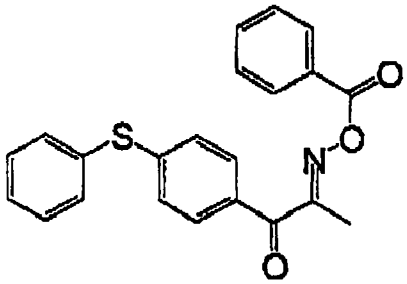
[0208] Preferable examples of the oxime ester compound used for the invention further include those described in "Progress in Organic Coatings" 13 (1985), 123 150; J. C. S. Perkin II (1979), 1653 1660; Journal of Photopolymer Science and Technology (1995), 205 232; J. C. S. Perkin II (1979), 156 162; JP-A No. 2000-66385; or JP-A No. 2000-80068.

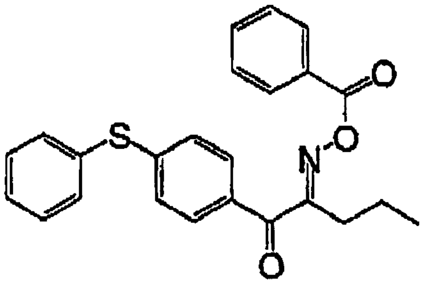
[0209] Specific examples of preferable oxime ether compounds for the invention are described below, while the invention should not be limited thereto.

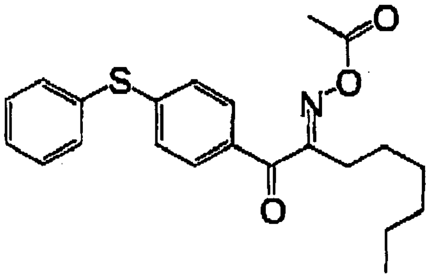
[0210]

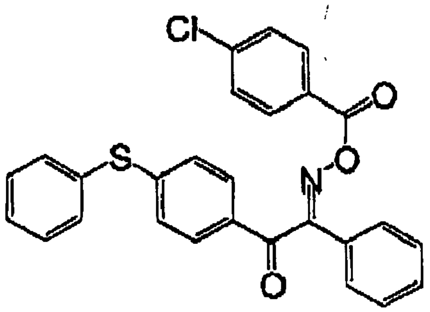


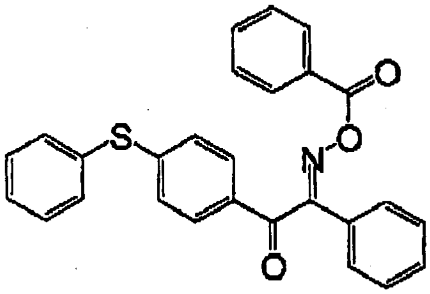


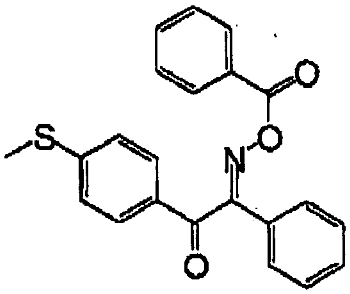


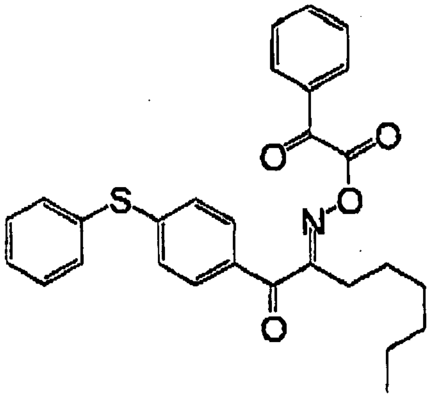


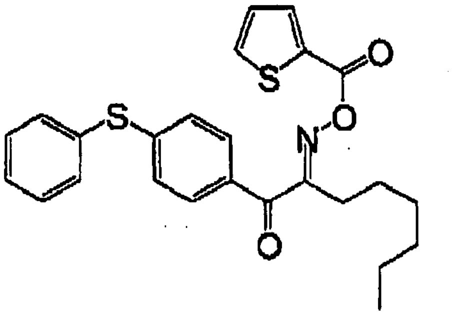












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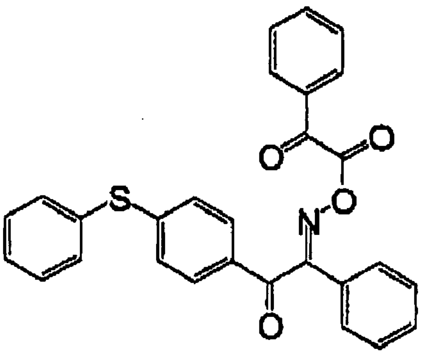
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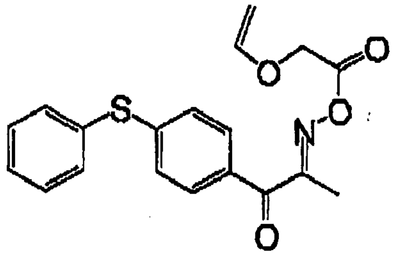
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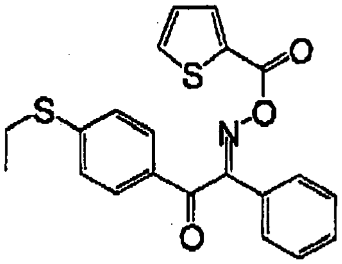
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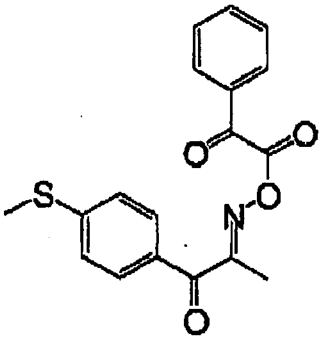
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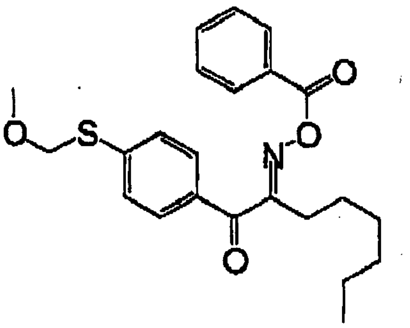
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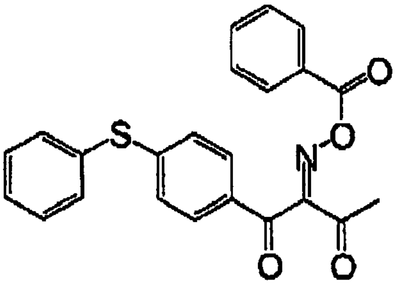
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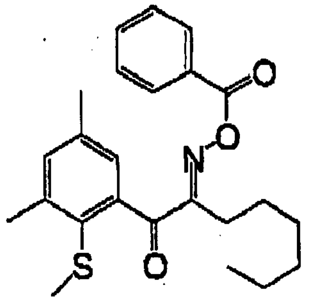
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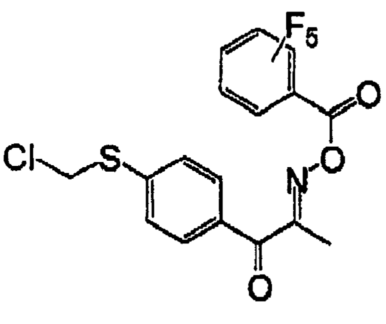
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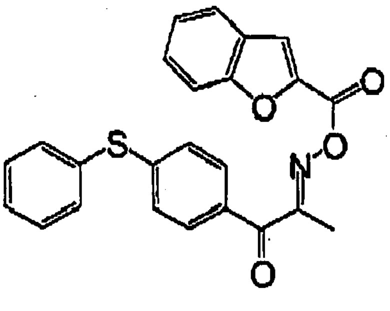
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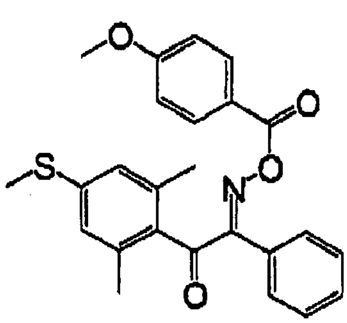
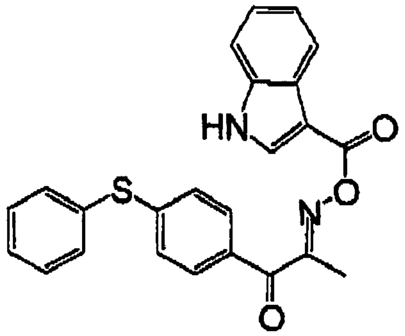
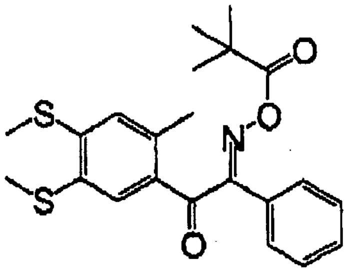
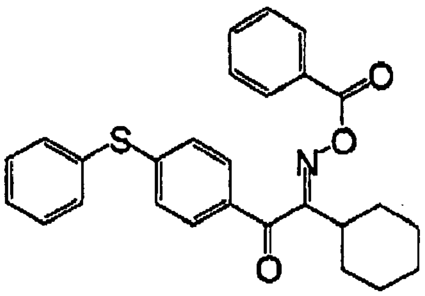
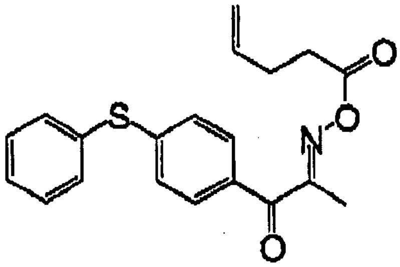
[0212]

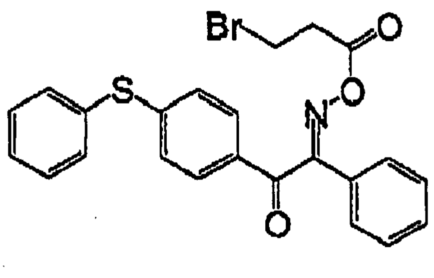


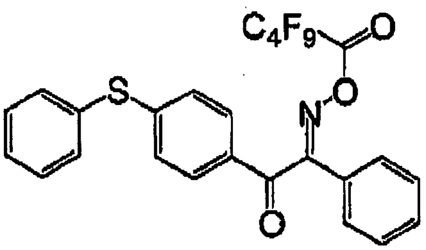












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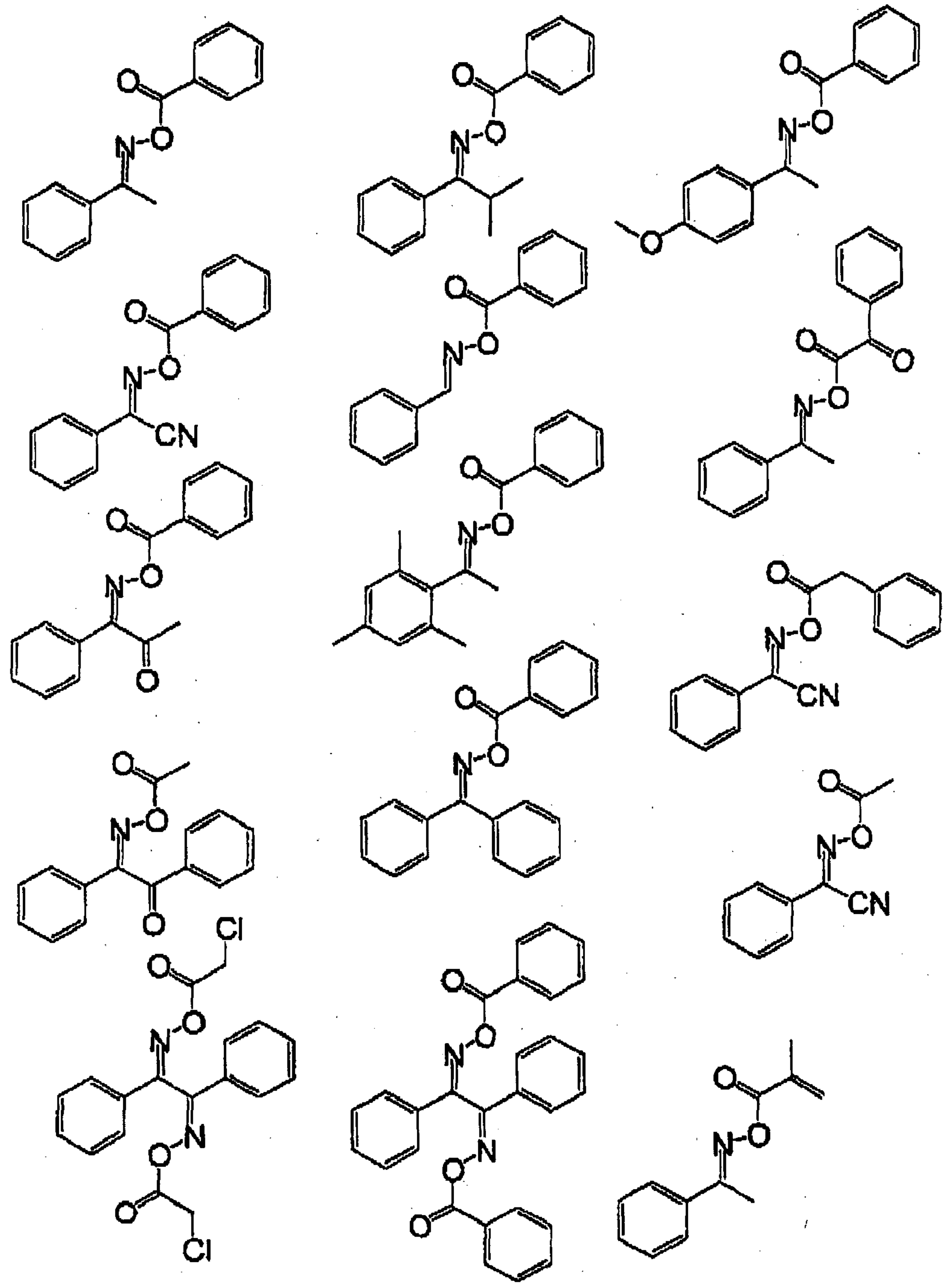

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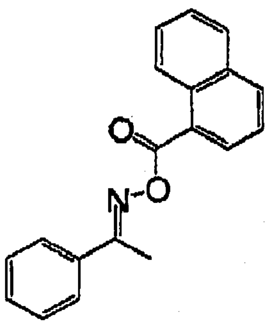

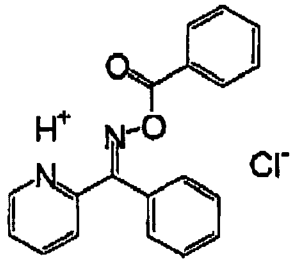

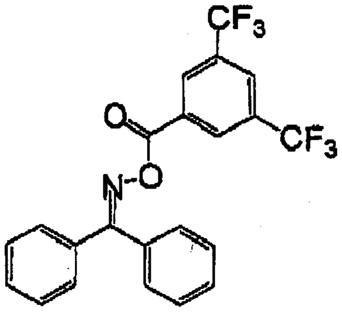

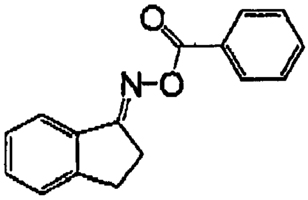

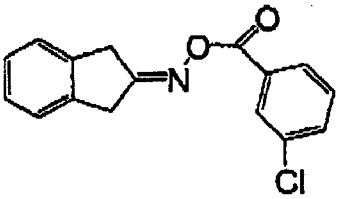

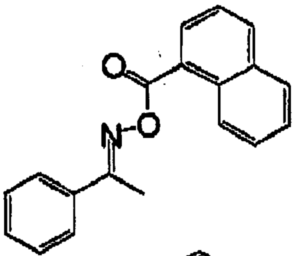

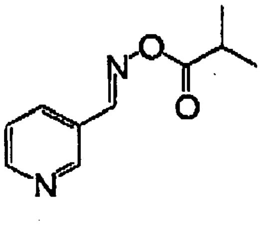

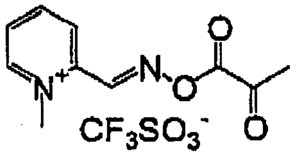

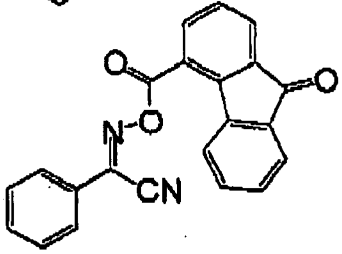

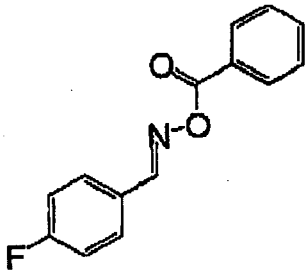

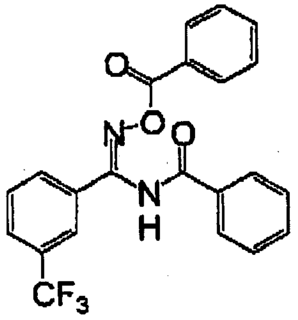

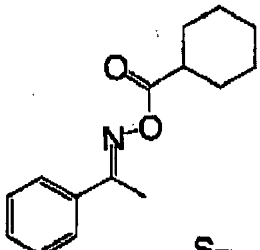

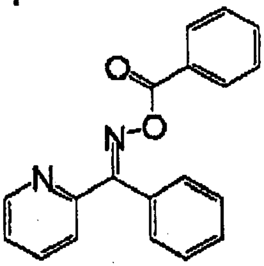

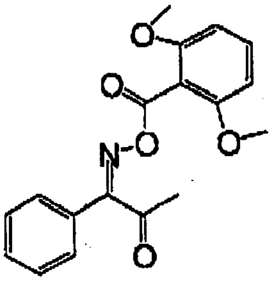

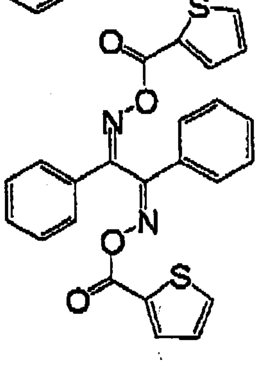

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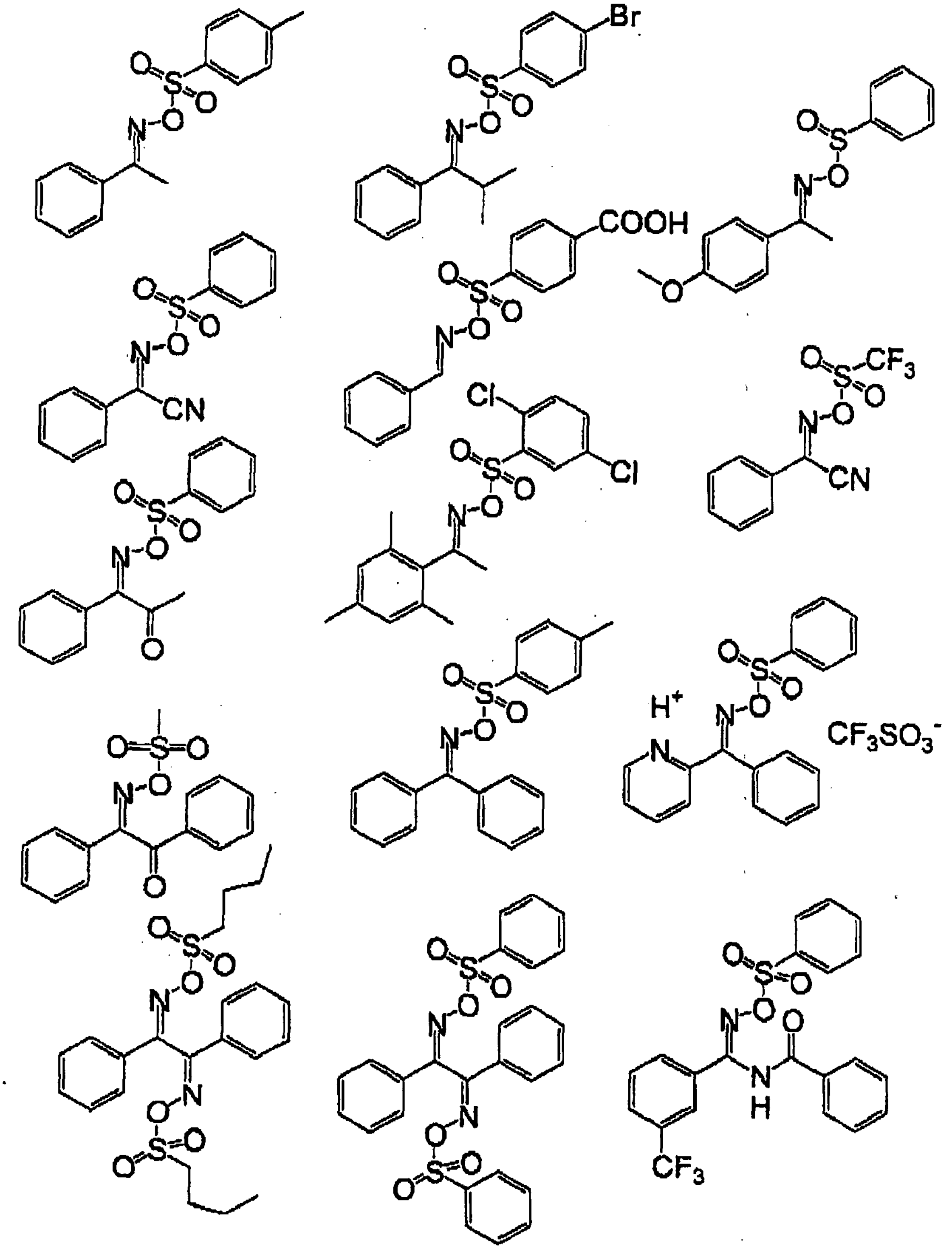

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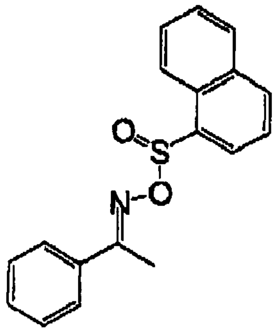
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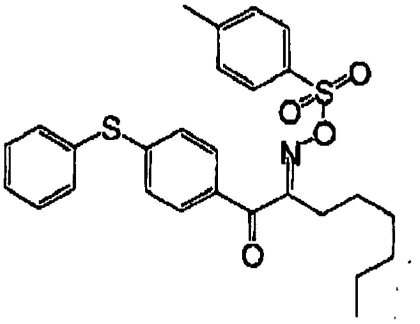
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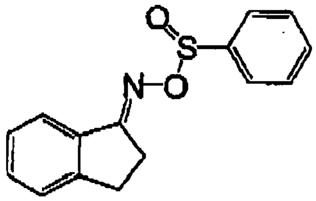
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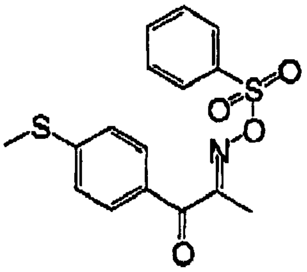
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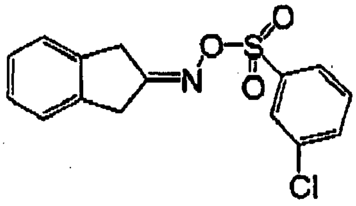
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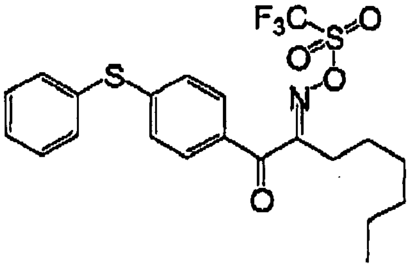
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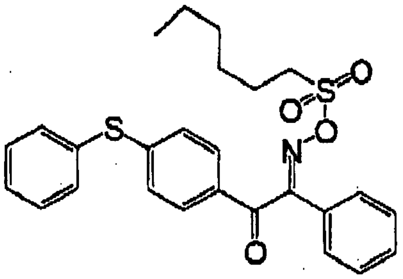
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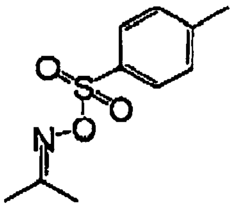
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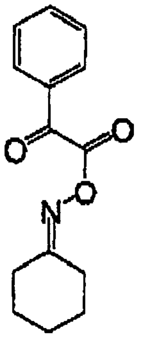
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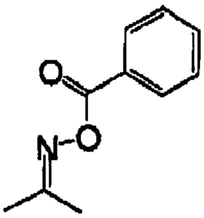
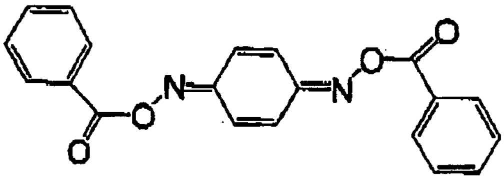
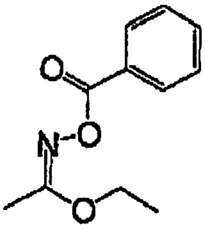
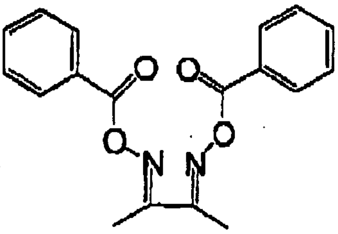
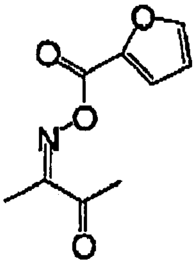
[0217]

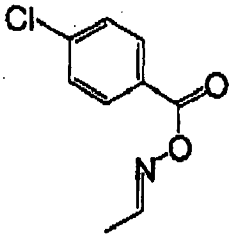


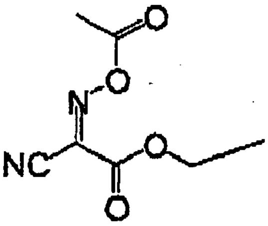


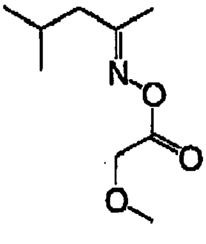


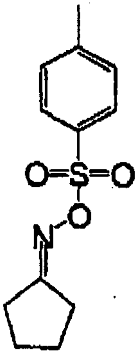


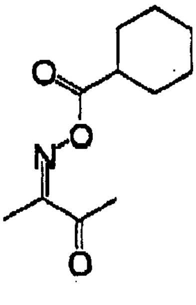


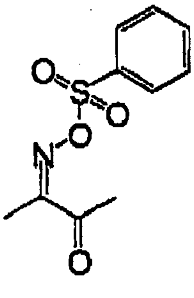




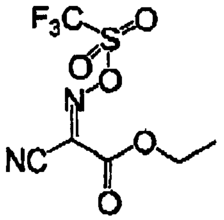


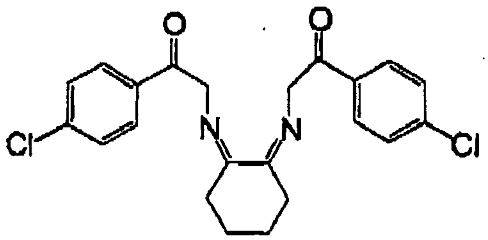


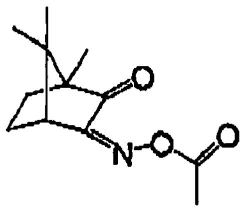


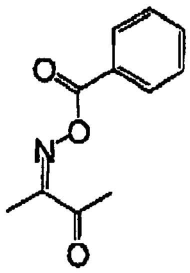


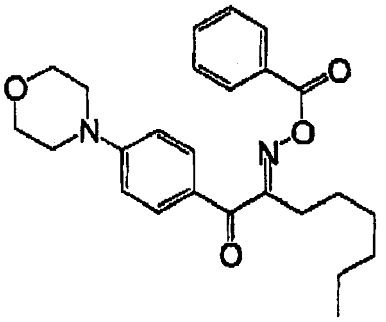
[0218]

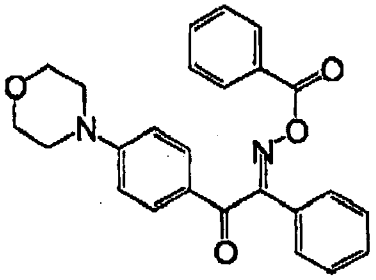


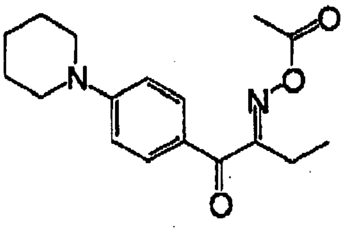


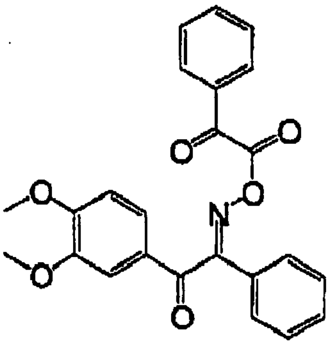












[0219] Among the polymerization initiators, it is more preferable that a titanocene compound, a sulfonium compound, or a hexaarylbiimidazole compound are used in the invention from the viewpoint of the polymerization initiation efficiency at the exposing process, and it is further preferable that the hexaarylbiimidazole compound is used in the invention.

