



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 584 978 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
12.10.2005 Bulletin 2005/41

(51) Int Cl.7: **G03C 1/498, G03C 5/17**

(21) Application number: **05006628.1**

(22) Date of filing: **24.03.2005**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR**
Designated Extension States:
AL BA HR LV MK YU

(72) Inventors:
• **Nakagawa, Hajime**
Minami-Ashigara-shi, Kanagawa (JP)
• **Tsukada, Yoshihisa**
Minami-Ashigara-shi, Kanagawa (JP)

(30) Priority: **26.03.2004 JP 2004093593**
14.01.2005 JP 2005008257

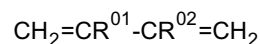
(74) Representative: **HOFFMANN EITLÉ**
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(71) Applicant: **FUJI PHOTO FILM CO., LTD.**
Kanagawa (JP)

(54) **Photothermographic material and image forming method**

(57) The invention provides a photothermographic material including, on at least one side of a support, an image forming layer containing at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent, and a binder, wherein:

the photosensitive silver halide has an average silver iodide content of 40 mol% or higher, and at least 50% of a projected area of total grains of the photosensitive silver halide is occupied by tabular grains having an aspect ratio of 2 or more; and 50% by weight or more of the binder is formed by a polymer latex containing the following monomer component from 10% by weight to 70% by weight:



wherein R⁰¹ and R⁰² each independently represent one selected from a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a halogen atom, and a cyano group, provided that both of R⁰¹ and R⁰² are not hydrogen atoms simultaneously.

The invention provides a photothermographic material and an image forming method utilizing the same which give an image with little haze, high image quality, and excellent pressure resistance.

Formula (M)

EP 1 584 978 A1

Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] The present invention relates to an improved photothermographic material and an image forming method. More specifically, the invention relates to a photothermographic material which exhibits a reduced degree of haze, high image quality, and excellent pressure resistance, and an image forming method utilizing the same.

10 Description of the Related Art

[0002] In recent years, decreases in the amount of processing liquid waste in the field of films for medical imaging have been keenly desired from the viewpoints of environmental protection and economy of space. For this reason, techniques related to photothermographic materials for medical diagnosis and graphic arts are required. Such that photothermographic materials can be exposed efficiently by laser image setters or laser imagers and can form clear black-toned images of high resolution and sharpness. Thermal development systems which do not require liquid processing chemicals are simpler and do not damage the environment and can therefore be supplied to customers.

20 **[0003]** While similar requirements also exist in the field of general image forming materials, images for medical imaging require a particularly high image quality excellent in sharpness and granularity since fine representation is required, and are characterized in that images of blue-black tones are preferred from the viewpoint of easy diagnosis. At present, various kinds of hard copy systems utilizing dyes or pigments such as ink jet printers and electrophotographic systems have been marketed as general image forming systems, but these are not satisfactory as output systems for medical images.

25 **[0004]** Thermal image forming systems utilizing organic silver salts are described, for example, in U.S. Patent (USP) Nos. 3152904 and 3457075, as well as in "Thermally Processed Silver Systems" by D. H. Klosterboer, appearing in "Imaging Processes and Materials", Neblette, 8th edition, edited by J. Sturge, V. Warlworth, and A. Shepp, Chapter 9, page 279, 1989. Such photothermographic materials generally comprise an image forming layer in which a catalytically active amount of photocatalyst (for example, a silver halide), a reducing agent, a reducible silver salt (for example, an organic silver salt), and if necessary, a toner for controlling the color tone of silver, are dispersed in a binder. A photothermographic material forms a black silver image by being heated to a high temperature (for example, 80°C or higher) after imagewise exposure to cause an oxidation-reduction reaction between a silver halide or a reducible silver salt and a reducing agent. The oxidation-reduction reaction is accelerated by the catalytic action of a latent image, which is generated on the silver halide grain by exposure. As a result, a black silver image is formed in the exposed region. This system has been described in USP No. 2910377 and Japanese Patent Application Publication (JP-B) No. 43-4924, as well as in many other documents, and the Fuji Medical Dry Imager FM-DP L is an example of a medical image forming system using a photothermographic material that has been made commercially available.

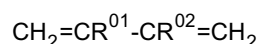
35 **[0005]** Attempts have also been made to apply the above-mentioned photothermographic material as a photosensitive material for photography. The photosensitive material for photography as described herein means a photosensitive material on which images are recorded by one-shot exposing by camera work, rather than by writing the image information by scanning exposure with a laser beam or the like. Conventionally, photosensitive materials for photography are generally used in the field of wet developing photosensitive materials, and direct or indirect radiography films, mammography films, and the like are widely known as photosensitive materials for use in medical imaging. For example, an X-ray photothermographic material coated on both sides using a blue fluorescent intensifying screen is described in Japanese Patent (JP) No. 3229344, and a photothermographic material using tabular silver iodobromide grains is described in Japanese Patent Application Laid-Open (JP-A) No. 59-142539. As another example, a photosensitive material for medical use containing tabular grains that have a high content of silver chloride and have (100) major faces, and that are coated on both sides of a support, is described in JP-A No. 10-282602. Double-sided coated photothermographic materials are disclosed in JP-A Nos. 2000-227642, 2001-22027, 2001-109101, and 2002-90941.

40 **[0006]** Because developed images can be obtained from photothermographic materials by heating alone, they have many beneficial features such as simple image forming operation, no need for controlling a wet processing solution or dispose thereof, and the like. However, there are also many technical problems that need to be resolved. One of these problems is deterioration of image quality caused by turbidity of a membrane (known as haze) which originates from silver halide grains remaining in the membrane after image formation. Another problem is an increase of fog known as print-out, which occurs because silver halide grains, unreacted organic silver salts, and reducing agents remain in the membrane.

SUMMARY OF THE INVENTION

[0007] A first aspect of the invention provides a photothermographic material comprising, on at least one side of a support, an image forming layer containing at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent, and a binder, wherein: the photosensitive silver halide has an average silver iodide content of 40 mol% or higher, and at least 50% of a projected area of total grains of the photosensitive silver halide is occupied by tabular grains having an aspect ratio of 2 or more; and 50% by weight or more of the binder is formed by a polymer latex containing the following monomer component in a range of from 10% by weight to 70% by weight:

Formula (M)



wherein R⁰¹ and R⁰² each independently represent one selected from a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a halogen atom and a cyano group, provided that R⁰¹ and R⁰² are not hydrogen atoms simultaneously.

[0008] A second aspect of the invention provides an image forming method using the photothermographic material according to the first aspect, wherein the method comprises: (a) providing an assembly for forming an image by placing the photothermographic material between a pair of fluorescent intensifying screens; (b) putting an analyte between the assembly and an X-ray source; (c) applying exposure to the analyte using X-rays having an energy level in a range of 25 kVp to 125 kVp; (d) taking the photothermographic material out of the assembly; and (e) heating the photothermographic material at a temperature at which the material can be developed thermally.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The present inventors found that for the above two problems of turbidity of the membrane (haze) and increase of fog known as print-out, the use of tabular photosensitive silver iodide grains is useful. Moreover the present invention solves the problem of generating a break at the surface of a photothermographic material when the material comprising the grains is impressed before thermal development by using a polymer having a specific monomer component for a binder in an image forming layer. In addition, the present invention provides a method for forming a radiation image with high sensitivity.

[0010] The present invention is explained below in detail.

1. Photothermographic material

[0011] The photothermographic material of the invention has an image forming layer comprising at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent, and a binder on at least one side of a support. Further, the image forming layer may have disposed thereon a surface protective layer, or a back layer, a back protective layer, or the like may be disposed on the opposite side of the image forming layer with respect to the support. The image forming layer of the present invention may be disposed on one side, or may be disposed on both sides of the support. Particularly, in the case of photothermographic material used for forming a radiation image, the image forming layer is preferably coated on both sides.

[0012] The constitutions and preferable components of these layers will be explained in detail below.

(Non-photosensitive organic silver salt)

1) Composition

[0013] The organic silver salt which can be used in the present invention is relatively stable to light but serves as to supply silver ions and forms silver images when heated to 80°C or higher under the presence of an exposed photosensitive silver halide and a reducing agent. The organic silver salt may be any organic material containing a source capable of supplying silver ions that are reducible by a reducing agent. Such a non-photosensitive organic silver salt is disclosed, for example, in JP-A No. 10-62899 (paragraph Nos. 0048 to 0049), European Patent (EP) No. 0803764A (page 18, line 24 to page 19, line 37), EP No. 0962812A1, JP-A Nos. 11-349591, 2000-7683, and 2000-72711, and the like. A silver salt of an organic acid, particularly, a silver salt of long chained aliphatic carboxylic acid (having 10 to 30 carbon atoms, and preferably having 15 to 28 carbon atoms) is preferable. Preferred examples of the silver salt of fatty acid can include, for example, silver lignocerate, silver behenate, silver arachidinate, silver stearate, silver oleate,

silver laurate, silver capronate, silver myristate, silver palmitate, silver erucate and mixtures thereof.

[0014] In the invention, among these silver salts of fatty acid, it is preferred to use a silver salt of fatty acid with a silver behenate content of 80 mol% to 99 mol%, more preferably, 85 mol% to 99 mol%, and further preferably, 95 mol% to 99 mol%. Further, it is preferred to use a silver salt of fatty acid with a silver erucate content of 2 mol% or less, more preferably, 1 mol% or less, and further preferably, 0.1 mol% or less.

2) Shape

[0015] There is no particular restriction on the shape of the organic silver salt usable in the invention and it may be needle-like, bar-like, tabular, or flake shaped.

[0016] As the particle size distribution of the organic silver salt, monodispersion is preferred.

[0017] In the monodispersion, the percentage for the value obtained by dividing the standard deviation for the length of minor axis and major axis by the minor axis and the major axis respectively is, preferably, 100% or less, more preferably, 80% or less and, further preferably, 50% or less. The shape of the organic silver salt can be measured by analyzing a dispersion of an organic silver salt as transmission type electron microscopic images. Another method of measuring the monodispersion is a method of determining of the standard deviation of the volume weighted mean diameter of the organic silver salt in which the percentage for the value defined by the volume weighted mean diameter (variation coefficient), is preferably, 100% or less, more preferably, 80% or less and, further preferably, 50% or less. For determination of such a value, a commercially available laser-beam scattering grain size analyzer can be used.

3) Preparation

[0018] Methods known in the art may be applied to the method for producing the organic silver salt used in the invention and to the dispersing method thereof. For example, reference can be made to JP-A No. 10-62899, EP Nos. 0803763A1 and 0962812A1, JP-A Nos. 11-349591, 2000-7683, 2000-72711, 2001-163889, 2001-163890, 2001-163827, 2001-33907, 2001-188313, 2001-83652, 2002-6442, 2002-49117, 2002-31870, and 2002-107868, and the like.

[0019] When a photosensitive silver salt is present together during dispersion of the organic silver salt, fog increases and sensitivity becomes remarkably lower, so that it is more preferred that the photosensitive silver salt is not substantially contained during dispersion. In the invention, the amount of the photosensitive silver salt to be disposed in the aqueous dispersion, is preferably, 1 mol% or less, more preferably, 0.1 mol% or less per 1 mol of the organic acid silver salt in the solution and, further preferably, positive addition of the photosensitive silver salt is not conducted.

[0020] In the invention, the photosensitive material can be prepared by mixing an aqueous dispersion of an organic silver salt and an aqueous dispersion of a photosensitive silver salt and the mixing ratio between the organic silver salt. A method of mixing two or more kinds of aqueous dispersions of organic silver salts and two or more kinds of aqueous dispersions of photosensitive silver salts upon mixing is used preferably for controlling the photographic properties.

4) Addition amount

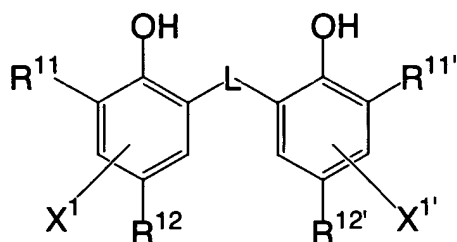
[0021] While an organic silver salt in the invention can be used in a desired amount, a total amount of coated silver including silver halide is preferably in a range from 0.1 g/m² to 5.0 g/m², more preferably from 0.3 g/m² to 3.0 g/m², and further preferably from 0.5 g/m² to 2.0 g/m². Particularly, in order to improve image storability, the total amount of coated silver is preferably 1.8 mg/m² or less, and more preferably 1.6 mg/m² or less.

(Reducing agent)

[0022] The photothermographic material of the invention preferably contains a reducing agent for the organic silver salt. The reducing agent may be any substance (preferably, organic substance) capable of reducing silver ions into metallic silver. Examples of the reducing agent are described in JP-A No. 11-65021 (column Nos. 0043 to 0045) and EP No. 0803764A1 (page 7, line 34 to page 18, line 12).

[0023] In the invention, a so-called hindered phenolic reducing agent or a bisphenol reducing agent having a substituent at the ortho-position to the phenolic hydroxy group is preferred. The compound represented by the following formula (R) is more preferred.

Formula (R)



5

10

15 **[0024]** In formula (R), R^{11} and $R^{11'}$ each independently represent an alkyl group having 1 to 20 carbon atoms. R^{12} and $R^{12'}$ each independently represent a hydrogen atom or a substituent capable of substituting for a hydrogen atom on a benzene ring. L represents an -S- group or a -CHR¹³-group. R^{13} represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms. X^1 and $X^{1'}$ each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring.

20 **[0025]** Formula (R) is to be described in detail.

1) R^{11} and $R^{11'}$

25 R^{11} and $R^{11'}$ each independently represent a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms. The substituent for the alkyl group has no particular restriction and can include, preferably, an aryl group, a hydroxy group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an acylamino group, a sulfonamide group, a sulfonyl group, a phosphoryl group, an acyl group, a carbamoyl group, an ester group, a ureido group, a urethane group, and a halogen atom.

2) R^{12} and $R^{12'}$, X^1 and $X^{1'}$

30 R^{12} and $R^{12'}$ each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring. X^1 and $X^{1'}$ each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring. Each of the groups capable of substituting for a hydrogen atom on the benzene ring can include, preferably, an alkyl group, an aryl group, a halogen atom, an alkoxy group, and an acylamino group.

3) L

35 L represents an -S- group or a -CHR¹³- group. R^{13} represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms in which the alkyl group may have a substituent. Specific examples of the unsubstituted alkyl group for R^{13} can include, for example, a methyl group, an ethyl group, a propyl group, a butyl group, a heptyl group, an undecyl group, an isopropyl group, a 1-ethylpentyl group, a 2,4,4-trimethylpentyl group, and the like. Examples of the substituent for the alkyl group can include, similar to substituent of R^{11} , a halogen atom, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an acylamino group, a sulfonamide group, a sulfonyl group, a phosphoryl group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, and the like.

4) Preferred substituents

45 R^{11} and $R^{11'}$ are, preferably, a secondary or tertiary alkyl group having 3 to 15 carbon atoms and can include, specifically, an isopropyl group, an isobutyl group, a t-butyl group, a t-amyl group, a t-octyl group, a cyclohexyl group, a cyclopentyl group, a 1-methylcyclohexyl group, a 1-methylcyclopropyl group, and the like. R^{11} and $R^{11'}$ each represent, more preferably, a tertiary alkyl group having 4 to 12 carbon atoms and, among them, a t-butyl group, a t-amyl group, and a 1-methylcyclohexyl group are further preferred and, a t-butyl group being most preferred.

50 **[0026]** R^{12} and $R^{12'}$ are, preferably, an alkyl group having 1 to 20 carbon atoms and can include, specifically, a methyl group, an ethyl group, a propyl group, a butyl group, an isopropyl group, a t-butyl group, a t-amyl group, a cyclohexyl group, a 1-methylcyclohexyl group, a benzyl group, a methoxymethyl group, a methoxyethyl group, and the like. More preferred are a methyl group, an ethyl group, a propyl group, an isopropyl group, and a t-butyl group.

55 **[0027]** X^1 and $X^{1'}$ are, preferably, a hydrogen atom, a halogen atom, or an alkyl group, and more preferably, a hydrogen atom.

[0028] L is preferably a -CHR¹³- group.

[0029] R^{13} is preferably a hydrogen atom or an alkyl group having 1 to 15 carbon atoms. Preferable examples of the alkyl group can include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a 2,4,4-trimethylpentyl

group. Particularly preferable R^{13} is a hydrogen atom, a methyl group, an ethyl group, a propyl group, or an isopropyl group.

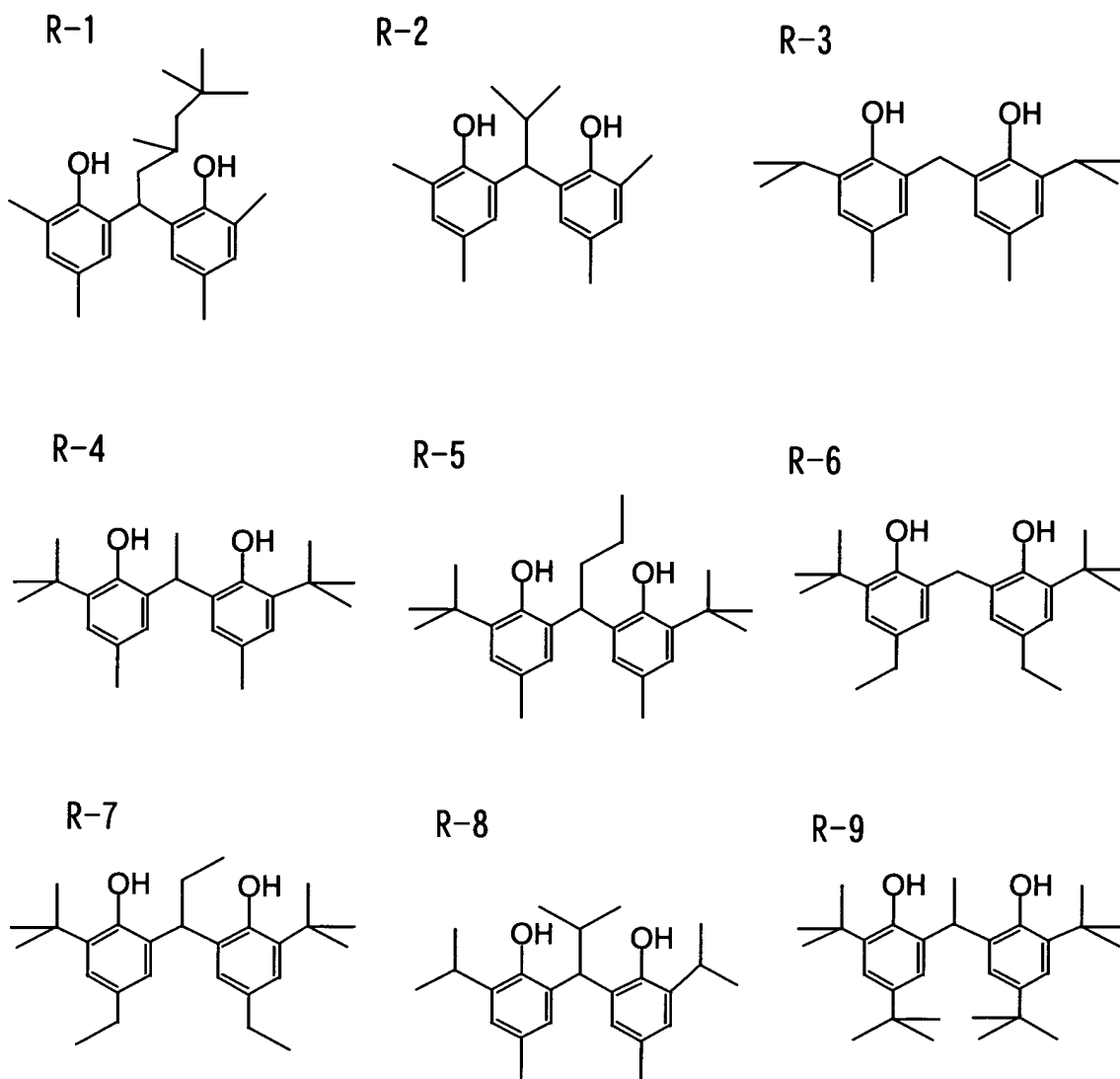
[0030] When R^{13} is a hydrogen atom, R^{12} and $R^{12'}$ are preferably an alkyl group having 2 to 5 carbon atoms, more preferably an ethyl group or a propyl group, and most preferably an ethyl group.

[0031] When R^{13} is a primary or secondary alkyl group having 1 to 8 carbon atoms, R^{12} and $R^{12'}$ are preferably a methyl group. The primary or secondary alkyl group having 1 to 8 carbon atoms as R^{13} is preferably a methyl group, an ethyl group, a propyl group, or an isopropyl group, and more preferably a methyl group, an ethyl group, or a propyl group.

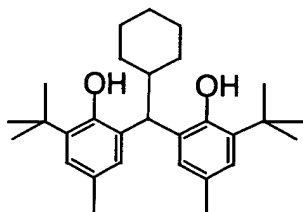
[0032] When all of R^{11} , $R^{11'}$, R^{12} and $R^{12'}$ are a methyl group, R^{13} is preferably a secondary alkyl group. In this case, the secondary alkyl group as R^{13} is preferably an isopropyl group, an isobutyl group, or a 1-ethylpentyl group, and more preferably an isopropyl group.

[0033] The reducing agent described above shows different thermal developing performances, color tones of developed silver images, or the like depending on the combination of R^{11} , $R^{11'}$, R^{12} , $R^{12'}$, and R^{13} . Since these performances can be controlled by using two or more kinds of reducing agents at various mixing ratios, it is preferred to use two or more kinds of reducing agents in combination depending on the purpose.

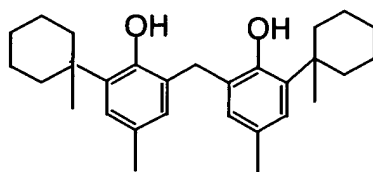
[0034] Specific examples of the reducing agents of the invention including the compounds represented by formula (R) according to the invention are shown below, but the invention is not restricted to them.



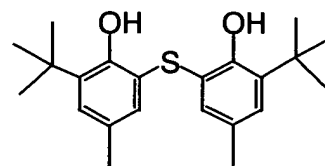
R-10



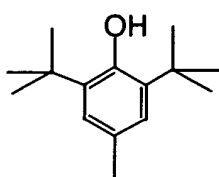
R-11



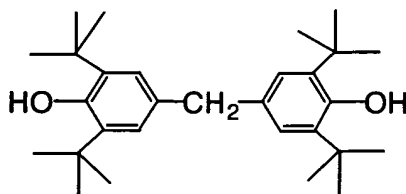
R-12



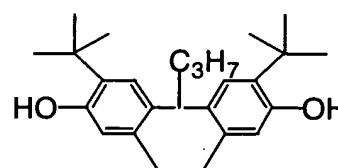
R-13



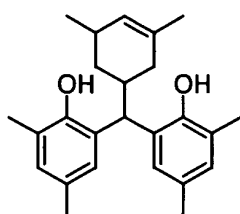
R-14



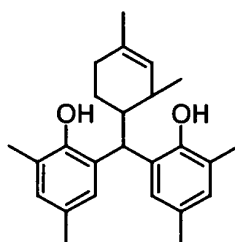
R-15



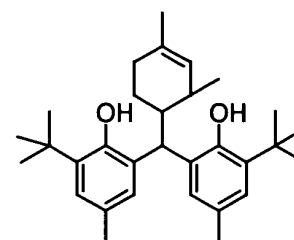
R-16



R-17



R-18



[0035] As preferred reducing agents of the invention other than those above, there can be mentioned compounds disclosed in JP-A Nos. 2001-188314, 2001-209145, 2001-350235, and 2002-156727.

[0036] In the invention, the addition amount of the reducing agent is, preferably, from 0.1 g/m² to 3.0 g/m², more preferably, 0.2 g/m² to 1.5 g/m² and, further preferably 0.3 g/m² to 1.0 g/m². It is preferably contained in a range of 5 mol% to 50 mol%, more preferably, 8 mol% to 30 mol% and, further preferably, 10 mol% to 20 mol% per 1 mol of silver in the image forming layer. The reducing agent of the invention is preferably contained in the image forming layer.

[0037] In the invention, the reducing agent may be incorporated into photothermographic material by being added into the coating solution, such as in the form of solution, emulsion dispersion, solid fine particle dispersion, and the like.

[0038] As a well known emulsion dispersing method, there can be mentioned a method comprising dissolving the reducing agent using an oil such as dibutyl phthalate, tricresyl phosphate, glyceryl triacetate, diethyl phthalate, or the like, as well as an auxiliary solvent such as ethyl acetate, cyclohexanone, or the like; from which an emulsion dispersion is mechanically produced.

[0039] As solid fine particle dispersing method, there can be mentioned a method comprising dispersing the powder of the reducing agent in a proper medium such as water, by means of ball mill, colloid mill, vibrating ball mill, sand mill, jet mill, roller mill, or ultrasonics, thereby obtaining solid dispersion. In this case, there can also be used a protective colloid (such as polyvinyl alcohol), or a surfactant (for instance, an anionic surfactant such as sodium triisopropylnaphthalenesulfonate (a mixture of compounds having the isopropyl groups in different substitution sites)). In the mills enumerated above, generally used as the dispersion media are beads made of zirconia and the like, and Zr and the like eluting from the beads may be incorporated in the dispersion. Although depending on the dispersing conditions,

the amount of Zr and the like generally incorporated in the dispersion is in the range from 1 ppm to 1000 ppm. It is practically acceptable so long as Zr is incorporated in an amount of 0.5 mg or less per 1 g of silver.

[0040] Preferably, an antiseptic (for instance, benzisothiazolinone sodium salt) is added in the water dispersion.

[0041] Particularly preferably, the reducing agent is used as a solid particle dispersion, and the reducing agent is added in the form of fine particles having mean particle size from 0.01 μm to 10 μm , and more preferably, from 0.05 μm to 5 μm , and further preferably, from 0.1 μm to 2 μm . In the invention, other solid dispersions are preferably used with this particle size range.

(Development accelerator)

[0042] In the photothermographic material of the invention, sulfonamide phenolic compounds described in the specification of JP-A No. 2000-267222, and represented by formula (A) described in the specification of JP-A No. 2000-330234; hindered phenolic compounds represented by formula (II) described in JP-A No. 2001-92075; hydrazine compounds described in the specification of JP-A No. 10-62895, represented by formula (I) described in the specification of JP-A No. 11-15116, represented by formula (D) described in the specification of JP-A No. 2002-156727, and represented by formula (1) described in the specification of JP-A No. 2002-278017; and phenolic or naphthalic compounds represented by formula (2) described in the specification of JP-A No. 2001-264929 are used preferably as a development accelerator. The development accelerator described above is used in a range from 0.1 mol% to 20 mol%, preferably, in a range from 0.5 mol% to 10 mol% and, more preferably, in a range from 1 mol% to 5 mol% with respect to the reducing agent. The introducing methods to the photothermographic material can include similar methods as those for the reducing agent and, it is particularly preferred to add as a solid dispersion or an emulsion dispersion. In a case of adding as an emulsion dispersion, it is preferred to add as an emulsion dispersion dispersed by using a high boiling solvent which is solid at a normal temperature and an auxiliary solvent at a low boiling point, or to add as a so-called oilless emulsion dispersion not using the high boiling solvent.

[0043] In the present invention, it is more preferred to use as a development accelerator, hydrazine compounds represented by formula (D) described in the specification of JP-A No. 2002-156727, and phenolic or naphthalic compounds represented by formula (2) described in the specification of JP-A No. 2001-264929.

[0044] Particularly preferred development accelerators of the invention are compounds represented by the following formulae (A-1) and (A-2).

Formula (A-1)

$Q_1\text{-NHNH-Q}_2$

(wherein Q_1 represents an aromatic group or a heterocyclic group which bonds to -NHNH-Q_2 at a carbon atom, and Q_2 represents one selected from a carbamoyl group, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a sulfonyl group, and a sulfamoyl group).

[0045] In formula (A-1), the aromatic group or the heterocyclic group represented by Q_1 is preferably a 5 to 7-membered unsaturated ring. Preferred examples include a benzene ring, a pyridine ring, a pyrazine ring, a pyrimidine ring, a pyridazine ring, a 1,2,4-triazine ring, a 1,3,5-triazine ring, a pyrrole ring, an imidazole ring, a pyrazole ring, a 1,2,3-triazole ring, a 1,2,4-triazole ring, a tetrazole ring, a 1,3,4-thiadiazole ring, a 1,2,4-thiadiazole ring, a 1,2,5-thiadiazole ring, a 1,3,4-oxadiazole ring, a 1,2,4-oxadiazole ring, a 1,2,5-oxadiazole ring, a thiazole ring, an oxazole ring, an isothiazole ring, an isooxazole ring, a thiophene ring, and the like. Condensed rings in which the rings described above are condensed to each other are also preferred.

[0046] The rings described above may have substituents and in a case where they have two or more substituents, the substituents may be identical or different from each other. Examples of the substituents can include a halogen atom, an alkyl group, an aryl group, a carbonamide group, an alkylsulfonamide group, an arylsulfonamide group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a carbamoyl group, a sulfamoyl group, a cyano group, an alkylsulfonyl group, an arylsulfonyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, and an acyl group. In the case where the substituents are groups capable of substitution, they may have further substituents and examples of preferred substituents can include a halogen atom, an alkyl group, an aryl group, a carbonamide group, an alkylsulfonamide group, an arylsulfonamide group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, a cyano group, a sulfamoyl group, an alkylsulfonyl group, an arylsulfonyl group, and an acyloxy group.

[0047] The carbamoyl group represented by Q_2 is a carbamoyl group preferably having 1 to 50 carbon atoms and, more preferably, having 6 to 40 carbon atoms, and examples can include unsubstituted carbamoyl, methyl carbamoyl, N-ethylcarbamoyl, N-propylcarbamoyl, N-sec-butylcarbamoyl, N-octylcarbamoyl, N-cyclohexylcarbamoyl, N-tert-butyl-

tylcarbamoyl, N-dodecylcarbamoyl, N-(3-dodecyloxypropyl)carbamoyl, N-octadecylcarbamoyl, N-{3-(2,4-tert-pentylphenoxy)propyl}carbamoyl, N-(2-hexyldecyl)carbamoyl, N-phenylcarbamoyl, N-(4-dodecyloxyphenyl)carbamoyl, N-(2-chloro-5-dodecyloxyphenyl)carbamoyl, N-naphthylcarbamoyl, N-3-pyridylcarbamoyl, and N-benzylcarbamoyl.