[0220] The amount of the polymerizable composition of the invention to be added is typically in a range of 0.1 to 50 mass%, is preferably in a range of 0.5 to 30 mass%, and is more preferably in a range of 1 to 20 mass% with respect to the total solid content of the polymerizable composition or the photosensitive layer, from the viewpoint of the sensitivity of the composition when the polymerizable composition is used in the photosensitive layer of the negative planographic printing plate precursor and the viewpoint of the staining resistance thereof in the non-image area in prints. The polymerization initiator may be used either singly or in combination of two or more different ones thereof. The polymerization initiator may be added to one layer in combination with other components, or may be added to an additional layer which is different from the layer containing other components.

[0221] From the viewpoint of improving the sensitivity of the polymerization initiator, the photosensitive layer of the invention may use a sensitizing dye (D) or an,infrared absorbing dye (D') depending on a wavelength of the laser used at the time of the exposing. The sensitizing dye and the infrared absorbing dye will be described in detail below. (D) Sensitizing dye

When the electron wave used for the polymerization is ultraviolet ray or visible ray, it is preferable to use a sensitizing dye having a maximum endothermic wave length that is in a range of 300 nm to 850 nm. More preferably, the sensitizing dye has an endothermic wave length in a range of 350 nm to 450 nm. Examples of the sensitizing dye include a spectrum sensitizing pigment and colorants or dyes which absorb the light and react with the photopolymerization initiator.

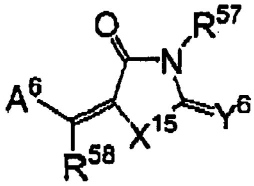
Preferable examples of the spectral sensitization colorants and dyes include polycyclic aromatic compounds (such as pyrene, perylene, or triphenylene), xanthenes (such as fluorescein, eosin, erythrosine, rhodamine B, or rose bengal), cyanines (such as thiacarbocyanine or oxacarbocyanine), merocyanines (such as merocyanine or carbomerocyanine), thiazines (such as thioene, methylene blue, or toluidine blue), acridines (such as acridine orange, chloroflavine, or acriflavine), phthalocyanines (such as phthalocyanine or metal phthalocyanines), porphyrins (such as tetraphenyl porphyrin, or central metal-substituted porphyrins), chlorophylls (such as chlorophyll, chlorophyllin, or central metal-substituted chlorophylls), metal complexes, anthraquinones (such as anthraquinone), squaryliums (such as squarylium), and the like.

[0222] Examples of more preferable spectral sensitization dyes and dyes include the styryl dyes described in JP-B No. 37-13034; the cation dyes described in JP-A No. 62-143044; the quinoxalinium salts described in JP-B No. 59-24147; the new methylene blue compound described in IP-A No. 64-33104; the anthraquinones described in JP-A No. 64-56767; the benzoxanthene dyes described in JP-A No. 2-1714; the acridines described in JP-A Nos. 2-226148 and 2-226149; the pyrylium salts described in JP-B No. 40-28499; the cyanines described in JP-B No. 46-42363; the benzofuran dyes described in JP-A No. 2-63053; the conjugate ketone dyesdescribed in JP-A Nos. 2-85858 and 2-216154; the dyes described in JP-A No. 57-10605; the azo cinnamylidene compounds described in JP-B No. 2-30321; the cyanine dyes described in JP-A No. 1-287105; the xanthene dyes described in JP-A Nos. 62-31844, 62-31848, and 62-143043; the aminostyrylketone described in JP-B No. 59-28325; the merocyaninedyes described in JP-B No. 61-9621; the dyes described in JP-A No. 2-179643; the merocyanine dyes described in JP-A No. 2-244050; the merocyanine dyes described in JP-B No. 59-28326; the merocyanine colorants described in, JP-A No. 59-89803; the merocyanine dyes described in JP-A No. 8-129257; the benzopyran dyes described in JP-A No. 8-3 34897; and the like.

[0223] The sensitizer for use in the invention is more preferably a compound represented by the following Formula (12).

[0224]

Formula (12)



[0225] In Formula (12), A^6 represents an aromatic or hetero ring that may be substituted; X^{15} represents an oxygen or sulfur atom or $-N(R^{56})-$; and Y^6 represents an oxygen atom or $-N(R^{56})-$.

R^{56}, R^{57}, and R^{58} each independently represents a hydrogen atom or a non-metal atom group; and each of A^6 and R^{56}, R^{57}, or R^{58} may be bonded to each other to form an aliphatic or aromatic ring.

[0226] When R^{56}, R^{57}, or R^{58} in Formula (12) is a monovalent non-metal atom group, it preferably represents an alkyl group or an aryl group which may be substituted or unsubstituted.

Hereinafter, preferable examples of the groups R^{56}, R^{57} and R^{58} in Formula (12) will be specifically described. Preferable examples of the alkyl group include straight-chain, branched, and cyclic alkyl groups having 1 to 20 carbon atoms; and specific examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, a hexadecyl group, an octadecyl group, an eicosyl group, an isopropyl group, an isobutyl group, a s-butyl group, a t-butyl group, an isopentyl group, a neopentyl group, a 1-methylbutyl group, an isohexyl group, a 2-ethylhexyl group, a 2-methylhexyl group, a cyclohexyl group, a cyclopentyl group, and a 2-norbornyl group. Among them, straight-chain alkyl groups having 1 to 12 carbon atoms, branched alkyl groups having 3 to 12 carbon atoms, and cyclic alkyl groups having 5 to 10 carbon atoms are more preferable.

[0227] The substituent group of the substituted alkyl group is a monovalent non-metal atom group other than hydrogen, and preferable examples thereof include halogen atoms (-F, -Br, -Cl, and -I), a hydroxyl group, alkoxy groups, aryloxy groups, a mercapto group, alkylthio groups, arylthio groups, alkyldithio groups, aryldithio groups, an amino group, N-alkylamino groups, N,N-dialkylamino groups, N-arylamino groups, N,N-diarylamino groups, N-alkyl-N-arylamino groups, acyloxy groups, carbamoyloxy groups; N-alkylcarbamoyloxy groups, N-arylcarbamoyloxy groups, N,N-dialkylcarbamoyloxy groups, N,N-diarylcarbamoyloxy groups, N-alkyl-N-arylcarbamoyloxy groups, alkylsulfoxy groups, arylsulfoxy groups, acyloxy groups, acylthio groups, acylamino groups, N-alkylacylamino groups, N-arylacylamino groups, a ureido group, N'-alkylureido groups, N',N'-dialkylureido groups, N'-arylureido groups, N',N'-diarylureido groups, N'-alkyl-N'-arylureido groups, N-alkylureido groups, N-arylureido groups, N'-alkyl-N-alkylureido groups, N'-alkyl-N-arylureido groups, N',N'-dialkyl-N-alkylureido groups, N',N'-dialkyl-N-arylureido groups, N'-aryl-N-alkylureido groups, N''-aryl-N-arylureido groups, N',N'-diaryl-N-alkylureido groups, N',N'-diaryl-N-arylureido groups, N'-alkyt-N'-aryl-N-alkylureido groups, N'-alkyl-N'-aryl-N-arylureido groups, alkoxycarbonylamino groups, aryloxycarbonylamino groups, N-alkyl-N-alkoxycarbonylamino groups, N-alkyl-N-aryloxycarbonylamino groups, N-aryl-N-alkoxycarbonylamino groups, N-aryl-N-aryloxycarbonylamino groups, a formyl group, acyl groups, a carboxyl group, alkoxycarbonyl groups, aryloxycarbonyl groups, carbamoyl groups, N-alkylcarbamoyl groups, N,N-diaikylcarbamoyl groups, N-arylcarbamoyl groups, N,N-diarylcarbamoyl groups, N-alkyl-N-arylcarbamoyl groups, alkylsulfinyl groups, arylsulfinyl groups, alkylsulfonyl groups, arylsulfonyl groups, a sulfo group ($-SO_3H$) and the conjugate base groups (hereinafter, referred to as sulfonato groups), alkoxysulfonyl groups, aryloxysulfonyl groups, sulfinamoyl groups, N-alkylsulfinamoyl groups, N,N-dialkylsulfinamoyl groups, N-arylsulfinamoyl groups, N,N-diarylsulfinamoyl groups, N-alkyl-N-arylsulfinamoyl groups, a sulfamoyl group, N-alkylsulfamoyl groups, N,N-dialkylsulfamoyl groups, N-arylsulfamoyl groups, N,N-diarylsulfamoyl groups, N-alkyl N-arylsulfamoyl groups, a phosphono group ($-PO_3H_2$) and the conjugate base groups thereof (hereinafter, referred to as phosphonato groups), dialkyl phosphono groups ($-PO_3(alkyl)_2$), diarylphosphono groups ($-PO_3(aryl)_2$), allcylarylphosphono groups ($-PO_3(alkyl)(aryl)$), monoalkylphosphono groups ($-PO_3H(alkyl)$) and the conjugate base groups thereof (hereinafter, referred to as allcylphosphonato groups), monoaryl phosphono groups ($-PO_3H(aryl)$) and the conjugate base groups thereof (hereinafter, referred to as arylphosphonato groups), a phosphonoxy group ($-OPO_3H_2$) and the conjugate base groups thereof (hereinafter, referred to as phosphonatoxy groups), dialkylphosphonoxy groups ($-OPO_3(alkyl)_2$), diarylphosphonoxy groups ($-OPO_3(aryl)_2$), alkylarylphosphonoxy groups ($-OPO_3(alkyl)(aryl)$), monoalkylphosphonoxy groups ($-OPO_3H(alkyl)$) and the conjugate base groups thereof (hereinafter, referred to as alkylphosphonatoxy groups), monoarylphosphonoxy groups ($-OP0_3H(aryl)$) and the conjugate base groups threreof (hereinafter, referred to as arylphosphonatoxy groups), a cyano group, a nitro group, aryl groups, heteroaryl groups, alkenyl groups, alkynyl groups, and silyl groups.

Specific examples of the alkyl groups in these substituent groups include the alkyl groups described above, and these groups may further have a substitutent.

[0228] Specific examples of the aryl groups include a phenyl group, a biphenyl group, a naphthyl group, a toluyl group, a xylyl group, a mesityl group, a cumenyl group, a chlorophenyl group, a bromophenyl group, a chloromethylphenyl group, a hydroxyphenyl group, a methoxyphenyl group, an ethoxyphenyl group, a phenoxyphenyl group, an acetoxyphenyl group, a benzyoloxyphenyl group, a methylthiophenyl group, a phenylthiophenyl group, a methylaminophenyl group, a dimethylaminophenyl group, an acetylaminophenyl group, a carboxyphenyl group, a methoxycarbonylphenyl group, an ethoxyphenylcarbonyl group, a phenoxycarbonylphenyl group, a N-phenylcarbamoylphenyl group, a cyanophenyl group, a sulfophenyl group, a sulfonatophenyl group, a phosphonophenyl group, a phosphonatophenyl group, and the like.

[0229] The heteroaryl group is a group derived from a monocyclic or polycyclic aromatic ring containing at least one of a nitrogen atom, an oxygen atom, and a sulfur atom, and particularly preferable examples of the heteroaryl rings in the heteroaryl group include thiophene, thiathrene, furan, pyran, isobenzofuran, chromane, xanthene, phenoxazine, pyrrole, pyrazole isothiazole, isoxazole, pyrazine, pyrimidine, pyridazine, indolizine, isoindolizine, indoyl, indazole, purine, quinolizine, isoquinoline, phthalazine, naphthyridine, quinazoline, cinnoline, pteridine, carbazole, carboline, phenanthrene, acridine, perimidine, phenanthroline, phthalazine, phenarsazine, phenoxazine, furazan, and the like, and these compounds may be fused with a benzene ring and may also have a substitutent.

[0230] Examples of the alkenyl group include a vinyl group, a 1-propenyl group, a 1-butenyl group, a cinnamyl group, a 2-chloro-I-ethenyl group, and other groups, and examples of the alkynyl group include an ethynyl group, a 1-propynyl group, a 1-butynyl group, a trimethylsilylethynyl group, and other groups. Examples of G^1 in the acyl group (G^1CO-) include hydrogen, the alkyl groups described above and the aryl groups described above. More preferable examples among the substituent groups include halogen atoms (-F, -Br, -Cl, and -1), alkoxy groups, aryloxy groups, alkylthio groups, arylthio groups, N-alkylamino groups, N,N-dialkylamino groups, acyloxy groups, N-alkylcarbamoyloxy groups, N-arylcarbamoyloxy groups, acylamino groups, a formyl group, acyl groups, a carboxyl group, alkoxycarbonyl groups, aryloxycarbonyl groups, carbamoyl groups, N-alkylcarbamoyl groups, N,N-dialkylcarbamoyl groups, N-arylcarbamoyl groups, N-alkyl-N-arylcarbamoyl groups, a sulfo group, sulfonato groups, sulfamoyl groups, N-alkylsulfamoyl groups, N,N-dialkylsulfamoyl groups, N-arylsulfamoyl groups, N-alkyl-N-arylsulfamoyl groups, a phosphono group, a phosphonato group, dialkylphosphono groups, diarylphosphono groups, monoalkylphosphono groups, alkyl phosphonato groups, monoarylphosphono groups, aryl phosphonato groups, phosphonooxy groups, phosphonatoxy groups, aryl groups, alkenyl groups, and alkylidene groups (methylene group and the like).

[0231] On the other hand, examples of the alkylene group in the substituted alkyl group include divalent organic residue formed by removing one of the hydrogen atoms from the alkyl groups having 1 to 20 carbon atoms described above, and preferable examples thereof include straight-chain alkylene groups having 1 to 12 carbon atoms, branched alkylene groups having 3 to 12 carbon atoms, and cyclic alkylene groups having 5 to 10 carbon atoms,

[0232] Specific examples of the substituted alkyl group preferable as R^1, R^2, or R^3 obtained by combining the substituent group with the alkylene group include a chloromethyl group, a bromomethyl group, a 2-chloroethyl group, a trifluoromethyl group, a methoxymethyl group, a methoxyethoxyethyl group, an allyloxymethyl group, a phenoxymethyl group, a methylthiomethyl group, a toluylthiomethyl group, an ethylaminoethyl group, a diethylaminopropyl group, a morpholinopropyl group, an acetyloxymethyl group, a benzoyloxymethyl group, a N-cyclohexylcarbamoyloxyethyl group, a N-pheylcarbamoyloxyethyl group, an acetylaminoethyl group, a N-methylbenzoylaminopropyl group, a 2-oxoethyl group, a 2-oxopropyl group, a carboxypropyl group, a methoxycarbonylethyl group, a nallyloxycarbonylbutyl group, a chlorophenoxycarbonylmethyl group, a carbamoylmethyl group, a N-methylcarbamoylethyl group, a N,N-dipropylcarbamoylmethyl group, a N-(methoxyphenyl)carbamoylethyl group, a N-methyl-N-(sulfophenyl)carbamoylmethyl group, a sulfobutyl group, a sulfonatopropyl group, a sulfonatobutyl group, a sulfamoylbutyl group, a N-ethylsulfamoylmethyl group, a N,N-dipropylsulfamoylpropyl group, a N-toluylsulfamoylpropyl group, a N-methyl-N-(phosphonophenyl)sulfamoyloctyl group, a phosphonobutyl group, a phosphonatohexyl group, a diethylphosphonobutyl group, a diphenylphosphonopropyl group, a methylphosphonobutyl group, a methylphosphonatobutyl group, a toluylphosphonohexyl group group, a toluylphosphonatohexyl group, a phosphonooxypropyl group, a phosphonatoxybutyl group, a benzyl group, a phenethyl group, an α-methylbenzyl group, a 1-methyl-1-phenylethyl group, a p-methylbenzyl group, a cinnamyl group, an allyl group, a 1-propenylmethyl group, a 2-butenyl group, a 2-methyl allyl group, a 2-methylpropenylmethyl group, a 2-propynyl group, a 2-butynyl group, a 3-butynyl group, and other groups.

[0233] Examples of the aryl groups preferable as R^{56}, R^{57}, or R^{58} include fused rings of one to three benzene rings and fused rings of a benzene ring and a five-membered unsaturated ring. Specific examples thereof include a phenyl group, a naphthyl group, an anthryl group, a phenanthryl group, an indenyl group, an acenaphthenyl group, and a fluorenyl group, and more preferable among them are a phenyl group, and a naphthyl group.

[0234] Examples of the substituted aryl groups preferable as R^{56}, R^{57}, or R^{58} include those having, as a substituent group on the ring-forming carbon atom of the aryl groups described above, a monovalent non-metal atom group (other than hydrogen atom). Preferable examples of the substituent groups for the substituted aryl groups include the alkyl group described above, the substituted alkyl group described above, and the substituent groups described as the substituent groups for the substituted alkyl group. Specific preferable examples of the substituted aryl groups include a biphenyl group, a toluyl group, a xylyl group, a mesityl group, a cumenyl group, a chlorophenyl group, a bromophenyl group, a fluorophenyl group, a chloromethylphenyl group, a trifluoromethylphenyl group, a hydroxyphenyl group, a methoxyphenyl group, a methoxyethoxyphenyl group, an allyloxyphenyl group, a phenoxyphenyl group, a methylthiophenyl group, a toluylthiophenyl group, an ethylaminophenyl group, a diethylaminophenyl group, a morpholino phenyl group, an acetyloxyphenyl group, a benzoyloxyphenyl group, a N-cyclohexylcarbamoyloxyphenyl group, a N-pheylcarbamoyloxyphenyl group, an acetylaminophenyl group, a N-methylbenzoylaminophenyl group, a carboxyphenyl group, a methoxycarbonylphenyl group, an allyloxycarbonylphenyl group, a chlorophenoxycarbonylphenyl group, a carbamoylphenyl group, a N-methylearbamoylphenyl group, a N,N-dipropylcarbamoylphenyl group, a N-(methoxyphenyl)carbamoylphenyl group, a N-methyl-N-(sulfophenyl)carbamoylphenyl group, a sulfophenyl group, a sulfonatophenyl group, a sulfamoylphenyl group, a N-ethylsulfamoylphenyl group, a N,N-dipropylsulfamoylphenyl group, a N-toluylsulfamoylphenyl group, a N-methyl-N-(phosphonophenyl)sulfamoylphenyl group, a phosphonophenyl group, a phosphonatophenyl group, a diethylphosphonophenyl group, a diphenylphosphonophenyl group, a methylphosphonophenyl group, a methyl phosphonatophenyl group, a toluylphosphonophenyl group, a toluylphosphonatophenyl group, an allylphenyl group, a 1 -propenylmethylphenyl group, a 2-butenylphenyl group, a 2-methyl allylphenyl group, a 2-methylpropenylphenyl group, a 2-propynylphenyl group, a 2-butynylphenyl group, a 3-butynylphenyl group, and other groups.

[0235] More preferable examples of R^{57} and R^{58} include substituted or unsubstituted alkyl groups. More preferable examples of R^{56} include substituted or unsubstituted aryl groups. Although the mechanism is not yet understood, it is assumed that presence of such a substituent leads to increase in interaction between the electronically excited state generated by photoabsorption and the initiator compound so as to improve efficiency of generating the radical, acid or base of the initiator compound.

[0236] Hereinafter, A^6 in Formula (12) will be described. A^6 represents an aromatic or hetero ring that may have a substitutent; and specific examples thereof include those exemplified above for R^{56}, R^{57}, or R^{58} in Formula (12).
Among these, preferable examples of A^6 include an alkoxy group-containing aryl group, a thioalkyl group-containing

aryl group, and an amino group-containing aryl group, and particularly preferable examples of A^6 are amino group-containing aryl groups.

[0237] Hereinafter, Y^6 in Formula (12) will be described. Y represents a non-metal atom group required for forming a heterocyclic ring, together with A^6 above and the adjacent carbon atoms. Examples of such a heterocyclic ring include five-, six- and seven-membered nitrogen- or sulfur-containing heterocyclic rings that may have one or more fused ring, and preferable examples thereof include five- and six-membered heterocyclic rings.

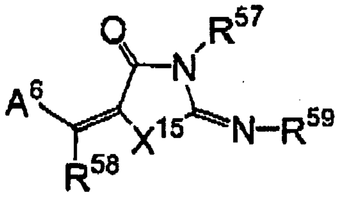
[0238] Preferable examples of the nitrogen-containing heterocyclic rings include those known as the base skeleton for merocyanine colorants described in L. G. Brooker et al., Journal of American Chemical Society (J. Am. Chem. Soc.) 73 (1951), pp. 5326 - 5358, and the reference literatures therein.
Specific examples thereof include thiazoles (such as thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4,5-di(p-methoxyphenylthiazole), 4-(2-thienyl)thiazole, and 4,5-di(2-furyl)thiazole), benzothiazoles (such as benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, S-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylene benzothiazole, 5-hydroxybenzothiaxole, 6-hydroxybenzothiazole, 6-dimethylaminobenzothiazole, and 5-ethoxycarbonylbenzothiazole), naphthothiazoles (such as naphtho[1,2]thiazole, naphtho[2,1]thiazole, 5-methoxynaphtho[2,1]thiazole, 5-ethoxynaphtho[2,1]thiazole, 8-methoxynaphtho[1,2]thiazole, and 7-ethoxynaphtho[1,2]thiazole), thianaphtheno-7',6',4,5-thiazoles (such as 4'-methoxythianaphtheno-7',6',4,5-thiazole), oxazoles (such as 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, and 5-phenyloxazole), benzoxazoles (benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methyl benzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 6-methoxybenzoxazole, 5-methoxybenzoxazole, 4-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, and 6-hydroxybenzoxazole), naphthoxazoles (such as naphtho[1,2]oxazole and naphtho[2,1] oxazole), selenazoles (such as 4-methylselenazole and 4-phenylselenazole), benzoselenazoles (such as benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, and tetrahydrobenzoselenazole), naphthoselenazoles (such as naphtho[1,2]selenazole and naphtho[2,1]selenazole), thiazolines (such as thiazoline, 4-methylthiazoline, 4,5-dimethylthiazoline, 4-phenylthiazoline, 4,5-di(2-furyl)thiazoline, 4,5-diphenylthiazoline, and 4,5-di(p-methoxyphenyl)thiazoline), 2-quinolines (such as quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, and 8-hydroxyquinoline), 4-quinolines (such as quinoline, 6-methoxyquinoline, 7-methylquinoline, and 8-methylquinoline), 1-isoquinolines (such as isoquinoline and 3,4-dihydroisoquinoline), 3-isoquinolines (such as isoquinoline), benzimidazoles (such as 1,3-dimethylbenzimidazole, 1,3-diethylbenzimidazole, and 1-ethyl-3-phenylbenzimidazole), 3,3-dialkylindolenines (such as 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, and 3,3,7-trimethylindolenine), 2-pyridines (such as pyridine and 5-methylpyridine), and 4-pyridines (such as pyridine). In addition, the substituent groups on these rings may be bound to each other to forming a ring.

[0239] Examples of the sulfur-containing heterocyclic rings include the dithiol partial structures in the colorants described in JP-A No. 3-296759.
Specific examples thereof include benzodithiols (such as benzodithiol, 5-t-butylbenzodithiol, and 5-methylbenzodithiol), naphthodithiols (such as naphtho[1,2]dithiol and naphtho[2,1]dithiol), and dithiols (such as 4,5-dimethyldithiols, 4-phenyldithiols, 4-methoxycarbonyldithiols, 4,5-dimethoxycarbonyldithiols, 4,5-diethoxycarbonyldithiols, 4,5-ditrifluoromethyldithiol, 4,5-dicyanodithiol, 4-methoxycarbonylmethyldithiol, and 4-carboxymethyldithiol).

[0240] Among the nitrogen- or sulfur-containing heterocyclic rings formed by Y^6, A^6 and the adjacent carbon atoms in Formula (12) described above, the dyes having a structure represented by the partial structural formula of the following Formula (13) are particularly preferable, because they give a photosensitive composition higher in sensitization potential and considerably superior in storage stability.

[0241]

Formula (13)

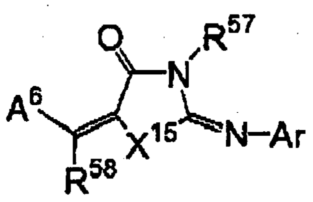


[0242] In Formula (13), each of A^6, X^{15}, R^{56}, R^{57}, and R^{58} have the same meanings as each of A^6, X^{15}, R^{56}, R^{57}, and R^{58} in Formula (12) respectively. R^{59} has the same meaning as R^{56}.

[0243] The compound represented by Formula (12) is further preferably a compound represented by the following Formula (14).

[0244]

Formula (14)

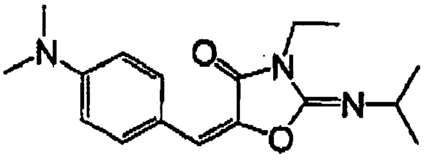


[0245] Each of A^6, X^{15}, R^{56}, R^{57}, and R^{58} in Formula (14) is similar to that in Formula (12) respectively.
Ar represents an aromatic ring or a hetero ring having one or more substituents, provided that a sum of Hammett values of the substituents on the Ar skeleton is greater than 0. The "sum of Hammett values greater than 0" may include the case where one substituent is provided on the Ar skeleton and this one substituent has the Hammett value greater than 0, and the case where plural substituents is rovided on the Ar skeleton and the sum of Hammett values of the plural substituents is greater than 0.
Specific examples of the Ar are similar to the specific examples of the aromatic ring or the hetero ring having the substituent described in the description of A^6 in Formula (12), while the substituent that may be introduced into Ar in Formula (14) is required to provide the sum of Hammett value greater than 0. Examples of the substituent include a trifluoromethyl group, a an carbonyl group, ester group, a halogen atom, a nitro group, a cyano group, a sulfoxide group, an amide group, and a carboxyl group.
The Hammett values of these substituent groups are shown below: trifluoromethyl group (-CF$_{3,}$ m: 0.43, p: 0.54), carbonyl group (e.g., -COH, m: 0.36, p: 0.43), ester group (-COOCH$_{3,}$ m: 0.37, p: 0.45), halogen atom (e.g., Cl, m: 0.37, p: 0.23), cyano group (-CN, m: 0.56, p: 0.66), sulfoxide group (e.g., -SOCH$_{3,}$ m: 0.52, p: 0.45), amido group (e.g.,-NHCOCH$_{3,}$ m: 0.21, p: 0.00), carboxyl group (-COOH, m: 0.37, p: 0.45), and the like. Each parenthesis above includes the site of the substituent group introduced on the aryl skeleton and its Hammett value. For example, (m: 0.50) means that the substituent group introduced at the meta position has a Hammett value of 0.50. Preferable examples of Ar among them include substituted phenyl groups, and preferable substituents on the Ar skeleton include ester and cyano groups. The substituent is particularly preferably introduced at the ortho site on the Ar skeleton.

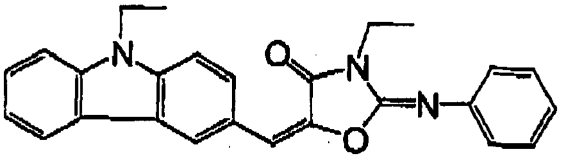
[0246] Hereinafter, preferable specific examples of the sensitizers represented by Formula (12) (exemplary compounds D1 to D57) will be shown, while the invention is not limited thereto. Among them, compounds corresponding to those represented by Formula (13) are exemplary compounds D2, D6, D10, D18, D21, D28, D31, D33, D35, D38, D41, and D45 to D57.

[0247]

(D1)



(D2)



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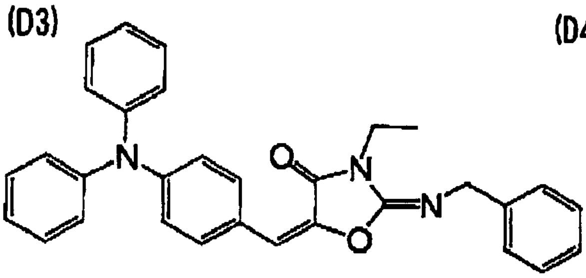

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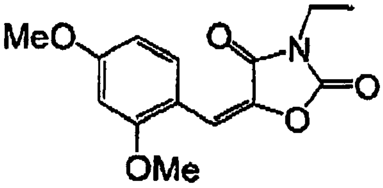

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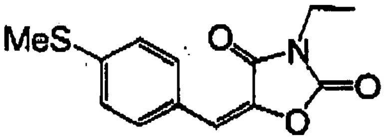

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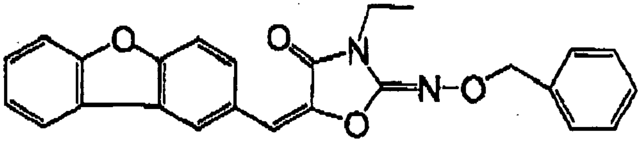

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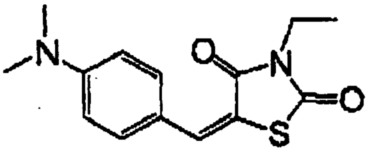

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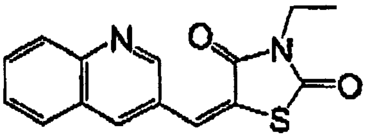

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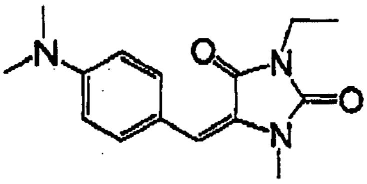

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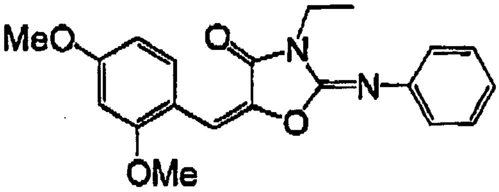

[0248]

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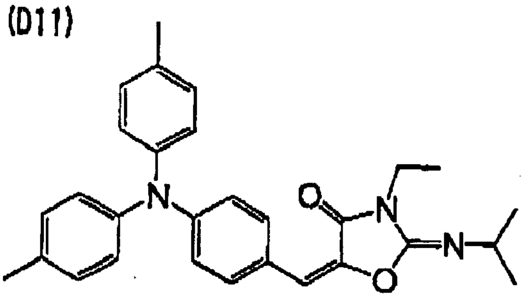

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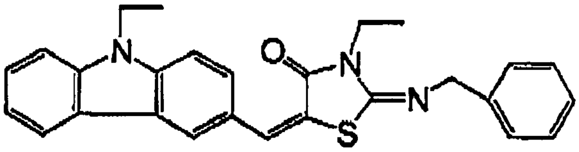

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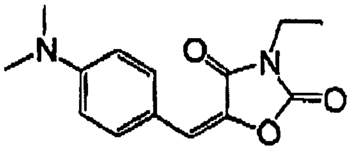

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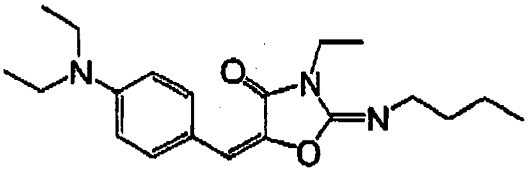

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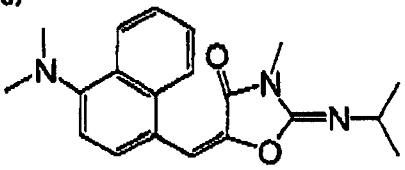

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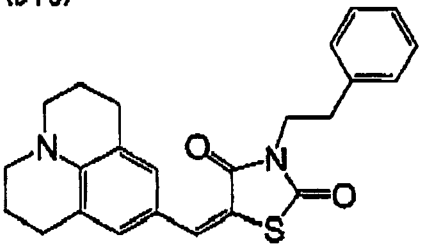

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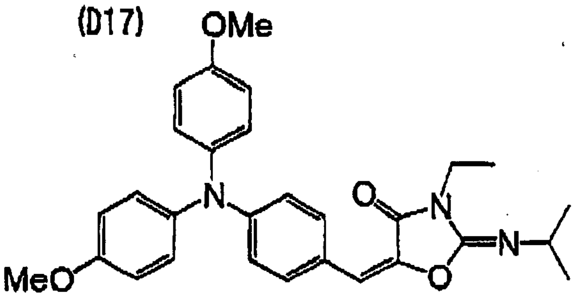

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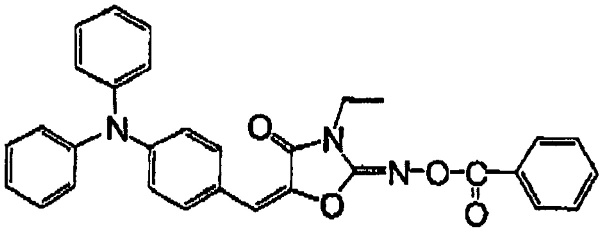

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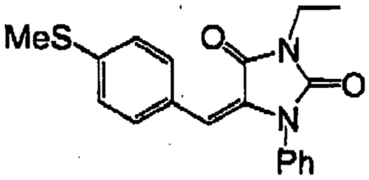
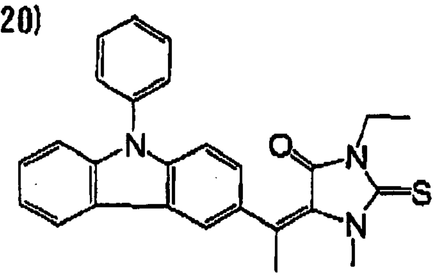


[0249]

(D20)



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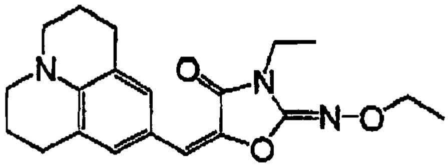

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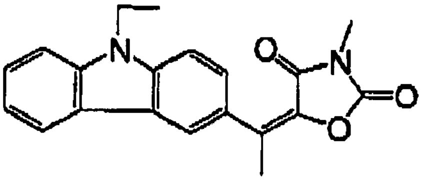

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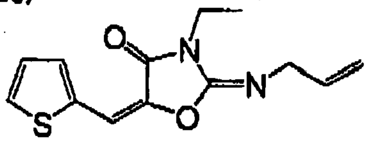

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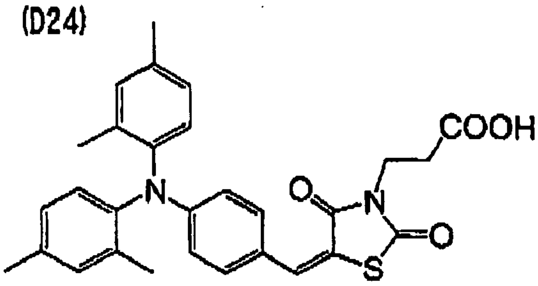

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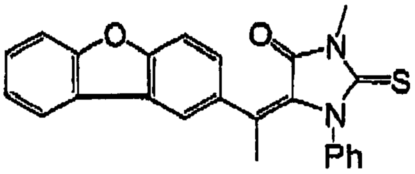

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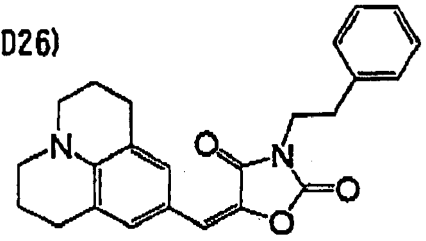

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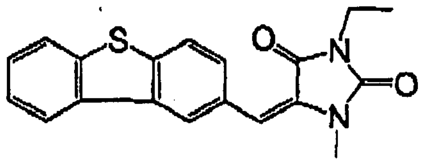

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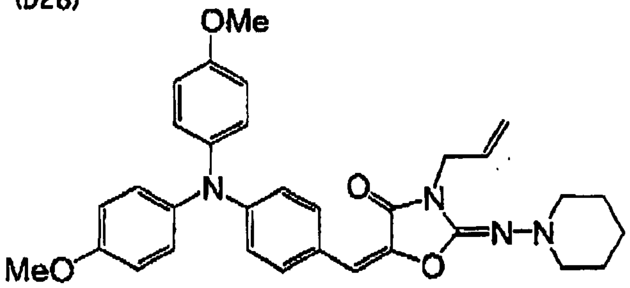

[0250]

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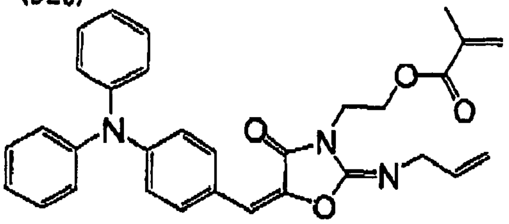

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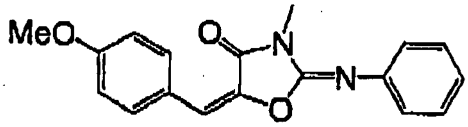

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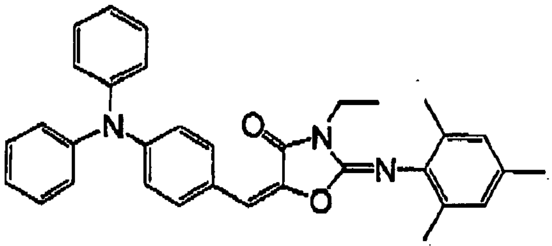

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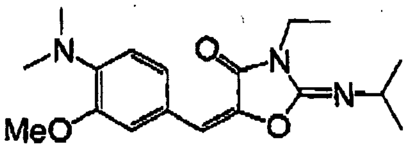

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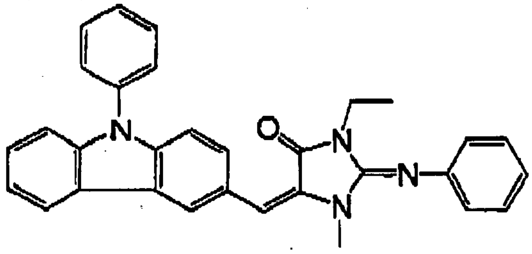

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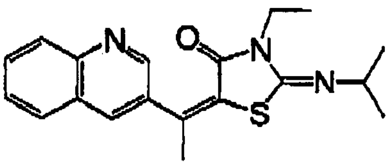

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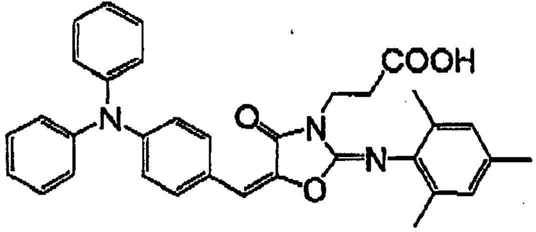

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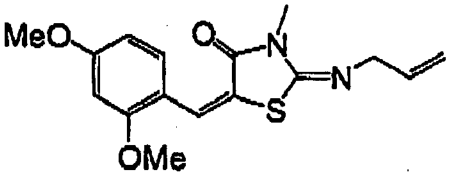

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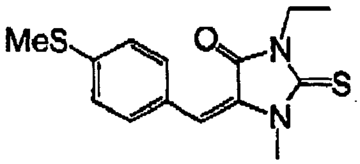

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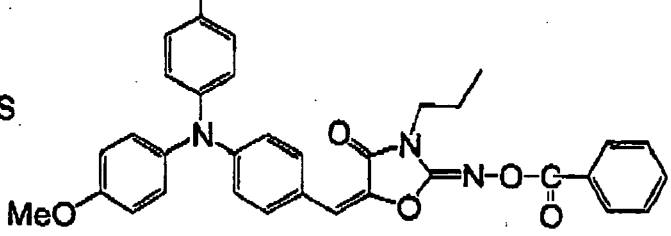

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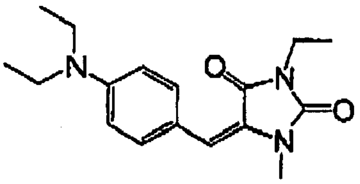

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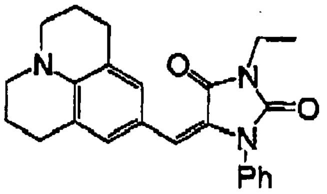

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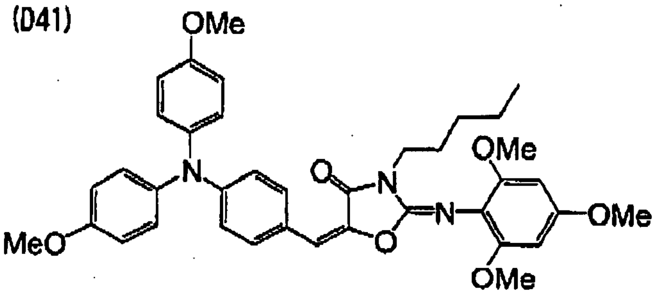

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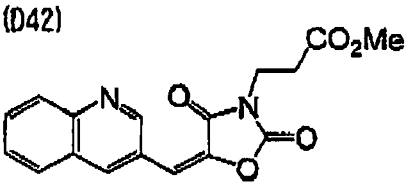

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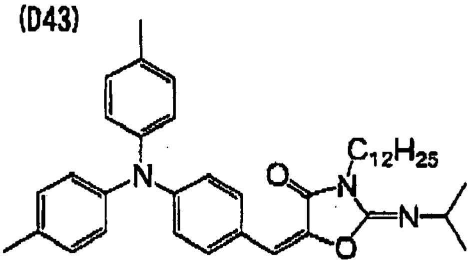

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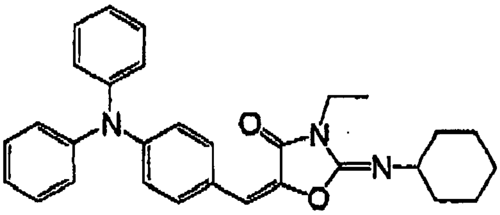

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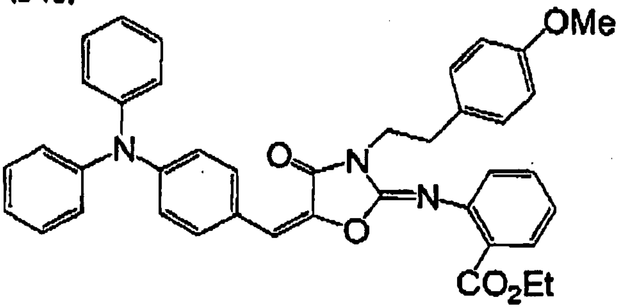

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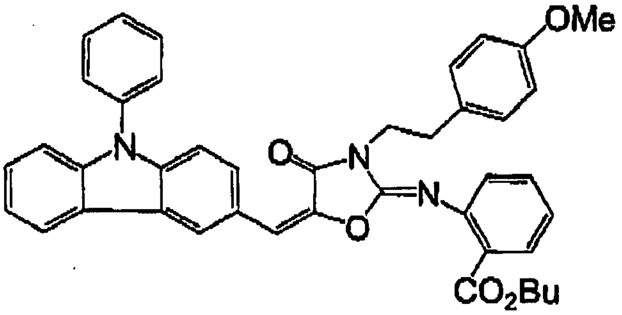

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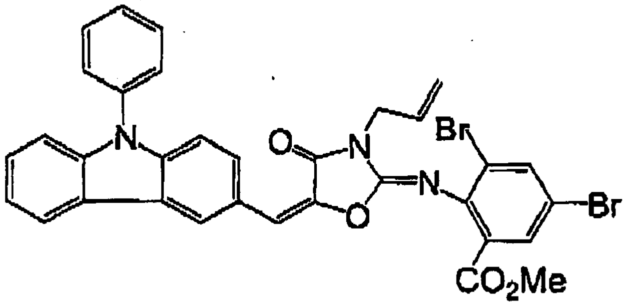

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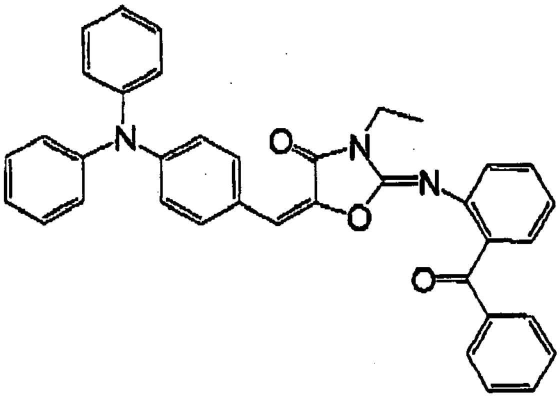

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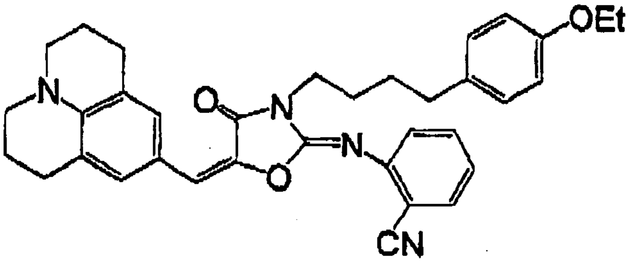
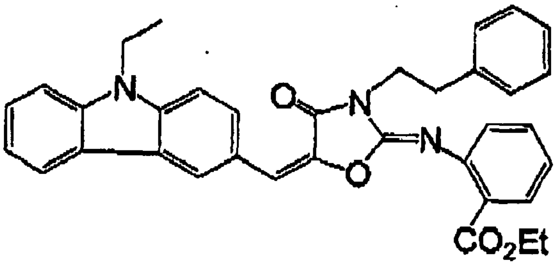


(D50)



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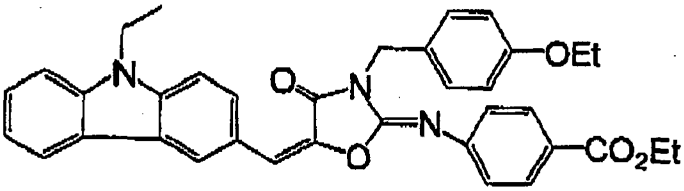

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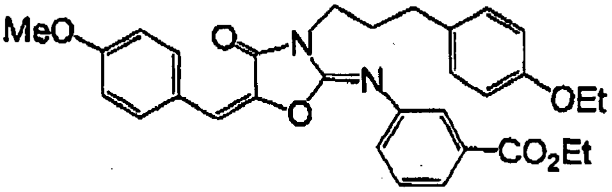

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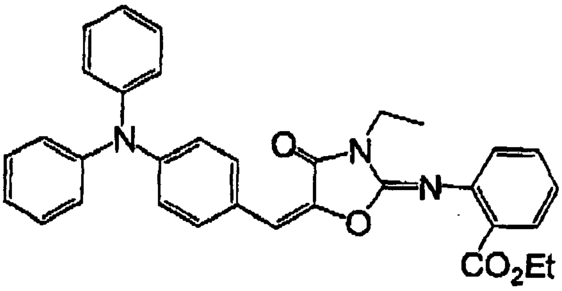
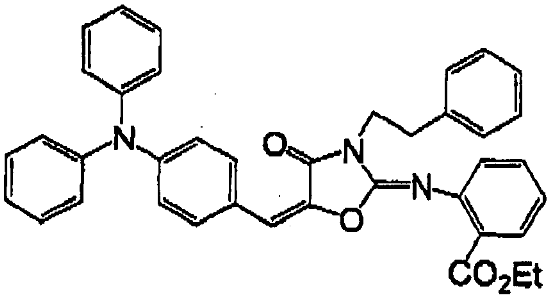


[0254]

(D54)



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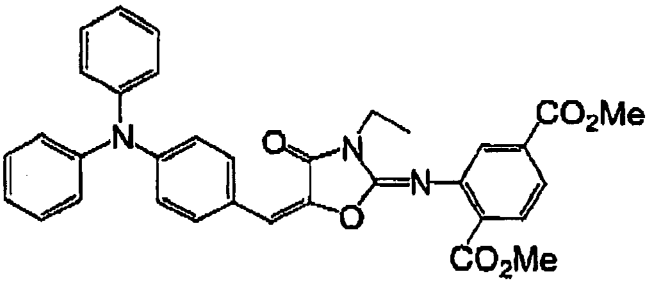

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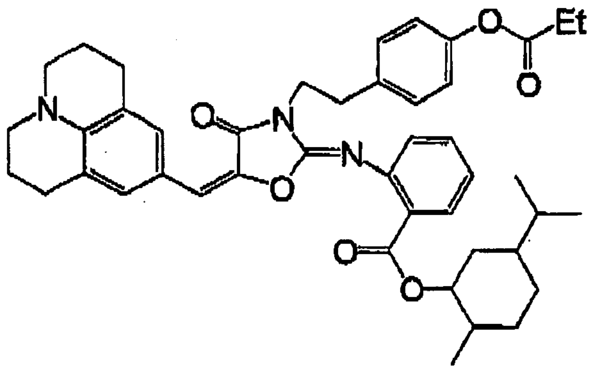

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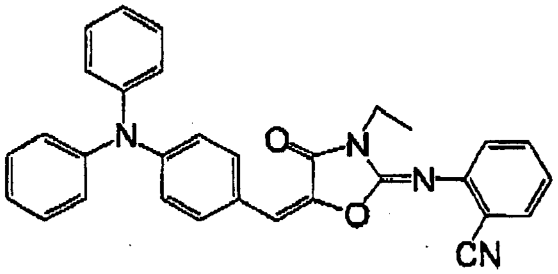
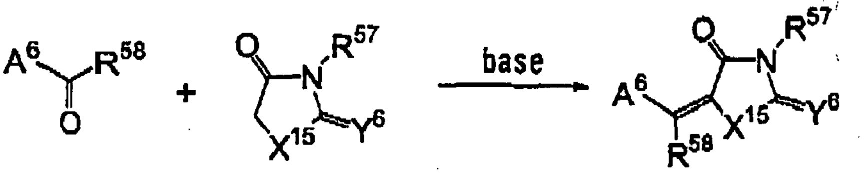


[0255] A method of synthesis of a compound represented by Formula (12) will be described. The compound represented by Formula (12) is usually obtained by condensation reaction of an acid nucleus having an active methylene group and a substituted or unsubstituted aromatic ring or heterocyclic ring. The compound represented by Formula (12) can be synthesized with referring to JP-B No. 59-28329. For example, a synthesis method utilizing condensation reaction of an acid nuclear compound and a basic nuclear raw material having an aldehyde group or a carbonyl group on a heterocyclic ring thereof, as shown in the following reaction scheme (1), may be used. The condensation reaction is carried out in the presence of a base, as the need arises. Examples of the base include generally employed bases such as amines or pyridines (for example, trialkylamines, dimethylaminopyridine, and diazabicycloundecene (DBU)), metal amides (for example, lithium diisopropylamide), metal alkoxides (for example, sodium methoxide and sodium t-butoxide), or metal hydrides (for example, sodium hydride and potassium hydride), which are not particularly limitated.

[0256]

Reaction scheme (1)



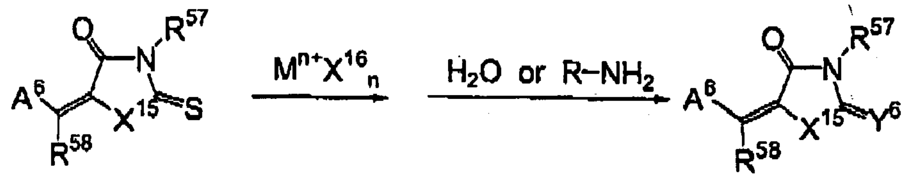
(1)

[0257] Also, as other desired synthesis method, a method according to the following reaction scheme (2) may be used. That is, this method includes carrying out the same procedures as those in the reaction scheme (1) until the step of synthesizing a dye precursor by using, as the starting material, an acid nuclear compound in the reaction scheme (1) in which Y^6 represents a sulfur atom and subjecting it to condensation reaction with a basic nuclear raw material having an aldehyde group or a carbonyl group on a heterocyclic ring thereof. The method according to the reaction scheme (2) further includes acting, to the dye precursor, a metal salt capable of mutually chemically acting to the sulfur atom to form a metal sulfide and water or a primary amine compound represented by R^{60}-NH_2 (wherein R^{60} represents a monovalent non-metallic atomic group).