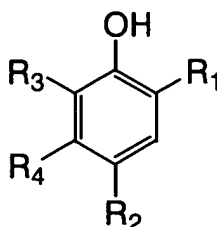
[0048] The acyl group represented by Q_2 is an acyl group, preferably having 1 to 50 carbon atoms and, more preferably having 6 to 40 carbon atoms and can include, for example, formyl, acetyl, 2-methylpropanoyl, cyclohexylcarbonyl, octanoyl, 2-hexyldecanoyl, dodecanoyl, chloroacetyl, trifluoroacetyl, benzoyl, 4-dodecyloxybenzoyl, and 2-hydroxymethylbenzoyl. The alkoxycarbonyl group represented by Q_2 is an alkoxycarbonyl group, preferably having 2 to 50 carbon atoms and, more preferably, having 6 to 40 carbon atoms and can include, for example, methoxycarbonyl, ethoxycarbonyl, isobutyloxycarbonyl, cyclohexyloxycarbonyl, dodecyloxycarbonyl, and benzyloxycarbonyl.

[0049] The aryloxy carbonyl group represented by Q_2 is an aryloxy carbonyl group, preferably having 7 to 50 carbon atoms and, more preferably having 7 to 40 carbon atoms, and can include, for example, phenoxycarbonyl, 4-octyloxyphenoxycarbonyl, 2-hydroxymethylphenoxycarbonyl, and 4-dodecyloxyphenoxycarbonyl. The sulfonyl group represented by Q_2 is a sulfonyl group, preferably having 1 to 50 carbon atoms and, more preferably having 6 to 40 carbon atoms, and can include, for example, methylsulfonyl, butylsulfonyl, octylsulfonyl, 2-hexadecylsulfonyl, 3-dodecyloxypropylsulfonyl, 2-octyloxy-5-tert-octylphenyl sulfonyl, and 4-dodecyloxyphenyl sulfonyl.

[0050] The sulfamoyl group represented by Q_2 is a sulfamoyl group, preferably having 0 to 50 carbon atoms and, more preferably having 6 to 40 carbon atoms, and can include, for example, unsubstituted sulfamoyl, N-ethylsulfamoyl group, N-(2-ethylhexyl)sulfamoyl, N-decylsulfamoyl, N-hexadecylsulfamoyl, N-{3-(2-ethylhexyloxy)propyl}sulfamoyl, N-(2-chloro-5-dodecyloxyphenyl)sulfamoyl, and N-(2-tetradecyloxyphenyl)sulfamoyl. The group represented by Q_2 may further have a group mentioned as the example of the substituent of 5 to 7-membered unsaturated ring represented by Q_1 at the position capable of substitution. In a case where the group has two or more substituents, such substituents may be the same or different from each other.

[0051] Then, preferred range for the compound represented by formula (A-1) is to be described. A 5 or 6-membered unsaturated ring is preferred for Q_1 , and a benzene ring, a pyrimidine ring, a 1,2,3-triazole ring, a 1,2,4-triazole ring, a tetrazole ring, a 1,3,4-thiadiazole ring, a 1,2,4-thiadiazole ring, a 1,3,4-oxadiazole ring, a 1,2,4-oxadiazole ring, a thioazole ring, an oxazole ring, an isothiazole ring, an isooxazole ring, and a ring in which the ring described above is condensed with a benzene ring or unsaturated hetero ring are further preferred. Further, Q_2 is preferably a carbamoyl group and, particularly, a carbamoyl group having a hydrogen atom on the nitrogen atom is particularly preferred.

Formula (A-2)



[0052] In formula (A-2), R_1 represents one selected from an alkyl group, an acyl group, an acylamino group, a sulfonamide group, an alkoxycarbonyl group, and a carbamoyl group. R_2 represents one selected from a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an acyloxy group, and a carbonate ester group. R_3 and R_4 each independently represent a group capable of substituting for a hydrogen atom on a benzene ring which is mentioned as the example of the substituent for formula (A-1). R_3 and R_4 may link together to form a condensed ring.

[0053] R_1 is preferably an alkyl group having 1 to 20 carbon atoms (for example, a methyl group, an ethyl group, an isopropyl group, a butyl group, a tert-octyl group, a cyclohexyl group, or the like), an acylamino group (for example, an acetylamino group, a benzoylamino group, a methylureido group, a 4-cyanophenylureido group, or the like), or a carbamoyl group (for example, a n-butylcarbamoyl group, an N,N-diethylcarbamoyl group, a phenylcarbamoyl group, a 2-chlorophenylcarbamoyl group, a 2,4-dichlorophenylcarbamoyl group, or the like). An acylamino group (including a ureido group and a urethane group) is more preferred.

[0054] R_2 is preferably a halogen atom (more preferably, a chlorine atom or a bromine atom), an alkoxy group (for example, a methoxy group, a butoxy group, an n-hexyloxy group, an n-decyloxy group, a cyclohexyloxy group, a benzyloxy group, or the like), or an aryloxy group (for example, a phenoxy group, a naphthoxy group, or the like).

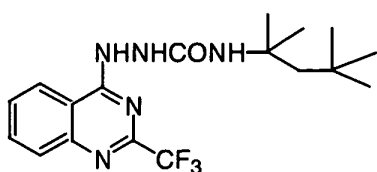
[0055] R_3 is preferably a hydrogen atom, a halogen atom, or an alkyl group having 1 to 20 carbon atoms, and most preferably a halogen atom. R_4 is preferably a hydrogen atom, an alkyl group, or an acylamino group, and more preferably an alkyl group or an acylamino group. Examples of the preferred substituent thereof are similar to those for R_1 . In the case where R_4 is an acylamino group, R_4 may preferably link with R_3 to form a carbostyryl ring.

[0056] In the case where R_3 and R_4 in formula (A-2) link together to form a condensed ring, a naphthalene ring is particularly preferred as the condensed ring. The same substituent as the example of the substituent referred to for formula (A-1) may bond to the naphthalene ring. In the case where formula (A-2) is a naphtholic compound, R_1 is preferably a carbamoyl group. Among them, a benzoyl group is particularly preferred. R_2 is preferably an alkoxy group or an aryloxy group and, particularly preferably an alkoxy group.

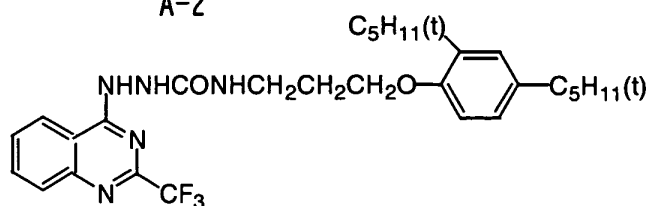
[0057] Preferred specific examples for the development accelerator of the invention are to be described below. The invention is not restricted to them.

[0058] Preferred specific examples for the development accelerator of the invention are to be described below. The invention is not restricted to them.

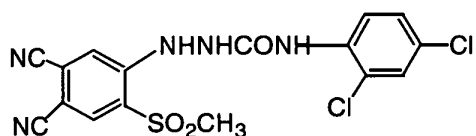
A-1



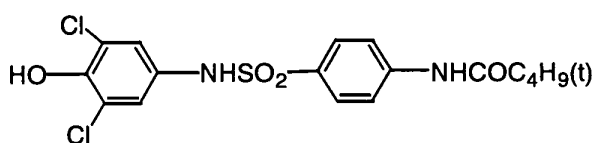
A-2



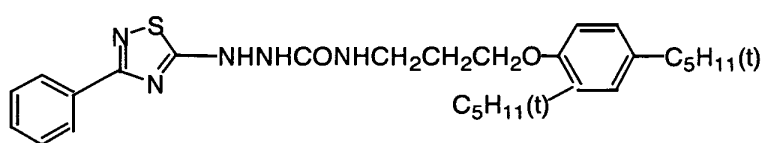
A-3



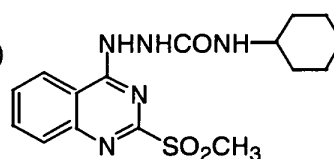
A-4



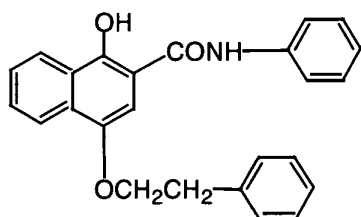
A-5



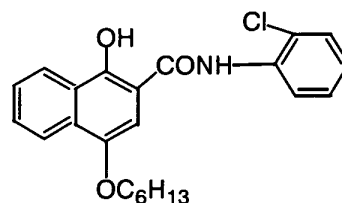
A-6



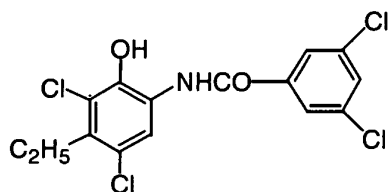
A-7



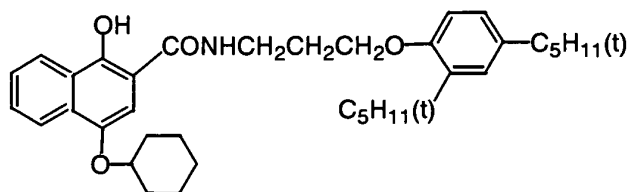
A-8



A-9



A-10



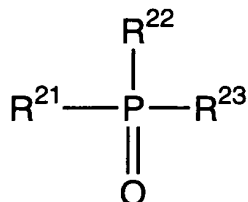
(Hydrogen bonding compound)

[0059] In the invention, in the case where the reducing agent has an aromatic hydroxy group (-OH) or an amino group (-NHR, R represents a hydrogen atom or an alkyl group), particularly in the case where the reducing agent is a bisphenol described above, it is preferred to use in combination, a nonreducing compound having a group capable of reacting with these groups, and that is also capable of forming a hydrogen bond therewith.

[0060] As a group forming a hydrogen bond with a hydroxy group or an amino group, there can be mentioned a phosphoryl group, a sulfoxide group, a sulfonyl group, a carbonyl group, an amide group, an ester group, a urethane group, a ureido group, a tertiary amino group, a nitrogen-containing aromatic group, and the like. Particularly preferred among them is a phosphoryl group, a sulfoxide group, an amide group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)), a urethane group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)), and a ureido group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)).

[0061] In the invention, particularly preferable as the hydrogen bonding compound is the compound expressed by formula (D) shown below.

Formula (D)



[0062] In formula (D), R^{21} to R^{23} each independently represent one selected from an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group, and a heterocyclic group, which may be substituted or unsubstituted.

[0063] In the case where R^{21} to R^{23} contain a substituent, examples of the substituent include a halogen atom, an alkyl group, an aryl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an alkylthio group, an arylthio group, a sulfonamide group, an acyloxy group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, a phosphoryl group, and the like, in which preferred as the substituents are an alkyl group or an aryl group, e.g., a methyl group, an ethyl group, an isopropyl group, a t-butyl group, a t-octyl group, a phenyl group, a 4-alkoxyphenyl group, a 4-acyloxyphenyl group, and the like.

[0064] Specific examples of an alkyl group expressed by R^{21} to R^{23} include a methyl group, an ethyl group, a butyl group, an octyl group, a dodecyl group, an isopropyl group, a t-butyl group, a t-amyl group, a t-octyl group, a cyclohexyl group, a 1-methylcyclohexyl group, a benzyl group, a phenetyl group, a 2-phenoxypropyl group, and the like.

[0065] As an aryl group, there can be mentioned a phenyl group, a cresyl group, a xylyl group, a naphthyl group, a 4-t-butylphenyl group, a 4-t-octylphenyl group, a 4-anisidyl group, a 3,5-dichlorophenyl group, and the like.

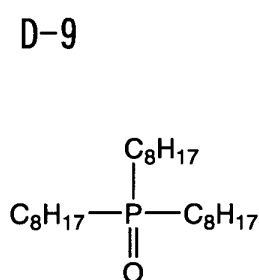
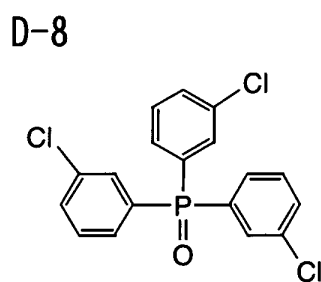
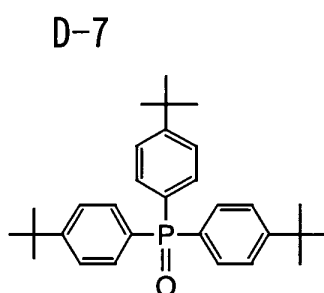
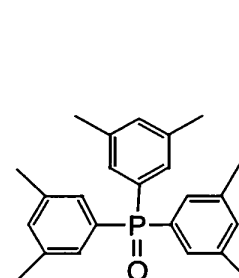
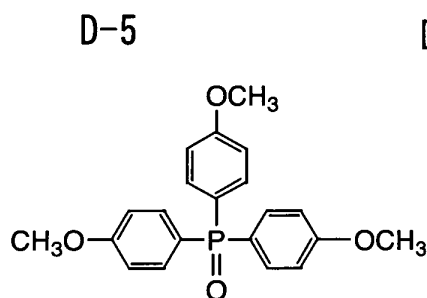
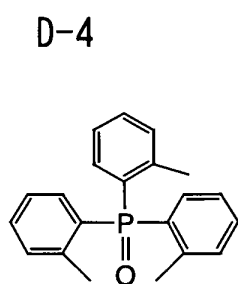
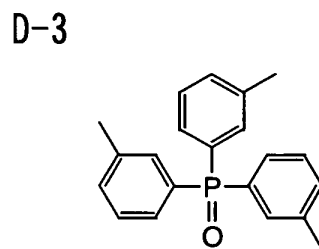
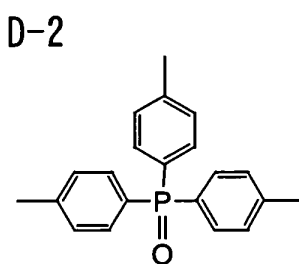
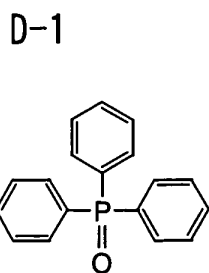
[0066] As an alkoxy group, there can be mentioned a methoxy group, an ethoxy group, a butoxy group, an octyloxy group, a 2-ethylhexyloxy group, a 3,5,5-trimethylhexyloxy group, a dodecyloxy group, a cyclohexyloxy group, a 4-methylcyclohexyloxy group, a benzyloxy group, and the like.

[0067] As an aryloxy group, there can be mentioned a phenoxy group, a cresyloxy group, an isopropylphenoxy group, a 4-t-butylphenoxy group, a naphthoxy group, a biphenyloxy group, and the like.

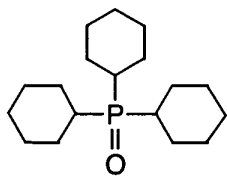
[0068] As an amino group, there can be mentioned are a dimethylamino group, a diethylamino group, a dibutylamino group, a dioctylamino group, an N-methyl-N-hexylamino group, a dicyclohexylamino group, a diphenylamino group, an N-methyl-N-phenylamino group, and the like.

5 **[0069]** Preferred as R^{21} to R^{23} is an alkyl group, an aryl group, an alkoxy group, or an aryloxy group. Concerning the effect of the invention, it is preferred that at least one or more of R^{21} to R^{23} are an alkyl group or an aryl group, and more preferably, two or more of them are an alkyl group or an aryl group. From the viewpoint of low cost availability, it is preferred that R^{21} to R^{23} are of the same group.

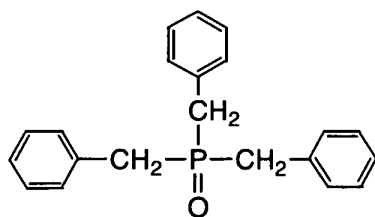
10 **[0070]** Specific examples of hydrogen bonding compounds represented by formula (D) of the invention and others are shown below, but it should be understood that the invention is not limited thereto.



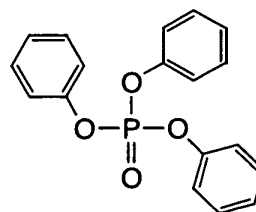
D-10



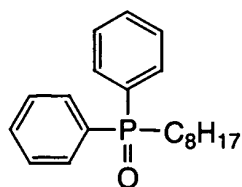
D-11



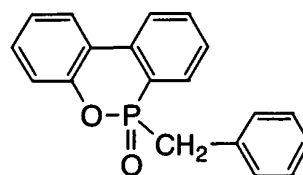
D-12



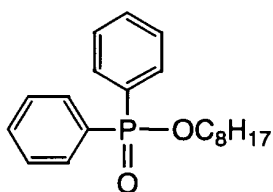
D-13



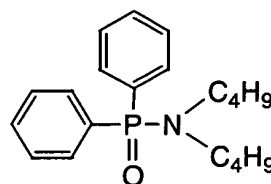
D-14



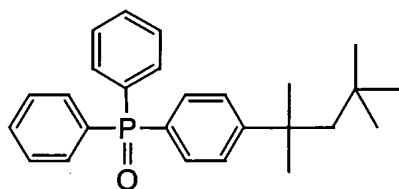
D-15



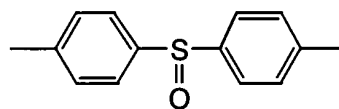
D-16



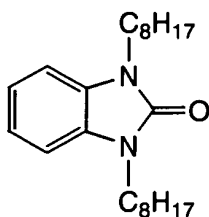
D-17



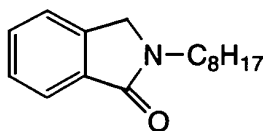
D-18



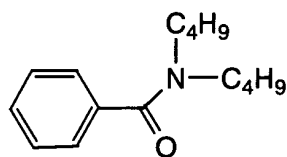
D-19



D-20



D-21



5

10

15

[0071] Specific examples of hydrogen bonding compounds other than those enumerated above can be found in those described in EP No. 1096310 and in JP-A Nos. 2002-156727 and 2002-318431.

20

[0072] The compound expressed by formula (D) used in the invention can be used in the photothermographic material by being incorporated into the coating solution in the form of solution, emulsion dispersion, or solid fine particle dispersion, similar to the case of reducing agent. However, it is preferred to use the compound in the form of solid dispersion. In the solution, the compound expressed by formula (D) forms a hydrogen-bonded complex with a compound having a phenolic hydroxy group or an amino group, and can be isolated as a complex in crystalline state depending on the combination of the reducing agent and the compound expressed by formula (D).

25

[0073] It is particularly preferred to use the crystal powder thus isolated in the form of solid fine particle dispersion, because it provides stable performance. Further, it is also preferred to use a method of leading to form complex during dispersion by mixing the reducing agent and the compound expressed by formula (D) in the form of powders and dispersing them with a proper dispersion agent using sand grinder mill or the like.

30

[0074] The compound expressed by formula (D) is preferably used in a range from 1 mol% to 200 mol%, more preferably from 10 mol% to 150 mol%, and further preferably, from 20 mol% to 100 mol%, with respect to the reducing agent.

(Photosensitive silver halide)

35

[0075] The photosensitive silver halide of the present invention has an average silver iodide content of 40 mol% or higher, and at least 50% of a projected area of total grains of the photosensitive silver halide is occupied by tabular grains having an aspect ratio of 2 or more.

1) Halogen composition

40

The photosensitive silver halide used in the present invention has an average silver iodide content of 40 mol% or higher, preferably 80 mol% or higher and, more preferably 90 mol% or higher. Other components are not particularly limited and can be selected from silver chloride, silver bromide, and organic silver salts such as silver thiocyanate, silver phosphate, or the like, and particularly, silver bromide and silver chloride are preferable. By using such a silver halide having a high silver iodide content, a preferable photothermographic material having excellent image storability after a developing process, particularly showing remarkably small increase in fogging in irradiation with light can be designed. The distribution of the halogen composition in a grain may be uniform or the halogen composition may be changed stepwise, or it may be changed continuously. Further, a silver halide grain having a core/shell structure can be used preferably. Preferred structure is a twofold to fivefold structure and, more preferably, core/shell grain having a twofold to fourfold structure can be used. A core-high-silver iodide-structure which has a high content of silver iodide in the core portion, and a shell-high-silver iodide-structure which has a high content of silver iodide in the shell portion can also be preferably used. Further, a technique of localizing silver chloride or silver bromide on the surface of a grain as form epitaxial parts can also be preferably used.

45

50

2) Average grain size

55

Concerning the average grain size of the photosensitive silver halide which can be used in the present invention, a mean equivalent spherical diameter of the silver halide is preferably 0.3 μm to 8.0 μm , and more preferably 0.3 μm to 5.0 μm . The term "mean equivalent spherical diameter" used here means an average diameter of a sphere having the same volume as the volume of silver halide grain. As for measuring method, the volume of a grain is calculated from projected area and thickness of individual grains by observation through electron microscope, and thereafter the equivalent spherical diameter is determined by converting the volume to a sphere having the volume equivalent to the obtained volume.

The tabular silver halide grains of the invention preferably have a mean thickness of 0.3 μm or less, more preferably 0.2 μm or less and, further preferably 0.1 μm or less.

The aspect ratio of the tabular silver halide grains of the invention is preferably 2 to 100, and more preferably 5 to 100.

3) Coating amount

The coating amount of the silver halide grains is in a range from 0.5 mol% to 15 mol%, preferably from 0.5 mol% to 12 mol%, further preferably from 0.5 mol% to 10 mol%, still more preferably from 1 mol% to 9 mol%, and particularly preferably from 1 mol% to 7 mol%, per 1 mol of silver contained in the non-photosensitive organic silver salt described below in each case.

4) Method of grain formation

The method of forming photosensitive silver halide is well-known in the relevant art and, for example, methods described in Research Disclosure No. 17029, June 1978 and USP No. 3700458 can be used. Specifically, a method of preparing a photosensitive silver halide by adding a silver-supplying compound and a halogen-supplying compound in a gelatin or other polymer solution and then mixing them with an organic silver salt is used. Further, a method described in JP-A No. 11-119374 (paragraph Nos. 0217 to 0224) and methods described in JP-A Nos. 11-352627 and 2000-347335 are also preferred.

5) Grain form

Silver iodide of the invention typically can assume either a β phase or a γ phase. The term " β phase" described above means a high silver iodide structure having a wurtzite structure of a hexagonal system and the term " γ phase" means a high silver iodide structure having a zinc blende structure of a cubic crystal system.

An average content of γ phase in the present invention is determined by a method presented by C. R. Berry. In the method, an average content of γ phase is calculated from the peak ratio of the intensity owing to γ phase (111) to that owing to β phases (100), (101), and (002) in powder X ray diffraction method. Detail description, for example, is described in Physical Review, volume 161, No.3, p. 848 to 851 (1967).

According to the method of forming tabular grains of silver iodide, preferably used are those described in JP-A Nos. 59-119350 and 59-119344. As for forming dodecahedral grains, tetradecahedral grains, and octahedral grains, the methods described in JP-A Nos. 2002-081020, 2003-287835, and 2003-287836 can be used for reference.

The silver halide having high silver iodide content of the invention can take a complicated form, and as the preferable form, there are listed, for example, connecting grains as shown in R. L. JENKINS et al., J. of Phot. Sci., vol. 28, p164, Fig. 1, (1980). Tabular grains as shown in Fig. 1 of the same literature can also be preferably used. Grains obtained by rounding corners of silver halide grains can also be preferably used. The surface indices (Miller indices) of the outer surface of a photosensitive silver halide grain is not particularly restricted, and it is preferable that the ratio occupied by the [100] face is large, because of showing high spectral sensitization efficiency when a spectral sensitizing dye is adsorbed. The ratio is preferably 50% or more, more preferably, 65% or more and, further preferably, 80% or more. The ratio of the [100] face, Miller indices, can be determined by a method described in T. Tani; J. Imaging Sci., vol. 29, page 165, (1985) utilizing adsorption dependency of the [111] face and [100] face in adsorption of a sensitizing dye.

6) Heavy metal

The photosensitive silver halide grain of the invention can contain metals or complexes of metals belonging to groups 6 to 13 of the periodic table (showing groups 1 to 18). Preferred are metals or complexes of metals belonging to groups 6 to 10. The metal or the center metal of the metal complex from groups 6 to 10 of the periodic table is preferably ferrum, rhodium, ruthenium, or iridium. The metal complex may be used alone, or two or more kinds of complexes comprising identical or different species of metals may be used together. A preferred content is in a range from 1×10^{-9} mol to 1×10^{-3} mol per 1 mol of silver. The heavy metals, metal complexes and the adding method thereof are described in JP-A No. 7-225449, in paragraph Nos. 0018 to 0024 of JP-A No.11-65021 and in paragraph Nos. 0227 to 0240 of JP-A No. 11-119374.

In the present invention, a silver halide grain having a hexacyano metal complex present on the outermost surface of the grain is preferred. The hexacyano metal complex includes, for example, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Ru}(\text{CN})_6]^{4-}$, $[\text{Os}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Rh}(\text{CN})_6]^{3-}$, $[\text{Ir}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{CN})_6]^{3-}$, and $[\text{Re}(\text{CN})_6]^{3-}$. In the invention, hexacyano Fe complex is preferred.

Since the hexacyano complex exists in ionic form in an aqueous solution, paired cation is not important and alkali metal ion such as sodium ion, potassium ion, rubidium ion, cesium ion and lithium ion, ammonium ion, alkyl ammonium ion (for example, tetramethyl ammonium ion, tetraethyl ammonium ion, tetrapropyl ammonium ion, and tetra(n-butyl) ammonium ion), which are easily miscible with water and suitable to precipitation operation of a silver halide emulsion are preferably used.

The hexacyano metal complex can be added while being mixed with water, as well as a mixed solvent of water and an appropriate organic solvent miscible with water (for example, alcohols, ethers, glycols, ketones, esters, or

amides) or gelatin.

The addition amount of the hexacyano metal complex is preferably from 1×10^{-5} mol to 1×10^{-2} mol and, more preferably from 1×10^{-4} mol to 1×10^{-3} mol, per 1 mol of silver in each case.

In order to allow the hexacyano metal complex to be present on the outermost surface of a silver halide grain, the hexacyano metal complex is directly added in any stage of: after completion of addition of an aqueous solution of silver nitrate used for grain formation, before completion of emulsion formation step prior to a chemical sensitization step, of conducting chalcogen sensitization such as sulfur sensitization, selenium sensitization and tellurium sensitization or noble metal sensitization such as gold sensitization, during a washing step, during a dispersion step and before a chemical sensitization step. In order not to grow the fine silver halide grain, the hexacyano metal complex is rapidly added preferably after the grain is formed, and it is preferably added before completion of the emulsion formation step.

Addition of the hexacyano complex may be started after addition of 96% by weight of an entire amount of silver nitrate to be added for grain formation, more preferably started after addition of 98% by weight and, particularly preferably, started after addition of 99% by weight.

When any of the hexacyano metal complex is added after addition of an aqueous silver nitrate just before completion of grain formation, it can be adsorbed to the outermost surface of the silver halide grain and most of them form an insoluble salt with silver ions on the surface of the grain. Since silver hexacyanoferrate (II) is a less soluble salt than AgI, re-dissolution with fine grains can be prevented and fine silver halide grains with smaller grain size can be prepared.

Metal atoms that can be contained in the silver halide grain used in the invention (for example, $[\text{Fe}(\text{CN})_6]^{4-}$), desalting method of a silver halide emulsion and chemical sensitizing method are described in paragraph Nos. 0046 to 0050 of JP-A No.11-84574, in paragraph Nos. 0025 to 0031 of JP-A No.11-65021, and paragraph Nos. 0242 to 0250 of JP-A No.11-119374.

7) Gelatin

As the gelatin contained the photosensitive silver halide emulsion used in the invention, various kinds of gelatins can be used. It is necessary to maintain an excellent dispersion state of a photosensitive silver halide emulsion in an organic silver salt containing coating solution, and a low molecular weight-gelatin having a molecular weight of 10,000 to 1,000,000 is preferably used. And phthalated gelatin is also preferably used. These gelatins may be used at grain formation step or at the time of dispersion after desalting treatment and it is preferably used at grain formation step.

8) Chemical sensitization

The photosensitive silver halide in the present invention can be used without chemical sensitization, but is preferably chemically sensitized by at least one of chalcogen sensitizing method, gold sensitizing method and reduction sensitizing method. As the chalcogen sensitizing method, sulfur sensitizing method, selenium sensitizing method, and tellurium sensitizing method are exemplary techniques.

In the present invention, it is preferred to use water-soluble thiocyanate salt (for example, potassium thiocyanate, sodium thiocyanate, ammonium thiocyanate, or the like) at chemical sensitization, particularly at chalcogen sensitization or gold sensitization. The addition amount thereof may be selected arbitrary, but is preferably 1×10^{-4} mol or more, more preferably 1×10^{-3} mol or more, further preferably in a range of from 2×10^{-3} mol to 8×10^{-1} mol, further preferably from 3×10^{-3} mol to 2×10^{-1} mol, and most preferably from 5×10^{-3} mol to 1×10^{-1} mol, per 1 mol of silver contained in silver halide in each case.

In sulfur sensitization, unstable sulfur compounds can be used. Such unstable sulfur compounds are described in *Chimie et Physique Photographique*, written by P. Graffkides, (Paul Momtel, 5th ed., 1987) and *Research Disclosure* (vol. 307, Item 307105), and the like.

As typical examples of sulfur sensitizer, known sulfur compounds such as thiosulfates (e.g., hypo), thioureas (e.g., diphenylthiourea, triethylthiourea, N-ethyl-N'-(4-methyl-2-thiazolyl)thiourea, and carboxymethyltrimethylthiourea), thioamides (e.g., thioacetamide), rhodanines (e.g., diethylrhodanine, and 5-benzylidene-N-ethylrhodanine), phosphinesulfides (e.g., trimethylphosphinesulfide), thiohydantoins, 4-oxo-oxazolidin-2-thione derivatives, disulfides or polysulfides (e.g., dimorphorinedisulfide, cystine, and hexathiocan-thione), polythionates, sulfur element, and active gelatin can be used. Specifically, thiosulfates, thioureas, and rhodanines are preferred.

In selenium sensitization, unstable selenium compounds can be used. These unstable selenium compounds are described in JP-B Nos. 43-13489 and 44-15748, JP-A Nos. 4-25832, 4-109340, 4-271341, 5-40324, 5-11385, 6-51415, 6-175258, 6-180478, 6-208186, 6-208184, 6-317867, 7-92599, 7-98483, and 7-140579, and the like.

As typical examples of selenium sensitizer, colloidal metal selenide, selenoureas (e.g., N,N-dimethylselenourea, trifluoromethylcarbonyl-trimethylselenourea and acetyltrimethylselenourea), selenamides (e.g., selenamide and N,N-diethylphenylselenamide), phosphineselenides (e.g., triphenylphosphineselenide and pentafluorophenyltriphenylphosphineselenide), selenophosphates (e.g., tri-p-tolylselenophosphate and tri-n-butylselenophosphate), selenoketones (e.g., selenobenzophenone), isoselenocyanates, selenocarbonic acids, selenoesters, and dia-

cylselenides can be used. Furthermore, non-unstable selenium compounds such as selenious acid, selenocyanic acid, selenazoles, and selenides described in JP-B Nos. 46-4553 and 52-34492 can also be used. Specifically, phosphineselenides, selenoureas, and salts of selenocyanic acids are preferred.

In the tellurium sensitization, unstable tellurium compounds are used. Unstable tellurium compounds described in JP-A Nos. 4-224595, 4-271341, 4-333043, 5-303157, 6-27573, 6-175258, 6-180478, 6-208186, 6-208184, 6-317867, 7-140579, 7-301879, 7-301880 and the like, can be used as tellurium sensitizer.

As typical examples of tellurium sensitizer, phosphinetellurides (e.g., butyl-diisopropylphosphinetelluride, tributylphosphinetelluride, tributoxyphosphinetelluride, and ethoxy-diphenylphosphinetelluride), diacyl(di)tellurides (e.g., bis(diphenylcarbamoyl)ditelluride, bis(N-phenyl-N-methylcarbamoyl)ditelluride, bis(N-phenyl-N-methylcarbamoyl)ditelluride, bis(N-phenyl-N-benzylcarbamoyl)telluride, and bis(ethoxycarbonyl)telluride), telluroureas (e.g., N,N'-dimethylethylenetellurourea and N,N'-diphenylethylenetellurourea), telluramides, telluroesters are used.

Specifically, diacyl(di)tellurides and phosphinetellurides are preferred. Especially, the compounds described in paragraph No. 0030 of JP-A No. 11-65021 and compounds represented by formulae (II), (III), and (IV) in JP-A No. 5-313284 are preferred.

Specifically, as for the chalcogen sensitization of the invention, selenium sensitization and tellurium sensitization are preferred, and tellurium sensitization is particularly preferred.

In gold sensitization, gold sensitizer described in *Chimie et Physique Photographique*, written by P. Grafkides, (Paul Momtel, 5th ed., 1987) and Research Disclosure (vol. 307, Item 307105) can be used. More specifically, chloroauric acid, potassium chloroaurate, potassium aurithiocyanate, gold sulfide, gold selenide and the like can be used. In addition to these, the gold compounds described in USP Nos. 2642361, 5049484, 5049485, 5169751, and 5252455, Belg. Patent No. 691857, and the like can also be used. Noble metal salts except gold such as platinum, palladium, iridium and so on described in *Chimie et Physique Photographique*, written by P. Grafkides, (Paul Momtel, 5th ed., 1987) and Research Disclosure (vol. 307, Item 307105) can also be used.

The gold sensitization can be used independently, but it is preferably used in combination with the above chalcogen sensitization. Specifically, these sensitizations are gold-sulfur sensitization (gold-plus-sulfur sensitization), gold-selenium sensitization, gold-tellurium sensitization, gold-sulfur-selenium sensitization, gold-sulfur-tellurium sensitization, gold-selenium-tellurium sensitization, and gold-sulfur-selenium-tellurium sensitization.

In the invention, chemical sensitization can be applied in the presence of silver halide solvent. Specifically, thiocyanates (e.g., potassium thiocyanate), thioethers (e.g., compounds described in USP Nos. 3021215 and 3271157, JP-B No. 58-30571 and JP-A No. 60-136736, especially, 3,6-dithia-1,8-octanediol), tetra-substituted thioureas (e.g., compounds described in JP-B No. 59-11892 and USP No. 4221863, especially, tetramethylthiourea), thione compounds described in JP-B No. 60-11341, selenoethers described in JP-B No. 63-29727, USP No. 4782013, and the like, telluroether compounds described in JP-A No. 2-118566, and sulfites can be described. Particularly among them, thiocyanates, thioethers, tetra-substituted thioureas, and thione compounds are preferable, and more preferable among them is thiocyanates. The addition amount of silver halide solvent preferably is from about 10^{-5} mol to 10^{-3} mol per 1 mol of silver halide.

In the invention, chemical sensitization can be applied at any time so long as it is after grain formation and before coating and it can be applied, after desalting, (1) before spectral sensitization, (2) simultaneously with spectral sensitization, (3) after spectral sensitization, (4) just before coating, or the like.

The addition amount of chalcogen sensitizer used in the invention may vary depending on the silver halide grain used, the chemical ripening condition, and the like, and it is about 10^{-8} mol to 10^{-1} mol, and preferably, about 10^{-7} mol to 10^{-2} mol, per 1 mol of silver halide.

Similarly, the addition amount of the gold sensitizer used in the invention may vary depending on various conditions and it is generally about 10^{-7} mol to 10^{-2} mol and, more preferably, 10^{-6} mol to 5×10^{-3} mol, per 1 mol of silver halide. There is no particular restriction on the condition for the chemical sensitization and, appropriately, the pAg is 8 or lower, preferably, 7.0 or lower, more preferably, 6.5 or lower and, particularly preferably, 6.0 or lower, and the pAg is 1.5 or higher, preferably, 2.0 or higher and, particularly preferably, 2.5 or higher; the pH is 3 to 10, preferably, 4 to 9; and the temperature is at 20°C to 95°C, preferably, 25°C to 80°C.

In the invention, reduction sensitization can also be used in combination with the chalcogen sensitization or the gold sensitization. It is specifically preferred to use in combination with the chalcogen sensitization.

As the specific compound for the reduction sensitization, ascorbic acid, thiourea dioxide, or dimethylamine borane is preferred, as well as use of stannous chloride, aminoimino methane sulfonic acid, hydrazine derivatives, borane compounds, silane compounds, polyamine compounds, and the like are preferred. The reduction sensitizer may be added at any stage in the photosensitive emulsion production process from crystal growth to the preparation step just before coating. Further, it is preferred to apply reduction sensitization by ripening while keeping the pH to 8 or higher and the pAg to 4 or lower for the emulsion, and it is also preferred to apply reduction sensitization by introducing a single addition portion of silver ions during grain formation.

The addition amount of the reduction sensitizer may also vary depending on various conditions and it is gen-

erally about 10^{-7} mol to 10^{-1} mol and, more preferably, 10^{-6} mol to 5×10^{-2} mol per 1 mol of silver halide.

In the silver halide emulsion used in the invention, a thiosulfonate compound may be added by the method shown in EP-A No. 293917.

The photosensitive silver halide grain in the invention is preferably chemically sensitized by at least one method of gold sensitizing method and chalcogen sensitizing method for the purpose of designing a high-sensitivity photothermographic material.

9) Compound that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons

The photothermographic material of the invention preferably contains a compound that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons. The said compound can be used alone or in combination with various chemical sensitizers described above to increase the sensitivity of silver halide.

As the compound that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons is a compound selected from the following Groups 1 and 2.

(Group 1) a compound that can be one-electron-oxidized to provide a one-electron oxidation product which further releases one or more electrons, due to being subjected to a subsequent bond cleavage reaction;

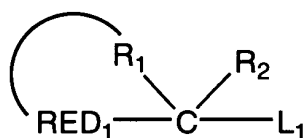
(Group 2) a compound that can be one-electron-oxidized to provide a one-electron oxidation product, which further releases one or more electrons after being subjected to a subsequent bond formation.

The compound of Group 1 will be explained below.

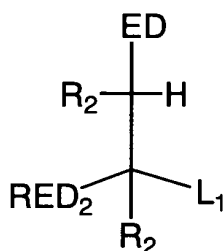
In the compound of Group 1, as for a compound that can be one-electron-oxidized to provide a one-electron oxidation product which further releases one electron, due to being subjected to a subsequent bond cleavage reaction, specific examples include examples of compound referred to as "one photon two electrons sensitizer" or "deprotonating electron-donating sensitizer" described in JP-A No. 9-211769 (Compound PMT-1 to S-37 in Tables E and F, pages 28 to 32); JP-A No. 9-211774; JP-A No. 11-95355 (Compound INV 1 to 36); JP-W No. 2001-500996 (Compound 1 to 74, 80 to 87, and 92 to 122); USP Nos. 5747235 and 5747236; EP No. 786692A1 (Compound INV 1 to 35); EP No. 893732A1; USP Nos. 6054260 and 5994051; etc. Preferred ranges of these compounds are the same as the preferred ranges described in the quoted specifications.

In the compound of Group 1, as for a compound that can be one-electron-oxidized to provide a one-electron oxidation product which further releases one or more electrons, due to being subjected to a subsequent bond cleavage reaction, specific examples include the compounds represented by formula (1) (same as formula (1) described in JP-A No. 2003-114487), formula (2) (same as formula (2) described in JP-A No. 2003-114487), formula (3) (same as formula (1) described in JP-A No. 2003-114488), formula (4) (same as formula (2) described in JP-A No. 2003-114488), formula (5) (same as formula (3) described in JP-A No. 2003-114488), formula (6) (same as formula (1) described in JP-A No. 2003-75950), formula (7) (same as formula (2) described in JP-A No. 2003-75950), and formula (8), and the compound represented by formula (9) among the compounds which can undergo the chemical reaction represented by reaction formula (1). And the preferable range of these compounds is the same as the preferable range described in the quoted specification.

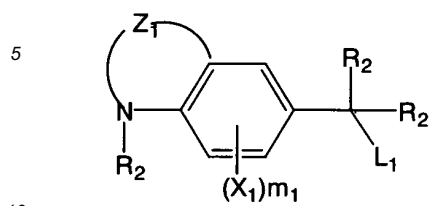
Formula (1)



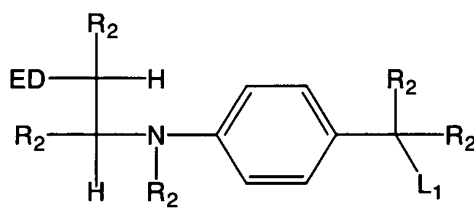
Formula (2)



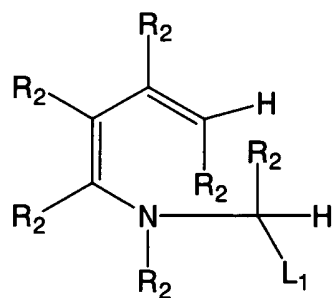
Formula (3)



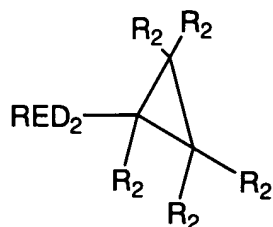
Formula (4)



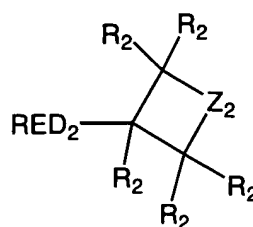
Formula (5)



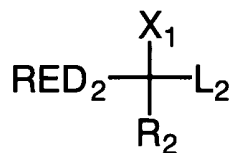
Formula (6)



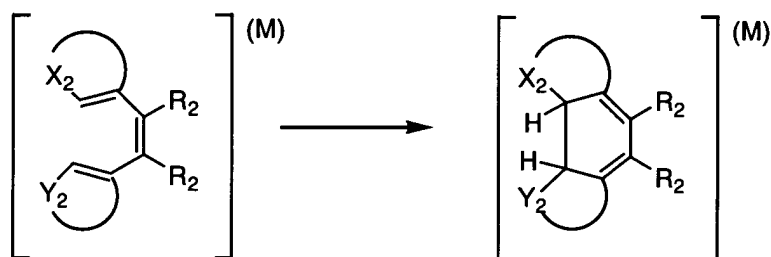
Formula (7)



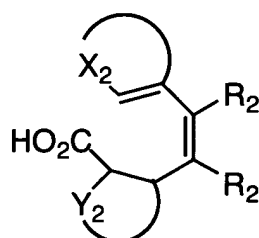
Formula (8)



Reaction formula (1)



Formula (9)



30

In the formulae, RED₁ and RED₂ represent a reducible group. R₁ represents a nonmetallic atomic group forming a cyclic structure equivalent to a tetrahydro derivative or an octahydro derivative of a 5 or 6-membered aromatic ring (including a hetero aromatic ring) with a carbon atom (C) and RED₁. R₂ represents a hydrogen atom or a substituent. In the case where plural R₂s exist in a same molecule, these may be identical or different from each other. L₁ represents a leaving group. ED represents an electron-donating group. Z₁ represents an atomic group capable to form a 6-membered ring with a nitrogen atom and two carbon atoms of a benzene ring. X₁ represents a substituent, and m₁ represents an integer of 0 to 3. Z₂ represents one selected from -CR₁₁R₁₂⁻, -NR₁₃⁻, or -O-. R₁₁ and R₁₂ each independently represent a hydrogen atom or a substituent. R₁₃ represents one selected from a hydrogen atom, an alkyl group, an aryl group, and a heterocyclic group. X₁ represents one selected from an alkoxy group, an aryloxy group, a heterocyclic oxy group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylamino group, an arylamino group, and a heterocyclic amino group. L₂ represents a carboxyl group or a salt thereof, or a hydrogen atom. X₂ represents a group to form a 5-membered heterocycle with C=C. M represents one selected from a radical, a radical cation, and a cation.

40

Next, the compound of Group 2 is explained.

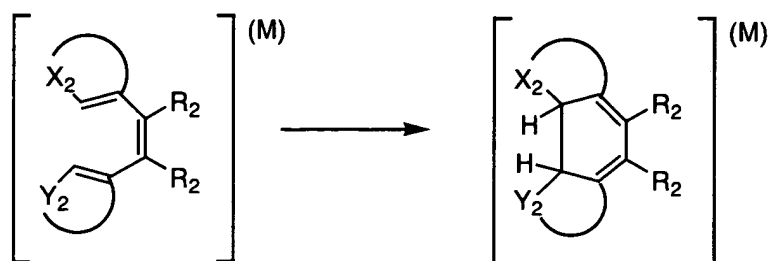
45

In the compound of Group 2, as for a compound that can be one-electron-oxidized to provide a one-electron oxidation product which further releases one or more electrons, after being subjected to a subsequent bond cleavage reaction, specific examples can include the compound represented by formula (10) (same as formula (1) described in JP-A No.2003-140287), and the compound represented by formula (11) which can undergo the chemical reaction represented by reaction formula (1). The preferable range of these compounds is the same as the preferable range described in the quoted specification.

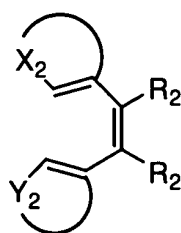
Formula (10)



Reaction formula (1)



Formula (11)



30

In the formulae described above, X represents a reducible group which can be one-electron-oxidized. Y represents a reactive group containing a carbon-carbon double bond part, a carbon-carbon triple bond part, an aromatic group part or benzo-condensed nonaromatic heterocyclic group which can react with one-electron-oxidized product formed by one-electron-oxidation of X to form a new bond. L_2 represents a linking group to link X and Y. R_2 represents a hydrogen atom or a substituent. In the case where plural R_2 s exist in a same molecule, these may be identical or different from each other. X_2 represents a group to form a 5-membered heterocycle with C=C. Y_2 represents a group to form a 5 or 6-membered aryl group or heterocyclic group with C=C. M represents one selected from a radical, a radical cation, and a cation.

35

The compounds of Groups 1 and 2 preferably are "the compound having an adsorptive group to silver halide in a molecule" or "the compound having a partial structure of a spectral sensitizing dye in a molecule". The representative adsorptive group to silver halide is the group described in JP-A No. 2003-156823, page 16 right, line 1 to page 17 right, line 12. A partial structure of a spectral sensitizing dye is the structure described in JP-A No. 2003-156823, page 17 right, line 34 to page 18 right, line 6.

40

As the compound of Groups 1 and 2, "the compound having at least one adsorptive group to silver halide in a molecule" is more preferred, and "the compound having two or more adsorptive groups to silver halide in a molecule" is further preferred. In the case where two or more adsorptive groups exist in a single molecule, those adsorptive groups may be identical or different with each other.

45

As preferable adsorptive group, a nitrogen-containing heterocyclic group substituted by a mercapto group (e.g., a 2-mercaptothiazole group, a 3-mercapto-1,2,4-triazole group, a 5-mercaptotetrazole group, a 2-mercapto-1,3,4-oxadiazole group, a 2-mercaptobenzoxazole group, a 2-mercaptobenzothiazole group, a 1,5-dimethyl-1,2,4-triazolium-3-thiolate group, or the like) or a nitrogen-containing heterocyclic group having -NH-group as a partial structure of heterocycle capable to form a silver imidate ($>NAg$) (e.g., a benzotriazole group, a benzimidazole group, an indazole group, or the like) are described. A 5-mercaptotetrazole group, a 3-mercapto-1,2,4-triazole group and a benzotriazole group are particularly preferable and a 3-mercapto-1,2,4-triazole group and a 5-mercaptotetrazole group are most preferable.

50

As an adsorptive group, the group which has two or more mercapto groups as a partial structure in a molecule is also particularly preferable. Herein, a mercapto group (-SH) may become a thione group in the case where it can tautomerize. Preferred examples of an adsorptive group having two or more mercapto groups as a partial structure (dimercapto-substituted nitrogen-containing heterocyclic group and the like) are a 2,4-dimercaptopyrimidine group, a 2,4-dimercaptotriazine group, and a 3,5-dimercapto-1,2,4-triazole group.

55

Further, a quaternary salt structure of nitrogen or phosphorus is also preferably used as an adsorptive group.

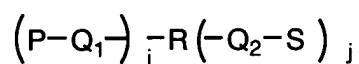
As typical quaternary salt structure of nitrogen, an ammonio group (a trialkylammonio group, a dialkylarylammonio group, a dialkylheteroarylammonio group, an alkyldiarylammonio group, an alkyldiheteroarylammonio group, or the like) and a nitrogen-containing heterocyclic group containing quaternary nitrogen atom can be used. As a quaternary salt structure of phosphorus, a phosphonio group (a trialkylphosphonio group, a dialkylarylphosphonio group, a dialkylheteroarylphosphonio group, an alkyldiarylphosphonio group, an alkyldiheteroarylphosphonio group, a triarylphosphonio group, a triheteroarylphosphonio group, or the like) is described. A quaternary salt structure of nitrogen is more preferably used and a 5 or 6-membered aromatic heterocyclic group containing a quaternary nitrogen atom is further preferably used.

Particularly preferably, a pyridinio group, a quinolinio group and an isoquinolinio group are used. These nitrogen-containing heterocyclic groups containing a quaternary nitrogen atom may have any substituent.

Examples of counter anion of quaternary salt are a halogen ion, carboxylate ion, sulfonate ion, sulfate ion, perchlorate ion, carbonate ion, nitrate ion, BF_4^- , PF_6^- , Ph_4B^- , and the like. In the case where the group having negative charge at carboxylate group and the like exists in a molecule, an inner salt may be formed with it. As a counter ion outside of a molecule, chloro ion, bromo ion and methanesulfonate ion are particularly preferable.

The preferred structure of the compound represented by Groups 1 and 2 having a quaternary salt of nitrogen or phosphorus as an adsorptive group is represented by formula (X).

Formula (X)



In formula (X), P and R each independently represent a quaternary salt structure of nitrogen or phosphorus, which is not a partial structure of a spectral sensitizing dye. Q_1 and Q_2 each independently represent a linking group and typically represent a single bond, an alkylene group, an arylene group, a heterocyclic group, $-\text{O}-$, $-\text{S}-$, $-\text{NR}_\text{N}$, $-\text{C}(=\text{O})-$, $-\text{SO}_2-$, $-\text{SO}-$, $-\text{P}(=\text{O})-$ and the group which consists of combination of these groups. Herein, R_N represents one selected from a hydrogen atom, an alkyl group, an aryl group, and a heterocyclic group. S represents a residue which is obtained by removing one atom from the compound represented by Group 1 or 2. i and j are an integer of one or more and are selected in a range of $i+j=2$ to 6. The case where i is 1 to 3 and j is 1 to 2 is preferable, the case where i is 1 or 2 and j is 1 is more preferable, and the case where i is 1 and j is 1 is particularly preferable. The compound represented by formula (X) preferably has 10 to 100 carbon atoms in total, more preferably 10 to 70 carbon atoms, further preferably 11 to 60 carbon atoms, and particularly preferably 12 to 50 carbon atoms in total.

The compounds of Groups 1 and 2 may be used at any time during preparation of the photosensitive silver halide emulsion and production of the photothermographic material. For example, the compound may be used in a photosensitive silver halide grain formation step, in a desalting step, in a chemical sensitization step, before coating, etc. The compound may be added in several times during these steps. The compound is preferably added after the photosensitive silver halide grain formation step and before the desalting step; in the chemical sensitization step (just before the chemical sensitization to immediately after the chemical sensitization); or before coating. The compound is more preferably added just before the chemical sensitization step to before mixing with the non-photosensitive organic silver salt.

It is preferred that the compound of Groups 1 and 2 used in the invention is dissolved in water, a water-soluble solvent such as methanol or ethanol, or a mixed solvent thereof. In the case where the compound is dissolved in water and solubility of the compound is increased by increasing or decreasing a pH value of the solvent, the pH value may be increased or decreased to dissolve and add the compound.

The compound of Groups 1 and 2 used in the invention is preferably used to the image forming layer comprising the photosensitive silver halide and the non-photosensitive organic silver salt. The compound may be added to a surface protective layer or an intermediate layer, as well as the image forming layer comprising the photosensitive silver halide and the non-photosensitive organic silver salt, to be diffused to the image forming layer in the coating step. The compound may be added before or after addition of a sensitizing dye. Each compound is contained in the image forming layer preferably in an amount of 1×10^{-9} mol to 5×10^{-1} mol, more preferably 1×10^{-8} mol to 5×10^{-2} mol, per 1 mol of silver halide.

10) Compound having adsorptive group and reducible group

The photothermographic material of the present invention preferably comprises a compound having an adsorptive group and a reducible group in a molecule. It is preferred that the compound having an adsorptive group and a reducible group used in the invention is represented by the following formula (I).

Formula (I)

A-(W)_n-B

5

In formula (I), A represents a group capable of adsorption to a silver halide (hereafter, it is called an adsorptive group), W represents a divalent linking group, n represents 0 or 1, and B represents a reducible group.

10 In formula (I), the adsorptive group represented by A is a group to adsorb directly to a silver halide or a group to promote adsorption to a silver halide. As typical examples, a mercapto group (or a salt thereof), a thione group (-C(=S)-), a nitrogen atom, a heterocyclic group containing at least one atom selected from a nitrogen atom, a sulfur atom, a selenium atom and a tellurium atom, a sulfide group, a disulfide group, a cationic group, an ethynyl group and the like are described.

15 The mercapto group as an adsorptive group means a mercapto group (and a salt thereof) itself and simultaneously more preferably represents a heterocyclic group or an aryl group or an alkyl group substituted by at least one mercapto group (or a salt thereof). Herein, as the heterocyclic group, a monocyclic or a condensed aromatic or nonaromatic heterocyclic group having at least a 5 to 7-membered ring, e.g., an imidazole ring group, a thiazole ring group, an oxazole ring group, a benzimidazole ring group, a benzothiazole ring group, a benzoxazole ring group, a triazole ring group, a thiadiazole ring group, an oxadiazole ring group, a tetrazole ring group, a purine ring group, a pyridine ring group, a quinoline ring group, an isoquinoline ring group, a pyrimidine ring group, a triazine ring group, and the like are described. A heterocyclic group having a quaternary nitrogen atom may also be adopted, wherein a mercapto group as a substituent may dissociate to form a mesoion. As a counter ion, whereby a mercapto group forms a salt thereof, a cation such as an alkali metal, an alkali earth metal, a heavy metal and the like (Li⁺, Na⁺, K⁺, Mg²⁺, Ag⁺, Zn²⁺ and the like), an ammonium ion, a heterocyclic group comprising a quaternary nitrogen atom, a phosphonium ion, and the like are described.

25 Further, the mercapto group as an adsorptive group may become a thione group by a tautomerization.

The thione group as an adsorptive group may also contain a chain or a cyclic thioamide group, a thioureido group, a thiouretane group or a dithiocarbamate ester group.

30 The heterocyclic group, as an adsorptive group, containing at least one atom selected from a nitrogen atom, a sulfur atom, a selenium atom and a tellurium atom represents a nitrogen-containing heterocyclic group having -NH- group, as a partial structure of heterocycle, capable to form a silver iminate (>NAg) or a heterocyclic group, having an -S- group, a -Se- group, a -Te- group or an =N- group as a partial structure of heterocycle, and capable to coordinate to a silver ion by a chelate bonding. As the former examples, a benzotriazole group, a triazole group, an indazole group, a pyrazole group, a tetrazole group, a benzimidazole group, an imidazole group, a purine group, and the like are described. As the latter examples, a thiophene group, a thiazole group, an oxazole group, a benzothiophene group, a benzothiazole group, a benzoxazole group, a thiadiazole group, an oxadiazole group, a triazine group, a selenoazole group, a benzoselenazole group, a tellurazole group, a benzotellurazole group, and the like are described.

The sulfide group or disulfide group as an adsorptive group contains all groups having "-S-" or "-S-S-" as a partial structure.

40 The cationic group as an adsorptive group means the group containing a quaternary nitrogen atom, such as an ammonio group or nitrogen-containing heterocyclic group including a quaternary nitrogen atom. As examples of the heterocyclic group containing a quaternary nitrogen atom, a pyridinio group, a quinolinio group, an isoquinolinio group, an imidazolium group, and the like are described.

45 The ethynyl group as an adsorptive group means -C≡CH group and the said hydrogen atom may be substituted.

The adsorptive group described above may have any substituent.

Further, as typical examples of an adsorptive group, the compounds described in pages 4 to 7 in the specification of JP-A No.11-95355 are described.

50 As an adsorptive group represented by A in formula (I), a mercapto-substituted heterocyclic group (e.g., a 2-mercaptothiadiazole group, a 2-mercapto-5-aminothiadiazole group, a 3-mercapto-1,2,4-triazole group, a 5-mercaptotetrazole group, a 2-mercapto-1,3,4-oxadiazole group, a 2-mercaptobenzimidazole group, a 1,5-dimethyl-1,2,4-triazolium-3-thiolate group, a 2,4-dimercaptopyrimidine group, a 2,4-dimercaptotriazine group, a 3,5-dimercapto-1,2,4-triazole group, a 2,5-dimercapto-1,3-thiazole group, or the like) or a nitrogen-containing heterocyclic group having a -NH- group capable to form an imino-silver (>NAg) as a partial structure of heterocycle (e.g., a benzotriazole group, a benzimidazole group, an indazole group, or the like) is preferable, and more preferable as an adsorptive group is a 2-mercaptobenzimidazole group or a 3,5-dimercapto-1,2,4-triazole group.

55 In formula (I), W represents a divalent linking group. The said linking group may be any divalent linking group, as far as it does not give a bad effect toward photographic properties. For example, a divalent linking group which

includes a carbon atom, a hydrogen atom, an oxygen atom, a nitrogen atom, or a sulfur atom can be used. As typical examples, an alkylene group having 1 to 20 carbon atoms (e.g., a methylene group, an ethylene group, a trimethylene group, a tetramethylene group, a hexamethylene group, or the like), an alkenylene group having 2 to 20 carbon atoms, an alkynylene group having 2 to 20 carbon atoms, an arylene group having 6 to 20 carbon atoms (e.g., a phenylene group, a naphthylene group, or the like), -CO-, -SO₂-, -O-, -S-, -NR₁-, and the combination of these linking groups are described. Herein, R₁ represents a hydrogen atom, an alkyl group, a heterocyclic group, or an aryl group.

The linking group represented by W may have any substituent.

In formula (I), a reducible group represented by B represents the group capable to reduce a silver ion. As the examples, a formyl group, an amino group, a triple bond group such as an acetylene group, a propargyl group and the like, a mercapto group, and residues which are obtained by removing one hydrogen atom from hydroxylamines, hydroxamic acids, hydroxyureas, hydroxyurethanes, hydroxysemicarbazides, reductones (reductone derivatives are contained), anilines, phenols (chroman-6-ols, 2,3-dihydrobenzofuran-5-ols, aminophenols, sulfonamidophenols and polyphenols such as hydroquinones, catechols, resorcinols, benzenetriols, bisphenols are contained), acylhydrazines, carbamoylhydrazines, 3-pyrazolidones, and the like can be described. They may have any substituent.

The oxidation potential of a reducible group represented by B in formula (I) can be measured by using the measuring method described in Akira Fujishima, "DENKIKAGAKU SOKUTEIHO" (pages 150 to 208, GIHODO SHUPPAN), and The Chemical Society of Japan, "ZIKKEN KAGAKUKOZA", 4th ed. (vol. 9, pages 282 to 344, MARUZEN). For example, the method of rotating disc voltammetry can be used; namely the sample is dissolved in the solution (methanol : pH 6.5 Britton-Robinson buffer = 10% : 90% (% by volume)) and after deaerated by nitrogen gas for 10 minutes, the voltamograph can be measured under the condition of 1000 rotations/minute, the sweep rate 20 mV/second, at 25°C by using a rotating disc electrode (RDE) made by glassy carbon as a working electrode, a platinum electrode as a counter electrode and a saturated calomel electrode as a reference electrode. The half wave potential (E_{1/2}) can be calculated by that obtained voltamograph.

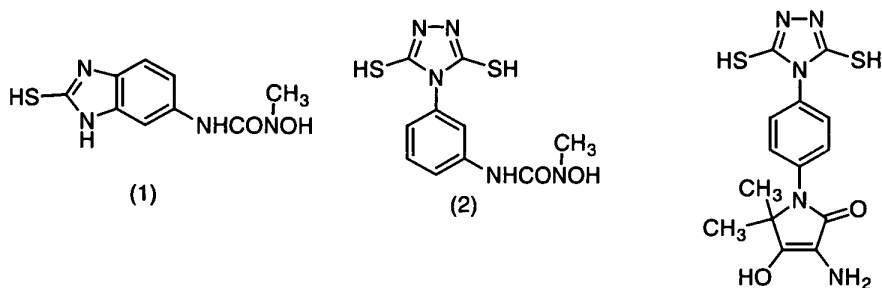
When a reducible group represented by B in the present invention is measured by the method described above, an oxidation potential is preferably in a range of about -0.3 V to about 1.0 V, more preferably about -0.1 V to about 0.8 V, and particularly preferably about 0 V to about 0.7 V.