Among these, the reaction represented by the reaction scheme (2) is especially preferable from the viewpoint of efficiency in synthesis because the yield is high in each of the reactions. Especially, in the case of synthesizing a compound represented by Formula (13), the reaction shown in the reaction scheme (2) is useful.

[0258]

Reaction scheme (2)



(2)

[0259] In the above reaction scheme (2), M_n $^{+}X^{16}_{n}$ represents a metal salt that is capable of forming a metal sulfide by chemically interacting with the sulfur atom in the thiocarbonyl group. Specific examples of the M include Al, Au, Ag, Hg, Cu, Zn, Fe, Cd, Cr, Co, Ce, Bi, Mn, Mo, Ga, Ni, Pd, Pt, Ru, Rh, Sc, Sb, Sr, Mg, Ti and the like. Specific examples of the X include F, Cl, Br, I, NO_3, SO_4, NO_2, PO_4, CH_3CO_2 and the like. Specific examples of the M_n $^{+}X^{16}_{n}$ includeAgBr, AgI, AgF, AgO, AgCl, Ag_2O, $Ag(NO_3)$, $AgSO_4$, $AgNO_2$, Ag_2CrO_4, Ag_3PO_4, $Hg_2(NO_3)_2$, $HgBr_2$, Hg_2Br_2, HgO, HgI_2, $Hg(NO_3)_2$, $Hg(NO_2)_2$, $HgBr_2$, $HgSO_4$, Hg_2I_2, Hg_2SO_4, $Hg(CH_3CO_2)_2$, AuBr, $AuBr_3$. AuI, AuI_3, AuF_3, Au_2O_3, AuCl, $AuCl_3$, CuCl, CuI, CuI_2, CuF_2, CuO, CuO_2, $Cu(NO_3)_2$, $CuSO_4$, $Cu_3(PO_4)_2$ and the like. Most preferable examples of the metal salt among these include a silver salt in view of interactivity with the sulfur atom.

[0260] A variety of chemical modifications can be further applied to the sensitizing dye represented by Formula (12) to be used in the invention for the purpose of improving the characteristics of the photosensitive layer. For example, by binding the sensitizing dye (D) with an addition polymerizable structure of the compound (B) (such as an acryloyl group or a methacryloyl group) by a method such as covalent bonding, ionic bonding, or hydrogen bonding, it becomes possible to enhance the strength of the exposed film and to suppress unnecessary precipitation of the dye from the exposed film. Also, by binding the sensitizing dye with a partial structure of the initiator compound having a radical generation ability as described above (such as alkyl halides, oniums, peroxides, biimidazoles, reduction decomposable sites of oniums, bimidazoles and the like, or oxidation cleavable sites of borates, amines, trimethylsilylmethyl, carboxymethyl, carbonyl, or imine, or the like), in particular, it becomes possible to remarkably enhance photosensitivity in the state where the concentration of constituents required for the initiation system is low.

[0261] Further, in the case where the photosensitive composition of the invention is used as a component of a photosensitive layer of a planographic printing plate precursor, which is a preferable aspect for use, it is useful to introduce a hydrophilic site (such as acid groups or polar groups such as a carboxyl group, an ester of a carboxyl group, a sulfonic acid group, an ester of a sulfonic acid group, or an ethylene oxide group) to the sensitizing dye represented by Formula (12) for enhancing adaptability to processes using an alkaline or aqueous developing solution. In particular, a hydrophilic group having an ester form has excellent affinity because it has a relatively hydrophobic structure in the photosensitive layer and is characterized in that it generates an acid group upon hydrolysis in the developing solution, whereby hydrophilicity increases.

Besides, for example, a substituent can be properly introduced to the sensitizing dye represented by Formula (12) for enhancing its affinity in the photosensitive layer and suppressing crystalline precipitation. For example, in a certain photosensitive system, there may be the case where an aryl group or an unsaturated bond such as an allyl group is very effective for enhancing the affinity. Also, by introducing a steric hindrance between dye π-planes by introduction of a branched alkyl structure or other methods, it is possible to remarkably suppress crystalline precipitation. Also, it is possible to enhance adhesion to an inorganic material such as metals or metal oxides by introduction of a phosphoric acid group, an epoxy group, a trialkoxysilyl group or the like. Besides, a method of polymerizing the sensitizing dye can be utilized depending upon the object.

[0262] It is preferable that at least one sensitizing dye represented by the foregoing Formula (12) is used as the sensitizing dye to be used in the invention. As long as the sensitizing dye is represented by Formula (12), details of the use method (for example: what kind of structure of the dye should be used (the dyes can be modified as described above); whether the dye should be used singly or in combination of two or more thereof; and what addition amount of the dye be employed) can be properly set up so as to coincide with the design of the final performance of the photosensitive material. For example, by using two or more kinds of sensitizing dyes in combination, it is possible to enhance affinity with the photosensitive layer.

In addition to the photosensitivity, a molar absorption coefficient at an emission wavelength of a light source to be used is an important factor in selecting the sensitizing dye. Use of a dye having a large molar absorption coefficient is economical and advantageous from the viewpoint of the film physical property of the photosensitive layer because the addition amount of the dye can be made relatively small.

As long as the effects of the invention are not hindered, other generally used sensitizing dyes can be used in addition to the sensitizing dye represented by Formula (12).

[0263] Since the photosensitivity and resolution of the photosensitive layer and the physical properties of the exposed film are largely influenced by an absorption at the light source wavelength, the addition amount of the sensitizing dye is properly selected while these are taken into consideration. For example, the sensitivity is lowered in a region where the absorption is 0.1 or lower. Also, the resolution becomes low due to influence of halation. However, for the purpose of curing a thick film of, for example, 5 μm or more, there may be the case where the degree of curing is rather increased at a low absorption. Also, in a region where the absorption is high (such as 3 or more), the major part of light is absorbed at the surface of the photosensitive layer, whereby curing in the inside thereof is hindered. For example, when such a photosensitive layer having high absorption is applied to a printing plate, the photosensitive layer may provide insufficient film strength or insufficient adhesion to a substrate.

For example, in the case where the photosensitive composition of the invention is applied to a photosensitive layer of a planographic printing plate precursor in which the photosensitive layer has a relatively thin film thickness, it is preferable to set up the addition amount of the sensitizing dye such that the absorption of the photosensitive layer is in a range of 0.1 to 1.5, and is preferably in a range of 0.25 to 1. Since the absorption of the photosensitive layer is determined by the addition amount of the sensitizing dye and the thickness of the photosensitive layer, a predetermined absorption can be obtained by controlling these conditions. The aborption of the photosensitive layer can be measered by an normal method. Examples of the measurement method include: a method inclding forming, on a transparent or white support, a photosensitive layer by applying the photosensitive composition so that the amount of the the photosensitive composition provides a thickness which is properly determined to be within a range after drying and is necessary for a planographic printing plate precursor and measuring the optical density of the photosensitive layer by a transmission optical densitometer; and a method inclding forming a recording layer on a reflective support such as aluminum, and measuring the reflection density of the photosensitive layer.

(D') Infrared absorbing dye

[0264] It is preferable that an infrared absorbing dye having an absorption maximum at a wavelength in a range of 750 to 1400 nm is contained in the photosensitive composition of the invention when exposure is conducted by using a laser emitting infrared ray as a light source. The infrared absorbing dye serves to convert absorbed infrared ray into heat. By thus generated heat, a radical generator (a polymerization initiator) is thermally decomposed to generate a radical. The infrared absorbing dye used in the invention is preferably a dye or pigment having an absorption maximum at a wavelength in a range of 750 to 1,400 nm.

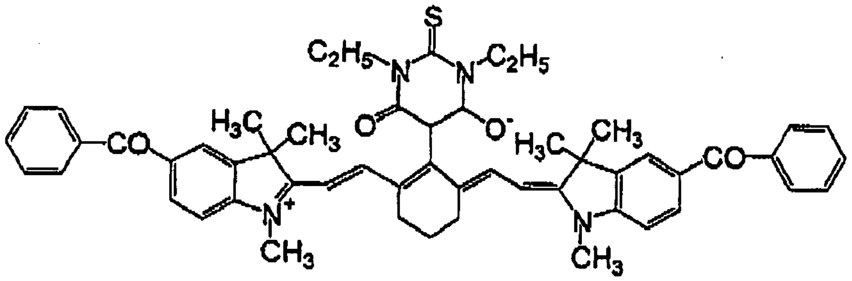
[0265] The dye may be any one of commercial dyes including known dyes described in e,g, "Senryo Binran" (Dye Handbook) (published in 1970 and compiled by Society of Synthetic Organic Chemistry, Japan). Examples of such dyes include azo dyes, metal complex salt azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinone imine dyes, methine dyes, cyanine dyes, squarylium colorants, pyrylium salts, metal thiolate complexes and the like.

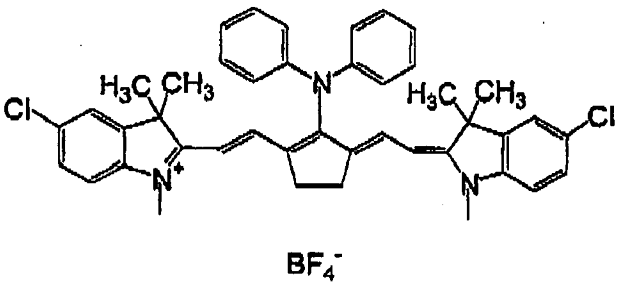
Examples of preferable dye include cyanine dyes described in JP-A Nos. 58-125246, 59-84336, 59-202829 or 60-78787, methine dyes described in JP-A Nos. 58-173696, 58-181690, or 58-194395, naphthoquinone dyes described in JP-A Nos. 58-112793, 58-224793, 59-48187, 59-73996, 60-52940, or 60-63744, squarylium colorants described in JP-A No. 58-112792, and cyanine dyes described in UK Patent No. 434,875.

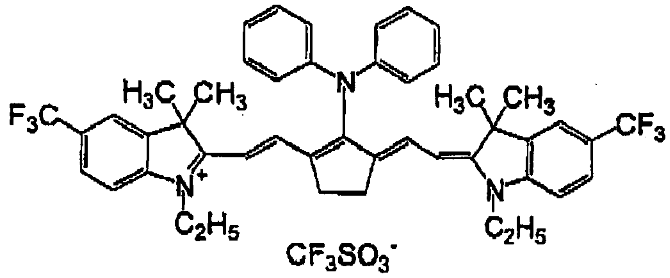
[0266] Near infrared ray-absorbing sensitizers described in US Patent No. 5,156,938 may be also preferably used. Also preferably used are substituted aryl benzo(thio) pyrylium salts described in US Patent No. 3,881,924, trimethine thiapyrylium salts described in JP-A No. 57-142645 (US Patent No. 4,327,169), pyrylium-containing compounds described in JP-A . Nos. 58-181051, 58-220143, 59-41363, 59-84248, 59-84249, 59-146043, or 59-146061, cyanine colorants described in JP-A No. 59-216146, pentamethine thiopyrylium salts described in US Patent No. 4,283,475, and pyrylium compounds described in JP-B Nos. 5-13514 or 5-19702. Examples of the preferable dye further include infrared ray-absorbing sensitizers represented by Formula (I) or (II) described in US Patent No. 4,756,993.

[0267] Examples of the infrared absorbing dye used in the invention further include specific indolenine cyanine dyes disclosed in JP-A Nos. 2002-278057 and 2002-278057 as shown below.

[0268]



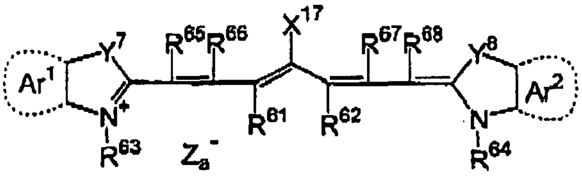




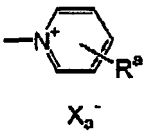
[0269] Specific examples among these dyes are cyanine dyes, squarylium colorants, pyrylium salts, nickel thiolate complexes, and indolenine cyanine dyes. Further preferable examples among these dyes are cyanine dyes and indolenine cyanine dyes. Particularly preferable examples among these dyes are cyanine dyes represented by any one of the following Formulae (a) to (e).

[0270]

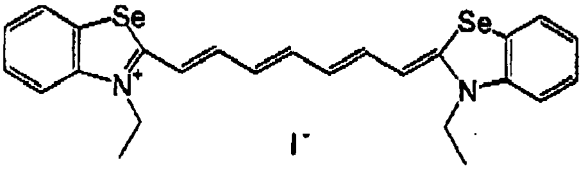
Formula (a)

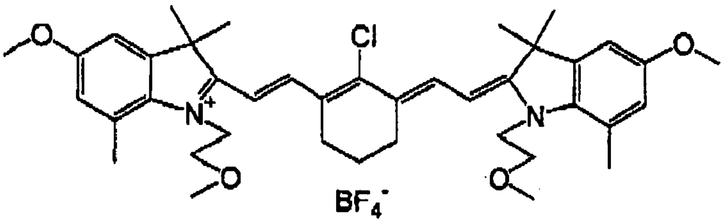


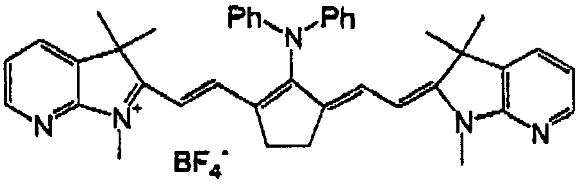
[0271] In Formula (a), X^{17} represents a hydrogen atom, halogen atom, $-NPh_2$, $-X^{16}-L^1$ or the group shown below.
[0272]

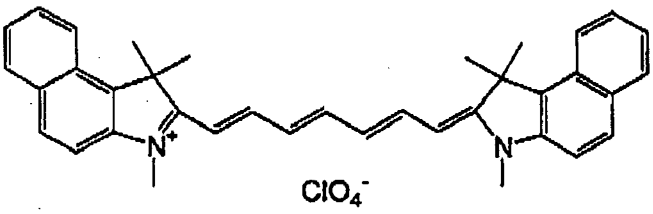


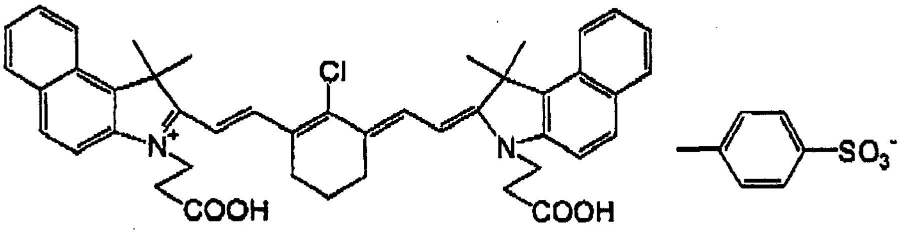
[0273] X^{16} represents an oxygen atom, a nitrogen atom, or a sulfur atom. L’ represents a hydrocarbon group having 1 to 12 carbon atoms, an aromatic ring having a heteroatom, or a hydrocarbon group having 1 to 12 carbon atoms and containing a heteroatom. The term "heteroatom" used herein refers to an atom selected from N, S, O, a halogen atom or Se, X_a^- has the same definition as that of Z_a^-, that is explained below, and R^a represents a hydrogen atom or a substituent selected from an alkyl group, an aryl group, a substituted or unsubstituted amino group, or a halogen atom.
[0274] R^{61} and R^{62} each independently represents a hydrocarbon group having 1 to 12 carbon atoms. For the storage stability of the recording layer coating liquid, each of R^{61} and R^{62} is preferably a hydrocarbon group containing two or more carbon atoms, and more preferably R^{61} and R^{62} are bound to each other to form a 5- or 6-memberred ring.
[0275] Ar^1 and Ar^2 may be the same or different, and each independently represents an aromatic hydrocarbon group which may have a substituent. The aromatic hydrocarbon group is preferably a benzene ring or a naphthalene ring. The substituent is preferably a hydrocarbon group containing 12 or less carbon atoms, a halogen atom or an alkoxy group containing 12 or less carbon atoms. Y1 and Y^2 may be the same or different, and each independently represents a sulfur atom or a dialkyl methylene group containing 12 or less carbon atoms. R^{63} and R^{64} may be the same or different, and each independently represents a hydrocarbon group containing 20 or less carbon atoms which may have a substituent. The substituent is preferably an alkoxy group containing 12 or less carbon atoms, a carboxyl group or a sulfo group. R^{65}, R^{66}, R^{67} and R^{68} may be the same or different, and each independently represents a hydrogen atom or a hydrocarbon group containing 12 or less carbon atoms. Each of R^{65}, R^{66}, R^{67} and R^{68} is preferably a hydrogen atom because the starting material is easily available. Z_a^- represents a counter anion. However, when the cyanine colorant represented by Formula (a) has an anionic substituent in its structure and does not necessitate neutralization of the charge, Z_a^- is not necessary. In view of the storage stability of the recording layer coating liquid, Z_a^- is preferably a halogen ion, a perchlorate ion, a tetrafluoroborate ion, a hexafluorophosphate ion or a sulfonate ion, and particularly preferably a perchlorate ion, a hexafluorophosphate ion or an aryl sulfonate ion.
[0276] In addition to the followings, specific examples of the cyanine dye that is represented by Formula (a) and can be preferably used in the invention further include those disclosed in [0017]-[0019] of JP-A No. 2001-133969, [0012]-[0038] of JP-A No. 2002-040638, [0012]-[0023] of JP-A No. 2002-023360 and the like.
[0277]



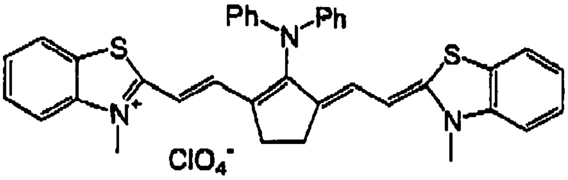

Cl
N+
N
O
O
BF4-

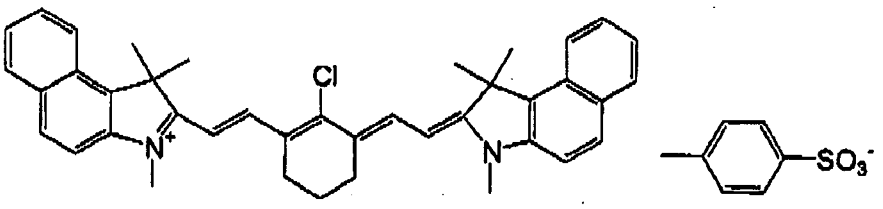

Ph
N
Ph
N
N+
N
N
BF4-

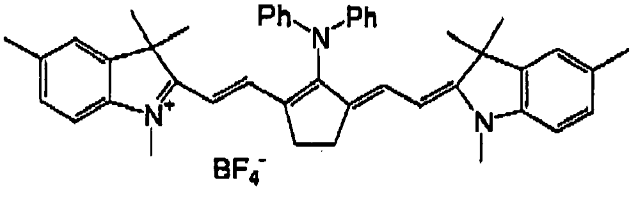

N+
N
ClO4-

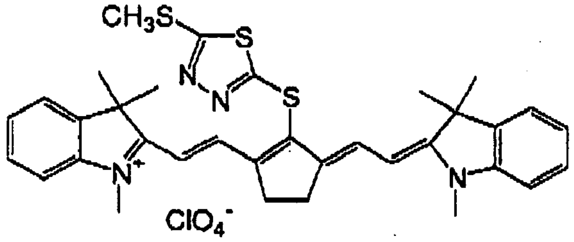

Cl
N+
N
COOH
COOH
SO3-

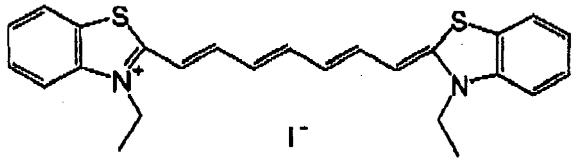
[0278]


Ph
N
Ph
S
N+
S
N
ClO4-

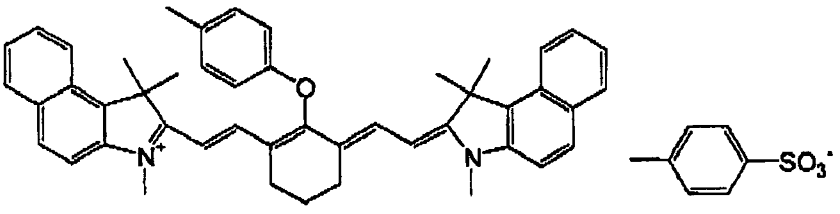


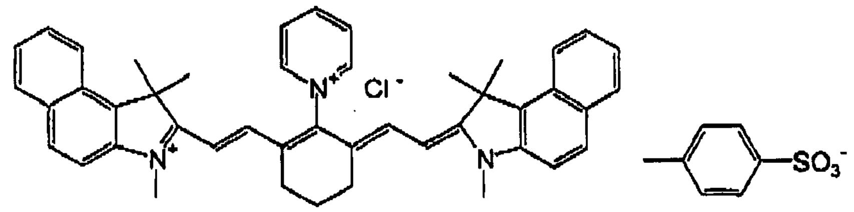


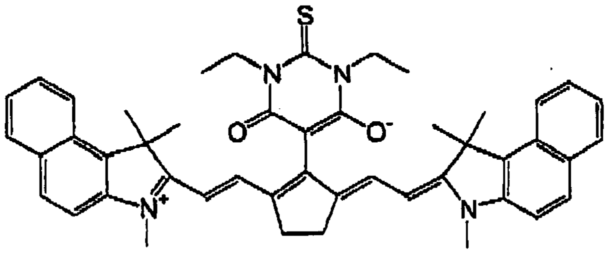




[0279]

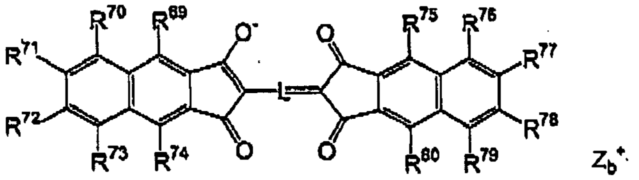






[0280]

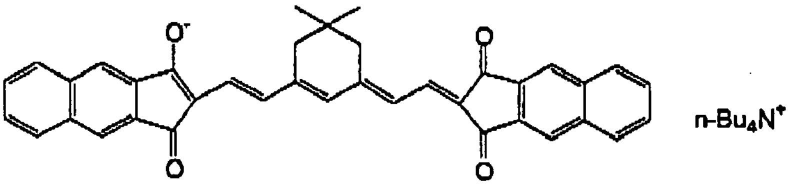
Formula (b)

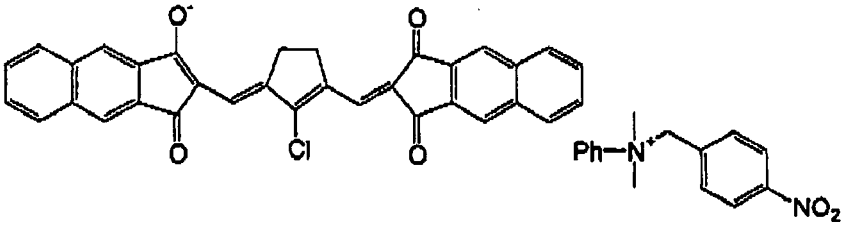


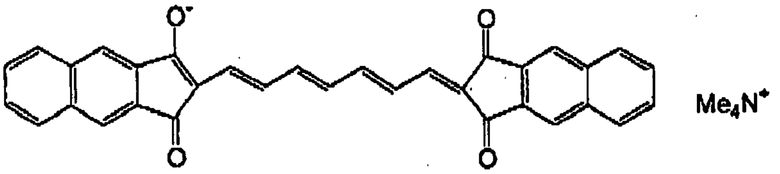
[0281] In Formula (b), L represents a methine chain containing 7 or more conjugated carbon atoms, and the methine chain may have a substituent, and the substituents may be bound to each other to form a ring structure. Z_b^+ represents a counter cation. The counter cation is preferably ammonium, iodonium, sulfonium, phosphonium, pyridinium or an alkali metal cation (such as Ni^+, K^+, or Li^+). R^{69} to R^{74} and R^{75} to R^{80} each independently represents 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, an oxy group or an amino group, or a substituent composed of a combination of two or three of these substituents which may be bound to each other to form a ring structure. Among the compounds of Formula (b), those having a methine chain containing 7 conjugated carbon atoms as L, and those in which each of R^9 to R^{74} and R^{75} to R^{80} represents a hydrogen atom, are preferable from the viewpoint of easy availability and effects.

[0282] Examples of the dyes represented by Formula (b), which can be used preferably in the invention, include those illustrated below:

[0283]

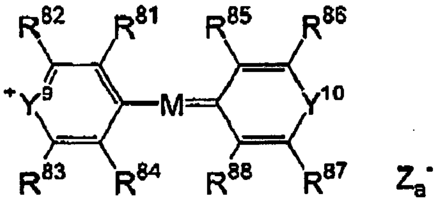






[0284]

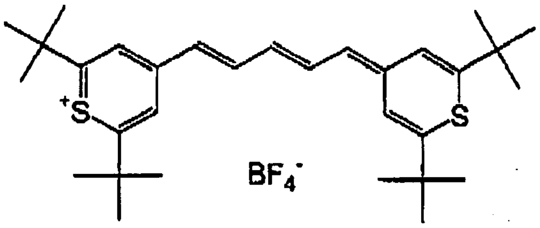
Formula (c)

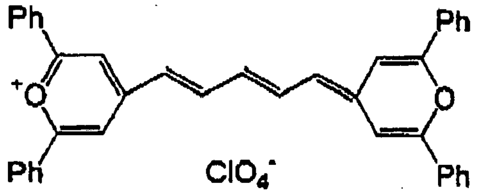


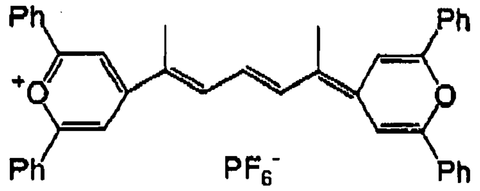
[0285] In Formula (c), Y^9 and Y^{10} each independently represents an oxygen atom, a sulfur atom, a selenium atom or a tellurium atom; M represents a methine chain containing 5 or more conjugated carbon atoms; R^{81} to R^{84} and R^{85} to R^{88} may be the same as or different from one another, and each independently represents 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; and $Z_a{}^-$ represents a counter anion and has the same definition as that of $Z_a{}^-$ in Formula (a) above.

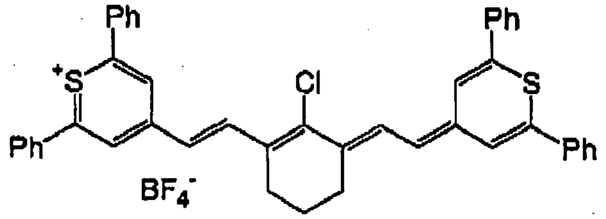
[0286] Examples of the dyes represented by Formula (c), which can be used preferably in the invention, include those illustrated below:

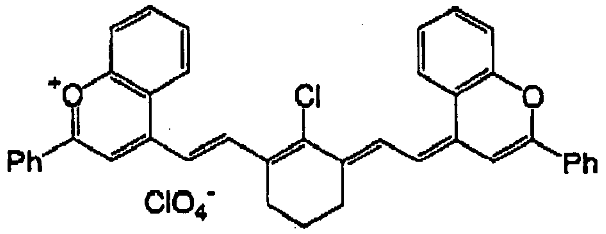
[0287]





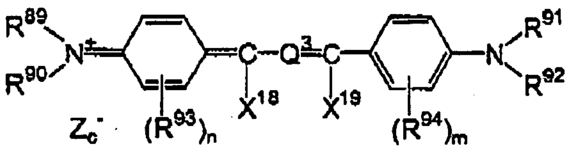






[0288]

Formula (d)

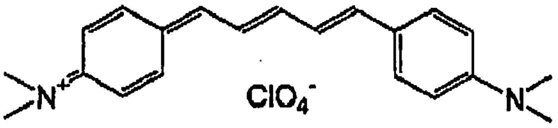


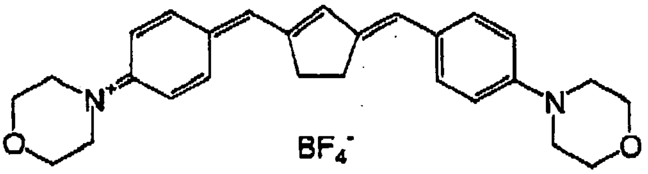
[0289] In Formula (d), R^{89} to R^{91} each independently represents a hydrogen atom, an alkyl group or an aryl group; R^{93} and R^{94} each independently represents an alkyl group, a substituted oxy group or a halogen atom; n and m each independently represents an integer of 0 to 4; R^{89} and R^{90}, or R^{91} and R^{92}, may be bound to each other to form a ring;

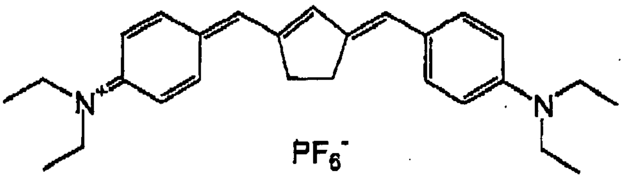
R^{89} and/or R^{90} may be bound to R^{93} to form a ring; R^{91} and/or R^{92} may be bound to R^{94} to form a ring; when plural R^{93}s are present, some of R^{93}s may be mutually bound to form a ring; when plural R^{94}s are present, some of R^{94}s may be mutually bound to form a ring; X^{18} and X^{19} each independently represents a hydrogen atom, an alkyl group or an aryl group, and at least one of X^{18} and X^{19} represents a hydrogen atom or an alkyl group; Q^3 is a trimethine group or a pentamethine group, each of which may have a substituent and may form a ring structure with a divalent organic group; and Zc· represents a counter anion and has the same definition as that of Z_a^- in Formula (a) above.

[0290] Examples of the dyes represented by Formula (d), which can be used preferably in the invention, include those illustrated below:

[0291]

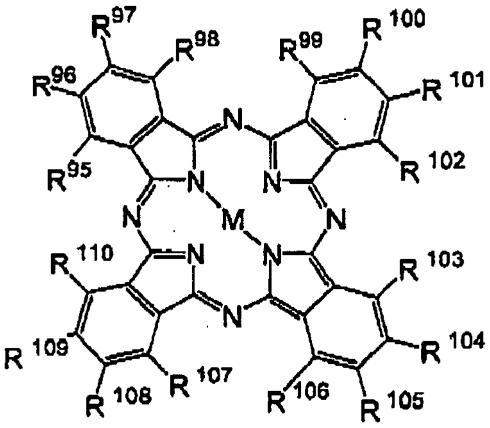






[0292]

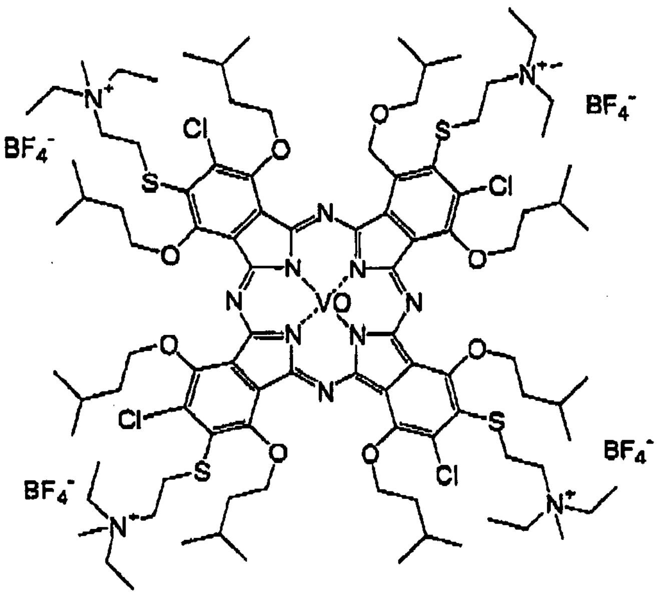
Formula (e)

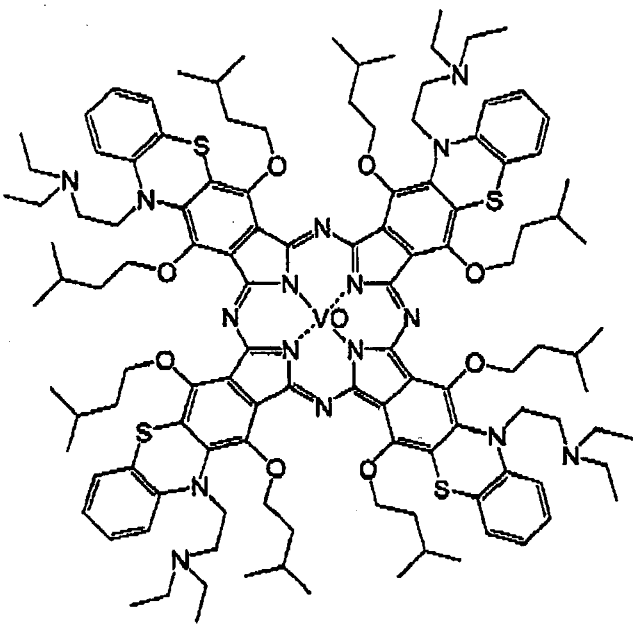


[0293] In Formula (e), R^{95} to R^{110} each independently represents a hydrogen atom, halogen atom, cyano group, alkyl group, aryl group, alkenyl group, alkynyl group, hydroxyl group, carbonyl group, thio group, sulfonyl group, sulfinyl group, oxy group, amino group, and onium salt structure, each of which may have a substituent; and M represents two hydrogen atoms, a metal atom, a halometal group or an oxymetal group, and examples of the metal atom contained therein include the groups IA, IIA, IIIB and IVB atoms in the periodic table, the transition metals in the first, second and third periods, and lanthanoid elements, and among these, copper, magnesium, iron, zinc, cobalt, aluminum, titanium and vanadium are preferable.

[0294] Examples of the dyes represented by Formula (e), which can be used preferably in the invention, include those illustrated below:

[0295]





[0296] Examples of the pigment used in the invention include commercial pigments and those described in Color Index (C. I.) Handbook, "Saishin Ganryo Binran" (Newest Dye Handbook) (published in 1977 and compiled by Japanese Society of Pigment Technology), "Saishin Ganryho Oyo Gijyutsu" (Newest Pigment Applied Technology) (published in 1986 by CMC), and "Insatsu Inki Gijyutsu" (Printing Ink Technology) (published in 1984 by CMC).

[0297] As to the type of the pigment, examples of usable pigments include black pigments, yellow pigments, orange pigments, brown pigments, red pigments, violet pigments, blue pigments, green pigments, fluorescent pigments, metallic powder pigments, and other pigments such as polymer-binding colorants. Specific examples thereof include insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyanine pigments, anthraquinone pigments, perylene pigments, perinone pigments, thioindigo pigments, quinacridone pigments, dioxazine pigments, isoindolinone pigments, quinophthalone pigments, dyed lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments, and carbon black. A preferable pigment among those described above is carbon black.

[0298] Such pigments may be used with or without being subjected to surface treatment. Examples of the method of surface treatment include a method of coating the surface with a resin or a wax, a method of allowing a surfactant to adhere to the surface, and a method of bonding a reactive substance (e.g., a silane coupling agent, an epoxy compound, a polyisocyanate etc.) onto the surface of the pigment. These methods of surface treatment are described in "Kinzoku Sekken No Seishitsu To Oyo" (Properties and Application of Metallic Soap) (Sachi Shobo), "Insatsu Inki Gijyutsu" (Printing Ink Technology) (published in 1984 by CMC Shuppan) and "Saishin Ganryho Oyo Gijyutsu" (Newest Pigment Applied Technology) (published in 1986 by CMC Shuppan).

[0299] The particle diameter of the pigment is preferably in a range of 0.01 to 10 μm, more preferably 0.05 to 1 μm, and still more preferably 0.1 to 1 μm. A pigment particle diameter of less than 0.01 μm may not be preferable in respect of the stability of a pigment dispersion in the image recording layer coating liquid, whereas a particle diameter of more than 10 μm may not be not preferable in respect of the uniformity of the image recording layer.

[0300] As the method of dispersing the pigments, any known dispersion techniques used in production of inks or toners can be used. Examples of the dispersing machine include a supersonic dispersing device, a sand mill, an attritor, a pearl mill, a super mill, a ball mill, an impeller, a disperser, a KD mill, a colloid mill, a dynatron, a triple roll mill, and a press kneader. Details thereof are described in "Saishin Ganryho Oyo Gijyutsu" (Newest Pigment Applied Technology) (published in 1986 by CMC Shuppan).

[0301] When the component (B) in the invention is used in the photosensitive layer of the negative planographic printing plate precursor, the sensitizing dye (D) and/or the infrared ray absorbing dye (D'), which can be added to promote the curing reaction of the component (B), may be added to the photosensitive layer or may be added to an another layer such as the undercoat layer. In view of the sensitivity of the photosensitive layer, it is preferable that the sensitizing dye (D) is selected so that an optical density of the photosensitive layer at an absorption maximum which is in a wavelength range of 350 nm to 450 nm falls in a range of 0.1 to 3.0, and/or the infrared ray absorbing dye (D') is selected so that an optical density of the photosensitive layer at an absorption maximum which is in a wavelength range of 750 nm to

1400 nm falls in a range of 0.1 to 3.0, when the component (B) of the invention is used in the photosensitive layer of the negative planographic printing plate precursor. Since the optical density is determined depending on the content of the sensitizing dye and/or the infrared ray absorption dye and the thickness of the photosensitive layer, a predetermined optical density of can be obtained by controlling these two conditions.
The optical density of the recording layer can be measured in a usual manner. Examples of methods for the measurement include a method comprising forming a recording layer on a transparent or white support such that the thickness of the recording layer is a predetermined thickness corresponding to an adequate dry coating weight as a planographic printing plate, and measuring the optical density by a transmission-type optical densitometer, and a method comprising forming a recording layer on a reflective support such as aluminum, and measuring the reflection density.

[0302] When the photosensitive composition of the invention is used as the photosensitive layer of the planographic printing plate precursor, the addition amount of the sensitizing dye (D) is typically in a range of 0.05 to 30 mass%, is preferably in a range of 0.1 to 20 mass%, and is further preferably in a range of 0.2 to 10 mass%, with respect to the total solid component of the photosensitive layer of 100 mass%.

(F) Other components

[0303] As needed, other components such as a co-sensitizer, a polymerization inhibitor, a coloring agent, a plasticizer and the like, which are suitable for the intended use, the production method etc., can further be added to the polymerizable composition according to the invention. Hereinafter, additives which are preferable in a case where the polymerizable composition according to the invention is specifically used for a photosensitive layer of a negative image recording material will be described.

Co-sensitizer

[0304] By use of a co-sensitizer in the photopolymerizable photosensitive layer, the sensitivity of the photosensitive layer can be further improved. The working mechanism of the co-sensitizer is not clear, but is considered to be mainly based on the following chemical process. That is, it is estimated that various intermediate active species (radials, peroxides, oxidants, reductants or the like) generated in the photo-reaction initiated by the absorption of light by the photopolymerization initiator (photopolymerization initiation system) and in the subsequent addition-polymerization reaction react with the co-sensitizer to form new active radicals. Such co-sensitizers can be roughly classified into (i) those capable of forming active radicals when reduced, (ii) those capable of forming active radicals when oxidized, and (iii) those converted into highly active radicals through reaction with radicals with low activity or those acting as chain transfer agents. There are many compounds whose classification is not commonly understood.

(i) Compound forming active radicals when reduced

[0305]

- Compounds having a carbon-halogen bond: It is considered that the carbon-halogen bond is reductively cleaved to generate active radicals. Specifically, for example, trihalomethyl-s-triazines and trilhalomethyl oxadiazoles can be preferably used.

[0306]

- Compounds having a nitrogen-nitrogen bond: It is considered that the nitrogen-nitrogen bond is reductively cleaved to form active radicals. Specifically, hexaryl biimidazoles can be preferably used.

[0307]

- Compounds having an oxygen-oxygen bond: It is considered that the oxygen-oxygen bond is reductively cleaved to generate active radicals. Specifically, organic peroxides can be preferably used.

[0308]

- Onium compounds: It is considered that a carbon-heteroatom bond or an oxygen-nitrogen bond is reductively cleaved to generate active radicals. Specifically, diaryl iodonium salts, triaryl sulfonium salts, and N-alkoxy pyridinium (azinium) salts can be preferably used.
- Ferrocene, iron arene complexes: Capable of forming active radicals reductively.

(ii) Compounds forming active radicals when oxidized

[0309]

- Alkylate complexes: It is considered that a carbon-heteroatom bond is oxidatively cleaved to generate active radicals. Specifically, for example, triaryl alkyl borates can be preferably used.

[0310]

- Alkyl amine compounds: It is considered that a C-X bond on a carbon adjacent to the nitrogen is cleaved by oxidation to form active radicals. X is preferably a hydrogen atom, a carboxyl group, a trimethylsilyl group, or a benzyl group. Specific examples of the alkyl amine compound include ethanol amines, N-phenyl glycines, N-phenyliminodiacetic acid and its modified compounds, and N-trimethylsilylmethyl anilines.

[0311]

- Sulfur- or tin-containing compounds: A compound obtained by replacing the nitrogen atom in any of the above-described amines with a sulfur atom or a tin atom can form active radicals in a similar mechanism. Further, compounds having S-S bonds are known to act as sensitizers by cleavage of the S-S bonds.

[0312]

- α-Substituted methyl carbonyl compounds: Capable of forming active radicals through the cleavage of the carbonyl-α carbon bond upon oxidation. Further, compounds obtained by replacing the carbonyl in such a compound with an oxime ether exhibit the same action. Specifically, examples include 2-alkyl-1-[4-(alkylthio) phenyl]-2-morpholino-pronone-1 and modified compounds thereof, as well as oxime ethers prepared by reacting such compounds with hydroxy amines and then etherifying N-OH.

[0313]

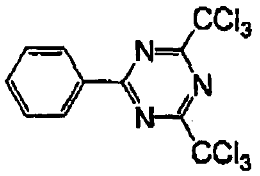
- Sulfinates: Capable of forming active radicals reductively. Specific examples of the sulfinates include sodium aryl sulfinates.

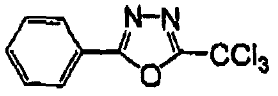
(iii) Compounds converted into highly active radicals through reaction with radicals, or compounds acting as chain transfer agents:

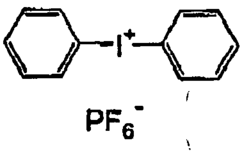
[0314] For example, compounds having SH, PH, SiH or GeH in the molecule are usable. These compounds can form radials by donating hydrogen to radicals having low-activity or by undergoing oxidization and subsequent deprotonation. Specific examples thereof include 2-mercaptobenzimidazoles.

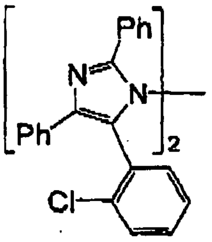
[0315] A large number of more specific examples of these co-sensitizers are described, for example, in JP-A No. 9-236913 as additives for improving sensitivity, and such compounds can also be used in the invention. Followings are shown for exemplifying a certain specific examples thereof, while the invention is not limited thereby.

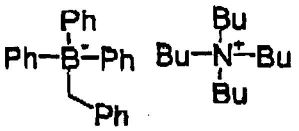
[0316]

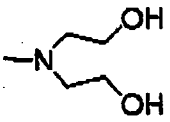


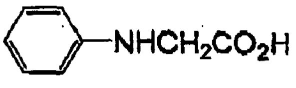


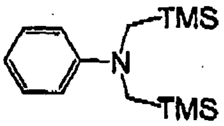


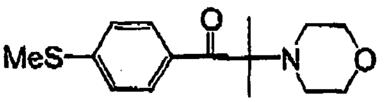


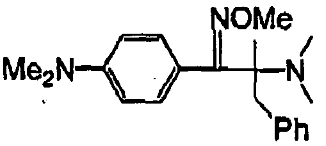


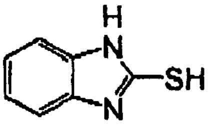












[0317] A variety of chemical modifications can be further applied the co-sensitizing dye for the purpose of improving the characteristics of the photosensitive layer. Examples of usable modification techniques include: bonding to a radical-generating part of, e.g., a sensitizing dye, titanocene or addition-polymerizable unsaturated compound; introduction of a hydrophilic group; introduction of a substituent for improvement of compatibility and inhibition of crystalline precipitation; introduction of a substituent for improving adhesion; and conversion into a polymer.

[0318] The co-sensitizer may be used singly or in a combination of two or more thereof. The amount of the co-sensitizer to be used may be in a range of 0.05 to 100 parts by mass, preferably 1 to 80 parts by mass, and more preferably 3 to 50 parts by mass, relative to 100 parts by mass of the polymerizable compound having an ethylenic unsaturated double bond.

Polymerization inhibitor

[0319] In the invention, a small amount of a heat-polymerization inhibitor is preferably added to the photo- or thermal-polymerizable negative photosensitive layer of the planographic plate precursor of the invention so as to inhibit unnecessary thermal polymerization of the polymerizable compound having a polymerizable ethylenic unsaturated double bond during production or storage of the negative photosensitive composition. Examples of suitable thermal-polymerization inhibitor include hydroquinone, p-methoxyphenol, di-t-butyl-p-cresol, pyrogallol, t-butyl catechol, benzoquinone, 4,4'-thiobis(3-methyl-6-t-butyl phenol), 2,2'-methylene bis(4-methyl-6-t-butyl phenol), and N-nitrosophenyl hydroxylamine primary cerium salts. The amount of the thermal-polymerization inhibitor to be added is preferably about 0.01 mass% to about 5 mass% relative to the amount of nonvolatile constituents in the entire of the polymerizable composition. To prevent the polymerization inhibition by oxygen, a higher fatty acid compound such as behenic acid or behenic amide may be added as needed so that the higher fatty acid compound localizes on the surface of the photosensitive layer during drying after application of the composition onto a support or the like during the production process of the planographic printing plate precursor. The amount of the higher fatty acid compound to be added is preferably about 0.5 mass% to about 10 mass% based on the amount of nonvolatile constituents in the entire of the polymerizable composition.

Coloring agent

[0320] In a case where the polymerizable composition of the invention is used in a photosensitive layer of a planographic printing plate precursor, a dye or pigment may be added to the polymerizable composition for the purpose of coloring of the photosensitive layer. The plate-checking property of the printing plate, such as visibility after plate-making and compatibility with an image densitometer, can thereby be improved. In consideration of the fact that many dyes lower the sensitivity of the photopolymerizable photosensitive layer, the coloring agent is preferably a pigment. Specific examples of the colorant include pigments such as phthalocyanine pigments, azo pigments, carbon black or titanium oxide, and dyes such as Ethyl Violet, Crystal Violet, azo dyes, anthraquinone dyes or cyanine dyes. The amount of the dyes and pigments to be added is preferably in a range of about 0.5 mass% to about 5 mass% based on the amount of nonvolatile constituents in the entire of the polymerizable composition.

Other additives

[0321] Known additives such as an inorganic filler for improving the physical properties of a cured film, a plasticizer, and a sensitizer which is capable of improving the inking property of the surface of the photosensitive layer in a case where the polymerizable composition of the invention is used in a photosensitive layer of a planographic printing plate precursor, can be added to the polymerizable composition of the invention.

[0322] Examples of the plasticizer include dioctyl phthalate, didodecyl phthalate, triethylene glycol dicaprylate, dimethyl glycol phthalate, tricresyl phosphate, dioctyl adipate, dibutyl sebacate, and triacetyl glycerin. When the plasticizer is used, it may be added in an amount of 10 mass% or less relative to the total mass of the polymer binder and the addition-polymerizable compound.

[0323] UV initiators and heat-crosslinking agents for enhancing the effects of heating and light exposure after development can also be added for the purpose of improving the layer strength (printing durability) described later.

Solvent

[0324] The planographic printing plate precursor according to the invention can be produced by dissolving the components of the photosensitive layer to a liquid which may be selected from various organic solvents, and coating the liquid onto the undercoat layer.

Examples of the solvent usable in the invention include acetone, methyl ethyl ketone, cyclohexane, ethyl acetate, ethylene dichloride, tetrahydrofuran, toluene, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, acetyl acetone, cyclohexanone, diacetone alcohol, ethylene glycol monomethyl ether acetate, ethylene glycol ethyl ether acetate, ethylene glycol monoisopropyl ether, ethylene glycol monobutyl ether acetate, 3-methoxy propanol, methoxy methoxy ethanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, 3-methoxy propyl acetate, N,N-dimethyl formamide, dimethyl sulfoxide, γ-butyrolactone, methyl lactate and ethyl lactate. These solvent may be used singly or in a mixture of two or more thereof. An adequate solids content of the coating liquid is from 2 to 50 mass%.

[0325] It is preferable that the coating amount of the photosensitive layer on the support be determined suitably depending on applications in consideration of the effects on the sensitivity and developability of the photosensitive layer and the strength and printing durability of the light-exposed film. When the coating amount is too small, printing durability may not be satisfactory. A too large coating amount is not preferable because sensitivity may be decreased, the time for light exposure may be prolonged, and the development treatment may also require a longer time. In a planographic printing plate precursor for scanning exposure, which is one of major application purposes of the invention, the coating amount of the photosensitive layer in terms of mass after drying is generally in a range of about 0.1 to about 10 g/m^2, and more preferably from 0,5 to 5 g/m^2,

Intermediate layer and Protective layer

[0326] The planographic printing plate precursor according to the invention may further include other layers such as an intermediate layer (undercoat layer), protective layer or the like.

Intermediate layer (undercoat layer)

[0327] For the purpose of improving the adhesiveness between the photosensitive layer and the support and stain resistance, the planographic printing plate precursor may have an intermediate layer (which may be also referred as an "undercoat layer" hereinafter). Specific examples of the intermediate layer include those described in JP-B No. 50-7481, JP-A Nos.51-71123, 54-72104, 59-101651, 60-149491, 60-232998, 2-304441, 3-56177, 4-282637, 5-16558, 5-246171, 5-341532, 7-159983, 7-314937, 8-202025, 8-320551, 9-34104, 9-236911, 9-269593, 10-69092, 10-115931, 10-161317, 10-260536, 10-282679, 10-282682, 11-84674, 10-69092, 10-115931, 11-38635, 11-38629, 10-282645, 10-301262, 11-24277, 11-109641, 10-319600, 11-84674, 11-327152, 2000-10292, 2000-235254, and 2000-352824, 2001-209170, and 2001-175001.

Protective layer

[0328] In a negative photosensitive planographic printing plate precursor having a photo-or thermal-polymerizable negative photosensitive layer as is in the invention, it is generally preferable to form a protective layer on the photosensitive layer since the photosensitive printing plate is exposed in the air. The protective layer prevents contamination of the photosensitive layer with low-molecular compounds such as oxygen or basic substances present in the air, which inhibit an image-forming reaction caused in the photosensitive layer by exposure. The protective layer thereby enables performing the exposure process in the air.

[0329] Accordingly, the protective layer is desirably a layer which has little peameability of low molecular compounds such as oxygen, does not substantially inhibit penetration of light used in light exposure, is excellent in adhesiveness to the recording layer, and can be easily removed in the development after light exposure. Conventionally, the protective layer has been devised in many ways and described in detail in US Patent No. 3,458,311 and JP-A No. 55-49729.

[0330] Examples of a material usable as a component in the protective layer is preferably a water-soluble polymer compound having relatively high crystallinity. Specifically, water-soluble polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, acidic celluloses, gelatin, gum arabic and polyacrylic acid are well-known in the art. Among these compounds, the use of polyvinyl alcohol as the major component may lead to the best results with respect to basic characteristics such as oxygen impermeability and removability at development. The polyvinyl alcohol used in the protective layer may be partially substituted by ester, ether or acetal insofar as it has unsubstituted vinyl alcohol units, which impart necessary oxygen impermeability and water solubility. Similarly, the polyvinyl alcohol may be a copolymer having a part that contains one or more other copolymerizable components.

Specific examples of the polyvinyl alcohol include PVA-105, PVA-110, PVA-117, PVA-117H, PVA-120, PVA-124, PVA-124H, PVA-CS, PVA-CST, PVA-HC, PVA-203, PVA-204, PVA-205, PVA-210, PVA-217, PVA-220, PVA-224, PVA-217EE, PVA-217E, PVA-220E, PVA-224E, PVA-405, PVA-420, PVA-613, and L-8 (all trade name, manufactured by Kuraray Co., Ltd.).

[0331] Examples of the copolymer described above include polyvinyl acetate, polyviny chloroacetate, polyviny propionate, polyvinyl formal and polyvinyl acetal which are hydrolyzed to 88 to 100%, and copolymers thereof. Examples of useful water-soluble polymer compounds further include polyvinyl pyrrolidone, gelatin and gum arabic. These water-soluble polymer compound may be used singly or in a combination of two or more thereof.

[0332] Polyvinyl alcohols preferably used in this embodiment include polyvinyl alcohols having a saponification degree of 71 to 100 % and a molecular weight in a range of 200 to 2,400. From the viewpoint of having excellent oxygen impermeability, excellent layer-forming property, and a surface of low adhesiveness, the use of polyvinyl alcohols having a saponification degree of 91 mol% or higher is more preferable.