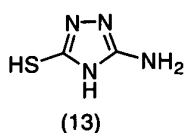
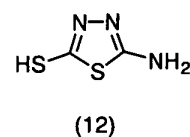
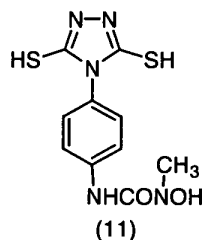
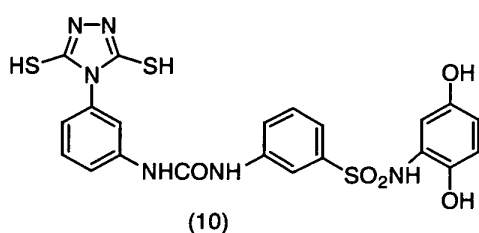
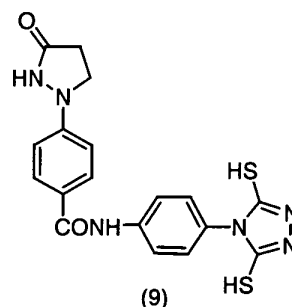
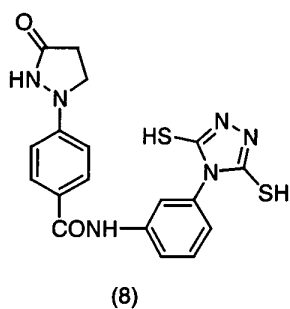
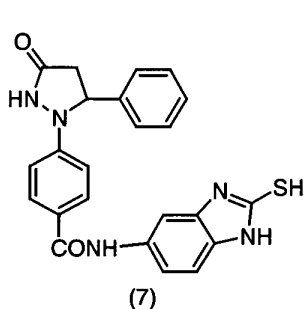
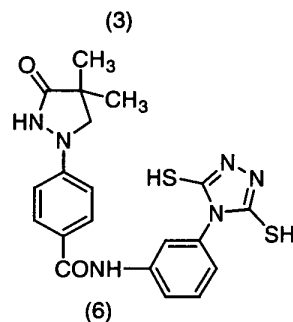
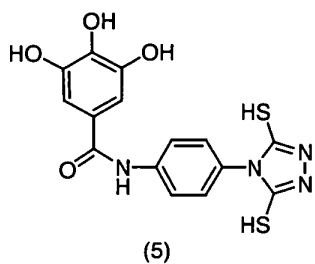
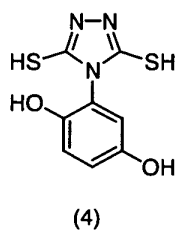
In formula (I), a reducible group represented by B is preferably a residue which is obtained by removing one hydrogen atom from hydroxylamines, hydroxamic acids, hydroxyureas, hydroxysemicarbazides, reductones, phenols, acylhydrazines, carbamoylhydrazines, 3-pyrazolidones, or the like.

The compound of formula (I) in the present invention may have the ballasted group or polymer chain in it generally used in the non-moving photographic additives as a coupler. And as a polymer, for example, the polymer described in JP-A No. 1-100530 can be selected.

The compound of formula (I) in the present invention may be bis or tris type of compound. The molecular weight of the compound represented by formula (I) in the present invention is preferably 100 to 10,000 and more preferably 120 to 1,000 and particularly preferably 150 to 500.

The examples of the compound represented by formula (I) in the present invention are shown below, but the present invention is not limited in these.





45 Further, example compounds 1 to 30 and 1⁻¹ to 1⁻⁷⁷ shown in EP No. 1308776A2, pages 73 to 87 are also described as preferable examples of the compound having an adsorptive group and a reducible group according to the invention.

50 These compounds can be easily synthesized by any known method. The compound of formula (I) in the present invention can be used alone, but it is preferred to use two or more kinds of the compounds in combination. When two or more kinds of the compounds are used in combination, those may be added to the same layer or the different layers, whereby adding methods may be different from each other.

55 The compound represented by formula (I) in the present invention preferably is added to an image forming layer and more preferably is to be added at an emulsion preparing process. In the case, where these compounds are added at an emulsion preparing process, these compounds may be added at any step in the process. For example, the compounds may be added during the silver halide grain forming step, the step before starting of desalting step, the desalting step, the step before starting of chemical ripening, the chemical ripening step, the step before preparing a final emulsion, or the like. Also, the addition can be performed in plural times during these processes. It is preferred to be added in an image forming layer, but may be added in a surface protective layer

or an intermediate layer adjacent to the image forming layer, as well as the image forming layer, to be diffused at the coating step.

The preferred addition amount is largely dependent on the adding method described above or the kind of the compound. It is generally 1×10^{-6} mol to 1 mol, preferably 1×10^{-5} mol to 5×10^{-1} mol, and more preferably 1×10^{-4} mol to 1×10^{-1} mol, per 1 mol of photosensitive silver halide in each case.

The compound represented by formula (I) in the present invention can be added by dissolving in water or water-soluble solvent such as methanol, ethanol or the like, or a mixed solution thereof. At this time, the pH may be arranged suitably by an acid or an alkaline and a surfactant can coexist. Further, these compounds may be added as an emulsified dispersion by dissolving them in an organic solvent having a high boiling point and also may be added as a solid dispersion.

11) Sensitizing dye

As the sensitizing dye applicable in the invention, those capable of spectrally sensitizing silver halide grains in a desired wavelength region upon adsorption to silver halide grains having spectral sensitivity suitable to the spectral characteristic of an exposure light source can be advantageously selected. Particularly, the photothermographic material of the invention is preferably spectrally sensitized to have a spectral sensitive peak in a range of 600 nm to 900 nm, or in a range of 300 nm to 500 nm. The sensitizing dyes and the adding method are disclosed, for example, in JP-A No. 11-65021 (paragraph Nos. 0103 to 0109), as a compound represented by the formula (II) in JP-A No. 10-186572, dyes represented by the formula (I) in JP-A No. 11-119374 (paragraph No. 0106), dyes described in USP Nos. 5510236 and 3871887 (Example 5), dyes disclosed in JP-A Nos. 2-96131 and 59-48753, as well as in page 19, line 38 to page 20, line 35 of EP No. 0803764A1, and in JP-A Nos. 2001-272747, 2001-290238, and 2002-23306. These sensitizing dyes may be used alone or, two or more kinds of them may be used in combination.

In the invention, the sensitizing dye may be added at any amount according to the properties of sensitivity and fog, but it is preferably added from 10^{-6} mol to 1 mol, and more preferably from 10^{-4} mol to 10^{-1} mol, per 1 mol of silver halide in the image forming layer.

The photothermographic material of the invention may also contain super sensitizers in order to improve the spectral sensitizing effect. The super sensitizers usable in the invention can include those compounds described in EP-A No. 587338, USP Nos. 3877943 and 4873184, JP-A Nos. 5-341432, 11-109547 and 10-111543, and the like.

12) Combined use of a plurality of silver halides

The photosensitive silver halide emulsion in the photothermographic material used in the invention may be used alone, or two or more kinds of them (for example, those of different average particle sizes, different halogen compositions, of different crystal habits and of different conditions for chemical sensitization) may be used together. Gradation can be controlled by using plural kinds of photosensitive silver halides of different sensitivity. The relevant techniques can include those described, for example, in JP-A Nos. 57-119341, 53-106125, 47-3929, 48-55730, 46-5187, 50-73627, and 57-150841. It is preferred to provide a sensitivity difference of 0.2 or more in terms of log E between each of the emulsions.

13) Mixing silver halide and organic silver salt

The photosensitive silver halide in the invention is particularly preferably formed in the absence of the non-photosensitive organic silver salt and chemically sensitized. This is because sometimes sufficient sensitivity can not be attained by the method of forming the silver halide by adding a halogenating agent to an organic silver salt.

The method of mixing the silver halide and the organic silver salt can include a method of mixing a separately prepared photosensitive silver halide and an organic silver salt by a high speed stirrer, ball mill, sand mill, colloid mill, vibration mill, or homogenizer, or a method of mixing a photosensitive silver halide completed for preparation at any timing in the preparation of an organic silver salt and preparing the organic silver salt. The effect of the invention can be obtained preferably by any of the methods described above.

14) Mixing silver halide into coating solution

In the invention, the time of adding silver halide to the coating solution for the image forming layer is preferably in a range from 180 minutes before to just prior to the coating, more preferably, 60 minutes before to 10 seconds before coating. But there is no restriction for mixing method and mixing condition as long as the effect of the invention is sufficient. As an embodiment of a mixing method, there is a method of mixing in a tank and controlling an average residence time. The average residence time herein is calculated from addition flux and the amount of solution transferred to the coater. And another embodiment of mixing method is a method using a static mixer, which is described in 8th edition of "Ekitai Kongo Gijyutu" by N. Harnby and M. F. Edwards, translated by Koji Takahashi (Nikkan Kogyo Shinbunsha, 1989).

(Compound which substantially reduces visible light absorption by photosensitive silver halide)

[0076] In the present invention, it is preferred that the photothermographic material contains a compound which substantially reduces visible light absorption by photosensitive silver halide after thermal development versus before thermal development.

[0077] In the present invention, it is particularly preferred that a silver iodide complex-forming agent is used as the compound which substantially reduces visible light absorption by photosensitive silver halide after thermal development.

<Silver iodide complex-forming agent>

[0078] As for the silver iodide complex-forming agent according to the present invention, at least one of a nitrogen atom or a sulfur atom in the compound can contribute to a Lewis acid-base reaction which gives an electron to a silver ion, as a ligand atom (electron donor: Lewis base). The stability of the complex is defined by successive stability constant or total stability constant, but it depends on the combination of silver ion, iodo ion and the silver complex forming agent. As a general guide, it is possible to obtain a large stability constant by a chelate effect from intramolecular chelate ring formation, by means of increasing the acid-base dissociation constant and the like.

[0079] In the present invention, the ultra violet-visible light absorption spectrum of the photosensitive silver halide can be measured by a transmission method or a reflection method. When the absorption derived from other compounds added to the photothermographic material overlaps with the absorption of photosensitive silver halide, the ultra violet-visible light absorption spectrum of photosensitive silver halide can be observed by using, independently or in combination, the means of difference spectrum and removal of other compounds by solvent and the like.

[0080] As a silver iodide complex-forming agent according to the present invention, a 5 to 7-membered heterocyclic compound containing at least one nitrogen atom is preferable. In the case where the compound does not have a mercapto group, a sulfide group, or a thione group as a substituent, the said 5 to 7-membered nitrogen-containing heterocycle may be saturated or unsaturated, and may have another substituent. The substituent on a heterocycle may bind to each other to form a ring.

[0081] As preferable examples of 5 to 7-membered heterocyclic compounds, pyrrole, pyridine, oxazole, isoxazole, thiazole, isothiazole, imidazole, pyrazole, pyrazine, pyrimidine, pyridazine, indole, isoindole, indolizine, quinoline, isoquinoline, benzimidazole, 1H-imidazole, quinoxaline, quinazoline, cinnoline, phthalazine, naphthylizine, purine, pterizine, carbazole, acridine, phenanthridine, phenanthroline, phenazine, phenoxazine, phenothiazine, benzothiazole, benzoxazole, 1,2,4-triazine, 1,3,5-triazine, pyrrolidine, imidazolidine, pyrazolidine, piperidine, piperazine, morpholine, indoline, isoindoline, and the like can be described.

[0082] More preferably, pyridine, imidazole, pyrazole, pyrazine, pyrimidine, pyridazine, indole, isoindole, indolizine, quinoline, isoquinoline, benzimidazole, 1H-imidazole, quinoxaline, quinazoline, cinnoline, phthalazine, 1,8-naphthylizine, 1,10-phenanthroline, benzotriazole, 1,2,4-triazine, 1,3,5-triazine, and the like can be described. Particularly preferably, pyridine, imidazole, pyrazine, pyrimidine, pyridazine, phtharazine, triazine, 1,8-naphthylizine, 1,10-phenanthroline, and the like can be described.

[0083] These rings may have a substituent and any substituent can be used as far as it does not negatively impact the photographic property. As preferable examples, a halogen atom (fluorine atom, chlorine atom, bromine atom, or iodine atom), an alkyl group (a straight, a branched, a cyclic alkyl group containing a bicycloalkyl group and an active methine group), an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group (substituted position is not asked), an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a heterocyclic oxycarbonyl group, a carbamoyl group, an N-acyl carbamoyl group, an N-sulfonyl carbamoyl group, an N-carbamoyl carbamoyl group, an N-sulfamoyl carbamoyl group, a carbazoyl group, a carboxyl group and a salt thereof, an oxalyl group, an oxamoyl group, a cyano group, a carbonimidoyl group, a formyl group, a hydroxy group, an alkoxy group (including the group in which ethylene oxy group units or propylene oxy group units are repeated), an aryloxy group, a heterocyclic oxy group, an acyloxy group, an alkoxy carbonyloxy group, an aryloxy carbonyloxy group, a carbamoyloxy group, a sulfonyloxy group, an amino group, an alkylamino group, an arylamino group, a heterocyclic amino group, an acylamino group, a sulfonamide group, a ureido group, a thioureido group, an imide group, an alkoxy carbonylamino group, an aryloxy carbonylamino group, a sulfamoylamino group, a semicarbazide group, an ammonio group, an oxamoylamino group, an N-alkylsulfonylureido group, an N-arylsulfonylureido group, an N-acylureido group, an N-acylsulfamoylamino group, a nitro group, a heterocyclic group containing a quaternary nitrogen atom (e.g., a pyridinio group, an imidazolio group, a quinolinio group, or an isoquinolinio group), an isocyano group, an imino group, an alkylsulfonyl group, an arylsulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a sulfo group and a salt thereof, a sulfamoyl group, an N-acylsulfamoyl group, an N-sulfonylsulfamoyl group and a salt thereof, a phosphino group, a phosphinyl group, a phosphinyloxy group, a phosphinylamino group, a silyl group, and the like are described.

[0084] Here, an active methine group means a methine group substituted by two electron-attracting groups, wherein

the electron-attracting group means an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group, a sulfamoyl group, a trifluoromethyl group, a cyano group, a nitro group, a carbonimidoyl group. Herein, two electron-attracting groups may bind each other to form a cyclic structure. And, the salt means a salt formed with positive ion such as an alkaline metal, an alkaline earth metal, a heavy metal, or the like, or organic positive ion such as an ammonium ion, a phosphonium ion, or the like. These substituents may be further substituted by these substituents.

[0085] These heterocycles may be further condensed by another ring. In the case where the substituent is an anion group (e.g., $-\text{CO}_2^-$, $-\text{SO}_3^-$, $-\text{S}^-$, or the like), the heterocycle containing nitrogen atom of the invention may become a positive ion (e.g., pyridinium, 1,2,4-triazolium, or the like) and may form an intramolecular salt.

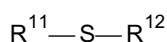
[0086] In the case where a heterocyclic compound is pyridine, pyrazine, pyrimidine, pyridazine, phthalazine, triazine, naththilazine, or phenanthroline derivative, the acid dissociation constant (pKa) of a conjugated acid of nitrogen-containing heterocyclic part in acid dissociation equilibrium of the said compound is preferably 3 to 8 in the mixture solution of tetrahydrofuran/water (3/2) at 25°C, and more preferably, the pKa is 4 to 7.

[0087] As the heterocyclic compound, pyridine, pyridazine, or phthalazine derivative is preferable, and particularly preferable is pyridine or phthalazine derivative.

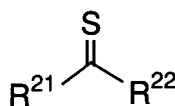
[0088] In the case where these heterocyclic compounds have a mercapto group, a sulfide group or a thione group as the substituent, pyridine, thiazole, isothiazole, oxazole, isoxazole, imidazole, pyrazole, pyrazine, pyrimidine, pyridazine, triazine, triazole, thiadiazole, and oxadiazole derivatives are preferable, and thiazole, imidazole, pyrazole, pyrimidine, pyridazine, triazine, and triazole derivatives are particularly preferable.

[0089] For example, as the said silver iodide complex-forming agent, the compound represented by the following formulae (1) or (2) can be used.

Formula (1)



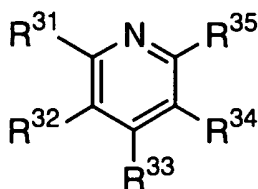
Formula (2)



[0090] In formula (1), R^{11} and R^{12} each independently represent a hydrogen atom or a substituent. In formula (2), R^{21} and R^{22} each independently represent a hydrogen atom or a substituent. However, both of R^{11} and R^{12} are not hydrogen atoms simultaneously and both of R^{21} and R^{22} are not hydrogen atoms simultaneously. As the substituent herein, the substituent explained as the substituent of a 5 to 7-membered nitrogen-containing heterocyclic type silver iodide complex-forming agent mentioned above can be described.

[0091] Further, the compound represented by formula (3) described below can also be used preferably.

Formula (3)



[0092] In formula (3), R^{31} to R^{35} each independently represent a hydrogen atom or a substituent. As the substituent represented by R^{31} to R^{35} , the substituent of a 5 to 7-membered nitrogen-containing heterocyclic type silver iodide complex-forming agent mentioned above can be used. In the case where the compound represented by formula (3)

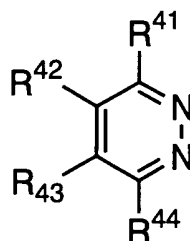
EP 1 584 978 A1

has a substituent, preferred substituting position is R³² to R³⁴. R³¹ to R³⁵ may bind each other to form a saturated or an unsaturated ring. A preferred substituent is a halogen atom, an alkyl group, an aryl group, a carbamoyl group, a hydroxy group, an alkoxy group, an aryloxy group, a carbamoyloxy group, an amino group, an acylamino group, a ureido group, an alkoxy-carbonylamino group, an aryloxy-carbonylamino group, or the like.

[0093] In the compound represented by formula (3), the acid dissociation constant (pKa) of conjugated acid of pyridine ring part preferably is 3 to 8 in the mixed solution of tetrahydrofuran /water (3/2) at 25°C, and particularly preferably 4 to 7.

[0094] Furthermore, the compound represented by formula (4) is also preferable.

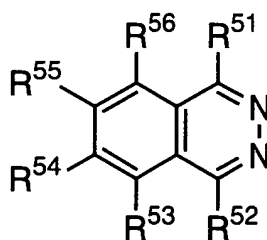
Formula (4)



[0095] In formula (4), R⁴¹ to R⁴⁴ each independently represent a hydrogen atom or a substituent. R⁴¹ to R⁴⁴ may bind each other to form a saturated or an unsaturated ring. As the substituent represented by R⁴¹ to R⁴⁴, the substituent of a 5 to 7-membered nitrogen-containing heterocyclic type silver iodide complex-forming agent mentioned above can be described. As preferred group, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, and a group which forms a phthalazine ring by benzo-condensation are described. In the case where a hydroxy group exists at the carbon atom adjacent to nitrogen atom of the compound represented by formula (4), there exists equilibrium between pyridazinone.

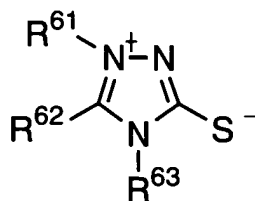
[0096] The compound represented by formula (4) more preferably forms a phthalazine ring represented by the following formula (5), and furthermore, this phthalazine ring particularly preferably has at least one substituent. As examples of R⁵¹ to R⁵⁶ in formula (5), the substituent of a 5 to 7-membered nitrogen-containing heterocyclic type silver iodide complex-forming agent mentioned above can be described. And as more preferable examples of the substituent, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a hydroxy group, an alkoxy group, an aryloxy group, and the like are described. An alkyl group, an alkenyl group, an aryl group, an alkoxy group, and an aryloxy group are preferable and an alkyl group, an alkoxy group, and an aryloxy group are more preferable.

Formula (5)



[0097] Further, the compound represented by formula (6) described below is also a preferable embodiment.

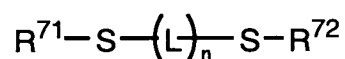
Formula (6)



[0098] In formula (6), R⁶¹ to R⁶³ each independently represent a hydrogen atom or a substituent. As examples of the substituent represented by R⁶², the substituent of a 5 to 7-membered nitrogen-containing heterocyclic type silver iodide complex-forming agent mentioned above can be described.

[0099] As the compound preferably used, the compound represented by the following formula (7) is described.

Formula (7)

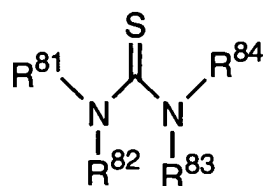


[0100] In formula (7), R⁷¹ and R⁷² each independently represent a hydrogen atom or a substituent. L represents a divalent linking group. n represents 0 or 1. As the substituent represented by R⁷¹ and R⁷², an alkyl group (containing a cycloalkyl group), an alkenyl group (containing a cycloalkenyl group), an alkynyl group, an aryl group, a heterocyclic group, an acyl group, an aryloxy carbonyl group, an alkoxy carbonyl group, a carbamoyl group, an imide group, and a complex substituent containing these groups are described as examples.

[0101] A divalent linking group represented by L preferably has the length of 1 to 6 atoms and more preferably has the length of 1 to 3 atoms, and furthermore, may have a substituent.

[0102] One more of the compounds preferably used is a compound represented by formula (8).

Formula (8)

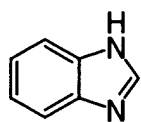


[0103] In formula (8), R⁸¹ to R⁸⁴ each independently represent a hydrogen atom or a substituent. As the substituent represented by R⁸¹ to R⁸⁴, an alkyl group (including a cycloalkyl group), an alkenyl group (including a cycloalkenyl group), an alkynyl group, an aryl group, a heterocyclic group, an acyl group, an aryloxy carbonyl group, an alkoxy carbonyl group, a carbamoyl group, an imide group, and the like are described as examples.

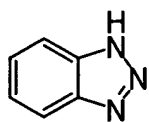
[0104] Among the silver iodide complex-forming agents described above, the compounds represented by formulae (3), (4), (5), (6) and (7) are more preferable and, the compounds represented by formulae (3) and (5) are particularly preferable.

[0105] Preferable examples of silver iodide complex-forming agent are described below, however the present invention is not limited in these.

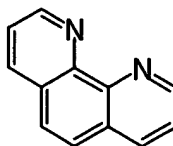
5



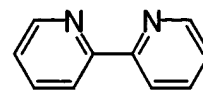
(1)



(2)

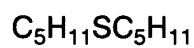


(3)

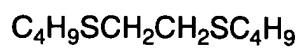


(4)

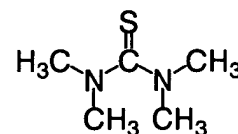
10



(5)

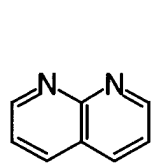


(6)

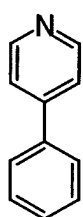


(7)

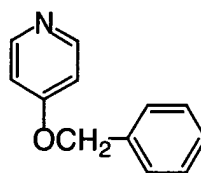
15



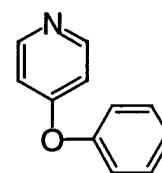
(8)



(9)



(10)

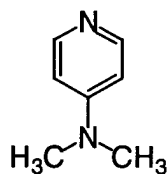


(11)

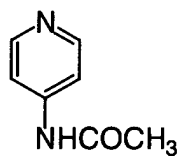
20

25

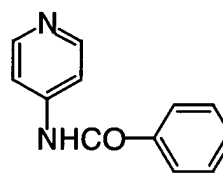
30



(12)



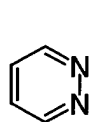
(13)



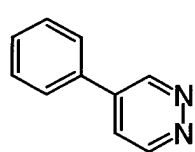
(14)

35

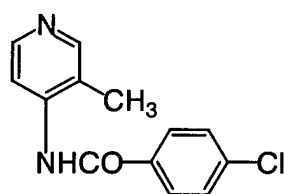
40



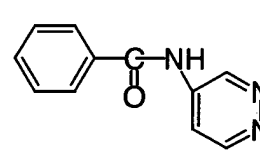
(15)



(16)



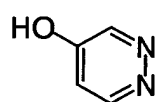
(17)



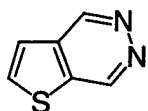
(18)

45

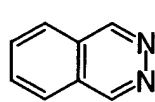
50



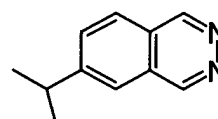
(19)



(20)

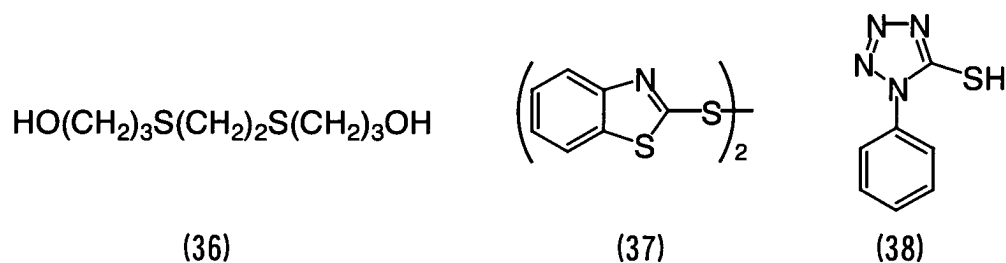
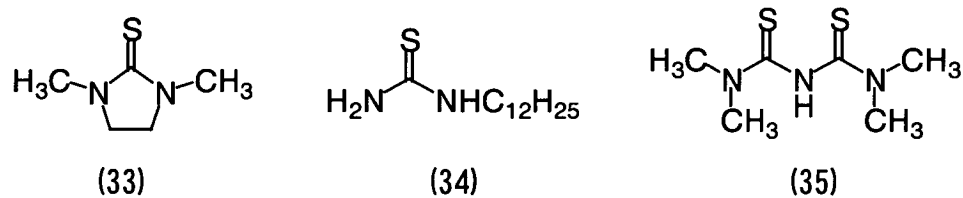
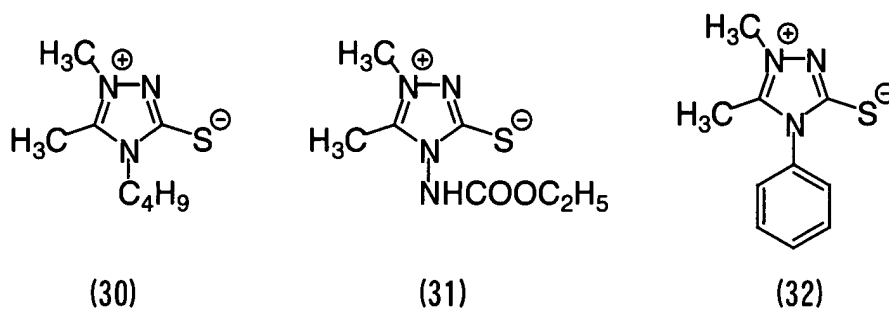
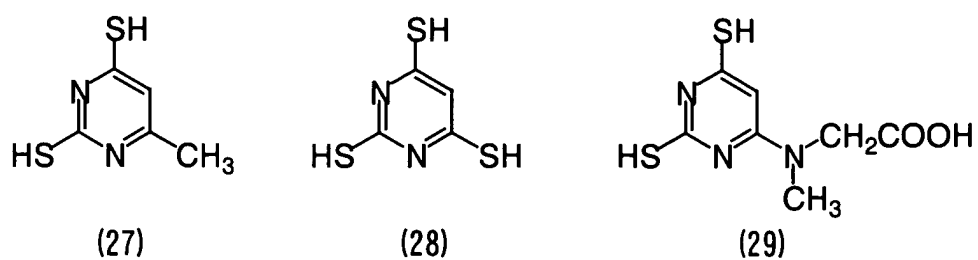
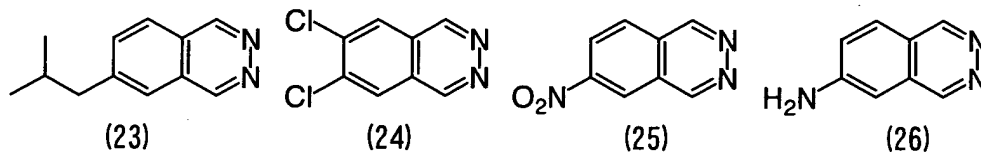


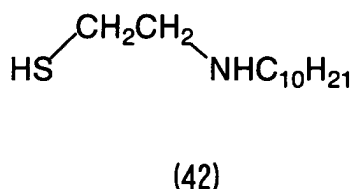
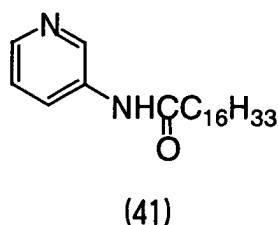
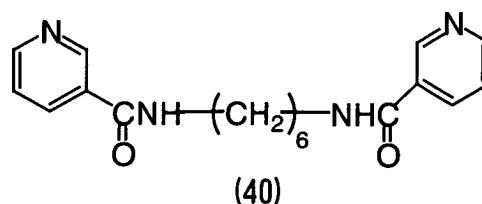
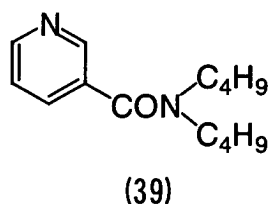
(21)



(22)

55





20 **[0106]** The silver iodide complex-forming agent according to the present invention can also be a compound common to a toner, in the case where the agent achieves the function of conventionally known toner. The silver iodide complex-forming agent according to the present invention can be used in combination with a toner. And, two or more kinds of the silver iodide complex-forming agents may be used in combination.

25 **[0107]** The silver iodide complex-forming agent according to the present invention preferably exists in a film under the state separated from a photosensitive silver halide, such as a solid state. It is also preferably added to the layer adjacent to the image forming layer. Concerning the silver iodide complex-forming agent according to the present invention, a melting point of the compound is preferably adjusted to a suitable range so that it can be dissolved when heated at thermal developing temperature.

30 **[0108]** In the present invention, an absorption intensity of ultra violet-visible light absorption spectrum of photosensitive silver halide after thermal development preferably becomes 80% or less as compared with before thermal development, more preferably 40% or less and, particularly preferably 10% or less.

[0109] The silver iodide complex-forming agent according to the invention may be incorporated into a photothermographic material by being added into the coating solution, such as in the form of a solution, an emulsion dispersion, a solid fine particle dispersion, or the like.

35 **[0110]** Well known emulsion dispersing methods include a method comprising dissolving the silver iodide complex-forming agent in an oil such as dibutylphthalate, tricresylphosphate, glyceryl triacetate, diethylphthalate, or the like, and an auxiliary solvent such as ethyl acetate, cyclohexanone, or the like, followed by mechanically forming an emulsified dispersion.

40 **[0111]** Solid fine particle dispersing methods include a method comprising dispersing the powder of the silver iodide complex-forming agent according to the invention in a proper solvent such as water or the like, by means of ball mill, colloid mill, vibrating ball mill, sand mill, jet mill, roller mill, or ultrasonics, thereby obtaining a solid dispersion. In this case, there can also be used a protective colloid (such as polyvinyl alcohol), or a surfactant (for instance, an anionic surfactant such as sodium triisopropylnaphthalenesulfonate (a mixture of compounds having the three isopropyl groups in different substitution sites)).

45 **[0112]** In the mills enumerated above, generally used as the dispersion media are beads made of zirconia and the like, and Zr and the like eluting from the beads may be incorporated in the dispersion. Depending on the dispersing conditions, the amount of Zr and the like generally incorporated in the dispersion is in a range of from 1 ppm to 1000 ppm. It is practically acceptable so long as Zr is incorporated in the photothermographic material in an amount of 0.5 mg or less per 1 g of silver.

50 **[0113]** Preferably, an antiseptic (for instance, benzisothiazolinone sodium salt) is added in the water dispersion.

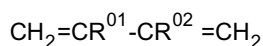
[0114] The silver iodide complex-forming agent according to the invention is preferably used in the form of a solid dispersion.

55 **[0115]** The silver iodide complex-forming agent according to the invention is preferably used in the range from 1 mol% to 5000 mol%, more preferably, from 10 mol% to 1000 mol% and, further preferably, from 50 mol% to 300 mol%, with respect to the photosensitive silver halide in each case.

(Binder)

[0116] 50% by weight or more of the binder used for the image forming layer of the present invention is formed by a polymer latex containing a monomer component represented by the following formula (M) within a range of from 10% by weight to 70% by weight.