Specific examples of the polyvinyl alcohol usable in the invention include PVA-102, PVA-103, PVA-104, PVA-105, PVA-110, PVA-117, PVA-120, PVA-124, PVA-117H, PVA-135H, PVA-HC, PVA-617, PVA-624, PVA-706, PVA-613, PVA-CS and PVA-CST (all trade names, manufactured by Kuraray Co., Ltd.), GOSENOL NL-05, NM-11, NM-14, AL-06, P-610, C-500, A-300 and AH-17 (all trade names, manufactured by Nippon Synthetic Chemical Industry Co., Ltd.), and JF-04, JF-05, JF-10, JF-17, JF-17L, JM-05, JM-10, JM-17, JM-17L, JT-05, JT-13 and JT-15 (all trade names, manufactured by JAPAN VAM&POVAL Co., Ltd.)

[0333] Acid-modified polyvinyl alcohols can also be preferably used. Preferable examples thereof include a carboxy-modified polyvinyl alcohol modified with itaconic acid or maleic acid, and a polyvinyl alcohol modified with sulfonic acid. Use of an acid-modified polyvinyl alcohol having a saponification degree of 91 mol% or higher is more preferable.

Specific examples of the acid-modified polyvinyl alcohol include KL-118, KM-618, KM-118, SK-5102, MP-102 and R-2105 (all trade names, manufactured by Kuraray Co., Ltd.), GOSENAL CKS-50, T-HS-1, T-215, T-350, T-330 and T-330H (all trade names, manufactured by Nippon Synthetic Chemical Industry Co., Ltd.), and AF-17, AT-17 (both trade names, manufactured by JAPAN VAM&POVAL CO., LTD) and the like.

[0334] In consideration of the sensitivity of the resultant negative planographic printing plate precursor and the adhesion between the planographic printing plate precursors when stacked, the water-soluble polymer compound described above is preferably contained in a range of 45 to 95 mass%, more preferably in a range of 50 to 90 mass%, based on the total solid content of the protective layer.

At least one water-soluble polymer compound may be used in the protective layer, and a combination of two or more water-soluble compounds may be used. When plural water-soluble polymer compounds are simultaneously used, the total mass thereof is preferably in the range described above.

[0335] The coating amount of the protective layer is preferably 0.1 g/m^2 to 4.0 g/m^2, and more preferably 0.3 g/m^2 to 3.0 g/m^2 from the viewpoints of the strength and scratch resistance of the resultant protective layer, maintenance of image quality, and maintenance of suitable oxygen permeability for imparting safelight compatibility.
Selections of the components (including selection of PVA, use of additives and the like) and the coating amount of the protective layer are conducted in consideration of the oxygen blocking ability, removability at development, fogging resistence, adhesive property and scratch resistance. In general, as the hydrolysis degree of PVA is higher (namely, as the unsubstituted vinyl alcohol unit content in the protective layer is higher) and as the layer thickness is larger, the oxygen blocking ability becomes higher, which is advantageous in view of sensitivity. However, if the oxygen blocking ability is excessively elevated, there arise problems such as an occurence of unnecessary polymerization reaction during the production or stock storage, or occurence of undesirable fogging or thickening of image at the time of image exposure.

[0336] The adhesiveness to an image portion of the recording layer and the scratch resistance are very important characteristics of the protective layer from the viewpoint of handling of the printing plate. That is, if a hydrophilic layer consisting of a water-soluble polymer is laminated on a lipophilic recording layer, layer separation easily occurs due to insufficient adhesiveness, and the released portion causes deficiency such as insufficient layer curing attributable to polymerization inhibition by oxygen. Against this problem, various proposals for improving the adhesion between the two layers have been made. For example, US Patent Application Nos. 292,501 and 44,563 describe that an acrylic emulsion, a water-insoluble vinyl pyrrolidone-vinyl acetate copolymer or the like is mixed in an amount of 20 to 60 mass% in a hydrophilic polymer mainly composed of polyvinyl alcohol and then the resultant composition is laminated on a recording layer, whereby satisfactory adhesiveness is obtained.

[0337] Any one of above-described conventionally-known methods can be used for applying the protective layer in the invention, and details of these methods are described in U.S. Patent No. 3,458,311, JP-A No. 55-49729 and the like. The protective layer may further appropriately contain various additives. Preferable additives which can be used in the invention are specifically explained hereinafter.

Filler

[0338] The protective layer according to the invention preferably further contains a filler. The filler incorporated into the protective layer has a mattifying function (a function to impart unevenness for reducing a surface area for adhesion) so that scratch resistance of the surface of the photosensitive layer can be improved, and the adhesion between the adjacent photosensitive printing plate precursors when stacked without an interleaf paper therebetween can be suppressed.

[0339] The filler used in the invention is added to the protective layer in order to prevent adhesion between the surface of the protective layer of the planographic printing plate precursor and the adjacent back surface of the support of the planographic printing plate precursor and scratches generated between the surface of the protective layer and the back surface of the aluminum support. These fillers preferably have primary characteristics of providing substantially no influenece to the transmission of light used for the exposure, resistence to softening and getting stickiness due to the moisture in air or heat at a temperature of 60°C or lower. In addition, the filler is required to have an effect of mattifying the surface of the protective layer (namely, an effect for decreasing surface area for adhesion by imparting irregularities). The Bekk smoothness, which serves as the index of the surface irregularities, of the surface of the protective layer is preferably 500 seconds or less, and is more preferably 150 seconds or less.

[0340] From the viewpoint of suppressing the scratches, the filler is preferably an organic particle which is relatively soft, exhibits elasticity, and can release stress generated when the protective layer contacts with the back surface of the support formed of hard aluminum. In consideration of avoiding deteriorations in such effects due to the pressure invloved in forming a stack of the planographic printing precursors, the filler is more preferably an organic resin fine particle. Among these, a cross-linked particle is preferable since it is not fused by heat. The fine particle of the filler preferably has a high affinity with a binder in the protective layer, is well kneaded in the protective layer, and are not taken off from the surface of the protective layer.

[0341] Examples of the organic resin having such characteristics include poly(meth)acrylic acid esters; polystyrenes and modified compounds thereof; polyamides; polyimides; polyolefins such as low density polyethylene, high density polyethylene, or polypropylene, copolymers formed of these polyolefins and poval; synthetic resin particles such as polyurethane, polyurea, or polyesters; and natural high molecular particles such as chitin, chitosan, cellulose, cross-linking cellulose or cross-linking starch. Among these, the synthetic resin particles are advantageous in that the particle size is easily controlled and a surface characteristic is easily desireably controlled by the surface modification. While a microparticulation method including grinding may be performed when a relatively hard resin is used, a method of synthesizing particles by a suspension polymerization has been generally adopted as a preparation method of the organic resin particles because of its easiness and precision in control of the particle diameter. The preparation method of fine particle powders is taught in "Preparation and Application for fine particle/powder", first edition, supervised by Haruma KAWAGUCHI and published by CMC Publishing Co.,Ltd, in 2005.

[0342] Examples of the organic resin fine particles which are commercially-available include crosslinked acrylic resins (such as MX-150, MX-180, MX-300, MX-500, MX-1000, MX-1500H, MX-2000, MR-2HG, MR-7HG, MR-10HG, MR-3GSN, MR-5GSN, MR-2G, MR-7G, MR-10G, MR-20G, MR-5C, or MR-7GC: all trade names, manufactured by Soken Chemical & Engineering Co., Ltd.), styryl resin fine particles (such as SX-350H or SX-500H: both trade names, manufactured by Soken Chemical & Engineering Co., Ltd.), acrylic resins (such as MBX-5, MBX-8, MBX-12, MBX-15, MBX-20, MB20X-5, MB30X-5, MB30X-8, MB30X-20, SBX-6, SBX-8, SBX-12 or SBX-17: all trade names, manufactured by Sekisui Plastics Co., Ltd.), and polyolefin resins (such as CHEMIPEARL W100, W200, W300, W308, W310, W400, W401, W4005, W410, W500, WF640, W700, W800, W900, W950 or WP100: all trade names, manufactured by Mitsui Chemicals, Inc.).

[0343] A mixture of two or more fillers selected from inorganic fillers, inorganic-organic composite fillers and the like may be also used in the invention.

[0344] Examples of the inorganic filler include metals and metal compounds such as oxides, oxide composites, hydroxides, carbonates, sulfates, silicates, phosphates, nitrides, carbides, sulfides, or complexes each containing at least two of such substances. Specific examples thereof include glass, zinc oxide, alumina, zirconium oxide, tin oxide, potassium titanate, strontium titanate, aluminum borate, magnesium oxide, magnesium borate, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, titanium hydroxide, basic magnesium sulfate, calcium carbonate, magnesium carbonate, calcium sulfate, magnesium sulfate, calcium silicate, magnesium silicate, calcium phosphate, silicon nitride, titanium nitride, aluminum nitride, silicon carbide, titanium carbide, zinc sulfide, or complexes each containing at least two of such substances.

Specific examples thereof include silica fine particles such as MIZUKASIL P-510, P-526, P-603, P-604, P-527, P-802, P-553A, P-73, P-78A, P-78F, P-705, or P-707 (all trade names, manufactured by Mizusawa Industrial Chemicals,Ltd.).

[0345] The inorganic-organic composite filler may be, for example, a composite of an organic filler selected from the above-described organic fillers and an inorganic filler selected from the above-described inorganic fillers. Examples of the inorganic filler used in such a composite include metal powder, particles of metal compounds (for example, oxides, nitrides, sulfides, carbides and composites thereof), preferable examples thereof include particles of oxides and sulfides, and more preferable examples thereof include particles of glass, SiO_2, ZnO, Fe_2O_3, ZrO_2, SnO_2, ZnS, CuS and the like.

[0346] Examples of the shape of the filler include a fiber, a needle, a plate, a sphere, a granule ("granule" refers to "amorphous granule", and the same applies hereinafter), a tetrapod, and a balloon. Among these, the filler is preferably in the form of a sphere or a granule. '

[0347] The particle-size distribution may be either monodisperse or polydisperse and is preferably monodisperse. As to the size of the filler, the average particle diameter is preferably 1 to 20 μm, more preferably 2 to 15 μm, and still more preferably 3 to 10 μm. Within these ranges, the effects of the invention can be exhibited more effectively.

[0348] The content of the filler in the protective layer is preferably in a range of 0.1 to 20 mass%, more preferably in a range of 1 to 15 mass%, and further preferably in a range of 2 to 10 mass% based on the total solid content of the protective layer.

[0349] These fine particles can be dispersed in an aqueous solution of polyvinyl alcohol of the protective layer by using a dispersion machine such as a homogenizer, a homomixer, a ball mill, or a paint shaker when the fine particle are provided in forms of powders. When a surfactant is added and dispersed therein as needed, the dispersed particles are further stabilized. Examples of the surfactant used for such dispersion include nonionic surfactant, anionic surfactant, and cationic surfactant. Examples of the nonionic surfactant include polyethylene glycol alkyl ether, alkenyl ethers, polyethylene glycol alkyl esters, polyethylene glycol aryl ethers, and the like. Examples of the anionic surfactant include alkyl or aryl sulfonic acid salts, alkyl or aryl sulfonate ester salts, alkyl or aryl phosphate esters, alkyl or aryl carboxylate salts, and the like. Examples of the cationic surfactant include alkyl amine salts, alkyl pyridinum salts, alkyl ammonium salts, and the like. Specifically, more specific examples of the surfactant are disclosed in 'The Latest Function creation, Material development, and Application Technique of Surfactant' edited by Teruo HORIUCHI and Toshiyuki SUZUKI and published in 2005 by Gijutsu Kyoiku Shuppan.

For example, the fine particles contained in CHEMIPEARL series (trade name, manufactured by Mitsui Chemicals, Inc. are supplied in a state where they are dispersed in water. Accordingly, the dispersion of the fine particles can be directly added and stirred in the aqueous solution for forming the protective layer so as to prepare a coating liquid.

Inorganic layered compound

[0350] The protective layer of the planographic printing plate precursor according to the invention preferably contains an inorganic layered compound. By further containing the inorganic layered compound, oxygen impermeability of the protective layer can be further improved, and the strength of the protective layer can be further improved so as to suppress deteriorations due to deformation and generations of scratches in the protective layer as well as the improvement of the oxygen impermeability.

Mica compound

[0351] Examples of the inorganic layered compound include natural- or synthetic mica compounds represented by the following formula.

[0352] Formula:

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

[0353] In the above formula, A represents K, Na, or Ca; each of B and C represents Fe(II), Fe(III), Mn, Al, Mg, or V; and D represents Si or Al.

[0354] Specific examples of the mica represented by the above formula and other micas which can be used in the invention are as follows. Namely, specific examples of the natural mica compounds include muscovite, paragonite, phlogopite, biotite and lepidolite. Specific examples of the synthetic mica compounds include non-swelling mica such as fluorphlogopite $KMg_3 (AlSi_3O_{10})F_2$ or potassium tetrasilicate mica $KMg_{2.5} (Si_4O_{10})F_2$, and swelling mica such as Na tetrasilyric mica $NaMg_{2.5} (Si_4O_{10})F_2$, Na teniolite or Li teniolite $(Na, Li)Mg_2Li (Si_4O_{10})F_2$, montmorillonite type Na- or Li-hectorite $(Na, Li)_{1/8}Mg_{2/5}Li_{1/8} (Si_4O_{10})F_2$. Synthetic smectite is also useful.

[0355] Among the mica compounds described above, fluorine swelling mica is particularly useful. That is, this swelling synthetic mica has a layered structure consisting of unit crystal lattice layers having a thickness of about 1 to 1.5 nm wherein intra-lattice metal atom substitution is far significant than in other clay minerals. As a result, the lattice layers are deficient in positive charge which is compensated for by adsorbing cations such as Li^+, Na^+, Ca^{2+} or Mg^{2+} between the layers. Cations that are present between the layers are called exchangeable cations, and are exchanged with various cations. In particular, when cations between the layers are Li^+ or Na^+, the ion radius thereof is small and the bonding between the layered crystal lattices is weak, thus showing great swelling in the presence of water. When shearing force is applied in this state, the layered structure is easily cleaved to form stable sol in water. This occurs easily in the swelling synthetic mica, which is useful in this embodiment; therefore, the swelling synthetic mica is particularly preferably used.

[0356] From the viewpoint of regulation of diffusion, the mica compound is preferably thinner, and the plane size of the mica compound is preferably larger insofar as the flatness of the coating surface and the permeation of active ray are not inhibited. Accordingly, the aspect ratio of the mica compound may be 20 or more, preferably 100 or more, and more preferably 200 or more. The "aspect ratio" used herein is the ratio of the thickness to the major axis of the particle, and can be measured from, for example, a projection view obtained from a photomicrograph of the particle. As the aspect ratio is increased, the obtained effects are greater.

[0357] The particle diameter of the mica compound may be 0.3 to 20 μm, preferably 0.5 to 10 μm, more preferably 1 to 5 μm, in terms of the average length of the major axis. The average thickness of the particles may be 0.1 μm or less, preferably 0.05 μm or less, and more preferably 0.01 μm or less. Specifically, the size of the swelling synthetic mica, that is a typical compound among mica compound, has a thicksness of 1 to 50 nm and a major axis length (plane size) of about 1 to 20 μm.

[0358] The Content of the inorganic lamellar compound such as mica compound in the oxygen barrier layer is preferably in a range of 5 to 50 % by mass, and is more preferably in a range of 10 to 40 % by mass, with respect to the total solid content of the oxygen barrier layer, in views of prevention of adhesion between stacked planographic printing plate precursors, scratching thereof, and reduction in sensitivity during laser exposure and for preservation of low oxygen permeability. When plural kinds of mica particles are used, the total amount of these mica particles is preferably in the above ranges by mass.

Oxygen permeability controlling agent

[0359] Examples of a method for controlling the oxygen permeability in the protective layer include adding, in combination with the polyvinylalcohol favorable as a binder polymer, another water-soluble polymer as an oxygen permeability controlling agent.

[0360] Examples of the other water-soluble polymers include polyvinylpyrrolidone, polyethylene glycol, soluble starch, carboxymethylcellulose, hydroxyethylcellulose, and copolymer compounds of ethyleneoxide and propyleneoxide. Particularly preferable among these are the compounds represented by the following Formula (A).

[0361]

$$HO\text{-}(CH_2CH_2O)_a(C_3H_6O)_b(CH_2CH_2O)_c\text{-}H \qquad \text{Formula (A):}$$

[0362] In Formula (A), a represents an integer of 1 to 100; b represents an integer of 1 to 100; and c an integer of 1 to 100.

[0363] The content of the oxygen permeability-controlling agent in the oxygen barrier layer is preferably 0.5 to 20 % by mass, more preferably 1 to 10 % by mass, with respect to the total solid content of the oxygen barrier layer.

Formation of Oxygen barrier layer

[0364] The oxygen barrier layer according to the invention is formed by coating an oxygen barrier layer coating liquid containing the components for the layer on the photosensitive layer described below.

[0365] Known additives, such as a surfactant for improvement in coatability and a water-soluble plasticizer for improvement in film physical properties, may be added to the oxygen barrier layer coating liquid. Examples of the water-soluble plasticizers include propionamide, cyclohexanediol, glycerol, sorbitol and the like. Alternatively, a water-soluble (meth)acrylic polymer may be added. In addition, known additives for improvement in the adhesiveness thereof to the layer formed on the support side surface of the oxygen barrier layer and also of stability of the coating liquid may be added to the coating liquid.

[0366] The method of forming the oxygen barrier layer according to the invention is not particularly limited, and examples thereof include those described in U.S. Patent No. 3,458,311 and JP-A No. 55-49729.

The coating amount of the oxygen barrier layer (coating amount after drying) is preferably 0.1 to 4.0 g/m^2, and more preferably 0.3 to 3.0 g/m^2, for preservation of film strength, abrasion resistance, maintaining image quality, and oxygen permeability favorable to exhibit safelight durability.

[0367] The coating amount of the oxygen impermeable layer is preferably 0.1 g/m^2 to 4.0 g/m^2, and is more preferably 0.3 g/m^2 to 3.0 g/m^2 from the viewpoints of the strength and scratch resistance of the resultant oxygen impermeable layer, maintenance of image quality, and maintenance of suitable oxygen permeability for imparting safelight compatibility.

[0368] In the planographic printing plate precursor according to the invention, a backcoat layer may be formed on a surface of the side of the support opposite to the surface provided with the photosensitive layer having photosensitivity to a laser beam. By forming the backcoat layer after setting an average surface roughness (Ra) of aluminum to 0.15 μm or less by the use of the above-mentioned method, it is possible to further reduce Ra. In a case where the backcoat layer is provided to the planographic printing plate precursor according to the invention, the average surface roughness (Ra) denotes an average surface roughness of the provided backcoat layer. There is no particular limitaion to a method for adjusting the Ra of the backcoat layer to be 0.15 μm or less, and examples thereof include a method including setting an average surface roughness of aluminum to 0.15 μm or less and then providing the backcoat layer thereon, and a method including controlling an application amount of a backcoat layer forming composition (such as a coating liquid) to be in a predetermined value (namely, a preferable amount described below). Among these, the method including setting an average surface roughness of aluminum to 0.15 μm or less and then providing the backcoat layer thereon is preferable.

The backcoat layer includes at least a resin having film property as a main component thereof, and may further include various additives if necessary.

Resin usable in Backcoat layer

[0369] Preferable examples of the resin usable in the backcoat layer that may be used in the invention include polyethylene, polypropylene, polybutene, polyamide (such as nylon), polybutadiene, nylon, polyurethane, polyurea, polyimide, polysiloxane, polycarbonate, polyester, epoxy resins, alkylphenol resin condensed with aldehyde, polyacetal resin, polybutyral resin, polyvinyl chloride, polyvinylidene chloride, polystyrene, resins having a phenolic hydroxyl group, acrylic resin, copolymer resins of any of these, hydroxyl cellulose, polyvinyl alcohol, cellulose acetate, and carboxymethyl cellulose. Particularly preferable examples thereof include polyester resin, resins having a phenolic hydroxyl group, and polyacetal resin in view of a film property and a resistance to adhesion to an outermost surface of the photosensitive recording layer.

A weight-average molecular weight of the resin usable in the backcoat layer is preferably 500 or more, is more preferably in the range of 1,000 to 500,000, is still more preferably in the range of 1,000 to 200,000, and is most preferably in the range of 1,000 to 100,000 in terms of polystyrene.

Typical examples of the resins are described hereinafter.

Polyester resin

[0370] The polyester resin includes a dicarboxylic acid unit and a diol unit.

Examples of the dicarboxylic acid unit include aromatic dicarboxylic acids such as a phthalic acid, a terephthalic acid, an isophthalic acid, a tetrabromophthalic acid, and a tetrachlorophthalic acid; and saturated aliphatic dicarboxylic acids such as an adiphic acid, an azelaic acid, a succinic acid, an oxalic acid, a suberic acid, a sebacic acid, a malonic acid, and a 1,4-cyclohexane dicarboxylic acid.

Examples of the diol unit include aliphatic chain diols such as ethylene glycol, diethyl glycol, triethyl glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, 1,3-butylene glycol, 2,3-butylene glycol, 1,4-butylene glycol, neopentyl glycol, hexane diol, or 2,2,4-trimethyl-1,3-pentane diol; and cyclic diols such as 1,4-bis-β-hydroxyethoxy cyclohexane, cyclohexane dimethanol, tricyclodecane dimethanol, bisphenol dioxyethyl ether, or bisphenol dioxypropyl ether.

The polyester preferably include at least one kind of the dicarboxylic acid unit and at least one kind of the diol unit, in which at least one of the dicarboxylic acid unit and the diol unit includes two or more kinds of units consisting a copolymerized unit. Characteristics of the copolymer are determined depending on a copolymerization composition and a molecular weight thereof.

Commercially-available products may be used as the polyester resin. Examples thereof include KEMIT 1294 (trade name, manufactured by Toray Industries Inc.).

[0371] The backcoat layer that may be used in the invention can be preferably formed by application of a liquid as described below, in view of efficiently formeing a thin film. In consideration of this, the polyester resin usable for forming the backcoat layer which may be provided to the invention is preferably amorphous and soluble in various industrial organic solvents.

Polyacetal resin

[0372] A polyacetal resin can be obtained by acetalizing polyvinyl alcohol by using aldehyde such as butyl aldehyde or formaldehyde. The polyacetal resins are different from each other in physical and chemical characteristics depending on acetalization degrees, composition ratios of a hydroxyl group and an acetyl group, and polymerization degrees. Resins with an acetalization degree of 60 mol% or more, a content of an acetyl group of 5 mol% or less, and a polymerization degree of 300 or more are preferably used in the backcoat layer that may be used in the invention.

[0373] Commercially-available products may be used as the polyacetal resin. Examples thereof include S-LEC BX-1, S-LEC BX-3, S-LEC BX-5, S-LEC KS-1, S-LEC KS-3, S-LEC KS-5, and S-LEC KS-10 (all of which are trade names, manufactured by SEKISUI CHEMICAL CO., LID.)

Resin having Phenolic hydroxyl group

[0374] Examples of the resin having a phenolic hydroxyl group include a novolac resin such as a condensation product of phenol and formaldehyde, a condensation product of m-cresol and formaldehyde, a condensation product of p-cresol and formaldehyde, a condensation product of formaldehyde and a mixture of m-cresol and p-cresol, and a condensation product of phenol, cresol (which may be one of m-cresol, p-cresol, and a mixture of m-cresol and p-cresol), and formaldehyde and a pyrogallol resin such as a condensation product of pyrogallol and acetone.

[0375] A copolymer obtained by copolymerizing a compound having a phenolic hydroxyl group can be also used as the resin having a phenolic hydroxyl group.

Examples of the compound having a phenolic hydroxyl group include acryl amide, methacryl amide, acrylic ester, methacrylate ester, and hydroxyl styrene, each of which has at least a phenolic hydroxyl group.

Other components

[0376] In order to improve the film property, in order to provide flexibility to the backcoat layer or to adjust slidability of the backcoat layer, a plasticizer, a surfactant, and other additives may be added thereto as needed.

[0377] Preferable examples of the effective plasticizer usable in the backcoat layer include ester phthalates such as dimethyl phthalate, diethyl phthalate, dibutyl phthalate, diisobutyl phthalate, dioctyl phthalate, octylcapryl phthalate, dicyclohexyl phthalate, ditridecyl phthalate, butylbenzyl phthalate, diisodecyl phthalate, or diallyl phthalate; glycol esters such as dimethylglycol phthalate, ethylphthalyl ethylgylcolate, methylphthalyl ethylglycolate, butylphthalylbutyl glycolate, or triethylene glyeoldicaprilic ester; ester phosphates such as tricresyl phosphate or triphenyl phosphate; aliphatic ester dichlorides such as diisobutyl adiphate, dioctyl adiphate, dimethyl sebacate, dibutyl sebacate, dioctyl azelate, or dibutyl maleate; polyglycidyl methacrylate; triethyl citrate; glycerin triacetyl ester; and butyl laurate. The amount of the plasticizers which can be added to the backcoat layer is in a range which may have the backcoat layer be free from getting stickness. The amount of the plasticizers may be defined in consideration of characteristics of the main used as a main component of the backcoat layer, flexibility required for the backcoat layer, and the like. In a case where any one or more of the typical resins such as a novolac resin having a phenolic hydroxyl group or a pyrogallol resin, the amount of the plasticizers may be in a range of 0.1 to 20 % by mass relative to a total solid content of a coating composition (such as a coating liquid) for forming the backcoat layer.

[0378] Preferable examples of the surfactant usable in the backcoat layer include nonionic surfactants such as polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene polystyrylphenyl ethers, polyoxyethylene polyoxypropylene alkyl ethers, partial esters of glycerin with fatty acids, partial esters of sorbitan with fatty acids, partial esters of pentaerythritol with fatty acids, propylene glycol mono fatty acid esters, partial esters of sucrose with fatty acids, partial esters of polyoxyethylene sorbitan with fatty acids, partial esters of polyoxyethylene sorbitol with fatty acids, polyethylene glycol fatty acid esters, partial esters of polyglycerin with fatty acids, polyoxyethylenated castor oils, partial esters of polyoxyethylene glycerin with fatty acids, fatty acid diethanol amides, N,N-bis-2-hydroxyalkyl amines, polyoxyethylene alkyl amines, triethanolamine fatty acid esters, and trialkylamine oxides; anionic surfactants such as fatty acid salts, abietates, hydroxyl alkane sulfonates; alkane sulfonates, dialkyl ester sulfosuccinates, straight-chained alkylbenzene sulfonates, branch-chained alkylbenzene sulfonates, alkylnaphthalene sulfonates, alkylphenoxy polyoxy ethylene propylsulfonates, polyoxyethylene alkylsulfophenyl ester salts, N-methyl-N-oleyltaurine sodium salts, N-alkylsulfosuccinate monoamide disodium salts, petroleum sulfonates, sulfate beef tallows, sulfate ester salts of fatty acid alkylester, alkyl sulfate ester salts, polyoxyethylene alkylether sulfate ester salts, fatty acid monogylceride sulfate ester salts, polyoxyethylene alkylphenylether sulfate ester salts, polyoxyethylene styrylphenylether sulfate ester salts, alkylphosphate ester salts, polyoxyethylene alkylether phosphate ester salts, polyoxyethylene alkylphenylether phosphate ester salts, partially saponified products of styrene/maleic acid anhydride copolymer, partially saponified products of olefin/maleic acid anhydride copolymer, and naphthalene sulfonate formalin condensation products; cationic surfactants such as alkylamine salts, quaternary ammonium salts, polyoxyethylene alkylamine salts, or polyethylene polyamine compounds; and amphoteric surfactants such as carboxy betaines, aminocarboxylic acids, sulfobetaines, aminosulfate esters, or imidazolines.