Formula (M) :



wherein R⁰¹ and R⁰² each independently represent one selected from a hydrogen atom, an alkyl groups having 1 to 6 carbon atoms, a halogen atom, and a cyano group, however both of R⁰¹ and R⁰² are not hydrogen atoms simultaneously.

[0117] As an alkyl group for R⁰¹ or R⁰², an alkyl group having 1 to 4 carbon atoms is preferred, and more preferably an alkyl group having 1 to 2 carbon atoms is used. As a halogen atom, a fluorine atom, a chlorine atom, or a bromine atom is preferred, and more preferred is a chlorine atom.

[0118] Particularly preferably, one of R⁰¹ and R⁰² represents a hydrogen atom and the other represents a methyl group or a chlorine atom.

[0119] Specific examples of monomer represented by the above formula (M) of the present invention include 2-ethyl-1,3-butadiene, 2-n-propyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene, 2-chloro-1,3-butadiene, 1-bromo-1,3-butadiene, 2-fluoro-1,3-butadiene, 2,3-dichloro-1,3-butadiene, and 2-cyano-1,3-butadiene.

[0120] The binder of the present invention are polymers obtained by copolymerizing monomers represented by formula (M), where the copolymerization ratio of the monomer represented by formula (M) for the polymer is in a range of from 10% by weight to 70% by weight, preferably from 15% by weight to 65% by weight, and more preferably from 20% by weight to 60% by weight.

[0121] When the copolymerization ratio of the monomer represented by formula (M) is less than 10% by weight, the bonding component of the binder is decreased and the membrane strength is deteriorated. When the copolymerization ratio of the monomer represented by formula (M) becomes more than 70% by weight, the bonding component of the binder is increased, mobility of the binder is increased, and as a result, image storability is deteriorated.

[0122] In the invention, the other monomers, which are capable to copolymerize with the monomer represented by formula (M), are not particularly restricted, and any monomers may be preferably used provided that they are polymerizable by usual radical polymerization or ion polymerization. As for the monomer which can be used preferably, it is capable to select the combination independently and freely from the monomer groups (a) to (j) described below.

-Monomer groups (a) to (j)-

(a) conjugated dienes: 1,3-butadiene, 1,3-pentadiene, 1-phenyl-1,3-butadiene, 1- α -naphthyl-1,3-butadiene, 1- β -naphthyl-1,3-butadiene, 1-bromo-1,3-butadiene, 1-chloro-1,3-butadiene, 1,1,2-trichloro-1,3-butadiene, cyclopentadiene, and the like;

(b) olefins: ethylene, propylene, vinyl chloride, vinylidene chloride, 6-hydroxy-1-hexene, 4-pentenoic acid, methyl 8-nonenate, vinylsulfonic acid, trimethylvinylsilane, trimethoxyvinylsilane, 1,4-divinylcyclohexane, 1,2,5-trivinylcyclohexane, and the like;

(c) α,β -unsaturated carboxylic acid and salts thereof: acrylic acid, methacrylic acid, itaconic acid, maleic acid, sodium acrylate, ammonium methacrylate, potassium itaconate, and the like;

(d) α,β -unsaturated carboxylate esters: alkyl acrylate (for example, methyl acrylate, ethyl acrylate, butyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, and the like), substituted alkyl acrylate (for example, 2-chloroethyl acrylate, benzyl acrylate, 2-cyanoethyl acrylate, and the like), alkyl methacrylate (for example, methyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, and the like), substituted alkyl methacrylate (for example, 2-hydroxyethyl methacrylate, glycidyl methacrylate, glycerine monomethacrylate, 2-acetoxyethyl methacrylate, tetrahydrofurfuryl methacrylate, 2-methoxyethyl methacrylate, polypropyleneglycol monomethacrylate (addition mole number of polyoxypropylene = 2 to 100), 3-N,N-dimethylaminopropyl methacrylate, chloro-3-N,N,N-trimethylammoniopropyl methacrylate, 2-carboxyethyl methacrylate, 3-sulfopropyl methacrylate, 4-oxysulfobutyl methacrylate, 3-trimethoxysilylpropyl methacrylate, allyl methacrylate, 2-isocyanatoethyl methacrylate, and the like), derivatives of unsaturated dicarboxylic acid (for example, monobutyl maleate, dimethyl maleate, monomethyl itaconate, dibutyl itaconate, and the like), and polyfunctional esters (for example, ethyleneglycol diacrylate, ethyleneglycol dimethacrylate, 1,4-cyclohexane diacrylate, pentaerythritol tetramethacrylate, pentaerythritol triacrylate, trimethylolpropane triacrylate, trimethylolethane triacrylate, dipentaerythritol pentamethacrylate, pentaerythritol hexaacrylate, 1,2,4-cyclohexane tetramethacrylate, and the like);

(e) amides of β -unsaturated carboxylic acid: for example, acrylamide, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-methyl-N-hydroxyethyl methacrylamide, N-tert-butyl acrylamide, N-tert-octyl methacrylamide, N-cyclohexyl acrylamide, N-phenyl acrylamide, N-(2-acetoacetoxyethyl) acrylamide, N-acryloyl morpholine, diacetone acrylamide, diamide itaconate, N-methyl maleimide, 2-acrylamide-methylpropanesulfonic acid, methyl-enebis acrylamide, dimethacryloyl piperazine, and the like;

(f) unsaturated nitriles: acrylonitrile, methacrylonitrile, and the like;

(g) styrene and derivatives thereof: styrene, vinyltoluene, p-tert-butylstyrene, vinylbenzoic acid, methyl vinylbenzoate, α -methylstyrene, p-chloromethylstyrene, vinylnaphthalene, p-hydroxymethylstyrene, sodium p-styrenesulfonate, potassium p-styrenesulfinate, p-aminomethylstyrene, 1,4-divinylbenzene, and the like;

(h) vinyl ethers: methylvinyl ether, butylvinyl ether, methoxyethylvinyl ether, and the like;

(i) vinyl esters: vinyl acetate, vinyl propionate, vinyl benzoate, vinyl salicylate, vinyl chloroacetate, and the like; and

(j) other polymerizable monomers: N-vinylimidazole, 4-vinylpyridine, N-vinylpyrrolidone, 2-vinylloxazoline, 2-isopropenyloxazoline, divinylsulfone, and the like.

[0123] Preferred examples of a polymer copolymerized with the monomer represented by formula (M) of the present invention include copolymers with styrene (for example, random copolymer, block polymer, or the like), copolymers with styrene and butadiene (for example, random copolymer, butadiene-isoprene-styrene block copolymer, styrene-butadiene-isoprene-styrene block copolymer, or the like), copolymers with ethylene and propylene, copolymers with acrylonitrile, copolymers with isobutylene, copolymers with acrylic esters (for example, as acrylic ester, ethyl acrylate, butyl acrylate, or the like can be used), and copolymers with acrylic ester and acrylonitrile (the same acrylic esters as mentioned above can be used). Among these, most preferred is a copolymer with styrene.

[0124] In addition to the above components, the polymer of the present invention is preferably copolymerized with a monomer having an acid group. As the acid group, preferred are a carboxylic acid, a sulfonic acid, and a phosphoric acid. The copolymerization ratio of a monomer having the acid group is preferably in a range of from 1% by weight to 20% by weight, and more preferably from 1% by weight to 10% by weight.

[0125] Examples of a monomer having the acid group include acrylic acid, methacrylic acid, itaconic acid, p-styrene sulfonic acid sodium salt, isoprene sulfonic acid, phoshyryl ethyl methacrylate, and the like. Any kind of polymer may be used in combination with the polymer copolymerized with the monomer represented by formula (M) as the binder of the invention. Suitable as the polymer which can be used in combination are those that are transparent or translucent, and that are generally colorless, such as natural resin or polymer and their copolymers; synthetic resin or polymer and their copolymer; or media forming a film; for example, included are gelatin, rubber, poly(vinyl alcohol), hydroxyethyl cellulose, cellulose acetate, cellulose acetate butyrate, poly(vinyl pyrrolidone), casein, starch, poly(acrylic acid), poly(methylmethacrylic acid), poly(vinyl chloride), poly(methacrylic acid), styrene-maleic anhydride copolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(vinyl acetal) (e.g., poly(vinyl formal) or poly(vinyl butyral)), polyester, polyurethane, phenoxy resin, poly(vinylidene chloride), polyepoxide, polycarbonate, poly(vinyl acetate), polyolefin, cellulose esters, and polyamide. A binder may be used with water, an organic solvent or emulsion to form a coating solution.

[0126] The binder of the invention preferably has a glass transition temperature (T_g) in a range of -30°C to 70°C , more preferably -10°C to 50°C , and further preferably 0°C to 40°C , considering work brittleness and image storability. Two or more kinds of polymers can be blended for the binder, and in this case, T_g of the blended polymer as a composition weighed average preferably falls within the range above. When the polymers exhibit phase separation or has a core-shell structure, T_g of each phase preferably falls within the range above.

[0127] In the specification, T_g is calculated according to the following equation.

$$1/T_g = \sum (X_i/T_{gi})$$

[0128] Where, the polymer is obtained by copolymerization of n monomer compounds (from $i=1$ to $i=n$); X_i represents the mass fraction of the i th monomer ($\sum X_i=1$), and T_{gi} is the glass transition temperature (absolute temperature) of the homopolymer obtained with the i th monomer. The symbol \sum stands for the summation from $i=1$ to $i=n$. Values for the glass transition temperature (T_{gi}) of the homopolymers derived from each of the monomers were obtained from J. Brandrup and E. H. Immergut, Polymer Handbook (3rd Edition) (Wiley-Interscience, 1989).

[0129] The polymer used in the invention can be readily obtained by a solution polymerization method, a suspension polymerization method, an emulsion polymerization method, a dispersion polymerization method, an anionic polymerization method, a cationic polymerization method, or the like, however most preferable is an emulsion polymerization method by which polymer can be obtained as a latex. For example, the polymer latex is obtained by emulsion polymerization at about 30°C to 100°C , preferably at 60°C to 90°C , for 3 hours to 24 hours with stirring using water or a mixed solvent of water and a water-miscible organic solvent (for example, methanol, ethanol, acetone, or the like) as

a dispersion medium, and using a monomer mixture in an amount of 5% by weight to 150% by weight with respect to the dispersion solvent, an emulsifying agent in an amount of 0.1 % by weight to 20% by weight with respect to a total amount of monomers, and a polymerization initiator. Conditions such as the dispersion medium, monomer concentration, the amount of the initiator, the amount of the emulsifying agent, the amount of the dispersing agent, the reaction temperature and the addition method of the monomer may be appropriately determined considering the kind of the monomer used. The dispersing agent is preferably used, if necessary.

[0130] Emulsion polymerization is usually carried out according to the following documents: "Gosei Jushi Emulsion (Synthetic Resin Emulsion)" ed. by Taira Okuda and Hiroshi Inagaki, Polymer Publishing Association (1978); "Gosei Latex no Oyo (Application of Synthetic Latex)" ed. by Taka-aki Sugimura, Yasuo Kataoka, Soichi Suzuki and Keiji Kasahara, Polymer Publishing Association (1993); and "Gosei Latex no Kagaku (Chemistry of Synthetic Latex)" by Soichi Muroi, Polymer Publishing Association (1970).

[0131] Emulsion polymerization method for synthesizing the polymer latex of the invention may be selected from an overall polymerization method, a monomer addition (continuous or divided) method, an emulsion addition method and a seed polymerization method. The overall polymerization method, monomer addition (continuous or divided) method, and emulsion addition method are preferable in view of productivity of the latex.

[0132] The polymerization initiator described above may have a radical generation ability, and examples of them available include inorganic peroxides such as persulfate salts and hydrogen peroxide, peroxides described in the catalogue of organic peroxides by Nippon Oil and Fat Co., and azo compounds described in azo polymerization initiator catalogue by Wako Pure Chemical Industries, Ltd. Among them, a water-soluble peroxides such as persulfate, and water-soluble azo compounds described in azo polymerization initiator catalogue by Wako Pure Chemical Industries, Ltd., are preferable. Ammonium persulfate, sodium persulfate, potassium persulfate, azobis(2-methylpropionamide) hydrochloride, azobis(2-methyl-N-(2-hydroxyethyl)propionamide and azobiscyanovaleric acid are more preferable, and particularly, peroxides such as ammonium persulfate, sodium persulfate and potassium persulfate are preferable from the viewpoint of image storability, solubility, and cost.

[0133] The addition amount of the polymerization initiator described above is preferably in a range from 0.3% by weight to 2.0% by weight, more preferably 0.4% by weight to 1.75% by weight, and particularly preferably 0.5% by weight to 1.5% by weight, based on a total amount of monomers. Image storability decreases when the amount of the polymerization initiator is less than 0.3% by weight, while the latex tends to be aggregated to deteriorate coating ability when the amount of the polymerization initiator exceeds 2.0% by weight.

[0134] As for the polymerization emulsifying agent mentioned above, any surfactants such as an anionic surfactant, a nonionic surfactant, a cationic surfactant, or an amphoteric surfactant can be employed. An anionic surfactant is preferably employed from the viewpoint of dispersibility and image storability, and more preferred is a sulfonic acid-type anionic surfactant which maintains the polymerization stability even in a small amount and has a hydrolysis resistance. Preferred is a long chain alkyl diphenylether disulfonate such as "PELEX SS-H" (trade name, available from Kao Co., Ltd.), and particularly preferred is a low electrolyte-type surfactant such as "PIONIN A-43-S" (trade name, available from Takemoto Oil & Fat Co., Ltd.).

[0135] As the polymerization emulsifying agent mentioned above, a sulfonic acid-type surfactant is preferably used in a range of from 0.1% by weight to 10.0% by weight based on the total amount of monomers, more preferably from 0.2% by weight to 7.5% by weight, and particularly preferably from 0.3% by weight to 5.0% by weight. Stability in the emulsion polymerization process can not secure when the addition amount of the polymerization emulsifying agent is less than 0.1% by weight, while image storability decreases when the addition amount exceeds 10.0 % by weight.

[0136] Chelating agents are preferably used for the synthesis of the polymer latex used in the invention. The chelating agent is a compound capable of coordinating multi-valent metal ions such as iron ion, and alkali earth metal ions such as calcium ion, and examples thereof include the compounds described in JP-B No. 6-8956; USP No. 5053322; and JP-A Nos. 4-73645, 4-127145, 4-247073, 4-305572, 6-11805, 5-173312, 5-66527, 5-158195, 6-118580, 6-110168, 6-161054, 6-175299, 6-214352, 7-114161, 7-114154, 7-120894, 7-199433, 7-306504, 9-43792, 8-314090, 10-182571, 10-182570, and 11-190892.

[0137] The chelating agent used in the invention is preferably an inorganic chelating compound (sodium tripolyphosphate, sodium hexametaphosphate, sodium tetrapolyphosphate, or the like), an aminopolycarboxylic acid chelating compound (nitrilotriacetic acid, ethylenediamine tetraacetic acid, or the like), an organic phosphonic acid chelating agent (compounds described in Research Disclosure No. 18170, JP-A Nos. 52-102726; 53-42730, 56-97347, 54-121127, 55-4024, 55-4025, 55-29883, 55-126241, 55-65955, 55-65956, 57-179843, and 54-61125; and West Germany Patent (WGP) No. 1045373), a polyphenol chelating agent, or a polyamine chelating agent. An aminopolycarboxylic acid derivative is particularly preferable.

[0138] Preferable examples of the aminopolycarboxylic acid derivative are described in the supplement table of "EDTA (-Chemistry of Complexane-)", Nankodo 1977. A part of the carboxyl group of these compounds may be substituted by a salt of alkali metal such as sodium or potassium, or an ammonium salt. Particularly preferable aminopolycarboxylic acid derivatives include iminodiacetic acid, N-methyliminodiacetic acid, N-(2-aminoethyl)iminodiacetic acid,

N-(carbamoyl)ethyl)iminodiacetic acid, nitrilotriacetic acid, ethylenediamine-N,N'-diacetic acid, ethylenediamine-N,N'-di- α -propionic acid, ethylenediamine-N,N'-di- β -propionic acid, N,N'-ethylene-bis(α -o-hydroxyphenyl)glycine, N,N'-di(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid, ethylenediamine-N,N'-diacetic acid-N,N'-diacetohydroxamic acid, N-hydroxyethylethylenediamine-N,N',N'-triacetic acid, ethylenediamine-N,N,N',N'-tetraacetic acid, 1,2-propylenediamine-N,N,N',N'-tetraacetic acid, d,1-2,3-diaminobutane-N,N,N',N'-tetraacetic acid, meso-2,3-diaminobutane-N,N,N',N'-tetraacetic acid, 1-phenylethylenediamine-N,N,N',N'-tetraacetic acid, d,1-1,2-diphenylethylenediamine-N,N,N',N'-tetraacetic acid, 1,4-diaminobutane-N,N,N',N'-tetraacetic acid, trans-cyclobutane-1,2-diamine-N,N,N',N'-tetraacetic acid, trans-cyclopentane-1,2-diamine-N,N,N',N'-tetraacetic acid, trans-cyclohexane-1,2-diamine-N,N,N',N'-tetraacetic acid, cis-cyclohexane-1,2-diamine-N,N,N',N'-tetraacetic acid, cyclohexane-1,3-diamine-N,N,N',N'-tetraacetic acid, cyclohexane-1,4-diamine-N,N,N',N'-tetraacetic acid, o-phenylenediamine-N,N,N',N'-tetraacetic acid, cis-1,4-diaminobutene-N,N,N',N'-tetraacetic acid, trans-1,4-diaminobutene-N,N,N',N'-tetraacetic acid, α,α' -diamino-o-xylene-N,N,N',N'-tetraacetic acid, 2-hydroxy-1,3-propanediamine-N,N,N',N'-tetraacetic acid, 2,2-oxy-bis(ethyliminodiacetic acid), 2,2'-ethylenedioxy-bis(ethyliminodiacetic acid), ethylenediamine-N,N'-diacetic acid-N,N'-di- α -propionic acid, ethylenediamine-N,N'-diacetic acid-N,N'-di- β -propionic acid, ethylenediamine-N,N,N',N'-tetrapropionic acid, diethylenetriamine-N,N,N',N'',N''-pentaacetic acid, triethylenetetramine-N,N,N',N'',N'',N''-hexaacetic acid, and 1,2,3-triaminopropane-N,N,N',N'',N''',N''''-hexaacetic acid. A part of the carboxylic group of these compounds may be substituted by a salt of alkali metal such as sodium or potassium, or an ammonium salt.

[0139] The addition amount of the chelating agent described above is preferable 0.01% by weight to 0.4% by weight, more preferably 0.02% by weight to 0.3% by weight, and particularly preferably 0.03% by weight to 0.15% by weight based on a total amount of monomers. Metal ions mingling in the production process of the polymer latex are insufficiently trapped when the amount of the chelating agent is less than 0.01% by weight to decrease stability of the latex against aggregation to deteriorate coating ability. When the content exceeds 0.4%, on the other hand, the viscosity of the latex increases to deteriorate coating ability.

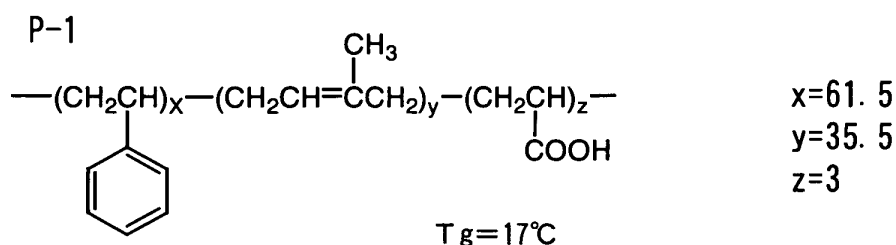
[0140] The chain transfer agent is preferably used in the synthesis of the polymer latex used in the invention. The compounds described in Polymer Handbook Third Edition (Wiley-Interscience, 1989) are preferable as the chain transfer agents. Sulfur compounds are preferable since they have high chain transfer ability to make the amount of use of the reagent small. Particularly preferable chain reaction agents are hydrophobic mercaptan chain transfer agents such as tert-dodecylmercaptan, n-dodecylmercaptan, and the like.

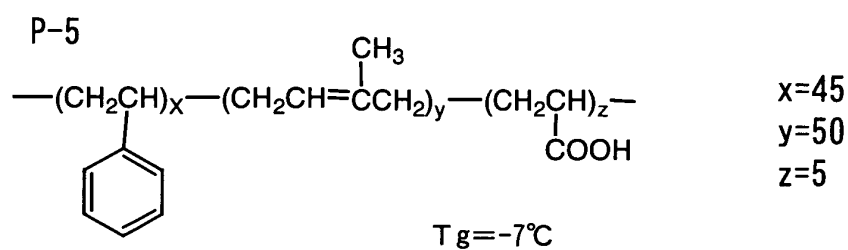
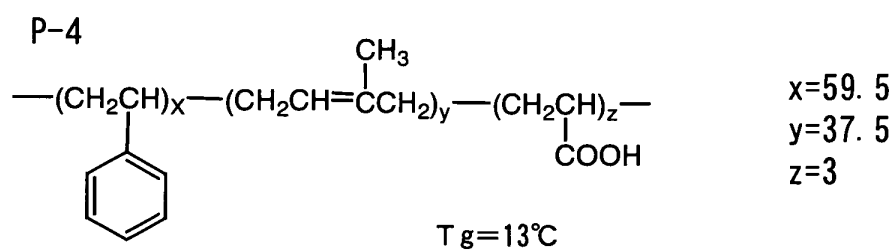
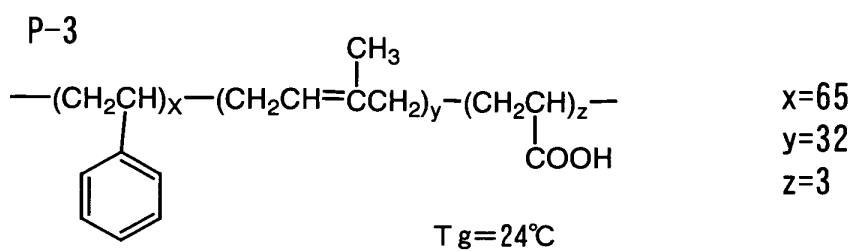
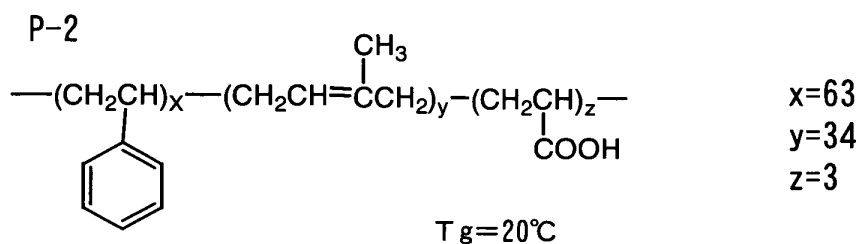
[0141] The amount of the chain transfer agent described above is preferable 0.2% by weight to 2.0% by weight, more preferably 0.3% by weight to 1.8% by weight, and particularly preferably 0.4% by weight to 1.6% by weight based on a total amount of monomers. Work brittleness is decreased when the amount of the chain transfer agent is less than 0.2% by weight, while image storability is deteriorated when the amount exceeds 2.0% by weight.

[0142] In the emulsion polymerization, additives such as an electrolyte, a stabilizer, a thickener, a defoaming agent, an antioxidant, a vulcanizing agent, an antifreeze agent, a gelling agent, vulcanization accelerator, and the like described in Synthetic Rubber Handbook and the like may be used in addition to the compounds above.

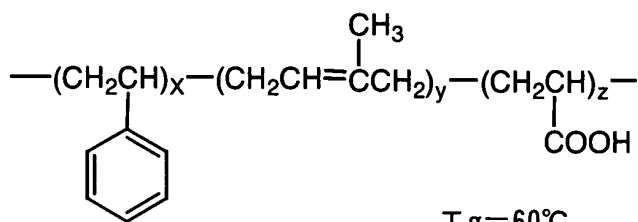
<Specific examples of polymer>

[0143] Specific examples of the polymer used in the present invention are listed below (compound P-1 to P-29), however the invention is not restricted to these. x, y, z, and z' in chemical formula show the mass ratios in the polymer composition, and the sum of x, y, z, and z' is equal to 100%. T_g represents the glass transition temperature of a dry film obtained from the polymer.



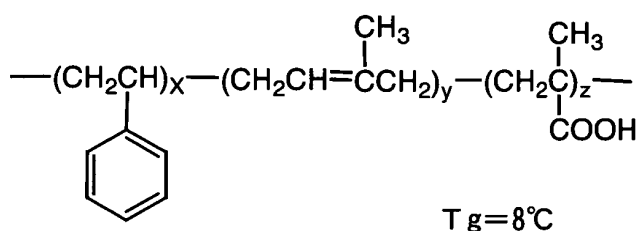


P-6



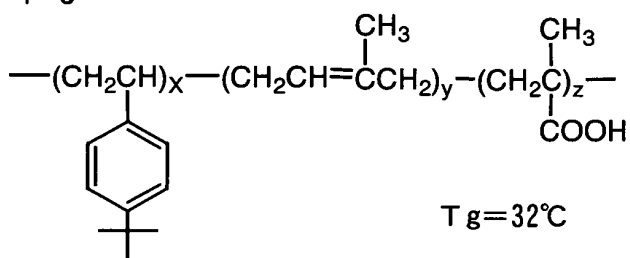
$x=79$
 $y=15$
 $z=6$

P-7



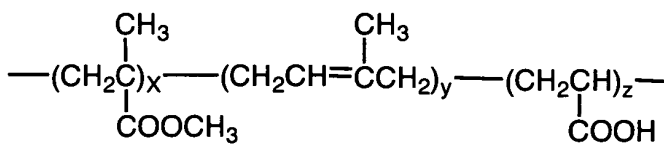
$x=55$
 $y=41$
 $z=4$

P-8



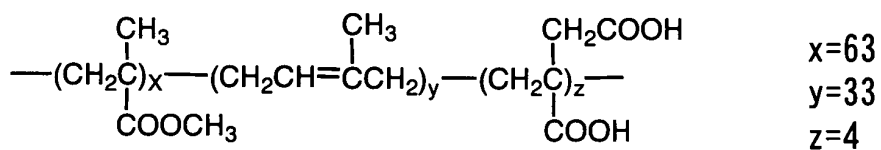
$x=60$
 $y=35$
 $z=5$

P-9



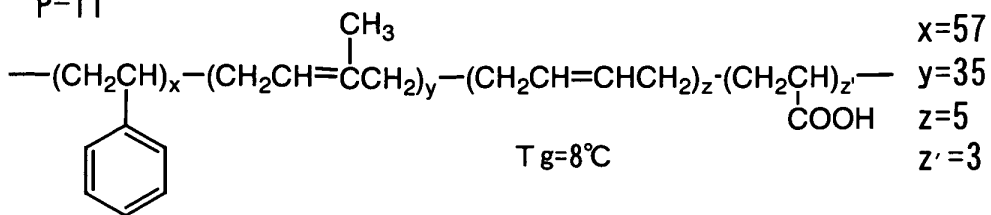
$x=62$
 $y=33$
 $z=5$

P-10

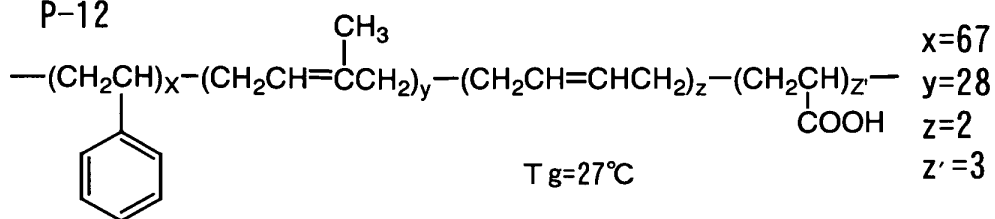


$T_g=28^\circ\text{C}$

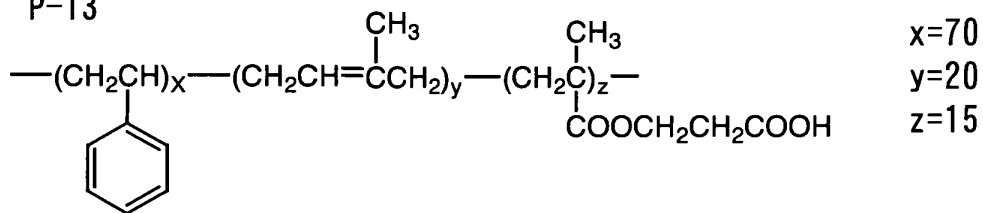
P-11



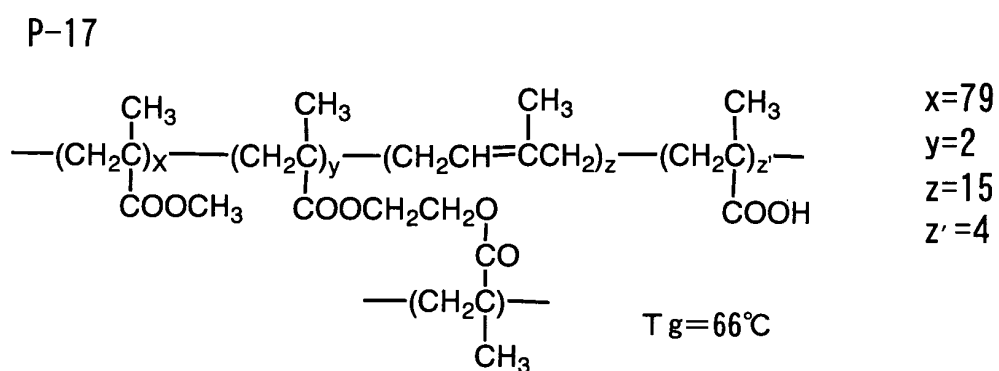
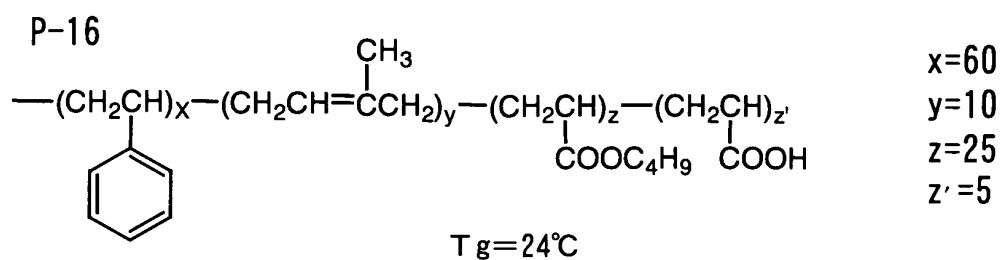
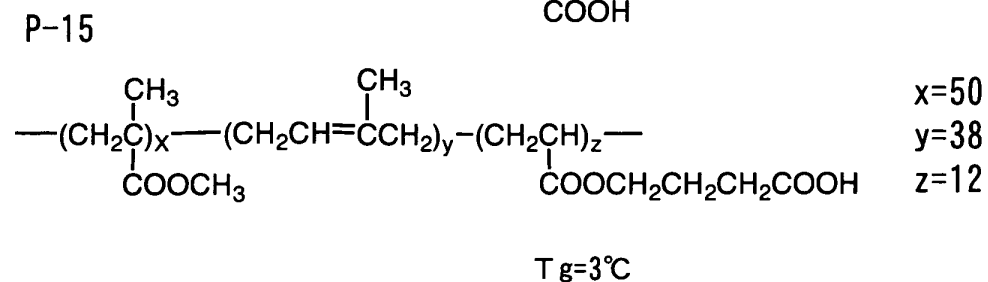
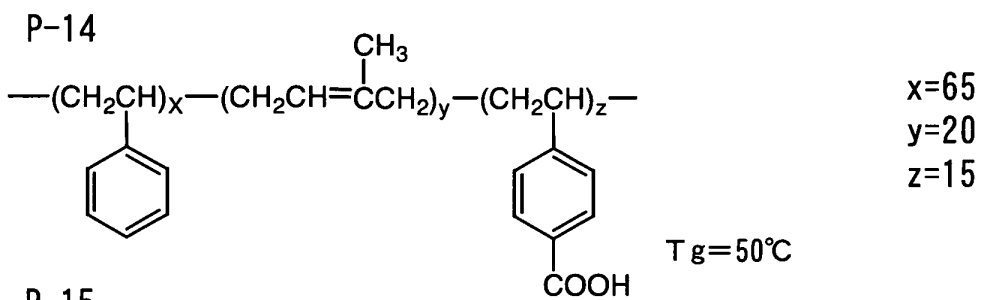
P-12