[0379] Preferable examples of the surfactants usable in the backcoat layer include surfactants obtained by replacing "polyethylene" in the above examples of the surfactants with polyoxyalkylenes such as polyoxymethylene, polyoxypropylene, or polyoxybutylene.

[0380] Fluorine-containing surfactants containing a perfluoroalkyl group in its molecule are more preferably used as the surfactant. Examples of the fluorine-containing surfactants include anionic surfactants such as perfluoroalkyl carboxylates, perfluoroalkyl sulfonates, or perfluoroalkyl phosphate esters; amphoteric surfactants such as perfluoroalkyl betaines; cationic surfactants such as perfluoroalkyl trimethyl ammonium salts; and nonionic surfactants such as perfluoroalkylamine oxides, adducts of perfluoroalkylethylene oxide, oligomers having a perfluoroalkyl group and a hydrophilic group, oligomers having a perfluoroalkyl group and a lyophilic group, oligomers having a perfluoroalkyl group, a hydrophilic group, and a lyophilic group, and urethanes having a perfluoroalkyl group and a lyophilic group.

[0381] The surfactants can be used alone or in combination of two or more kinds thereof. The amount of the surfactants to be added is preferably in the range of 0.001 to 10 wt%, and is more preferably in the range of 0.001 to 5 wt%, in terms of the weight of solid contents in the backcoat layer.

[0382] One or more of o-naphthoquinone diazide compounds, photosensitive azide compounds, photopolymerizable compounds having a unsaturated double bond-containing monomer as a major component, photocrosslinking compounds having a cinnamic acid or a dimethyl maleimide group, and diazo resins obtained by condensing an organic condensing agent (particularly, acetals or aldehydes such as formaldehyde and acetoaldehyde) having a reactive carbonyl group with a diazonium monomer or aromatic diazonium salt and in an acidic medium can be added to the backcoat layer for the purpose of improving resistance to chemical agents. The o-naphthoquinone diazide compounds are very suitably used which are known as positive photosensitive compounds.

Formation of Backcoat layer

[0383] The backcoat layer that may be used in the invention can be formed by the use of thermal compression of a film, a melt lamination method, a coating method or the like. It is preferable that the backcoat layer is formed by application of a liquid in view of efficiently forming a thin film.

[0384] In the invention, the resin used in the backcoat layer is preferably amorphous and soluble in various industrial organic solvents.

[0385] Examples of the solvent used in preparation of the backcoat layer include acetone, methylethyl ketone, cyclohexane, ethyl acetate, ethylene dichloride, tetrahydrofuran, toluene, ethyleneglycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, acetyl acetone, cyclohexanone, diacetone alcohol, ethylene glycol monomethylether acetate, ethylene glycol ethylether acetate, ethylene glycol monoisopropyl ether, ethylene glycol monobutylether acetate, 3-methoxypropanol, methoxymethoxy ethanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, propylene glycol monomethylether acetate, propylene glycol monoethylether acetate, 3-methoxypropyl acetate, N,N-dimethyl formamide, dimethyl sulfoxide, γ-butyrolactone, methyl lactate, and ethyl lactate.

The solvent may be used singly or in combination of two or more thereof. The concentration of the solid components in the backcoat layer-forming coating liquid is preferably in the range of 0.5 to 50 wt%.

[0386] The amount of backcoat layer that may be used in the invention is preferably in the range of 0.01 to 10 g/m^2, is more preferably in the range of 0.05 to 7 g/m^2, is still more preferably in the range of 0.1 to 5 g/m^2, and is particularly preferably in the range of 0.3 to 0.8 g/m^2 in terms of a dry mass.

Bekk smoothness

[0387] From the viewpoint of obtaining a conveying characteristic by using a setter at the time of laminating the planographic printing plate precursor of the invention without interposing an interleaf paper, the planographic printing plate precursor has a surface which has a sensitivity to a laser light and a Bekk smoothness which is preferably 10,000 seconds or less, and is more preferably 5,000 seconds or less. By selecting the kind, content and/or particle diameter of the filler which can be included in the protective layer, the Bekk smoothness can fall within such a range.
Here, the "Bekk smoothness of the surface having a sensitivity to laser light' means a Bekk smoothness of the outermost surface of the photosensitive layer provided on or above the surface of the support. For example, when only the photosensitive layer is formed on the surface of the support, the Bekk smoothness referres to that of the surface of the photosensitive layer, and when the protective layer is formed on the photosensitive layer, the Bekk smoothness referres to that of the surface of the protective layer.
The Bekk smoothness is determined by a time (seconds) required for allowing a predetermined amount of atmospheric air to flow between a specimen and a ring-shaped surface contacting each other with a predetermined condition under a predetermined initial pressure difference. The Bekk smoothness on the outermost surface of the protective layer can be measured by a method defined in ISO 5627 (1995). The measurement can be performed by using a Bekk smoothness test machine manufactured by Kumagai Riki Kogyo Co., Ltd. and 1/10 of a reference amount of air, that is, the amount of air of 1ml. The values of the Bekk smoothness used in the present application are obtained by this measuring method.

Stack of planographic printing plate precursors

[0388] A stack of planographic printing plate precursors of the invention is formed of a plurality of planographic printing plate precursors, each of which directly contacts with an adjacent planographic printing plate precursor at an uppermost layer thereof and at the back surface of the support.
A stackof a conventional planographic printing plate precursor required an interleaf paper which serves to prevent adhesion between planographic printing plate precursors or prevent scratches generated when contacting with an aluminum support. In contrast, since the stack of the invention does not require such an interleaf paper, productivity can be improved.

Production of Planographic printing plate precursor

[0389] In order to produce the planographic printing plate precursor of the invention, at least an exposing process and a developing process are performed.
A known light source may be used as a light source used for an exposure of the negative planographic printing plate precursor of the invention without any limitation. The wavelength of a laser light emitted from the light source is preferably in a range of 300 to 1,200 nm. Various kinds of the light source can be used in the invention, and examples among these include a light source providing infrared laser having a wavelength of 780 nm to 1,200 nm.
The exposure mechanism may be any of an internal surface drum system, an external surface drum system, and a flat bed system.
[0390] Furthermore, various mercury lamps of ultrahigh pressure, high pressure, medium pressure, and low pressure, a chemical lamp, a carbon arc lamp, a xenon lamp, a metal halide lamp, various laser lamps of a visible ray and a an ultraviolet ray, a fluorescent lamp, a tungsten lamp, or a solar light may be used as other exposing rays for the planographic printing plate precursor of the invention.
[0391] The planographic printing plate precursor which is subjected to exposure treatment is further subjected to development. The development may be conducted by using distilled water, alkali aqueous solution or washing water, a surfactant-containing rinse, or a desensitizing gum solution containing gum arabic or a starch compounds such as described in JP-A No. 54-8002, JP-A No. 55-115045 or JP-A No. 59-58431.
An aqueous alkaline solution having pH of 14 or less is particularly preferably used, and an anion aqueous alkaline solution having pH of 8 to 12 containing anion surfactant is more preferably used as a developing solution in the invention.
Examples of alkaline agents include inorganic alkali agents such as sodium tertiary phosphate, potassium tertiary phosphate, ammonium tertiary phosphate, sodium secondary phosphate, potassium secondary phosphate, ammonium secondary phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogencarbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide, or lithium hydroxide. In addition, organic alkaline agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, or pyridine may be used in the invention. These alkaline agents may be used singly or in combination of two or more of them.

[0392] An anionic surfactant is preferably added to the developing solution for use in developing the planographic printing plate precursor of the invention in an amount of generally from 1 to 20 mass%, preferably 3 to 10 mass%, relative to the total amount of the developing solution. When the amount of the anionic surfactant is too small, developability may be impaired, while when it is too large, disadvantageous influences such as the deterioration of the image areas in strength, such as wearing resistance, may occur. Examples of the anionic surfactant include sodium lauryl alcohol sulfate, ammonium lauryl alcohol sulfate, sodium octyl alcohol sulfate, salts of alkylarylsulfonic acids such as sodium isopropylnaphthalenesulfonate, sodium isobutylnaphthalenesulfonate, the sodium salt of polyoxyethylene glycol mononaphthyl ether sulfate, sodium dodecylbenzenesulfonate, or sodium meta-nitrobenzenesulfonate; sulfuric acid esters of higher alcohols having 8 to 22 carbon atoms, such as disodium alkyl sulfates; phosphoric acid esters of aliphatic alcohols, such as sodium salt of cetyl alcohol phosphate; alkylamide sulfonic acid salts such as $C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3Na$; and sulfonic acid salts of dibasic aliphatic ester, such as sodium dioctyl sulfosuccinate and sodium dihexyl sulfosuccinate.

[0393] A water-miscible organic solvent such as benzyl alcohol can be added to the developing solution according to need. Suitable organic solvents have a solubility to water of about 10 mass% or lower. Preferably, an appropriate organic solvent is selected from those having a solubility in water of 5 mass% or lower. Examples thereof include 1-phenylethanol, 2-phenylethanol, 3-phenylpropanol, 1,4-phenylbutanol, 2,2-phenylbutanol, 1,2-phenoxyethanol, 2-benzyloxyethanol, o-methoxybenzyl alcohol, m-methoxybenzyl alcohol, p-methoxybenzyl alcohol, benzyl alcohol, cyclohexanol, 2-methylcyclohexanol, 4-methylcyclohexanol, and 3-methylcyclohexanol. The content of such an organic solvent is preferably in a range of 1 to 5 mass% based on the total weight of the developing solution in use. The amount of the organic solvent to be used is closely related to the amount of the surfactant to be used. It is preferable to increase the amount of the anionic surfactant as the amount of the organic solvent increases. This is because, if a large amount of an organic solvent is added to a developing solution containing a small amount of an anionic surfactant, the organic solvent partly remains undissolved, making it impossible to expect satisfactory developability.

[0394] The developing solution may further contain additives such as a deforming agent or a water softener. Examples of the water softener include polyphosphates such as $Na_2P_2O_7$, $Na_5P_3O_3$, $Na_3P_3O_9$, $Na_2O_4P(NaO_3P)PO_3Na_2$, and Calgon (sodium polymetaphosphate), aminopolycarboxylic acids (for example, ethylenediaminetetraacetic acid, and potassium salts or sodium salts thereof; diethylenetriaminepentaacetic acid, and potassium salts or sodium salts thereof; triethylenetetraminehexaacetic acid, and potassium salts or sodium salts thereof; hydroxyethylenediaminetriacetic acid, and potassium salts or sodium salts thereof; nitrilotriacetic acid, and potassium salts or sodium salts thereof; 1,2-diaminocyclohexanetetraacetic acid, and potassium salts or sodium salts thereof; and 1,3-diamino-2-propanol tetraacetic acid, and potassium salts or sodium salts thereof); other polycarboxylic acids (for example, 2-phosphonobutanetricarboxylic acid-1,2,4, and potassium salts or sodium salts thereof; and 2-phosphonobutanonetricarboxylic acid-2,3,4, and potassium salts or sodium salts thereof), organic phosphonic acids (for example, 1-phosphonoethanetricarboxylic acid-1,2,2, potassium salt thereof, and potassium salts or sodium salts thereof; and 1-hydroxyethane-1,1-diphosphonic acid, potassium salt thereof, sodium salt thereof; and aminotri(methylene phosphonic acid), and potassium salts or sodium salts thereof).

The optimum amount of the water softener varies depending on the hardness and amount of hard water used. In general, the water softener is contained in a range of 0.01 to 5 mass%, more preferably 0.01 to 0.5 mass%, relative to the amount of the developing solution at use.

[0395] In a case where an automatic developing machine is used for developing the planographic printing plate precursor of the invention, in order to restore the processing power of the developer a replenisher or a fresh developing solution may be further used because the processing ability of the machine is made to be deteriorated in accordance with the increase of the amount of the precursors processed thereby. In this case, the replenishing can be conducted by a method described in US Patent No. 4,882,246. Developers described in JP-A No. 50-26601, JP-A No. 58-54341, JP-B No. 56-39464, JP-B No. 56-42860 or JP-B No. 57-7427 are also preferable.

[0396] The planographic printing plate precursor which was subjected to development treatment in this manner may be post-treated with washing water, a surfactant-containing rinse, or a desensitizing gum solution containing gum arabic or a starch derivative, as described in JP-A Nos. 54-8002, 55-115045 or 59-58431. Various combinations of these treatments can be used.

[0397] In a process for making the planographic printing plate precursor in of the invention, an entire surface of the plate may be heated before exposure, during exposure, and/or during the period of the exposure to development according to need. This heating accelerates an image-forming reaction in the photosensitive layer to bring about advantages of improved sensitivity, improved printing durability, and stabilized sensitivity. Furthermore, the technique in which an entire surface of the image formed through development is subjected to post-heating or exposure is effective in improving image area strength and printing durability.

It is generally preferable that the heating before development is conducted under such mild conditions that the plate is heated at 150°C or lower from the viewpoint of avoiding an occurrence of an undesired curing reaction. Exceedingly severe conditions may be used for the heating after development. Usually, this heating is conducted at a temperature in a range of 200 to 500°C in consideration of improvment in the image area strength and pyrolysis of the image areas.

[0398] The planographic printing plate obtained by these treatments is loaded onto an offset printing machine, and used for printing on a large number of sheets.
At the time of printing, a plate cleaner may be used for removing dirt from the plate. PS plate cleaners conventionally-known in the art may be used therefor, and examples thereof include Multi-cleaner CL-1, CL-2, CP, CN-4, CN, CG-1, PC-1, SR or IC (all trade names, manufactured by Fuji Film Corporation).

EXAMPLES

[0399] Hereinafter, the present invention will be described in more detail by reference to Examples, but the invention is not limited thereto.
Planographic printing plate precursors which are within the scope of preferable embodiments of the invention are prepared and evaluated in the following Examples.

Example 1

[0400] A molten aluminum alloy including the following elements other than aluminum, (hereinafter, suitably referred to as 'molten Al') was prepared.

- Si: 0.06% by weight
- Fe: 0.30% by weight
- Cu: 0.017% by weight
- Mn: 0.00 % by weight
- Mg: 0.001% by weight
- Zn: 0.001 % by weight
- Ti: 0.03% by weight

[0401] After cleaning a molten Al by filtration, an ingot having a thickness of 500 mm and a width of 1,200 mm was obtained by DC casting. The surface of the obtained ingot was scraped by means of a surface scraping machine so that the portion which was removed from the ingot had an average thickness of 10 mm. Thereafter, the ingot was kept at 550°C for about 5 hours. When the temperature thereof was lowered to 400°C, a rolled plate having a thickness of 2.7 mm was formed from the ingot using a hot rolling machine. Furthermore, a continuously annealing machine was used to subject the rolled plate to thermal treatment at 500°C, and then the plate was subjected to cold rolling so as to give an aluminum alloy plate having a thickness of 0.24 mm. As the rolls of the cold rolling machine, rolls having various surface roughnesses were used for conducting the cold rolling, and aluminum alloy plates, the mean roughnesses of the back surfaces of which (surface which is opposite to the side where a photosensitive layer is formed) are different from each others, were thus formed.

[0402] Each of the surfaces of the various aluminum alloy plates (namely, the surface which was not subjected to adjustment of the surface roughness by the cold rolling treatment) was subjected to an alkali etching treatment (amount of dissolved aluminum: 5.5 g/m^2), followed by a rinsing treatment and a desmutting treatment using nitric acid spray. Then, the surface was subjected to an electrolytic graining (amount of electricity: 270 C/dm^2) by employing an alternating current to roughen the surface. After that, the resultant was subjected to an alkali etching treatment (amount of dissolved aluminum: 0.2 g/m^2), followed by a desmutting treatment by using sulfuric acid spray. Furthermore, by using an apparatus for an anodic oxidation treatment which has the configuration which is similar to that shown in Fig. 5, an anodic oxidized film was formed on the surface and the back surface of the aluminum alloy plate (amount of the surface film: 2.6 g/m^2, amount of back surface film: 0.1 g/m^2). After that, a surfactant treatment was performed by using sodium silicate. Supports having various average surface roughnesses in the width direction and the longitudinal direction of the back surface were thus produced. The results are shown in Table 1.

Undercoat layer

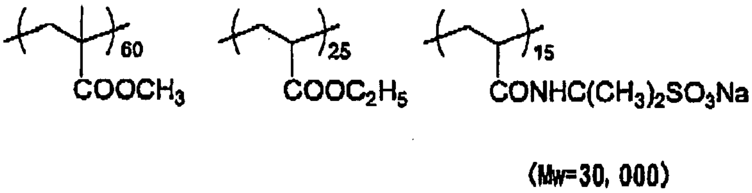
[0403] Then, this aluminum support was coated with an undercoat layer coating liquid having the following formulation, using a wire bar, and then dried at 90°C for 30 seconds. The coating amount was 10 mg/m^2.

[0404] Formulation of Undercoat layer coating liquid

- Polymer compound A having the structure below (weight-average molecular weight: 10,000) 0.05 g
- Methanol 27 g
- Ion-exchange water 3 g

[0405]

Polymer compound A



Photosensitive layer [P-1]

[0406] Then, a photosensitive layer coating liquid [P-1] having the following formulation was prepared and applied with a wire bar onto the aluminum support to form a photosensitive layer. Drying of the photosensitive layer was carried out at 115°C for 34 seconds with a hot-air drying apparatus. The coating amount of the photosensitive layer after drying was 1.36 g/m^2.

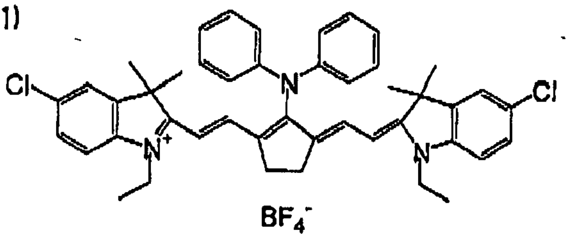
Formulation of Photosensitive layer coating liquid [P-1]

[0407]

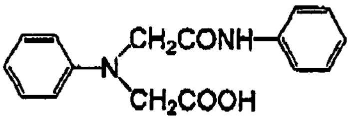
- Infrared absorber (IR-1) 0.074 g
- Polymerization initiator (OS-12) 0.280 g
- Additive (PM-1) 0.151 g
- Polymerizable compound (AM-1) 1.00 g
- Specific binder polymer (BT-1) [Component (A)] 1.00 g
- Ethyl Violet (C-1) 0.04 g
- Fluorine-containing surfactant 0.015 g
  (trade name: MEGAFAC F-780-F, manufactured by Dainippon Ink and Chemicals, Inc.: 30 mass% solution in methyl isobutyl ketone (MIBK))
- Methyl ethyl ketone 10.4 g
- Methanol 4.83 g
- 1-Methoxy-2-propanol 10.4 g

[0408] The polymerization initiator (OS-12) used in the coating liquid of the photosensitive layer is the compound shown as an example of the onium salts represented by Formula (1).
The structures of the infrared absorbent (IR-1), additive (PM-1), polymerizable compound (AM-1), binder polymer (BT-1), binder polymer (BT-2), and ethyl violet (C-1) are shown below.
[0409]

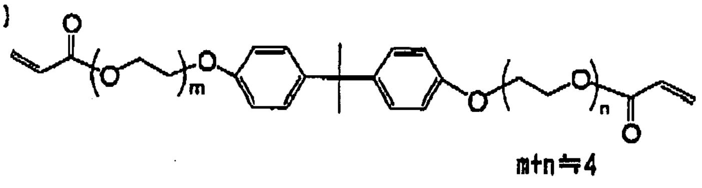
(IR-1)



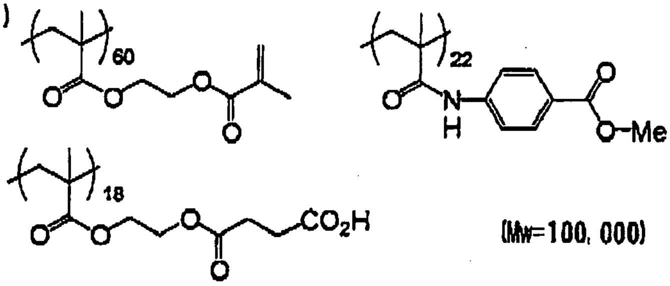
(PM-1)



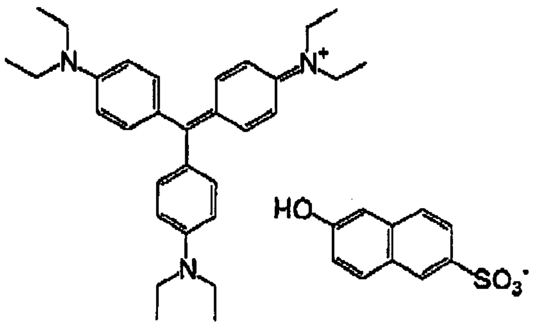
(AM-1)



(BT-1)



(C-1)



Protective layer

[0410] A mixed aqueous solution (protective layer coating liquid) containing polyvinylalcohol (trade name: GOHSERAN CKS-50, manufactured by Nippon Synthetic Chemical Industry Co., Ltd., saponification degree: 99 mol%, polymerization degree: 300, sulfonic acid-modified polyvinylalcohol), a surfactant (trade name: EMALEX 710, manufactured by Nihon-Emulsion Co., Ltd.), and a filler (trade name: CHEMIPEARL W-308, manufactured by Mitsui Chemicals, Inc., high-density polyethylene particle, particle diameter: 6 μm) was coated on the oxygen barrier layer surface with a wire bar and dried in a hot air dryer at 125°C for 75 seconds. The content ratio of filler/polyvinylalcohol/surfactant in the mixed aqueous solution (protective layer-coating liquid) was 2.5/93/4.5 (mass %), and the total coating amount (coating amount after drying) was 1.60 g/m^2.
The Bekk smoothness of the thus-prepared protective layer on the surface of the support was 125 seconds.

[0411] The planographic printing plate precursors thus obtained were stacked in orders in the same direction without interposing an interleaf paper therebetween, thereby obtaining a stack of the planographic printing plate precursors.

Examples 2 to 5

[0412] In each of Examples 2 to 5, a stack of planographic printing plate precursors was obtained in the same manner as Example 1 except that the support having the average surface roughness in the width direction and the longitudinal direction of the back surface of the support as shown in Table 1 was used.

Examples 6 to 10

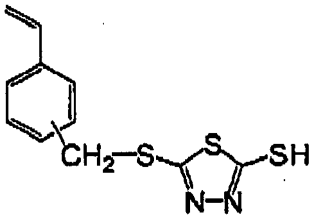
[0413] Planographic printing plate precursors of Examples 6 to 10 were obtained in the same manner as Examples 1 to 5, except that a synthetic mica (trade name: SOMASIF MEB-3L: manufactured by Co-op Chemical Co., Ltd.; 3.2% water dispersion) was added instead of the filler (trade name: CHEMIPEARL W308: manufactured by Mitsui Chemical Co., Ltd.; 40% water dispersion of high density polyethylene particle having particle diameter of 6 μm).
The content ratio of the synthetic mica/polyvinyl alcohol/surfactant after drying in this mixed aqueous solution (coating liquid for protective layer) was 12/83.5/4.5 (mass%) and the total amount of coating (coating amount after drying) was 1.60 g/m^2.

Example 11

[0414] First, synthesis examples of (B) a polymer having a phenyl group substituted with a vinyl group in a side chain thereof and (C) a compound representative of a monomer having 2 or more of phenyl groups substituted with the vinyl group are described below.

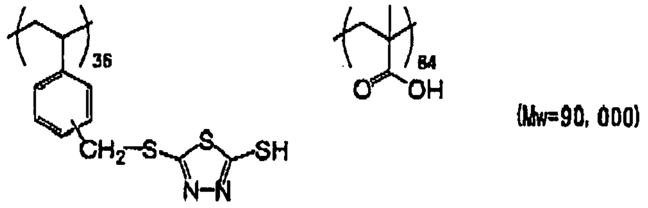
Synthesis Example 1: Synthesis example of (B) Specific polymer (P-1)

[0415] 150 g of bismuthyol (2,5-dimercapto-1,3,4-thiamidazole) was suspended in 600 mL of methanol, and 101 g of triethylamine was gradually added thereto while the resultant was cooled, thereby obtaining a homogenous solution. The solution was kept at a room temperature, and p-chloromethyl styrene (manufactured by SEIMI CHEMICAL CO., LTD.; CMS-14) was added thereto dropwise over 10 minutes, and then the mixture was stirred for 3 hours. The reaction products were gradually precipitated, and the resultant then stirred was transferred to an ice bath to cool the internal temperature down to 10°C. The resultant was then isolated by a suction filtration. The resultant was rinsed by methanol and dried in a vacuum dryer for one day-and-night, thereby obtaining a compound (monomer) with 75% yield.
[0416]



[0417] A four neck flask which hasg a capacity of 1-liter and is equipped with a stirrer, a nitrogen-iducing tube, a thermometer, and a reflux condenser was charged with 40 g of the monomer. 70 g of methacrylic acid, 200 ml of ethanol, and 50 ml of distilled water were added thereto. While the mixture was stirred, 110g of triethylamine was added in a water bath. The solution was heated to have the internal temperature of 70°C under nitrogen atmosphere, and 1g of azobisisobutylonitrile (AIBN) was added thereto so as to initialize polymerization at this temperature. The heating was continued with stirring for 6 hours and then the polymerized system was cooled to room temperature. A portion of the resultant was taken out of the system and pH thereof was regulated to 3 by adding a diluted hydrochloric acid. The resultant was poured in water so that a polymer having a structure shown below was obtained.
[0418]

P-1



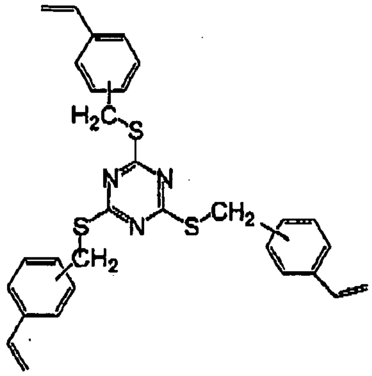
[0419] 100g of 1,4-dioxane and 23g of p-chloromethyl styrene were added to the polymer solution from which the portion of the polymer was taken out, and the resulted mixture was stirred at room temperature for additional 15 hours. After that, 80 to 90 g of a concentrated hydrochloric acid (35 to 37% aqueous solution) was added thereto, and after confirming that pH of the system is 4 or lower, the whole solution was moved to 3 liter of distilled water. The polymer thus precipitated was separated by the filtration, rinsed by distilled water several times, and then dried in a vacuum drier for 24 hours. The aimed (B) specific polymer (P-1) was thus obtained to provide a yield of 90%. It was confirmed that the polymer has a weight average molecular weight of 90,000 (in terms of polystyrene) according to a molecular weight measurement with a gel permeation chromatography, and an analysis of a proton NMR supported that the polymer has a structure of (B) specific polymer (P-1).