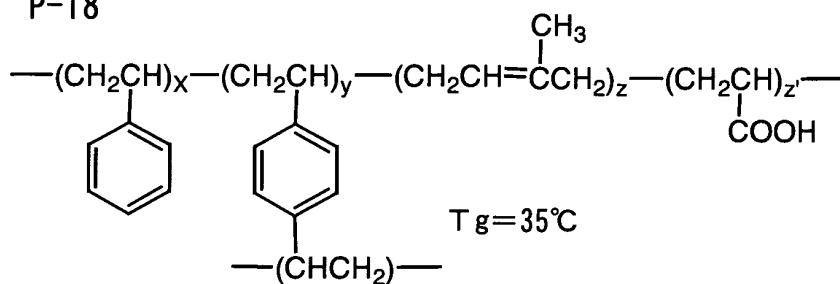
P-13



$T_g=32^\circ\text{C}$

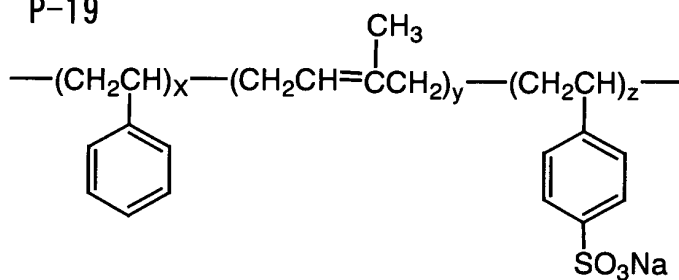


P-18



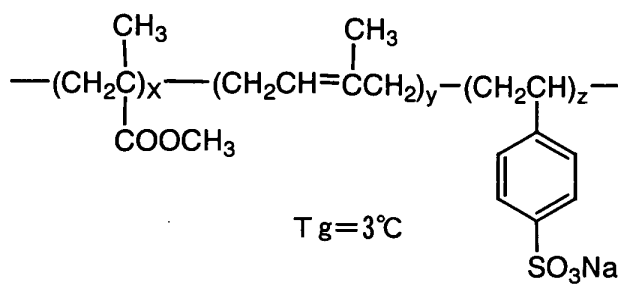
x=66
y=2
z=29
z'=3

P-19



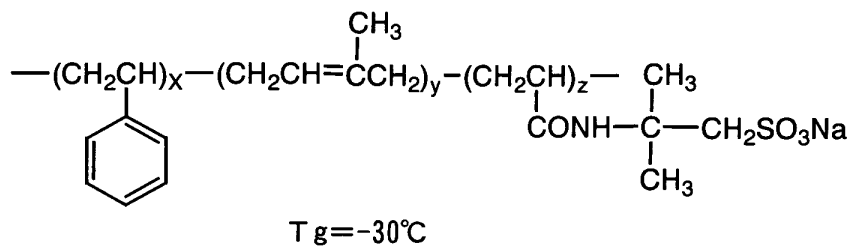
x=63
y=35
z=2

P-20



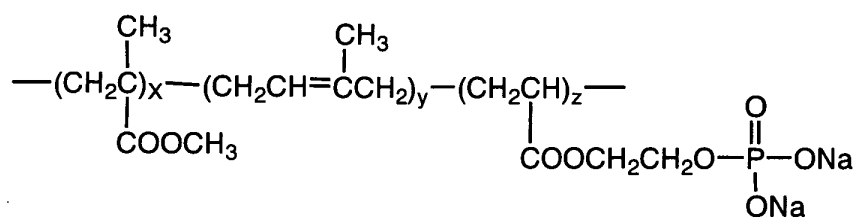
x=51
y=45
z=4

P-21



x=29
y=70
z=1

P-22



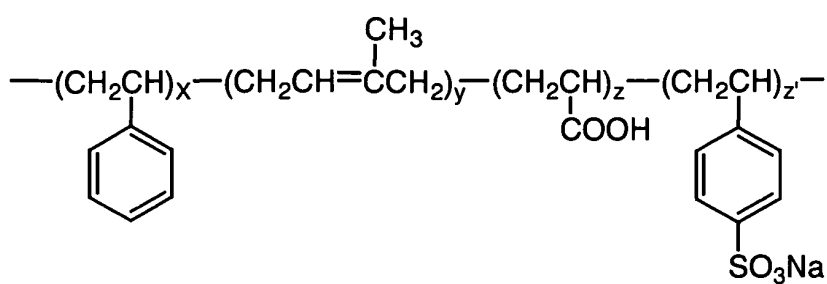
x=43

y=54

z=3

T_g = -12°C

P-23



x=67

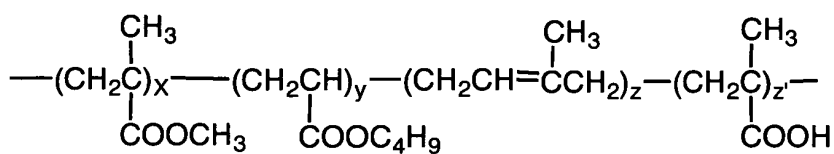
y=30

z=1

z'=2

T_g = 28°C

P-24



x=70

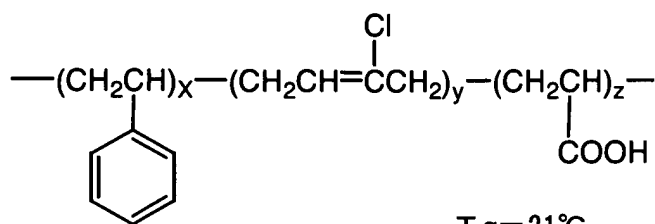
y=22

z=5

z'=3

T_g = 42°C

P-25



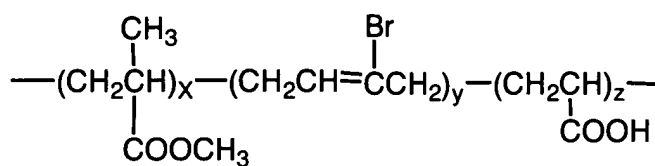
x=55

y=42

z=3

T_g=21°C

P-26



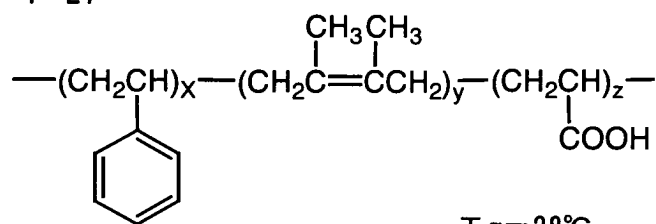
x=49

y=58

z=3

T_g=-10°C

P-27



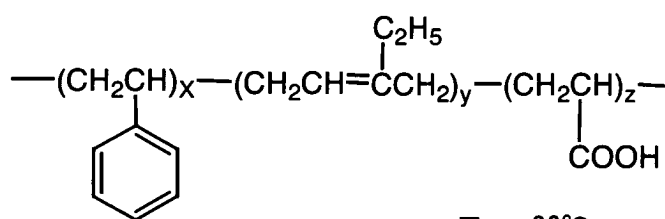
x=40

y=57

z=3

T_g=28°C

P-28

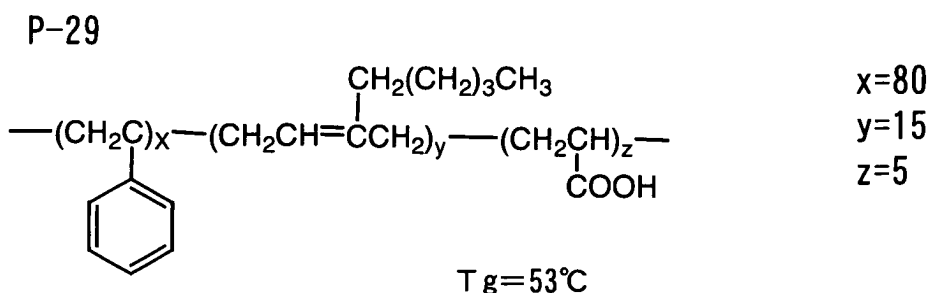


x=68

y=28

z=4

T_g=26°C



[0144] While examples of synthesis of the polymers used in the invention are shown below, the invention is not restricted to the synthetic methods shown below. Similar synthetic method may be used for other compounds in the examples.

<Synthetic Example 1: synthesis of compound P-1>

[0145] Into the polymerization vessel of gas monomer reaction apparatus (type TAS-2J, manufactured by Taiatsu Techno Corp.), 1500 g of distilled water were poured and heated for 3 hours at 90°C to make passive film over the stainless-steel vessel surface and stainless-steel stirring device. Into the polymerization vessel after this treatment were added 584.86 g of distilled water which was bubbled with nitrogen gas for 1 hour, 9.45 g of a surfactant (PIONIN A-43-S produced by Takemoto Oil and Fats Cp.), 20.25 g of 1 mol/L sodium hydroxide, 0.216 g of ethylenediamine tetraacetic acid tetrasodium salt, 332.1 g of styrene, 191.7 g of isoprene, 16.2 g of acrylic acid, and 4.32 g of tert-dodecyl mercaptan. And then the reaction vessel was sealed the mixture was stirred at 225 rpm, followed by elevating the inner temperature to 60°C. To the aforementioned mixture was added a solution prepared through dissolving 2.7 g of ammonium persulfate in 50 mL of water, and kept for 7 hours with stirring.

[0146] Furthermore, the mixture was heated to 90°C with stirring for 3 hours. After the reaction was completed, the inner temperature of the reaction vessel was cooled to room temperature. The polymer obtained was filtered through a filter cloth (mesh: 225), then 1145 g of the example compound P-1 (solid content of 45 % by weight, particle diameter of 112 nm) was obtained.

<Synthetic Example 2: synthesis of compound P-2>

[0147] Into the reaction vessel of gas monomer reaction apparatus (type TAS-2J manufactured by Tiatsu Garasu Kogyo Ltd.) pretreated to make passive film similar to the above-described Synthetic Example 1, 350.92 g of distilled water which was bubbled with nitrogen gas for 1 hour, 3.78 g of the surfactant (PIONIN A-43-S produced by Takemoto Oil and Fats Cp.), 20.25 g of 1 mol/L sodium hydroxide, 0.216 g of ethylenediamine tetraacetic acid tetrasodium salt, 34.02 g of styrene, 18.36 g of isoprene, 1.62 g of acrylic acid, and 2.16 g of tert-dodecyl mercaptan were added. Thereafter, the reaction vessel was sealed and the mixture was stirred at 225 rpm, followed by elevating the inner temperature to 65°C.

[0148] To this mixture was added a solution prepared through dissolving 1.35 g of ammonium persulfate in 50 mL of water and kept for 2 hours with stirring. An emulsion was separately prepared by adding, with stirring, 233.94 g of distilled water, 5.67 g of the surfactant (PIONIN A-43-S produced by Takemoto Oil and Fats Cp.), 306.18 g of styrene, 165.24 g of isoprene, 14.58 g of acrylic acid, 2.16 g of tert-dodecyl mercaptan, and 1.35 g of ammonium persulfate. The emulsion was poured dropwise over 8 hours into the reaction vessel described above. The reaction solution was further stirred for 2 hours after completing the addition.

[0149] Thereafter the resulting mixture was further stirred for 3 hours by elevating the temperature at 90°C. After the reaction was completed, the inner temperature of the reaction vessel was cooled to room temperature. The polymers obtained was filtered through a filter cloth (mesh: 225), then 1147 g of the example compound P-2 (solid content of 45 % by weight, particle diameter of 121 nm) was obtained.

<Synthetic Example 3: synthesis of compound P-4>

[0150] Into the reaction vessel of gas monomer reaction apparatus (type TAS-2J manufactured by Tiatsu Garasu Kogyo Ltd.) pretreated to make passive film similar to the above-described Synthetic Example 1, 578.11 g of distilled water which was bubbled with nitrogen gas for one hour, 16.2 g of the surfactant (PELEX SS-H produced by Kao Co.,

Ltd.), 20.25 g of 1 mol/L sodium hydroxide, 0.216 g of ethylenediamine tetraacetic acid tetrasodium salt, 321.3 g of styrene, 202.5 g of isoprene, 1.62 g of acrylic acid, and 4.32 g of tert-dodecyl mercaptan were added. Thereafter the reaction vessel was sealed and the mixture was stirred at the stirring rate of 225 rpm, followed by elevating the inner temperature to 60°C.

[0151] To the aforesaid mixture was added a solution prepared through dissolving 2.7 g of ammonium persulfate in 25 mL of water, and kept for 5 hours with stirring. Furthermore a solution obtained dissolving 1.35 g of ammonium persulfate dissolved in 25 mL of water was added to the mixture. Then the mixture was heated to 90°C and stirred for 3 hours. After the reaction was completed, the inner temperature of the vessel was cooled to room temperature. The polymers obtained was filtered through filter cloth (mesh: 225), then 1139 g of the example compound P-4 (solid content of 45 % by weight, particle diameter of 105 nm) was obtained.

[0152] In the invention, for the solvent of a coating solution for the polymer latex, water solvent can be used and any of water-admixing organic solvents may be used in combination.

[0153] As water-admixing organic solvents, there can be used, for example, alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, and the like; cellosolves such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, and the like; ethyl acetate, dimethylformamide, and the like. The addition amount of the organic solvent is 50% by weight or less, and more preferably 30% by weight or less, with respect to the solvent.

[0154] As for the polymer latex of the invention, the concentration of the polymer is preferably 10% by weight to 70% by weight, more preferably 20% by weight to 60% by weight, and particularly preferably 30% by weight to 55% by weight, with respect to the latex solution in each case.

[0155] The equilibrium water content under 25°C and 60%RH is preferably 2% by weight or lower, but is more preferably, 0.01% by weight to 1.5% by weight, and is further preferably, 0.02% by weight to 1.0% by weight.

[0156] The term "equilibrium water content under 25°C and 60%RH" as referred herein can be expressed as follows:

Equilibrium water content under 25°C and 60%RH

$$= [(W1 - W0)/W0] \times 100 \text{ (\% by weight)}$$

wherein W1 is the weight of the polymer in moisture-controlled equilibrium under the atmosphere of 25°C and 60%RH, and W0 is the absolutely dried weight at 25°C of the polymer.

[0157] For the definition and the method of measurement for water content, reference can be made to Polymer Engineering Series 14, "Testing methods for polymeric materials" (The Society of Polymer Science, Japan, published by Chijin Shokan).

[0158] In the invention, polymers capable of being dispersed in an aqueous solvent are particularly preferable. Examples of dispersed states may include a latex, in which water-insoluble fine particles of hydrophobic polymer are dispersed, or such in which polymer molecules are dispersed in molecular states or by forming micelles, but preferred are latex-dispersed particles. The average particle size of the latex-dispersed particles is in a range of from 1 nm to 50,000 nm, preferably from 5 nm to 1,000 nm, more preferably 10 nm to 500 nm, and further preferably 50 nm to 200 nm. There is no particular limitation concerning particle size distribution of the dispersed particles, and they may be widely distributed or may exhibit a monodisperse particle size distribution. From the viewpoint of controlling the physical properties of the coating solution, preferred mode of usage includes mixing two or more types of particles each having monodisperse particle distribution.

[0159] In the image forming layer of the present invention, if necessary, there can be added hydrophilic polymers such as gelatin, polyvinyl alcohol, methyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, and the like. The hydrophilic polymers above are added at an amount of 30% by weight or less, preferably 20% by weight or less, with respect to the total weight of the binder incorporated in the image forming layer.

[0160] The image forming layer of the present invention is preferably formed by using a polymer latex. Concerning the amount of the binder for the image forming layer, the weight ratio for total binder to organic silver salt (total binder/organic silver salt) is preferably in a range of from 1/10 to 10/1, more preferably from 1/3 to 5/1, and further preferably 1/1 to 3/1.

[0161] The weight ratio for total binder to photosensitive silver halide (total binder/photosensitive silver halide) is preferably in a range of from 400 to 5, and more preferably, from 200 to 10.

[0162] The total amount of binder in the image forming layer of the invention is preferably in a range from 0.2 g/m² to 30 g/m², more preferably from 1 g/m² to 15 g/m², and further preferably 2 g/m² to 10 g/m². As for the image forming layer of the invention, there may be added a crosslinking agent for crosslinking, or a surfactant and the like to improve coating properties.

(Antifoggant)

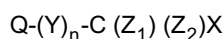
[0163] As an antifoggant, stabilizer and stabilizer precursor usable in the invention, there can be mentioned those disclosed as patents in paragraph number 0070 of JP-A No. 10-62899 and in line 57 of page 20 to line 7 of page 21 of EP-A No. 0803764A1, the compounds described in JP-A Nos. 9-281637 and 9-329864, in USP No. 6,083,681, and in EP-A No. 1048975.

[0164] Furthermore, the antifoggant preferably used in the invention is an organic halogen compound, and those disclosed in paragraph Nos. 0111 to 0112 of JP-A No. 11-65021 can be enumerated as examples thereof. In particular, the organic halogen compound expressed by formula (P) in JP-A No. 2000-284399, the organic polyhalogen compound expressed by formula (II) in JP-A No. 10-339934, and organic polyhalogen compounds described in JP-A Nos. 2001-31644 and 2001-33911 are preferred.

1) Organic polyhalogen compound

Organic polyhalogen compounds preferably used in the invention are specifically described below. In the invention, preferred organic polyhalogen compounds are the compounds expressed by formula (H) below:

Formula (H)



[0165] In formula (H), Q represents one selected from an alkyl group, an aryl group, and a heterocyclic group; Y represents a divalent linking group; n represents 0 or 1; Z₁ and Z₂ each represent a halogen atom; and X represents a hydrogen atom or an electron-attracting group.

[0166] In formula (H), Q is preferably an aryl group, or a heterocyclic group.

[0167] In formula (H), in the case where Q is a heterocyclic group, Q is preferably a nitrogen-containing heterocyclic group having 1 or 2 nitrogen atoms, and particularly preferably a 2-pyridyl group or a 2-quinolyl group.

[0168] In formula (H), in the case where Q is an aryl group, Q preferably is a phenyl group substituted by an electron-attracting group whose Hammett substituent coefficient σ_p yields a positive value. For the details of Hammett substituent coefficient, reference can be made to Journal of Medicinal Chemistry, vol. 16, No. 11 (1973), pp. 1207 to 1216, and the like.

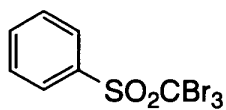
[0169] As such electron-attracting group, examples include, halogen atoms (fluorine atom (σ_p value: 0.06), chlorine atom (σ_p value: 0.23), bromine atom (σ_p value: 0.23), iodine atom (σ_p value: 0.18)), trihalomethyl groups (tribromomethyl σ_p value: 0.29), trichloromethyl (σ_p value: 0.33), trifluoromethyl (σ_p value: 0.54)), a cyano group (σ_p value: 0.66), a nitro group (σ_p value: 0.78), an aliphatic aryl sulfonyl group or a heterocyclic sulfonyl group (for example, methanesulfonyl (σ_p value: 0.72)), an aliphatic aryl acyl group or a heterocyclic acyl group (for example, acetyl (σ_p value: 0.50) and benzoyl (σ_p value: 0.43)), an alkynyl (e.g., C \equiv CH (σ_p value: 0.23)), an aliphatic aryl oxycarbonyl group or a heterocyclic oxycarbonyl group (for example, methoxycarbonyl (σ_p value: 0.45) and phenoxy carbonyl (σ_p value: 0.44)), a carbamoyl group (σ_p value: 0.36), a sulfamoyl group (σ_p value: 0.57), a sulfoxido group, a heterocyclic a group, a phosphoryl group, and the like. Preferred range of the σ_p value is from 0.2 to 2.0, and more preferably, from 0.4 to 1.0. Particularly preferred as the electron-attracting groups are a carbamoyl group, an alkoxy carbonyl group, an alkylsulfonyl group, and an alkylphosphoryl group, and most preferred among them is a carbamoyl group.

[0170] X is preferably an electron-attracting group, and more preferably, a halogen atom, an aliphatic aryl sulfonyl group, a heterocyclic sulfonyl group, an aliphatic aryl acyl group, a heterocyclic acyl group, an aliphatic aryl oxycarbonyl group, a heterocyclic oxycarbonyl group, a carbamoyl group, or a sulfamoyl group; particularly preferred among them is a halogen atom. Among halogen atoms, preferred are chlorine atom, bromine atom, and iodine atom; more preferred are chlorine atom and bromine atom; and particularly preferred is bromine atom.

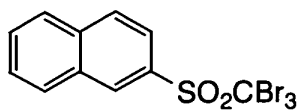
[0171] Y preferably represents -C(=O)-, -SO-, or -SO₂-; more preferably, -C(=O)- or -SO₂-; and particularly preferred is -SO₂-. n represents 0 or 1, and preferably represents 1.

[0172] Specific examples of the compounds expressed by formula (H) of the invention are shown below.

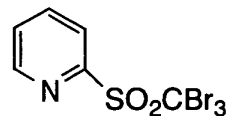
H-1



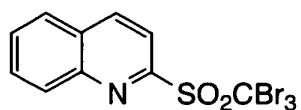
H-2



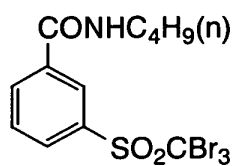
H-3



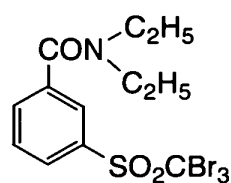
H-4



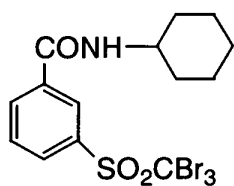
H-5



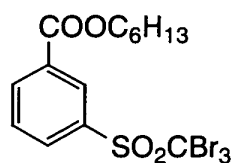
H-6



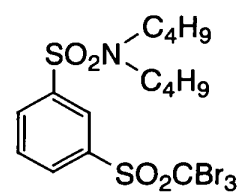
H-7



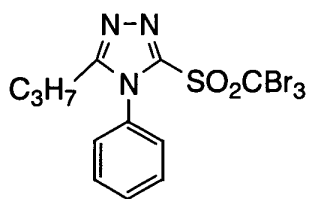
H-8



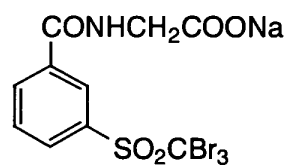
H-9



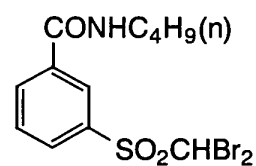
H-10



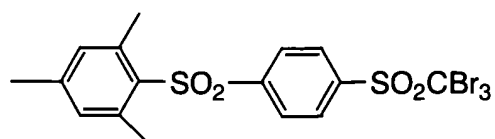
H-11



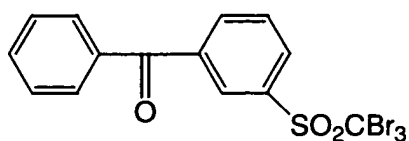
H-12



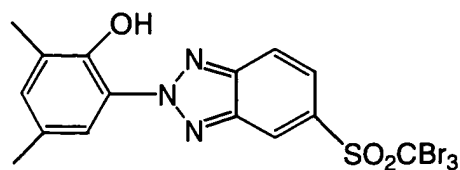
H-13



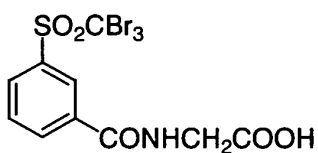
H-14



H-15



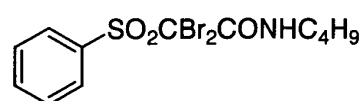
H-16



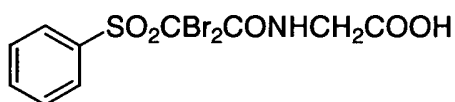
H-17



H-18



H-19



[0173] As preferred organic polyhalogen compounds of the invention other than those above, there can be mentioned compounds disclosed in JP-A Nos. 2001-31644, 2001-56526, and 2001-209145.

[0174] The compounds expressed by formula (H) of the invention are preferably used in an amount of from 10^{-4} mol to 1 mol, more preferably, 10^{-3} mol to 0.5 mol, and further preferably, 1×10^{-2} mol to 0.2 mol, per 1 mol of non-photosensitive silver salt incorporated in the image forming layer.

[0175] In the invention, usable methods for incorporating the antifoggant into the photosensitive material are those described above in the method for incorporating the reducing agent. Furthermore, the organic polyhalogen compound is also preferably used in the form of solid fine particle dispersion.

2) Other antifoggants

[0176] As other antifoggants, there can be mentioned a mercury (II) salt described in paragraph number 0113 of JP-A No. 11-65021, benzoic acids described in paragraph number 0114 of the same literature, a salicylic acid derivative described in JP-A No. 2000-206642, a formaline scavenger compound expressed by formula (S) in JP-A No. 2000-221634, a triazine compound related to Claim 9 of JP-A No. 11-352624, a compound expressed by formula (III), 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and the like, described in JP-A No. 6-11791.

[0177] The photothermographic material of the invention may further contain an azolium salt in order to prevent fogging. Azolium salts useful in the present invention include a compound expressed by formula (XI) described in JP-A No. 59-193447, a compound described in JP-B No. 55-12581, and a compound expressed by formula (II) in JP-A No. 60-153039. The azolium salt may be added to any part of the photothermographic material, but as an additional layer, it is preferred to select a layer on the side having thereon the image forming layer, and more preferred is to select the image forming layer itself. The azolium salt may be added at any time of the process of preparing the coating solution; in the case where the azolium salt is added into the image forming layer, any time of the process may be selected, from the preparation of the organic silver salt to the preparation of the coating solution, but preferred is to add the salt after preparing the organic silver salt and just before coating. As the method for adding the azolium salt, any method using a powder, a solution, a fine-particle dispersion, and the like, may be used.

[0178] Furthermore, it may be added as a solution having mixed therein other additives such as sensitizing agents, reducing agents, toners, and the like.

[0179] In the invention, the azolium salt may be added at any amount, but preferably, it is added in a range from 1×10^{-6} mol to 2 mol, and more preferably, from 1×10^{-3} mol to 0.5 mol, per 1 mol of silver.

(Other additives)

[0180]

1) Mercapto compounds, disulfides and thiones

In the invention, mercapto compounds, disulfide compounds, and thione compounds can be added in order to control the development by suppressing or enhancing development, to improve spectral sensitization efficiency, and to improve storage properties before and after development. Descriptions can be found in paragraph Nos. 0067 to 0069 of JP-A No. 10-62899, a compound expressed by formula (I) of JP-A No. 10-186572 and specific examples thereof shown in paragraph Nos. 0033 to 0052, in lines 36 to 56 in page 20 of EP No. 0803764A1. Among them, mercapto-substituted heterocyclic aromatic compound, which is described in JP-A Nos. 9-297367, 9-304875, 2001-100358, 2002-303954, 2002-303951 and the like, is preferred.

2) Toner

In the photothermographic material of the present invention, the addition of a toner is preferred. The description of the toner can be found in JP-A No.10-62899 (paragraph Nos. 0054 to 0055), EP No.0803764A1 (page21, lines 23 to 48), JP-A Nos. 2000-356317 and 2000-187298. Preferred are phthalazinones (phthalazinone, phthalazinone derivatives and metal salts thereof, e.g., 4-(1-naphthyl)phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxyphthalazinone, and 2,3-dihydro-1,4-phthalazinedione); combinations of phthalazinones and phthalic acids (e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, diammonium phthalate, sodium phthalate, potassium phthalate, and tetrachlorophthalic anhydride); phthalazines (phthalazine, phthalazine derivatives and metal salts thereof, (e.g., 4-(1-naphthyl)phthalazine, 6-isopropylphthalazine, 6-tert-butylphthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine, and 2,3-dihydrophthalazine); and combinations of phthalazines and phthalic acids. Particularly preferred is a combination of phthalazines and phthalic acids.

Among them, particularly preferable are the combination of 6-isopropylphthalazine and phthalic acid, and the combination of 6-isopropylphthalazine and 4-methylphthalic acid.

3) Plasticizer and lubricant

In the invention, well-known plasticizer and lubricant can be used to improve physical properties of film. Particularly, to improve handling facility during manufacturing process or scratch resistance during thermal development, it is preferred to use a lubricant such as a liquid paraffin, a long chain fatty acid, an amide of fatty acid, an ester of fatty acid and the like. Particularly preferred are a liquid paraffin obtained by removing components having low boiling point and an ester of fatty acid having a branch structure and a molecular weight of 1000 or more.

As for plasticizers and lubricants usable in the image forming layer and in the non-photosensitive layer, compounds described in paragraph No. 0117 of JP-A No. 11-65021 and in JP-A Nos. 2000-5137, 2004-219794, 2004-219802, and 2004-334077 are preferable.

4) Dyes and pigments

From the viewpoint of improving image tone, preventing the generation of interference fringes and preventing irradiation on laser exposure, various kinds of dyes and pigments (for instance, C.I. Pigment Blue 60, C.I. Pigment Blue 64, and C.I. Pigment Blue 15:6) can be used in the image forming layer of the invention. Detailed description can be found in WO No. 98/36322, JP-A Nos. 10-268465 and 11-338098, and the like.

5) Nucleator

As for the photothermographic material of the invention, it is preferred to add a nucleator into the image forming layer. Details on the nucleators, method for their addition and addition amount can be found in paragraph No. 0118, paragraph Nos. 0136 to 0193 of JP-A No. 11-223898, as compounds expressed by formulae (H), (1) to (3), (A), and (B) in JP-A No. 2000-284399; as for a nucleation accelerator, description can be found in paragraph No. 0102 of JP-A No. 11-65021, and in paragraph Nos. 0194 to 0195 of JP-A No. 11-223898.

[0181] In the case of using formic acid or formates as a strong fogging agent, it is preferably incorporated into the side having thereon the image forming layer containing photosensitive silver halide, at an amount of 5 mmol or less, and preferably 1 mmol or less, per 1 mol of silver.

[0182] In the case of using a nucleator in the photothermographic material of the invention, it is preferred to use an acid resulting from hydration of diphosphorus pentoxide, or a salt thereof in combination. Acids resulting from the hydration of diphosphorus pentoxide or salts thereof include metaphosphoric acid (salt), pyrophosphoric acid (salt), orthophosphoric acid (salt), triphosphoric acid (salt), tetraphosphoric acid (salt), hexametaphosphoric acid (salt), and the like. Particularly preferred acids obtainable by the hydration of diphosphorus pentoxide or salts thereof include orthophosphoric acid (salt) and hexametaphosphoric acid (salt). Specifically mentioned as the salts are sodium ortho-

phosphate, sodium dihydrogen orthophosphate, sodium hexametaphosphate, ammonium hexametaphosphate, and the like.

[0183] The addition amount of the acid obtained by hydration of diphosphorus pentoxide or the salt thereof (i.e., the coating amount per 1 m² of the photothermographic material) may be set as desired depending on sensitivity and fogging, but preferred is an amount of from 0.1 mg/m² to 500 mg/m², and more preferably, from 0.5 mg/m² to 100 mg/m².

(Preparation of coating solution and coating)

[0184] The temperature for preparing the coating solution for the image forming layer of the invention is preferably from 30°C to 65°C, more preferably, from 35°C or more to less than 60°C, and further preferably, from 35°C to 55°C. Furthermore, the temperature of the coating solution for the image forming layer immediately after adding the polymer latex is preferably maintained in the temperature range from 30°C to 65°C.

(Image forming method using a fluorescent intensifying screen)

[0185] The photothermographic material of the present invention may be either "single-sided type" having an image forming layer on one side of the support, or "double-sided type" having image forming layers on both sides of the support.

<Double-sided type photothermographic material>

[0186] The black and white photothermographic material of the present invention is preferably applied for an image forming method to record radiation images using a fluorescent intensifying screen.

[0187] For the image forming method, the photothermographic material can be preferably employed as described below: where the photothermographic material is exposed with a monochromatic light having the same wavelength as the main emission peak wavelength of the fluorescent intensifying screen and having a half band width of 15 ± 5 nm, and after a thermal developing process, an exposure value required for a density of fog+0.5 for an image obtained by removing the image forming layer that is disposed on the opposite side of an exposure face is 0.005 Lux·sec to 0.07 Lux·sec.

[0188] The image forming method using the photothermographic materials described above comprises:

- (a) providing an assembly for forming an image by placing the photothermographic material between a pair of fluorescent intensifying screens;
- (b) putting an analyte between the assembly and an X-ray source;
- (c) applying X-rays having an energy level in a range of 25 kVp to 125 kVp to the analyte;
- (d) taking the photothermographic material out of the assembly; and
- (e) heating the removed photothermographic material at a temperature at which the image can be developed.

[0189] The photothermographic material used for the assembly in the present invention is subjected to X-ray exposure through a step wedge tablet and thermal development. On the photographic characteristic curve having an optical density (D) and an exposure value (log E) along the rectangular coordinates having the equal axis-of-coordinate unit, it is preferred to adjust so that the thermal developed image may have the photographic characteristic curve where the average gamma (γ) made at the points of a density of fog+0.1 and a density of fog+0.5 is from 0.5 to 0.9, and the average gamma (γ) made at the points of a density of fog+1.2 and a density of fog+1.6 is from 3.2 to 4.0.

[0190] For the X-ray radiography employed in the practice of the present invention, the use of photothermographic material having the aforesaid photographic characteristic curve would give the radiation images with excellent photographic properties that exhibit an extended bottom portion and high gamma value at a middle density area. According to this photographic property, the photographic properties mentioned have the advantage of that the depiction in a low density portion on the mediastinal region and the heart shadow region having little X-ray transmittance becomes excellent, and that the density becomes easy to view, and that the contrast in the images on the lung field region having much X-ray transmittance becomes excellent.

[0191] The photothermographic material having the preferred photographic characteristic curve mentioned above can be easily prepared, for example, by the method where each of the image forming layer of both sides may be constituted of two or more image forming layers containing silver halide and having a sensitivity different from each other. Especially, the aforesaid image forming layer preferably comprises an emulsion of high sensitivity for the upper layer and an emulsion with photographic properties of low sensitivity and high contrast for the lower layer.

[0192] In the case of preparing the image forming layer comprising two layers, the sensitivity difference between the silver halide emulsion in each layer is preferably from 1.5 times to 20 times, and more preferably from 2 times to 15

times. The ratio of the amount of emulsion used for forming each layer may depend on the sensitivity difference between emulsions used and the covering power. Generally, as the sensitivity difference is large, the ratio of the using amount of high sensitivity emulsion is reduced. For example, if the sensitivity difference is two times, and the covering power is equal, the ratio of the amount of high sensitivity emulsion to low sensitivity emulsion would be preferably adjusted to be in a range from 1:20 to 1:50 based on silver amount.

[0193] The techniques such as an emulsion sensitizing method, kinds of additives and constituents employed in the production of the photothermographic material of the present invention are not particularly limited. For example, various kinds of techniques described in JP-A Nos. 2-68539, 2-103037 and 2-115837 can be applied.

[0194] As the techniques for crossover cut (in the case of double-sided photosensitive material) and anti-halation (in the case of single-sided photosensitive material), dyes or combined use of dye and mordant described in JP-A. No. 2-68539, (from page 13, left lower column, line 1 to page 14, left lower column, line 9) can be employed.

[0195] Next the fluorescent intensifying screen employed in the practice of the present invention is explained below. The radiographic intensifying screen essentially comprises a support and a fluorescent substance layer coated on one side of the support as the fundamental structure. The fluorescent substance layer is a layer where the fluorescent substance is dispersed in binders. On the surface of a fluorescent substance layer opposite to the support side (the surface of the side that does not face on the support), a transparent protective layer is generally disposed to protect the fluorescent substance layer from chemical degradation and physical shock.

[0196] Preferred fluorescent substances of the present invention are described below. Tungstate fluorescent substances (CaWO_4 , MgWO_4 , $\text{CaWO}_4\text{:Pb}$ and the like), terbium activated rare earth sulfoxide fluorescent substances ($\text{Y}_2\text{O}_2\text{S:Tb}$, $\text{Gd}_2\text{O}_2\text{S:Tb}$, $\text{La}_2\text{O}_2\text{S:Tb}$, $(\text{Y,Gd})_2\text{O}_2\text{S:Tb}$, $(\text{Y,Gd})\text{O}_2\text{S:Tb}$, Tm, and the like), terbium activated rare earth phosphate fluorescent substances ($\text{YPO}_4\text{:Tb}$, $\text{GdPO}_4\text{:Tb}$, $\text{LaPO}_4\text{:Tb}$, and the like), terbium activated rare earth oxyhalogen fluorescent substances (LaOBr:Tb , LaOBr:Tb , Tm, LaOCl:Tb , LaOCl:Tb , Tm, LaOBr:Tb , GdOBr:Tb , GdOCl:Tb , and the like), thulium activated rare earth oxyhalogen fluorescent substances (LaOBr:Tm , LaOCl:Tm , and the like), barium sulfate fluorescent substances ($\text{BaSO}_4\text{:Pb}$, $\text{BaSO}_4\text{:Eu}^{2+}$, $(\text{Ba,Sr})\text{SO}_4\text{:Eu}^{2+}$, and the like), divalent europium activated alkali earth metal phosphate fluorescent substances ($(\text{Ba}_2\text{PO}_4)_2\text{:Eu}^{2+}$, $(\text{Ba}_2\text{PO}_4)_2\text{:Eu}^{2+}$, and the like), divalent europium activated alkali earth metal fluorinated halogenide fluorescent substances (BaFCl:Eu^{2+} , BaFBr:Eu^{2+} , BaFCl:Eu^{2+} , Tm, BaFBr:Eu^{2+} , Tm, $\text{BaF}_2\text{:BaCl}\cdot\text{KCl:Eu}^{2+}$, $(\text{Ba,Mg})\text{F}_2\text{:BaCl}\cdot\text{KCl:Eu}^{2+}$, and the like), iodide fluorescent substances (CsI:Na , CsI:T1 , NaI , KI:T1 , and the like), sulfide fluorescent substances (ZnS:Ag(Zn,Cd)S:Ag , $(\text{Zn,Cd)S:Cu}$, $(\text{Zn,Cd)S:Cu}$, Al, and the like), hafnium phosphate fluorescent substances ($\text{HfP}_2\text{O}_7\text{:Cu}$ and the like). However, the fluorescent substance used in the present invention is not particularly limited to these specific examples, so long as to emit light in visible or near ultraviolet region by exposure to a radioactive ray.

[0197] In the fluorescent intensifying screen used in the present invention, the fluorescent substances are preferably packed in the grain size graded structure. Especially, fluorescent substance particles having a large particle size is preferably coated at the side of the surface protective layer and fluorescent substance particles having a small particle size is preferably coated at the side of the support. Hereto, the small particle size of fluorescent substance is preferably in a range from 0.5 μm to 2.0 μm and the large size is preferably in a range from 10 μm to 30 μm .

<Single-sided type photothermographic material>

[0198] The single-sided type photothermographic material of the present invention is preferably applied for an X-ray photosensitive material used for mammography.

[0199] To use the single-sided type photothermographic material for that purpose, it is very important to design the contrast of the obtained image in the suitable range.

[0200] The method to draw the photographic characteristic curve of the photothermographic material of the present invention is explained below. As for mammography, molybdenum target tube, which emits a low pressure X-ray, is usually employed as beam source. However, as far as the intensifying screen comprising substantially the fluorescent substance comprising $\text{Gd}_2\text{O}_2\text{S:Tb}$ is used, the photographic characteristic curve obtained by changing the X-ray exposure value by the method of distance using the X-ray beam emitted by tungsten target tube as the beam source, may give substantially the same result obtained above.

[0201] Specifically for the measurement employed in the present invention, X-ray emitted from tungsten target tube operated by three-phase electric power supply at 50 KVp and penetrated through an aluminum plate having a thickness of 3 mm is used. The commercially available UM-Fine screen and the photosensitive material to be measured are made contact and installed in ECMA cassette produced by Fuji Photo Film Co., Ltd. After arranging so that the top plate of cassette, the photothermographic material and the screen may be set, from X-ray tube, in turn, X-ray irradiation is performed. By changing the X-ray exposure value by the method of distance, the assembly is subjected to exposure with a step wedge tablet having a width of 0.15 in terms of log E.

[0202] The exposed photothermographic material is thermally developed under the determined condition. Thereafter, density is measured, and then the photographic characteristic curve is obtained where the logarithm of radiation ex-

posure value is plotted on abscissa axis, and the optical density is plotted on ordinate axis. The contrast is determined from the gradient ($\tan \theta$, when the angle to the abscissa axis is θ) of the straight line connecting the points at a density of fog+0.25 and a density of fog+2.0.

[0203] Next, the measuring method of the sensitivity of the photosensitive material is explained. As for the light source, a monochromatic light having the same wavelength as a main emission peak wavelength of the fluorescent intensifying screen is employed. As a means of obtaining such a required monochromatic light, a method using the filter system where interference filters are combined can be used. According to the aforesaid method, usually the monochromatic light having a required exposure value and a half band width of 15 ± 5 nm can be obtained easily, although it depends also on the combination of interference filters used.

[0204] The monochromatic light whose intensity is correctly measured by an illuminometer in advance is employed as the light source. Thereby the photothermographic material is subjected to exposure with a step wedge tablet through a neutral filter for one second, where the photothermographic material and the light source are one meter apart. The density is measured after a thermal developing process, the sensitivity can be obtained by determining the exposure value required to give a density of fog+0.5 and can be expressed by Lux · second.

[0205] Preferred sensitivity of the photothermographic material used for mammography according to the invention is 0.01 Lux·sec to 0.07 Lux·sec. Preferred contrast for the photothermographic material used for mammography according to the present invention is from 3.0 to 5.0.

[0206] The fluorescent intensifying screen for mammography used in the invention is explained in detail below. The fluorescent intensifying screen used for photographic assembly of mammography used in the present invention is required to have high image sharpness in comparison with the conventional chest diagnosis. Generally, the image sharpness of commercially available fluorescent intensifying screen used for mammography is usually enhanced by coloring the fluorescent substance layer. However, the light emitted by X-ray beam absorbed in the inner side of the fluorescent substance to the X-ray irradiation plane cannot effectively be taken out from the colored screen. For the fluorescent intensifying screen according to the present invention, it is required to provide the intensifying screen coated with the amount of fluorescent substances enough to absorb X-ray and having high image sharpness without coloring the fluorescent substance layer substantially.

[0207] In order to attain the object of the aforesaid screen, the particle size of fluorescent substances preferably may be below a fixed size. The measurement of the particle size is performed by Coulter counter or observation through electron microscope. As for the preferred particle size of the fluorescent substance, the mean equivalent spherical diameter of the fluorescent substance particles is preferably in a range from 1 μm to 5 μm , and more preferably from 1 μm to 4 μm . Although the above condition is not important to the conventional intensifying screen for mammography whose fluorescent substance layer is colored, it is very important to the present invention.

[0208] Moreover, in order to raise the sharpness of the screen mentioned above, the use of fewer binders is preferred in regard to the weight ratio of binder to fluorescent substance in the fluorescent substance layer. The weight ratio of binder/fluorescent substance is preferably from 1/50 to 1/20, and more preferably from 1/50 to 1/25.

[0209] As for the binder, known substances described in JP-A No. 6-75097, from line 45 on right column at page 4 to line 10 on left column at page 5, can be employed. The thermoplastic elastomer having a softening temperature or a melting temperature of 30°C to 150°C can be preferably used alone or in combination with the other binder polymer. Especially for the screen of the present invention, which contains very small amount of binder to enhance the image sharpness, the proper selection of the binder used is very important to resist to the defect, because of the poor durability of the screen. It is desirable to choose entirely flexible binders as the solution for the defect. And also plasticizers and the like are preferably added in the fluorescent substance layer. As specific examples as the thermoplastic elastomer, polystyrenes, polyolefines, polyurethanes, polyesters, polyamides, polybutadienes, ethylene vinyl acetates, natural rubbers, fluorinated rubbers, polyisoprenes, ethylene chlorides, styrene-butadiene rubbers, silicone rubbers, and the like can be described. Among them, polyurethanes are particularly preferred. Moreover, the selection of the binder for the undercoat of the fluorescent substance layer is very important. Acrylate binders are preferably employed.

[0210] To the allowable limit with respect to the anti-scratch and anti-stain properties of the screen, the thickness of the surface protective layer is preferably thin. The preferred thickness of the surface protective layer is in a range of from 2 μm to 7 μm .

[0211] As the materials for the surface protective layer of the screen, films such as PET (especially, stretched type), PEN, nylon, and the like can be preferably stuck thereon. The surface protective layer of the screen is preferably formed by coating the fluorinated resins dissolved in a suitable solvent from the standpoint of preventing stain. The preferred embodiments of the fluorinated resins are described in detail in JP-A No. 6-75097, line 4 on left column at page 6 to line 43 on right column at the same page. As for specific examples of the resin suited for solvent coating type to form the surface protective layer, polyurethane resins, polyacrylate resins, cellulose derivatives, polymethyl methacrylates, polyester resins, epoxy resins, and the like can be mentioned other than fluorinated resins.

[0212] Moreover, it is important that filling factor of the fluorescent substances is sufficiently high to obtain a screen with high image sharpness and high sensitivity. Specifically, the volume filling factor of the fluorescent substance is

preferably from 60% to 80%, and more preferably from 65 % to 80%. In order to keep the volume filling factor of fine particles of the fluorescent substances high as in the present invention, the compression processes of fluorescent substance layer described in JP-A No. 6-75097, line 29 on right column at page 4 to line 1 on left column at page 6, are preferably applied.

[0213] The fluorescent substance used in the present invention preferably comprises substantially $Gd_2O_2S:Tb$. The term "substantially" described here means that main component of the fluorescent substance is $Gd_2O_2S:Tb$, and several % of any other additives to improve the property of the screen, and silica and the like to decorate the surface can preferably be included. And also, in place of Gd, Y, La, or Lu can be possibly mixed inside the ratio of several ten %.

[0214] Generally, fluorescent substance having a heavy density is preferred to absorb X-ray effectively. As such fluorescent substance that shows a desirable X-ray absorption ability in beam source used for mammography, $YTaO_4$ and the one adding various kinds of activator as the emission center thereto, $CaWO_4$, $BaFBr:Eu$, and the like can be mentioned besides $Gd_2O_2S:Tb$.

<Combined use with ultraviolet fluorescent intensifying screen>

[0215] As for the image forming method using photothermographic material according to the present invention, it is preferred that the image forming method is performed in combination with a fluorescent substance having a main emission peak at 400 nm or lower. And more preferably, the image forming method is performed in combination with a fluorescent substance having a main emission peak at 380 nm or lower. Either single-sided photosensitive material or double-sided photosensitive material can be applied for the assembly. As the screen having a main emission peak at 400 nm or lower, the screens described in JP-A No. 6-11804 and WO No. 93/01521 and the like are used, but the present invention is not limited to these. As the techniques of crossover cut (for double-sided photosensitive material) and anti-halation (for single-sided photosensitive material) of ultraviolet light, the technique described in JP-A No. 8-76307 can be applied. As ultraviolet absorbing dyes, the dye described in JP-A No. 2001-144030 is particularly preferred.

(Layer constitution and other constituting components)

[0216] The photothermographic material according to the invention can have a non-photosensitive layer in addition to the image forming layer. The non-photosensitive layers can be classified depending on the layer arrangement into (a) a surface protective layer provided on the image forming layer (on the side farther from the support), (b) an intermediate layer provided among plural image forming layers or between the image forming layer and the protective layer, (c) an undercoat layer provided between the image forming layer and the support, and (d) a back layer provided to the side opposite to the image forming layer.

[0217] Furthermore, a layer that functions as an optical filter may be provided as (a) or (b) above. An antihalation layer may be provided as (c) or (d) to the photothermographic material.

1) Surface protective layer

The photothermographic material of the invention can comprise a surface protective layer with an object to prevent adhesion of the image forming layer. The surface protective layer may be a single layer, or plural layers.

Description of the surface protective layer may be found in paragraph Nos. 0119 to 0120 of JP-A No. 11-65021 and in JP-A No. 2000-171936.

Preferred as the binder of the surface protective layer of the invention is gelatin, but polyvinyl alcohol (PVA) may be used preferably instead, or in combination. As gelatin, there can be used an inert gelatin (e.g., Nitta gelatin 750), a phthalated gelatin (e.g., Nitta gelatin 801), and the like. Usable as PVA are those described in paragraph Nos. 0009 to 0020 of JP-A No. 2000-171936, and preferred are the completely saponified product PVA-105 and the partially saponified PVA-205 and PVA-335, as well as modified polyvinyl alcohol MP-203 (trade name of products from Kuraray Ltd.). The coating amount of polyvinyl alcohol (per 1 m² of support) in the protective layer (per one layer) is preferably in a range from 0.3 g/m² to 4.0 g/m², and more preferably, from 0.3 g/m² to 2.0 g/m².

The coating amount of total binder (including water-soluble polymer and latex polymer) (per 1 m² of support) in the surface protective layer (per one layer) is preferably in a range from 0.3 g/m² to 5.0 g/m², and more preferably, from 0.3 g/m² to 2.0 g/m².

2) Antihalation layer

The photothermographic material of the present invention can comprise an antihalation layer provided to the side farther from the light source with respect to the image forming layer.

Descriptions on the antihalation layer can be found in paragraph Nos. 0123 to 0124 of JP-A No. 11-65021, in JP-A Nos. 11-223898, 9-230531, 10-36695, 10-104779, 11-231457, 11-352625, 11-352626, and the like.

The antihalation layer contains an antihalation dye having its absorption at the wavelength of the exposure

light. In the case the exposure wavelength is in the infrared region, an infrared-absorbing dye may be used, and in such a case, preferred are dyes having no absorption in the visible region.

In the case of preventing halation from occurring by using a dye having absorption in the visible region, it is preferred that the color of the dye would not substantially remain after image formation, and is preferred to employ a means for decoloring by the heat of thermal development; in particular, it is preferred to add a thermal bleaching dye and a base precursor to the non-photosensitive layer to impart function as an antihalation layer. Those techniques are described in JP-A No. 11-231457 and the like.

The addition amount of the bleaching dye is determined depending on the usage of the dye. In general, it is used at an amount as such that the optical density (absorbance) exceeds 0.1 when measured at the desired wavelength. The optical density is preferably in a range from 0.15 to 2, and more preferably from 0.2 to 1. The addition amount of dyes to obtain optical density in the above range is generally from about 0.001 g/m² to 1 g/m².

By decoloring the dye in such a manner, the optical density after thermal development can be lowered to 0.1 or lower. Two or more kinds of bleaching dyes may be used in combination in a photothermographic material. Similarly, two or more kinds of base precursors may be used in combination.

In the case of thermal decolorization by the combined use of a bleaching dye and a base precursor, it is advantageous from the viewpoint of thermal decolorization efficiency to further use a substance capable of lowering the melting point by 3°C or more when mixed with the base precursor (e.g., diphenylsulfone, 4-chlorophenyl(phenyl)sulfone, 2-naphthyl benzoate, or the like) as disclosed in JP-A No. 11-352626.

3) Back layer

Back layers, which can be used in the invention, are described in paragraph Nos. 0128 to 0130 of JP-A No. 11-65021.

In the invention, coloring matters having maximum absorption in a wavelength range from 300 nm to 450 nm can be added in order to improve color tone of developed silver images and a deterioration of the images during aging. Such coloring matters are described in, for example, JP-A Nos. 62-210458, 63-104046, 63-103235, 63-208846, 63-306436, 63-314535, 01-61745, 2001-100363, and the like.

Such coloring matters are generally added in a range from 0.1 mg/m² to 1 g/m², preferably to the back layer which is provided to the side opposite to the image forming layer. Further, in order to control the basic color tone, it is preferred to use a dye having an absorption peak in a wavelength range from 580 nm to 680 nm. As a dye satisfying this purpose, preferred are oil-soluble azomethine dyes described in JP-A Nos. 4-359967 and 4-359968, or water-soluble phthalocyanine dyes described in JP-A No. 2003-295388, which have low absorption intensity on the short wavelength side. The dyes for this purpose may be added to any of the layers, but more preferred is to add them in the non-photosensitive layer on the image forming side, or in the back side.

4) Matting agent

A matting agent is preferably added to the photothermographic material of the invention in order to improve transportability. Description of the matting agent can be found in paragraphs Nos. 0126 to 0127 of JP-A No. 11-65021. The addition amount of the matting agents is preferably in a range from 1 mg/m² to 400 mg/m², and more preferably, from 5 mg/m² to 300 mg/m², with respect to the coating amount per 1 m² of the photothermographic material.

The shape of the matting agents in the invention may be fixed form or non-fixed form. Preferred is to use those having fixed form and globular shape. Average particle size is preferably in a range of from 0.5 μm to 10 μm, more preferably, from 1.0 μm to 8.0 μm, and most preferably, from 2.0 μm to 6.0 μm. Furthermore, a particle size distribution of the matting agent is preferably set as such that the variation coefficient may become 50% or lower, more preferably, 40% or lower, and most preferably, 30% or lower. The variation coefficient, herein, is defined by (the standard deviation of particle diameter)/(mean diameter of the particle) × 100. Furthermore, it is preferred to use by blending two types of matting agents having low variation coefficient and the ratio of their mean diameters is more than 3.

The level of matting on the image forming layer surface is not restricted as far as star-dust trouble occurs, but the level of matting of 30 seconds to 2000 seconds is preferred, particularly preferred, 40 seconds to 1500 seconds as Beck's smoothness. Beck's smoothness can be calculated easily, using Japan Industrial Standard (JIS) P8119 "The method of testing Beck's smoothness for papers and sheets using Beck's test apparatus", or TAPPI standard method T479.

The level of matting of the back layer in the invention is preferably in a range of 1200 seconds or less and 10 seconds or more; more preferably, 800 seconds or less and 20 seconds or more; and further preferably, 500 seconds or less and 40 seconds or more, when expressed by Beck smoothness.

In the invention, the matting agent is preferably contained in an outermost layer of the photothermographic material, in a layer which can function as an outermost layer, or in a layer nearer to outer surface, and also is preferably contained in a layer which can function as a so-called protective layer.

5) Polymer latex

A polymer latex is preferably incorporated in the surface protective layer and the back layer of the present invention. As for such polymer latex, descriptions can be found in "Gosei Jushi Emulsion (Synthetic resin emulsion)" (Taira Okuda and Hiroshi Inagaki, Eds., published by Kobunshi Kankokai (1978)), "Gosei Latex no Oyo (Application of synthetic latex)" (Takaaki Sugimura, Yasuo Kataoka, Soichi Suzuki, and Keiji Kasahara, Eds., published by Kobunshi Kankokai (1993)), and "Gosei Latex no Kagaku (Chemistry of synthetic latex)" (Soichi Muroi, published by Kobunshi Kankokai (1970)). More specifically, there can be mentioned a latex of methyl methacrylate(33.5% by weight)/ethyl acrylate(50% by weight)/methacrylic acid (16.5% by weight) copolymer, a latex of methyl methacrylate(47.5% by weight)/butadiene(47.5% by weight)/itaconic acid(5% by weight) copolymer, a latex of ethyl acrylate/methacrylic acid copolymer, a latex of methyl methacrylate(58.9% by weight)/2-ethylhexyl acrylate(25.4% by weight)/styrene (8.6% by weight)/2-hydroethyl methacrylate(5.1% by weight)/acrylic acid(2.0% by weight) copolymer, a latex of methyl methacrylate(64.0% by weight)/styrene(9.0% by weight)/butyl acrylate(20.0% by weight)/2-hydroxyethyl methacrylate(5.0% by weight)/acrylic acid(2.0% by weight) copolymer, and the like.

Furthermore, as the binder for the surface protective layer, there can be applied the technique described in paragraph Nos. 0021 to 0025 of the specification of JP-A No. 2000-267226, and the technique described in paragraph Nos. 0023 to 0041 of the specification of JP-A No. 2000-19678. The polymer latex in the surface protective layer is preferably contained in an amount of 10% by weight to 90% by weight, particularly preferably, of 20% by weight to 80% by weight of the total weight of binder.

6) Surface pH

The surface pH of the photothermographic material according to the invention preferably yields a pH of 7.0 or lower, more preferably, 6.6 or lower, before thermal developing process. Although there is no particular restriction concerning the lower limit, the lower limit of pH value is about 3, and the most preferred surface pH range is from 4 to 6.2. From the viewpoint of reducing the surface pH, it is preferred to use an organic acid such as phthalic acid derivative or a non-volatile acid such as sulfuric acid, or a volatile base such as ammonia for the adjustment of the surface pH. In particular, ammonia can be used preferably for the achievement of low surface pH, because it can easily vaporize to remove it before the coating step or before applying thermal development.

It is also preferred to use a non-volatile base such as sodium hydroxide, potassium hydroxide, lithium hydroxide, or the like, in combination with ammonia. The method of measuring surface pH value is described in paragraph No. 0123 of the specification of JP-A No. 2000-284399.

7) Hardener

A hardener may be used in each of image forming layer, protective layer, back layer, and the like. As examples of the hardener, descriptions of various methods can be found in pages 77 to 87 of T. H. James, "THE THEORY OF THE PHOTOGRAPHIC PROCESS, FOURTH EDITION" (Macmillan Publishing Co., Inc., 1977). Preferably used are, in addition to chromium alum, sodium salt of 2,4-dichloro-6-hydroxy-s-triazine, N,N-ethylene bis(vinylsulfonacetamide), and N,N-propylene bis(vinylsulfonacetamide), polyvalent metal ions described in page 78 of the above literature and the like, polyisocyanates described in USP No. 4281060, JP-A No. 6-208193 and the like, epoxy compounds of USP No. 4791042 and the like, and vinyl sulfone based compounds of JP-A No. 62-89048.

The hardener is added as a solution, and the solution is added to the coating solution for protective layer 180 minutes before coating to just before coating, preferably 60 minutes before to 10 seconds before coating. However, so long as the effect of the invention is sufficiently exhibited, there is no particular restriction concerning the mixing method and the conditions of mixing. As specific mixing methods, there can be mentioned a method of mixing in the tank, in which the average stay time calculated from the flow rate of addition and the feed rate to the coater is controlled to yield a desired time, or a method using static mixer as described in Chapter 8 of N. Harnby, M. F. Edwards, A. W. Nienow (translated by Koji Takahashi) "EKITAI KONGO GIJUTSU (Liquid Mixing Technology)" (Nikkan Kogyo Shinbunsha, 1989), and the like.

8) Surfactant

As for the surfactant and the solvent applicable in the invention, there can be mentioned those disclosed in paragraph Nos. 0132 and 0133, respectively, of JP-A No. 11-65021.

In the invention, preferably used are fluorocarbon surfactants. Specific examples of fluorocarbon surfactants can be found in those described in JP-A Nos. 10-197985, 2000-19680, 2000-214554, and the like. Polymer fluorocarbon surfactants described in JP-A 9-281636 can be also used preferably. For the photothermographic material of the invention, fluorocarbon surfactants described in JP-A Nos. 2002-82411, 2003-57780, and 2001-264110 are preferably used. Especially, the usage of the fluorocarbon surfactants described in JP-A Nos. 2003-57780 and 2001-264110 in an aqueous coating solution is preferred viewed from the standpoint of capacity in static control, stability of the coating surface state and sliding facility. The fluorocarbon surfactants described in JP-A No. 2001-264110 are most preferred because of high capacity in static control and that it needs small amount to use.

According to the invention, the fluorocarbon surfactant can be used on either side of image forming layer side or back layer side, but is preferred to use on the both sides. Further, it is particularly preferred to use in combination with electrically conductive layer including aforementioned metal oxides. In this case, the amount of the fluorocar-

bon surfactant on the side of the electrically conductive layer can be reduced or removed.

The addition amount of the fluorocarbon surfactant is preferably in a range from 0.1 mg/m² to 100 mg/m² on each side of image forming layer and back layer, more preferably from 0.3 mg/m² to 30 mg/m², and further preferably from 1 mg/m² to 10 mg/m². Especially, the fluorocarbon surfactant described in JP-A No. 2001-264110 is effective, and used preferably in a range from 0.01 mg/m² to 10 mg/m², and more preferably from 0.1 mg/m² to 5 mg/m².