Synthesis Example 2: Synthesis example of (C) Specific monomer (C-5)

[0420] 89g of thiocyanate was suspended in 1.5 liter of methanol, and a 30% aqueous solution containing 84g of potassium hydroxide dissolved therein was gradually added thereto while the resultant was cooled, so as to obtain a homogenous solution. The solution was kept at a room temperature and 230g of p-chloromethyl styrene was gradually given thereto in a dropwise manner so that the internal temperature thereof does not exceed 40°C. The reaction products were soon precipitated after adding the solution, while the resultant was continuously stirred. After the resultant was stirred for 3 hours, the resultant was isolated by a suction filtration. The resultant was rinsed by methanol and dried in a vacuum dryer for one day-and-night so as to obtain (C) a specific monomer (c-5) with 90% yield.

[0421]

C-5



Preparation of Support

[0422] One surface side of an aluminum plate (Al: 99.50% or more, Si: 0.25%, Fe:0.40%, Cu:0.05%, Mn:0.05%, Mg: 0.05%, Zn:0.05%, and Ti:0.03%) having a thickness of 0.30 mm and a width of 1030 mm was polished by buffing so as to obtain a support having an average surface roughness in a width direction (Ra1) of 0.13 μm and an average surface roughness in a longitudinal direction (Ra2) of 0.10 μm. The polished side was used as a back surface, and a surface (namely, an opposite side of the back surface) was subjected to the following surface treatment.

Surface treatment

[0423] In the surface treatment, the following treatments (a) to (f) were successively conducted. After each treatment and water washing, a remaining liquid was removed with nip rollers.

[0424]

(a) The aluminum support was subjected to etching treatment with an aqueous solution containing sodium hydroxide at a concentration of 26 mass% and aluminum ion at a concentration of 6.5 mass% at a temperature of 70°C, whereby the aluminum support was dissolved in an amount of 5 g/m^2. Thereafter, the aluminum plate was washed with water.

(b) The aluminum plate was subjected to desmutting treatment with a spray of an aqueous solution of 1 mass% nitric acid (also containing 0.5 mass% of an aluminum ion) at a temperature of 30°C, and then was washed with water.

[0425] (c) The plate was subjected to continuous electrochemical surface roughening treatment with an alternating voltage of 60 Hz. The electrolytic solution used was 1 mass% aqueous nitric acid solution (containing 0.5 mass% of aluminum ion and 0.007 mass% of ammonium ion) at a temperature of 30°C. The electrochemical surface roughening treatment was carried out with a carbon electrode as a counter electrode, using a trapezoid rectangular wave alternating current wherein the time TP required for the electric current to change from 0 to the peak value was 2 msec and the duty ratio was 1:1. Ferrite was used as an assistant anode. The current density was 25 A/dm^2 in terms of the electric current peak value, and the quantity of electricity was 250 C/dm^2 in terms of total quantity of electricity at the time the aluminum plate works as the anode. 5% of the electric current from the power source was distributed to the assistant anode. Thereafter, the plate was washed with water.

[0426] (d) The aluminum plate was subjected to etching treatment by spraying with an aqueous solution containing sodium hydroxide at a concentration of 26 mass% and aluminum ion at a concentration of 6.5 mass% at a temperature of 35°C, whereby the aluminum plate was dissolved in an amount of 0.2 g/m^2 to remove smut components mainly composed of aluminum hydroxide generated during the electrochemical surface roughening treatment using the alternating current in the previous stage, and smoothen the edge portion of the generated pit through dissolution of the edge portion. Thereafter, the aluminum plate was washed with water.

(e) The aluminum plate was subjected to desmutting treatment with a spray of an aqueous solution of 25 mass% sulfuric acid (also containing 0.5 mass% aluminum ion) at a temperature of 60°C and then was washed with sprayed water.

[0427] (f) The aluminum plate was subjected to anodizing treatment for 50 seconds in an aqueous solution of sulfuric acid at a concentration of 170 g/L (containing 0.5 mass% aluminum ion) at a temperature of 33°C and a current density of 5 (A/dm^2). Thereafter, washing by spraying with water was carried out. The amount of the anodized coating was 2.7 g/m^2.

[0428] The surface roughness (Ra) of the aluminum support obtained in this manner was 0.27 (measured with SURFCOM (trade name, manufactured by Tokyo Seimitsu Co., Ltd.) provided with a sensing pin tip diameter of 2 micrometer), the surface area ratio (ΔS) thereof was 75%, and the steepness (a45) thereof was 44% (measured with SPA300 or SPI3800N: both trade names, manufactured by Seiko Instruments Inc.)

Formation of Negative photosensitive layer

[0429] Next, the photosensitive coating liquid having the following composition was prepared and coated on the aluminum support which had been subjected to the surface treatment to give a thickness after drying of 1.4 μm, and the resultant was dried in a dryer of 70°C for 5 minutes, so as to provide a planographic printing plate precursor.

Coating liquid for photosensitive layer

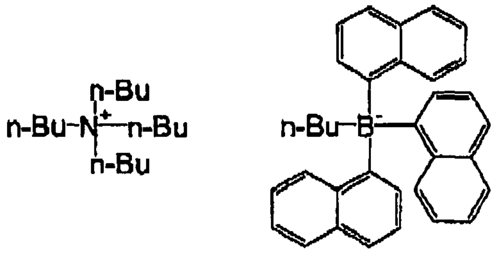
[0430]

- (A) Radical generator (BC-6) 2.5 mass%
- (B) Specific polymer (P-1) 10,0 mass%
- (C) Specific monomer (C-5) 3.5 mass%
- (D) Infrared ray absorbing dye (S-4) 0.5 mass%
- Dioxane 70.0 mass%
- Cyclohexane 20.0 mass%

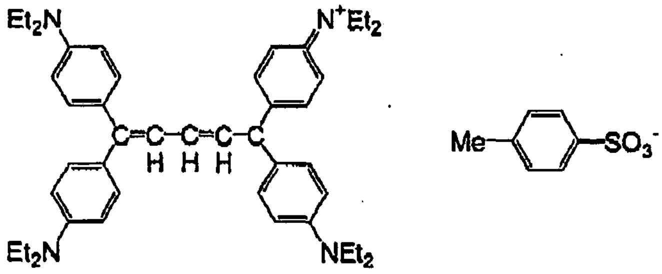
[0431] The (B) and (C) are the compounds represented in Synthesis Examples 1 and 2. The (A) and (D) are compound shown below. The planographic printing plate precursors thus obtained were stacked in orders in the same direction without interposing the interleaf paper therebetween, thereby obtaining a stack of the planographic printing plate precursors.

[0432]

Radical generator (BC-6)



Infrared ray absorbing dye (S-4)



Example 12

[0433] A stack of Example 12 was prepared in the same manner as that of Example 1, except that a support having an average surface roughness (Ral) of 0.13 μm in the width direction of the back surface of the support obtained by chainging a buff grinding condition of the support and an average surface roughness (Ras) of 0.10 μm in the longitudinal direction was used, a high sensitive photopolymerizable composition P-1 having the following composition was applied on the undercoat described in Example I to give the coating amount of 1.4 g/m^2 after the drying, and then the resultant was dried at 100°C for 1 minute so as to form the photosensitive layer of a planographic printing plate precursor.
The planographic printing plate precursors thus obtained were stacked in orders in the same direction without interposing the interleaf paper therebetween, thereby obtaining a stack of the planographic printing plate precursors.

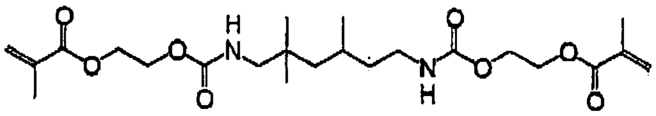
Photopolymerizable composition P-1

[0434]

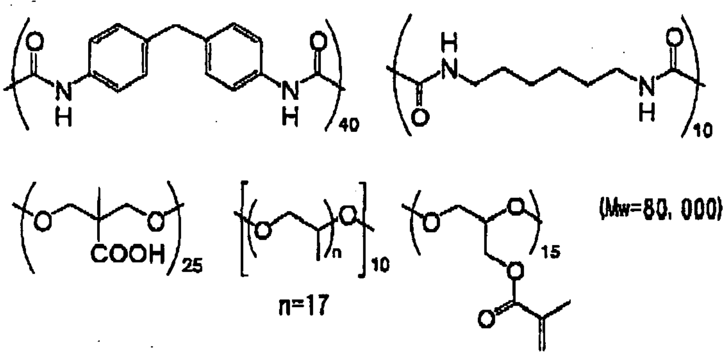
· Polymerizable compound (A-1)	4.2 mass%
· Binder polymer (B-1)	3.6 mass%
· Sensitizing dye (C-1)	0.21 mass%
· Polymerization initiator (D-1)	0.81 mass%
· Chain transfer agent (E-1)	0.3 mass%
· Dispersants of s-phtalocyanine dye (dye: 15 mass%, dispersion aryl methacrylate/methacrylic acid copolymer (molar ratio of copolymerization 83/17): 10 mass%, cyclohexanone: 15 mass%)	0.76 mass%
· Fluorine surface active agent (trade name: MEGAFAC F780, manufactured by Dainippon Ink and Chemicals, Inc.)	0.05 g
· Thermal polymerization inhibitor of N-nitroso-phenylhydroxylamine aluminium salt	0.03 mass%
· Methyl ethyl ketone	58 mass%
· Propylene glycol monomethylether acetate	53 mass%

[0435]

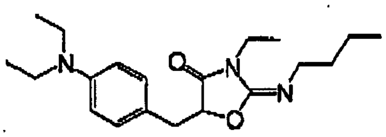
A-1



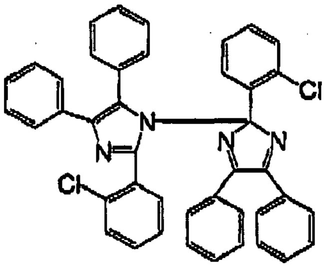
B-1



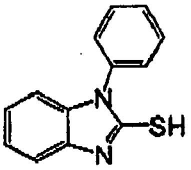
C-1



D-1



[0436]



E-1

Formation of Protective layer

[0437] A mixture aqueous solution of polyvinyl alcohol (safonification degree of 98 mol%, polymerization degree of 500) and polyvinyl pyrrolidone(trade name: RUBISCOL K30, manufactured by BASF JAPAN LTD.) was coated on the photosensitive layer by a wire bar and dried in an hot air dryer at 125°C for 75 seconds so as to obtain a planographic printing plate precursor. The content of the polyvinyl alcohol/polyvinyl pyrrolidone was 4/1 mass% and the coating amount (coating amount after drying) was 2.45 g/m^2.

Comparative Examples 1 to 4

[0438] Stacks of the planographic printing plate precursors of Comparative examples 1 to 4 were obtained in the same manner as Examples 1, 6, 11, and 12 respectively, except that a support having an average surface roughness (Ral) of 0.16 μm in the width direction of the back surface of the support obtained by chainging a buff grinding condition of the support and an average surface roughness (Ras) of 0.12 μm in the longitudinal direction was used.

Example 13

[0439] A planographic printing plate precursor of Example 13 was obtained in the same manner as Example 1, except that a backcoat layer was further provided on a rear surface of the support. Details of the preparation of the backcoat layer are explained in the followings.

Preparation of Backcoat layer

[0440] The rear surface of the aluminum support was coated with a backcoat layer coating liquid [BC-1] having the following formulation, using a wire bar, and then dried at 100°C for 70 seconds so as to form a backcoat layer on the rear surface of the aluminum support. The coating amount was 0.46 mg/m^2.

Formulation of Backcoat layer coating liquid [BC-1]

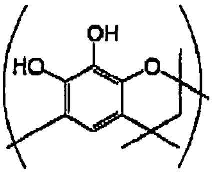
[0441]

- Novolac resin A
  (phenol/m-cresol/p-cresol = 5/3/2 (mol ratio), weight average molecular weight: 5,300) 1.00 g
- Fluorine-containing surfactant
  (trade name: MEGAFAC F-780-F, manufactured by Dainippon Ink and Chemicals, Inc.: 30 mass% solution in methyl isobutyl ketone (MIBK)) 0.015 g
- Methyl ethyl ketone 22.5 g
- 1-Methoxy-2-propanol 2.5 g

Example 14

[0442] A planographic printing plate precursor of Example 14 was obtained in the same manner as Example 13, except that a pyrogallol resin formed by polymerizing the unit having the following chemical structure and a weight average molecular weight of 3,000 was used in place of the novolac resin A. The amount of the pyrogallol resin used therein was an equivalent amount to that of the novolac resin A.

[0443]



Example 15

[0444] A planographic printing plate precursor of Example 15 was obtained in the same manner as Example 13, except that a commarcially-availabe butyral resin (trade name: S-LEC KS-10, manufactured by Sekisui Chemical Co.,Ltd.) was used in place of the novolac resin A. The amount of the butyral resin used therein was an equivalent amount to that of the novolac resin A.

Comparative example 5

[0445] A planographic printing plate precursor of Comparative example 5 was obtained in the same manner as Example 13, except that the aluminum support was changed to an aluminum support having subjected to an anodic oxidation treatment and having a rear surface with an average roughness in the widthwise direction (Ral) of 0.25 and an average surface roughness in the longitudinal direction (Ras) of 0.21.

Evaluation of Average surface roughness (Ra)

[0446] The average surface roughness in the width direction (Ral) and the longitudinal direction (Ras) of the back surface of the support in Examples and Comparative Examples was measured by a 3D surface roughness measuring instrument (trade name: SURFCOM, manufactured by TOKYO SEIMITSU CO., LTD).

Evaluation of Resistance to Scratch

[0447] A plurality of the planographic printing plate precursors were stacked in orders in the same direction without interposing an interleaf paper between 20 sheets of the precursors thus obtained so as to provide a stack. This stack was put to be displaced by 5 cm from the edges of the planographic printing plate precursor of the invention (so as to form a state where the 20 stacked sheets of the plate are projected by 5 cm from the edges of the plate in the cassette), and then the edges of the projected 20 sheets of the precursors were pushed in the horizontal direction, so that a back surface of an aluminum support of the precursor positioned at the lowest in the stacked 20 sheets was provided in the cassette while the surface of the uppermost plate in the cassette is rubbed by the back surface of the aluminum support. The precursor having the protective layer rubbed by the back surface of the aluminum support was used for the evaluation of scratch resistance of the precursor of each of the examples and comparative examples. The plate was conveyed to a CTP machine (trade name: TRENDSETTER 3244, manufacture by Creo Corporation) by an autoloader, and the 50% screen tint image was exposed by a resolution of 2400 dpi under conditions of output 7W, outer surface drum rotation of 150 rpm, and a plate surface energy of 110 mJ/cm^2. Then an exposure treatment was performed in a simmilar manner as that in the sensitivity evaluation. A presence or absence of scratches generated on the screen tint image of the planographic printing plate precursor thus obtained was evaluated by eyes. This evaluation was performed so as to count the number of the scratches in 100 plates of each of the examples. Each of the evaluation was indicated by "P" for practicable revel or "X" for impracticable level.

[0448] The results are shown in Table 1.

Table 1

	Average surface roughness (Ra) (μm)			Resistance to Scratch	
	Widthwise direction (Ral)	Longitudinal direction (Ras)	Ral/Ras	Visial Observation	Number*
Example 1	0.15	0.11	1.36	P	4
Example 2	0.13	0.10	1.30	P	2
Example 3	0.10	0.07	1.43	P	2
Example 4	0.08	0.03	2.67	P	1
Example 5	0.02	0.01	2.00	P	0
Example 6	0.15	0.11	1.36	P	2
Example 7	0.13	0.10	1.30	P	1
Example 8	0.10	0.07	1.43	P	1
Example 9	0.08	0.03	2.67	P	0
Example 10	0.02	0.01	2.00	P	0
Example 11	0.13	0.10	1.30	P	1

(continued)

	Average surface roughness (Ra) (μm)			Resistance to Scratch	
	Widthwise direction (Ral)	Longitudinal direction (Ras)	Ral/Ras	Visial Observation	Number*
Example 12	0.13	0.10	1.30	P	1
Comparative example 1	0.16	0.12	1.33	X	10
Comparative example 2	0.16	0.12	1.33	X	8
Comparative example 3	0.16	0.12	1.33	X	8
Comparative example 4	0.16	0.12	1.33	X	8
Example 13	0.13	0.08	1.62	P	0
Example 14	0.13	0.09	1.44	P	1
Example 15	0.12	0.10	1.20	P	0
Comparative example 5	0.20	0.18	1.11	X	9
* Number: The numbers of scratches found on 100 sheets of samples were counted.					

[0449] From the results shown in Table 1, it is understood that the planographic printing plate precursor having Ra of 0.15 or less of Examples 1 to 12 do not have scratches due to rubbing on the surfaces of their photosensitive materials contacting with others, the positive friction coefficients thereof are within the range to allow handling, and can be used without interposing an interleaf paper. On the other hand, the planographic printing plate precursor having Ra of greater than 0.15 in each of Comparative Examples 1 to 4 is practically problematic since it has scratches due to rubbing on its photosensitive material.

The remarkable effects of the invention are also achieved in Examples 13 to 15, each of which is provided with a backcoat layer, in a case where the average roughness in the widthwise direction (Ral) and the average surface roughness in the longitudinal direction (Ras) are within the ranges required in the invention. However, as is clearly understood from the results of Comparative example 5, a planographic printing plate precursor having the widthwise direction (Ral) and the average surface roughness in the longitudinal direction (Ras) of outside the scope of the invention exhibits inferior resistence to scrach even if a backcoat layer is further provided thereto.

Claims

1. A planographic printing plate precursor comprising a photosensitive layer that has sensitivity to laser light and is provided on or above a surface of a support, wherein an average surface roughness (Ra) of a back surface of the support in both of a longitudinal direction and a width direction is 0.15 μm or less.

2. The planographic printing plate precursor of claim 1, wherein the average surface roughness (Ra) in both of the longitudinal direction and the width direction is 0.13 μm or less.

3. The planographic printing plate precursor of claim 1 or 2, wherein the support comprises aluminum.

4. The planographic printing plate precursor of any one of claims 1 to 3, wherein a Bekk smoothness of a surface of the planographic printing plate precursor that has sensitivity to laser light, is 10,000 seconds or less.

5. **The planographic printing plate precursor of any one of claims 1 to 4, wherein** the photosensitive layer comprises a photosensitive polymerization initiator.

6. The planographic printing plate precursor of any one of claims 1 to 5, further comprising a protective layer formed

on or above the photosensitive layer.

7. The planographic printing plate precursor of claim 6, wherein the protective layer comprises a filler.

8. The planographic printing plate precursor of any one of claims 1 to 7, wherein the photosensitive layer comprises an infrared absorbing dye having a maximum absorption wavelength in a range of from 750 to 1,400 nm,

9. The planographic printing plate precursor of any one of claims 1 to 7, wherein the photosensitive layer comprises a sensitizing dye having a maximum absorption wavelength in a range of from 350 to 450 nm.

10. A stack comprising a plurality of planographic printing plate precursors, wherein:

each of the planographic printing plate precursors is the planographic printing plate precursor of any one of claims 1 to 9; and
each of the planographic printing plate precursors directly contacts with an adjacent planographic printing plate precursor at an uppermost layer thereof and at the back surface of the support.

FIG. 1

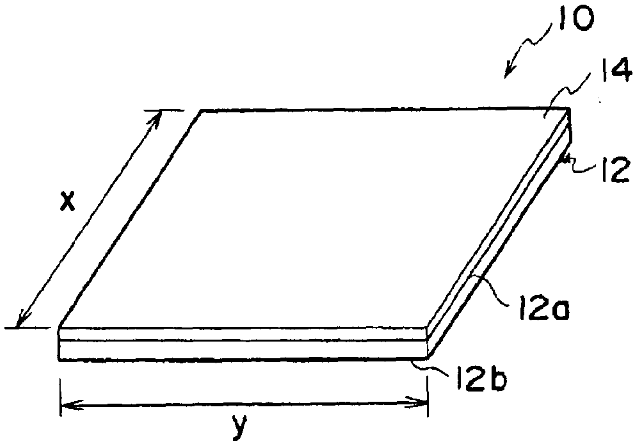


FIG. 2

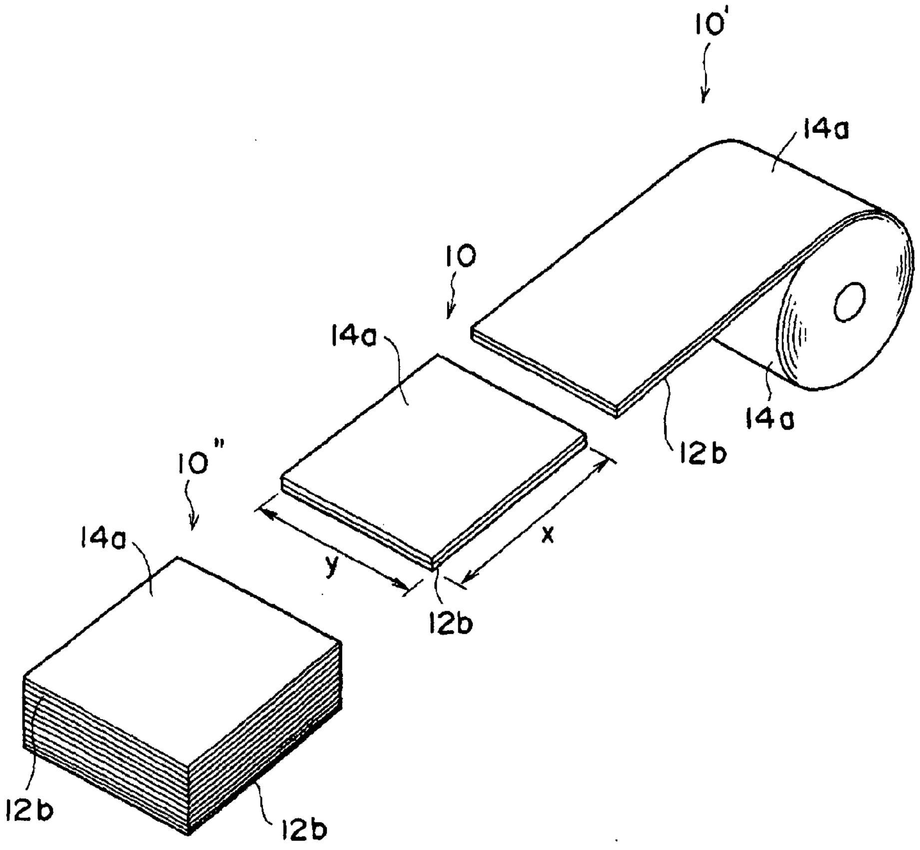


FIG. 3

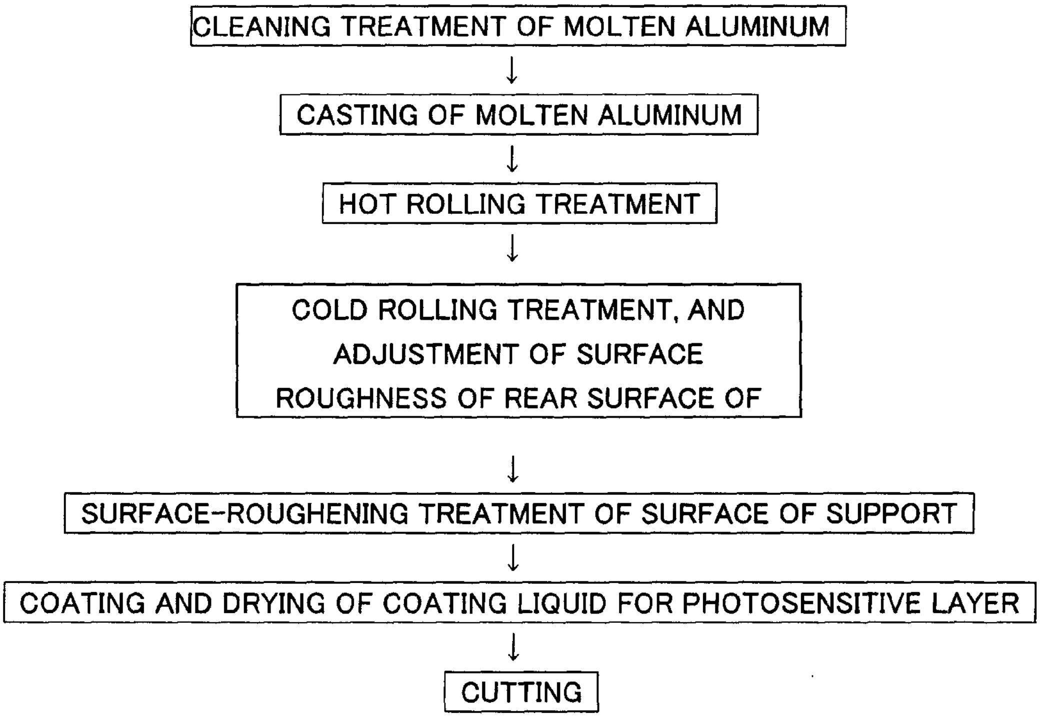
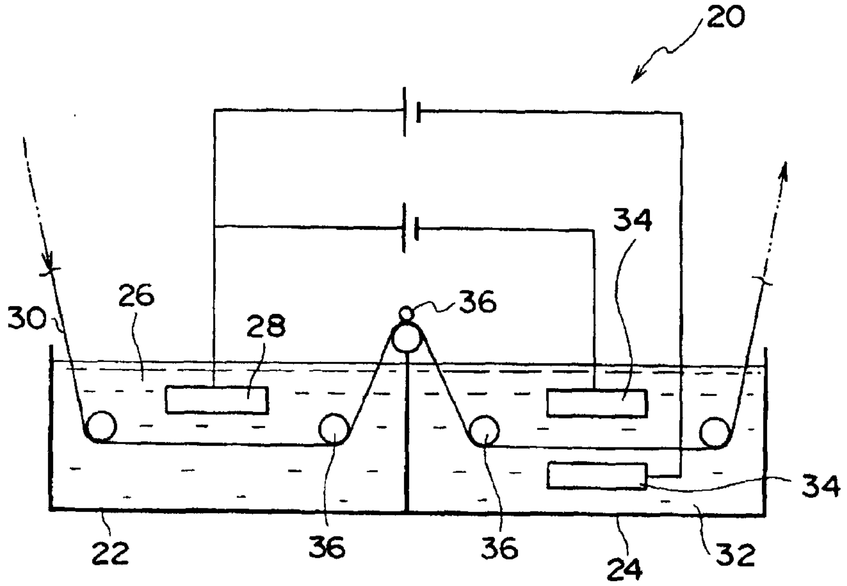

CLEANING TREATMENT OF MOLTEN ALUMINUM
CASTING OF MOLTEN ALUMINUM
HOT ROLLING TREATMENT
COLD ROLLING TREATMENT, AND ADJUSTMENT OF SURFACE ROUGHNESS OF REAR SURFACE OF
SURFACE-ROUGHENING TREATMENT OF SURFACE OF SUPPORT
COATING AND DRYING OF COATING LIQUID FOR PHOTOSENSITIVE LAYER
CUTTING

FIG. 4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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	6 July 2007	Bacon, Alan

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X : particularly relevant if taken alone
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06-07-2007

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