9) Antistatic agent

The photothermographic material of the invention preferably contains an electrically conductive layer including various kinds of metal oxides or electrically conductive polymers known to the public. The antistatic layer may serve as an undercoat layer described above, or a back surface protective layer, and the like, but can also be placed specially. As an electrically conductive material of the antistatic layer, metal oxides having enhanced electric conductivity by the method of introducing oxygen defects or different types of metallic atoms into the metal oxides are preferably for use. Examples of metal oxides are preferably selected from ZnO, TiO₂ and SnO₂. As the combination of different types of atoms, preferred are ZnO combined with Al, In; SnO₂ with Sb, Nb, P, halogen atoms, and the like; TiO₂ with Nb, Ta, and the like; Particularly preferred for use is SnO₂ combined with Sb.

The addition amount of different types of atoms is preferably in a range from 0.01 mol% to 30 mol%, and more preferably, in a range from 0.1 mol% to 10 mol%. The shape of the metal oxides can include, for example, spherical, needle-like, or plate-like shape. The needle-like particles, with the rate of (the major axis)/(the minor axis) is 2.0 or more, and more preferably, 3.0 to 50, is preferred viewed from the standpoint of the electric conductivity effect. The metal oxides is used preferably in a range from 1 mg/m² to 1000 mg/m², more preferably from 10 mg/m² to 500 mg/m², and further preferably from 20 mg/m² to 200 mg/m².

The antistatic layer can be laid on either side of the image forming layer side or the back layer side, it is preferred to set between the support and the back layer. Examples of the antistatic layer in the invention include described in JP-A Nos. 11-65021, 56-143430, 56-143431, 58-62646, and 56-120519, and in paragraph Nos. 0040 to 0051 of JP-A No. 11-84573, USP No. 5575957, and in paragraph Nos. 0078 to 0084 of JP-A No. 11-223898.

10) Support

As the transparent support, preferably used is polyester, particularly, polyethylene terephthalate, which is subjected to heat treatment in the temperature range of from 130°C to 185°C in order to relax the internal strain caused by biaxial stretching and remaining inside the film, and to remove strain ascribed to heat shrinkage generated during thermal development. In the case of a photothermographic material for medical use, the transparent support may be colored with a blue dye (for instance, dye-1 described in the example of JP-A No. 8-240877), or may be uncolored.

As to the support, it is preferred to apply undercoating technology, such as water-soluble polyester described in JP-A No. 11-84574, a styrene-butadiene copolymer described in JP-A No. 10-186565, a vinylidene chloride copolymer described in JP-A No. 2000-39684 and the like. The moisture content of the support is preferably 0.5% by weight or less when coating for image forming layer and back layer is conducted on the support.

11) Other additives

Furthermore, antioxidant, stabilizing agent, plasticizer, UV absorbent, or a film-forming promoting agent may be added to the photothermographic material. Each of the additives is added to either of the image forming layer or the non-photosensitive layer. Reference can be made to WO No. 98/36322, EP No. 803764A1, JP-A Nos. 10-186567 and 10-18568, and the like.

12) Coating method

The photothermographic material of the invention may be coated by any method. More specifically, various types of coating operations inclusive of extrusion coating, slide coating, curtain coating, immersion coating, knife coating, flow coating, or an extrusion coating using the kind of hopper described in USP No. 2681294 are used. Preferably used is extrusion coating or slide coating described in pages 399 to 536 of Stephen F. Kistler and Petert M. Schweizer, "LIQUID FILM COATING" (Chapman & Hall, 1997), and particularly preferably used is slide coating. Example of the shape of the slide coater for use in slide coating is shown in Figure 11b.1, page 427, of the same literature. If desired, two or more layers can be coated simultaneously by the method described in pages 399 to 536 of the same literature, or by the method described in USP No. 2761791 and British Patent No. 837095.

Particularly preferable coating method in the invention is the method described in JP-A Nos. 2001-194748, 2002-153808, 2002-153803, and 2002-182333.

The coating solution for the image forming layer in the invention is preferably a so-called thixotropic fluid. For the details of this technology, reference can be made to JP-A No. 11-52509. Viscosity of the coating solution for the image forming layer in the invention at a shear velocity of 0.1 S⁻¹ is preferably from 400 mPa·s to 100,000 mPa·s, and more preferably, from 500 mPa·s to 20,000 mPa·s. At a shear velocity of 1000 S⁻¹, the viscosity is preferably from 1 mPa·s to 200 mPa·s, and more preferably, from 5 mPa·s to 80 mPa·s.

In the case of mixing two types of liquids on preparing the coating solution of the invention, known in-line mixer

and in-plant mixer can be used preferably. Preferred in-line mixer of the invention is described in JP-A No. 2002-85948, and the in-plant mixer is described in JP-A No. 2002-90940.

The coating solution of the invention is preferably subjected to defoaming treatment to maintain the coated surface in a fine state. Preferred defoaming treatment method in the invention is described in JP-A No. 2002-66431.

In the case of applying the coating solution of the invention to the support, it is preferred to perform dielectrification in order to prevent the adhesion of dust, particulates, and the like due to charge up. Preferred example of the method of dielectrification for use in the invention is described in JP-A No. 2002-143747.

Since a non-setting coating solution is used for the image forming layer in the invention, it is important to precisely control the drying wind and the drying temperature. Preferred drying method for use in the invention is described in detail in JP-A Nos. 2001-194749 and 2002-139814.

In order to improve the film-forming properties in the photothermographic material of the invention, it is preferred to apply a heat treatment immediately after coating and drying. The temperature of the heat treatment is preferably in a range from 60°C to 100°C at the film surface, and time period for heating is preferably in a range from 1 second to 60 seconds. More preferably, the temperature of the heat treatment is in a range from 70°C to 90°C at the film surface and the time period for heating is from 2 seconds to 10 seconds. A preferred method of heat treatment for the invention is described in JP-A No. 2002-107872.

Furthermore, the production methods described in JP-A Nos. 2002-156728 and 2002-182333 are favorably used in the invention in order to stably and continuously produce the photothermographic material of the invention.

The photothermographic material is preferably of mono-sheet type (i.e., a type which can form image on the photothermographic material without using other sheets such as an image-receiving material).

13) Wrapping material

In order to suppress fluctuation from occurring on the photographic property during a preservation of the photothermographic material of the invention before thermal development, or in order to improve curling or winding tendencies when the photothermographic material is manufactured in a roll state, it is preferred that a wrapping material having low oxygen transmittance and/or vapor transmittance is used. Preferably, oxygen transmittance is $50 \text{ mL} \cdot \text{atm}^{-1}\text{m}^{-2}\text{day}^{-1}$ or lower at 25°C, more preferably, $10 \text{ mL} \cdot \text{atm}^{-1}\text{m}^{-2}\text{day}^{-1}$ or lower, and further preferably, $1.0 \text{ mL} \cdot \text{atm}^{-1}\text{m}^{-2}\text{day}^{-1}$ or lower. Preferably, vapor transmittance is $10 \text{ g} \cdot \text{atm}^{-1}\text{m}^{-2}\text{day}^{-1}$ or lower, more preferably, $5 \text{ g} \cdot \text{atm}^{-1}\text{m}^{-2}\text{day}^{-1}$ or lower, and further preferably, $1 \text{ g} \cdot \text{atm}^{-1}\text{m}^{-2}\text{day}^{-1}$ or lower.

As specific examples of a wrapping material having low oxygen transmittance and/or vapor transmittance, reference can be made to, for instance, the wrapping material described in JP-A Nos. 8-254793 and 2000-206653.

14) Other applicable techniques

Techniques which can be used for the photothermographic material of the invention also include those in EP No. 803764A1, EP No. 883022A1, WO No. 98/36322, JP-A Nos. 56-62648, and 58-62644, JP-A Nos. 09-43766, 09-281637, 09-297367, 09-304869, 09-311405, 09-329865, 10-10669, 10-62899, 10-69023, 10-186568, 10-90823, 10-171063, 10-186565, 10-186567, 10-186569 to 10-186572, 10-197974, 10-197982, 10-197983, 10-197985 to 10-197987, 10-207001, 10-207004, 10-221807, 10-282601, 10-288823, 10-288824, 10-307365, 10-312038, 10-339934, 11-7100, 11-15105, 11-24200, 11-24201, 11-30832, 11-84574, 11-65021, 11-109547, 11-125880, 11-129629, 11-133536 to 11-133539, 11-133542, 11-133543, 11-223898, 11-352627, 11-305377, 11-305378, 11-305384, 11-305380, 11-316435, 11-327076, 11-338096, 11-338098, 11-338099, and 11-343420, JP-A Nos. 2000-187298, 2000-10229, 2000-47345, 2000-206642, 2000-98530, 2000-98531, 2000-112059, 2000-112060, 2000-112104, 2000-112064, and 2000-171936.

(Image forming method)

[0218] Although any method may be used for development of the photothermographic material of the invention, thermal development process is usually performed by elevating the temperature of the photothermographic material exposed imagewise. The temperature for development is preferably 90°C to 180°C, more preferably 95°C to 140°C, and further preferably 100°C to 130°C. Time period for development is generally 1 second to 60 seconds, preferably 3 seconds to 30 seconds, and more preferably 5 seconds to 15 seconds.

[0219] As for the process for thermal development, either a drum type heater or a plate type heater may be used. However, a plate type heater process is preferred. A preferable process for thermal development by a plate type heater is a process described in JP-A No. 11-133572, which discloses a thermal developing device in which a visible image is obtained by bringing a photothermographic material with a formed latent image into contact with a heating means at a thermal developing portion, wherein the heating means comprises a plate heater, and a plurality of pressing rollers are oppositely provided along one surface of the plate heater, the thermal developing device is characterized in that thermal development is performed by passing the photothermographic material between the pressing rollers and the plate heater.

[0220] It is preferred that the plate heater is divided into 2 to 6 portions, with the leading end having a lower temper-

ature by 1°C to 10°C. For example, 4 sets of plate heaters, which can be independently subjected to the temperature control, are used, and are controlled so that they respectively become 112°C, 119°C, 121°C, and 120°C.

[0221] For downsizing the thermal developing apparatus and for shortening the time period for thermal development, it is preferable that the heater is more stably controlled, and a top part of one sheet of the photothermographic material is exposed and thermal development of the exposed portion is started before exposure of the end part of the sheet has completed,

[0222] Preferred imagers capable of rapid processing for use in the invention are described in, for example, JP-A Nos. 2002-289804 and 2002-287668. When such imagers are used, thermal development within 14 seconds is possible with a plate type heater having three heating plates which are controlled, for example, at 107°C, 121°C, and 121°C, respectively. Thus, the output time period for the first sheet can be reduced to about 60 seconds.

[0223] In a rapid developing process like this, there exists various problems as mentioned above, and it is particularly preferable to use in combination with the photothermographic material of the invention.

(Application of the invention)

[0224] The photothermographic material and the image forming method of the invention are employed for forming black and white images by silver imaging. Preferably, the photothermographic material and the image forming method of the invention can be employed for medical imaging.

EXAMPLES

[0225] The present invention is specifically explained by way of Examples below, which should not be construed as limiting the invention thereto.

EXAMPLE 1

1. Preparation of PET Support

1-1. Film Manufacturing

[0226] PET having IV (intrinsic viscosity) of 0.66 (measured in phenol/tetrachloroethane = 6/4 (weight ratio) at 25°C) was obtained according to a conventional manner using terephthalic acid and ethylene glycol. The product was pelletized, dried at 130°C for 4 hours, melted at 300°C. Thereafter, the mixture was extruded from a T-die and rapidly cooled to form a non-tentered film.

[0227] The film was stretched along the longitudinal direction by 3.3 times using rollers of different peripheral speeds, and then stretched along the transverse direction by 4.5 times using a tenter machine. The temperatures used for these operations were 110°C and 130°C, respectively. Then, the film was subjected to thermal fixation at 240°C for 20 seconds, and relaxed by 4% along the transverse direction at the same temperature. Thereafter, the chucking part was slit off, and both edges of the film were knurled. Then the film was rolled up at the tension of 4 kg/cm² to obtain a roll having the thickness of 175 μm.

1-2. Surface Corona Discharge Treatment

[0228] Both surfaces of the support were treated at room temperature at 20 m/minute using Solid State Corona Discharge Treatment Machine Model 6KVA manufactured by Piller GmbH. It was proven that treatment of 0.375 KV·A·minute·m⁻² was executed, judging from the readings of current and voltage on that occasion. The frequency upon this treatment was 9.6 kHz, and the gap clearance between the electrode and dielectric roll was 1.6 mm.

1-3. Undercoating

[0229]

1) Preparation of Coating Solution for Undercoat Layer

Pesresin A-520 manufactured by Takamatsu Oil & Fat Co., Ltd. (30% by weight solution) 46.8 g
 BAIRONAARU WD-1200 manufactured by Toyo Boseki Co., Ltd. 10.4 g
 Polyethylene glycol monononylphenylether (average ethylene oxide number = 8.5) (1% by weight solution) 11.0 g

MP-1000 manufactured by Soken Chemical & Engineering Co., Ltd. (PMMA polymer fine particle, mean particle diameter of 0.4 μm) 0.91 g
distilled water 931 mL

5 2) Undercoating

Both surfaces of the aforementioned biaxially tented polyethylene terephthalate support having the thickness of 175 μm were subjected to the corona discharge treatment as described above. Thereafter, the aforementioned formula of coating solution for the undercoat was coated with a wire bar so that the amount of wet coating became 6.6 mL/m² (per one side), and dried at 180°C for 5 minutes. Thus, an undercoated support was produced.

10 2. Image Forming Layer, Intermediate Layer, and Surface Protective Layer

2-1. Preparation of Coating Material

15 1) Preparations of Silver Halide Emulsion

<Preparation of Silver Halide Emulsion A>

20 **[0230]** A solution was prepared by adding 4.3 mL of a 1% by weight potassium iodide solution, and then 3.5 mL of 0.5 mol/L sulfuric acid, 36.5 g of phthalated gelatin, and 160 mL of a 5% by weight methanol solution of 2,2'-(ethylene dithio)diethanol to 1421 mL of distilled water. The solution was kept at 75°C while stirring in a stainless steel reaction vessel, and thereto were added total amount of: solution A prepared through diluting 22.22 g of silver nitrate by adding distilled water to give the volume of 218 mL; and solution B prepared through diluting 36.6 g of potassium iodide with distilled water to give the volume of 366 mL. A method of controlled double jet was executed through adding total amount of the solution A at a constant flow rate over 16 minutes, accompanied by adding the solution B while maintaining the pAg at 10.2.

25 **[0231]** Thereafter, 10 mL of a 3.5 % by weight aqueous solution of hydrogen peroxide was added thereto, and 10.8 mL of a 10% by weight aqueous solution of benzimidazole was further added. Moreover, a solution C prepared through diluting 51.86 g of silver nitrate by adding distilled water to give the volume of 508.2 mL and a solution D prepared through diluting 63.9 g of potassium iodide with distilled water to give the volume of 639 mL were added. A method of controlled double jet was executed through adding total amount of the solution C at a constant flow rate over 80 minutes, accompanied by adding the solution D while maintaining the pAg at 10.2.

30 **[0232]** Potassium hexachloroiridate (III) was added in its entirety to give 1×10^{-4} mol per 1 mol of silver, at 10 minutes post initiation of the addition of the solution C and the solution D. Moreover, at 5 seconds after completing the addition of the solution C, potassium hexacyanoferrate (II) in an aqueous solution was added in its entirety to give 3×10^{-4} mol per 1 mol of silver. And after that, 32.7 g of phthalated gelatin was added. The mixture was adjusted to the pH of 3.8 with 0.5 mol/L sulfuric acid. After stopping stirring, the mixture was subjected to precipitation/ desalting/ water washing steps. The mixture was adjusted to the pH of 5.9 with 1 mol/L sodium hydroxide to produce a silver halide dispersion having the pAg of 11.0.

35 **[0233]** The silver halide emulsion A was a pure silver iodide emulsion, and the obtained silver halide grains had a mean projected area equivalent diameter of 0.93 μm , a variation coefficient of a projected area equivalent diameter distribution of 17.7%, a mean thickness of 0.057 μm and a mean aspect ratio of 16.3. Tabular grains having an aspect ratio of 2 or more occupied 80% or more of the total projected area. The mean equivalent spherical diameter of the grains was 0.42 μm . 90% or more of the silver iodide existed in γ phase from the result of powder X-ray diffraction analysis.

40 <Preparation of Silver Halide Emulsion B>

45 **[0234]** 1 mol of the tabular silver iodide emulsion prepared in the silver halide emulsion A was added to the reaction vessel. The pAg measured at 38°C was 10.2. 0.5 mol/L potassium bromide solution and 0.5 mol/L silver nitrate solution were added at an addition speed of 10 mL/min over 10 minutes by double jet addition to precipitate substantially a 5 mol% of silver bromide on the silver iodide host grain in an epitaxial form while keeping the pAg at 10.2 during the operation.

50 **[0235]** Furthermore, the mixture was adjusted to the pH of 3.8 with 0.5 mol/L sulfuric acid. After stopping stirring, the mixture was subjected to precipitation/ desalting/ water washing steps. The mixture was adjusted to the pH of 5.9 with 1 mol/L sodium hydroxide to produce a silver halide dispersion having the pAg of 11.0.

55 **[0236]** The above-mentioned silver halide dispersion was kept at 38°C with stirring, and thereto was added 5 mL of a 0.34% by weight methanol solution of 1,2-benzisothiazoline-3-one, and after 40 minutes the temperature was ele-

vated to 60°C. At 20 minutes after elevating the temperature, sodium benzene thiosulfonate in a methanol solution was added at 7.6×10^{-5} mol per 1 mol of silver. At additional 5 minutes later, tellurium sensitizer C in a methanol solution was added at 2.0×10^{-5} mol per 1 mol of silver and subjected to ripening for 91 minutes. And then, 1.3 mL of a 0.8% by weight N,N'-dihydroxy-N",N"-diethylmelamine in methanol was added thereto, and at additional 4 minutes thereafter, 5-methyl-2-mercaptobenzimidazole in a methanol solution at 4.8×10^{-3} mol per 1 mol of silver, 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole in a methanol solution at 5.4×10^{-3} mol per 1 mol of silver, and 1-(3-methylureido phenyl)-5-mercaptotetrazole in an aqueous solution at 8.5×10^{-3} mol per 1 mol of silver were added to produce silver halide emulsion B.

<Preparation of Silver Halide Emulsion C>

[0237] Preparation of silver halide emulsion C was conducted in a similar manner to the process in the preparation of the silver halide emulsion A except that adequately changing the addition amount of a 5 % by weight methanol solution of 2,2'-(ethylene dithio)diethanol, the temperature at grain formation step, and the time for adding the solution A. The silver halide emulsion C was a pure silver iodide emulsion. The obtained silver halide grains had a mean projected area equivalent diameter of 1.369 μm , a variation coefficient of a projected area equivalent diameter distribution of 19.7%, a mean thickness of 0.130 μm and a mean aspect ratio of 11.1. Tabular grains having an aspect ratio of 2 or more occupied 80% or more of the total projected area. The mean equivalent spherical diameter of the grains was 0.71 μm . 90% or more of the silver iodide existed in γ phase from the result of powder X-ray diffraction analysis.

<Preparation of Silver Halide Emulsion D>

[0238] Preparation of silver halide emulsion D was conducted in a similar manner to the process in the preparation of silver halide emulsion B, except that using silver halide emulsion C. Thereby, silver halide emulsion D containing 5 mol% of epitaxial silver bromide was prepared.

<Preparation of Mixed Emulsion for Coating Solution>

[0239] The silver halide emulsion B and the silver halide emulsion D at the rate of (silver halide emulsion B : silver halide emulsion D =) 3 : 2 by mole of silver were dissolved, and thereto was added benzothiazolium iodide at 7×10^{-3} mol per 1 mol of silver with a 1% by weight aqueous solution. Further, as "a compound that can be one-electron-oxidized to provide a one-electron oxidation product, which releases one or more electrons", the compounds Nos. 1, 2, and 3 were added respectively in an amount of 2×10^{-3} mol per 1 mol of silver in silver halide.

[0240] Thereafter, as "a compound having an adsorptive group and a reducible group", the compound Nos. 1 and 2 were added respectively in an amount of 8×10^{-3} mol per 1 mol of silver halide.

[0241] Further, water was added thereto to give the content of silver halide of 15.6 g in terms of silver, per 1 liter of the mixed emulsion for a coating solution.

2) Preparation of Dispersion A of Silver Salt of Fatty Acid

<Preparation of Recrystallized Behenic Acid>

[0242] Behenic acid manufactured by Henkel Co. (trade name: Edenor C22-85R) in an amount of 100 kg was admixed with 1200 kg of isopropyl alcohol, and dissolved at 50°C. The mixture was filtrated through a 10 μm filter, and cooled to 30°C to allow recrystallization. Cooling speed for the recrystallization was controlled to be 3 °C/hour. The resulting crystal was subjected to centrifugal filtration, and washing was performed with 100 kg of isopropyl alcohol. Thereafter, the crystal was dried. The resulting crystal was esterified, and subjected to GC-FID analysis to give the results of the content of behenic acid being 96 mol%, lignoceric acid 2 mol%, and arachidic acid 2 mol%. In addition, erucic acid was included at 0.001 mol%.

<Preparation of Dispersion A of Silver Salt of Fatty Acid>

[0243] 88 kg of the recrystallized behenic acid, 422 L of distilled water, 49.2 L of 5 mol/L sodium hydroxide aqueous solution, 120 L of t-butyl alcohol were admixed, and subjected to a reaction with stirring at 75°C for one hour to give a solution of sodium behenate. Separately, 206.2 L of an aqueous solution of 40.4 kg of silver nitrate (pH 4.0) was provided, and kept at a temperature of 10°C. A reaction vessel charged with 635 L of distilled water and 30 L of t-butyl alcohol was kept at 30°C, and thereto were added the total amount of the solution of sodium behenate and the total amount of the aqueous silver nitrate solution with sufficient stirring at a constant flow rate over 93 minutes and 15

seconds, and 90 minutes, respectively. Upon this operation, during first 11 minutes following the initiation of adding the aqueous silver nitrate solution, the added material was restricted to the aqueous silver nitrate solution alone. The addition of the solution of sodium behenate was thereafter started, and during 14 minutes and 15 seconds following the completion of adding the aqueous silver nitrate solution, the added material was restricted to the solution of sodium behenate alone. The temperature inside of the reaction vessel was then set to be 30°C, and the temperature outside was controlled so that the liquid temperature could be kept constant. In addition, the temperature of a pipeline for the addition system of the solution of sodium behenate was kept constant by circulation of warm water outside of a double wall pipe, so that the temperature of the liquid at an outlet in the leading edge of the nozzle for addition was adjusted to be 75°C.

[0244] Further, the temperature of a pipeline for the addition system of the aqueous silver nitrate solution was kept constant by circulation of cool water outside of a double wall pipe. Position at which the solution of sodium behenate was added and the position, at which the aqueous silver nitrate solution was added, was arranged symmetrically with a shaft for stirring located at a center. Moreover, both of the positions were adjusted to avoid contact with the reaction liquid.

[0245] After completing the addition of the solution of sodium behenate, the mixture was left to stand at the temperature as it was for 20 minutes. The temperature of the mixture was then elevated to 35°C over 30 minutes followed by ripening for 210 minutes. Immediately after completing the ripening, solid matters were filtered out with centrifugal filtration. The solid matters were washed with water until the electric conductivity of the filtrated water became 30 μ S/cm. A silver salt of fatty acid was thus obtained. The resulting solid matters were stored as a wet cake without drying.

[0246] When the shape of the resulting particles of the silver behenate was evaluated by an electron micrography, a crystal was revealed having $a = 0.21 \mu\text{m}$, $b = 0.4 \mu\text{m}$ and $c = 0.4 \mu\text{m}$ on the average value, with a mean aspect ratio of 2.1, and a variation coefficient of an equivalent spherical diameter distribution of 11 % (a , b and c are as defined aforementioned.).

[0247] To the wet cake corresponding to 260 kg of a dry solid matter content, were added 19.3 kg of polyvinyl alcohol (trade name: PVA-217) and water to give the total amount of 1000 kg. Then, a slurry was obtained from the mixture using a dissolver blade. Additionally, the slurry was subjected to preliminary dispersion with a pipeline mixer (manufactured by MIZUHO Industrial Co., Ltd.: PM-10 type).

[0248] Next, a stock liquid after the preliminary dispersion was treated three times using a dispersing machine (trade name: Microfluidizer M-610, manufactured by Microfluidex International Corporation, using Z type Interaction Chamber) with the pressure controlled to be 1150 kg/cm² to give a dispersion of the silver behenate. For the cooling manipulation, coiled heat exchangers were equipped in front of and behind the interaction chamber respectively, and accordingly, the temperature for the dispersion was set to be 18°C by regulating the temperature of the cooling medium.

3) Preparations of Reducing Agent Dispersion

<Preparation of Reducing Agent-1 Dispersion>

[0249] To 10 kg of reducing agent-1 (2,2'-methylenebis-(4-ethyl-6-tertbutylphenol)) and 16 kg of a 10% by weight aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP-203) was added 10 kg of water, and thoroughly mixed to give a slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by AIMEX Co., Ltd.) packed with zirconia beads having a mean particle diameter of 0.5 mm for 3 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the reducing agent to be 25% by weight. This dispersion was subjected to heat treatment at 60°C for 5 hours to obtain reducing agent-1 dispersion. Particles of the reducing agent included in the resulting reducing agent dispersion had a median diameter of 0.40 μm , and a maximum particle diameter of 1.4 μm or less. The resultant reducing agent dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 μm to remove foreign substances such as dust, and stored.

<Preparation of Reducing Agent-2 Dispersion>

[0250] To 10 kg of reducing agent-2 (6,6'-di-*t*-butyl-4,4'-dimethyl-2,2'-butylidenediphenol)) and 16 kg of a 10% by weight aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP-203) was added 10 kg of water, and thoroughly mixed to give a slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by AIMEX Co., Ltd.) packed with zirconia beads having a mean particle diameter of 0.5 mm for 3 hours and 30 minutes. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the reducing agent to be 25% by weight.

[0251] This dispersion was warmed at 40°C for one hour, followed by a subsequent heat treatment at 80°C for one hour to obtain reducing agent-2 dispersion. Particles of the reducing agent included in the resulting reducing agent-2

EP 1 584 978 A1

dispersion had a median diameter of 0.50 μm , and a maximum particle diameter of 1.6 μm or less.

[0252] The resultant reducing agent-2 dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 μm to remove foreign substances such as dust, and stored.

5 4) Preparation of Hydrogen Bonding Compound Dispersion

<Preparation of Hydrogen Bonding Compound-1 Dispersion>

10 **[0253]** To 10 kg of hydrogen bonding compound-1 (tri(4-t-butylphenyl)phosphineoxide) and 16 kg of a 10% by weight aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP-203) was added 10 kg of water, and thoroughly mixed to give a slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by AIMEX Co., Ltd.) packed with zirconia beads having a mean particle diameter of 0.5 mm for 4 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the hydrogen bonding compound to be 25% by weight.

15 **[0254]** This dispersion was warmed at 40°C for one hour, followed by a subsequent heat treatment at 80°C for one hour to obtain hydrogen bonding compound-1 dispersion. Particles of the hydrogen bonding compound included in the resulting hydrogen bonding compound dispersion had a median diameter of 0.45 μm , and a maximum particle diameter of 1.3 μm or less. The resultant hydrogen bonding compound dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 μm to remove foreign substances such as dust, and stored.

20

5) Preparations of Dispersions of Development Accelerator and Color-tone-adjusting Agent

<Preparation of Development Accelerator-1 Dispersion>

25 **[0255]** To 10 kg of development accelerator-1 and 20 kg of a 10% by weight aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP-203) was added 10 kg of water, and thoroughly mixed to give a slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by AIMEX Co., Ltd.) packed with zirconia beads having a mean particle diameter of 0.5 mm for 3 hours and 30 minutes. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby

30 adjusting the concentration of the development accelerator to be 20% by weight. Accordingly, development accelerator-1 dispersion was obtained.

[0256] Particles of the development accelerator included in the resulting development accelerator dispersion had a median diameter of 0.48 μm , and a maximum particle diameter of 1.4 μm or less. The resultant development accelerator dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 μm to remove foreign substances such as dust, and stored.

35

<Preparations of Solid Dispersions of Development Accelerator-2 and Color-tone-adjusting Agent-1 >

40 **[0257]** Also concerning solid dispersions of development accelerator-2 and color-tone-adjusting agent-1, dispersion was executed similar to the development accelerator-1, and thus dispersions of 20% by weight and 15% by weight were respectively obtained.

6) Preparations of Organic Polyhalogen Compound Dispersion

45 <Preparation of Organic Polyhalogen Compound-1 Dispersion>

[0258] 10 kg of organic polyhalogen compound-1 (tribromomethane sulfonylbenzene), 10 kg of a 20% by weight aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP-203), 0.4 kg of a 20% by weight aqueous solution of sodium triisopropylphthalenesulfonate and 14 kg of water were thoroughly admixed

50 to give a slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by AIMEX Co., Ltd.) packed with zirconia beads having a mean particle diameter of 0.5 mm for 5 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the organic polyhalogen compound to be 30% by weight. Accordingly, organic polyhalogen compound-1 dispersion was obtained.

55 **[0259]** Particles of the organic polyhalogen compound included in the resulting organic polyhalogen compound dispersion had a median diameter of 0.41 μm , and a maximum particle diameter of 2.0 μm or less. The resultant organic polyhalogen compound dispersion was subjected to filtration with a polypropylene filter having a pore size of 10.0 μm to remove foreign substances such as dust, and stored.

<Preparation of Organic Polyhalogen Compound-2 Dispersion>

[0260] 10 kg of organic polyhalogen compound-2 (N-butyl-3-tribromomethane sulfonylbenzamide), 20 kg of a 10% by weight aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP-203) and 0.4 kg of a 20% by weight aqueous solution of sodium triisopropyl naphthalenesulfonate were thoroughly admixed to give a slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by AIMEX Co., Ltd.) packed with zirconia beads having a mean particle diameter of 0.5 mm for 5 hours. Thereafter, 0.2 g of a benzisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the organic polyhalogen compound to be 30% by weight.

[0261] This fluid dispersion was heated at 40°C for 5 hours to obtain organic polyhalogen compound-2 dispersion. Particles of the organic polyhalogen compound included in the resulting organic polyhalogen compound dispersion had a median diameter of 0.40 μm, and a maximum particle diameter of 1.3 μm or less.

[0262] The resultant organic polyhalogen compound dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 μm to remove foreign substances such as dust, and stored.

7) Preparation of Silver Iodide Complex-forming Agent Solution

[0263] 8 kg of modified polyvinyl alcohol MP-203 was dissolved in 174.57 kg of water, and thereto were added 3.15 kg of a 20% by weight aqueous solution of sodium triisopropyl naphthalenesulfonate and 14.28 kg of a 70% by weight aqueous solution of silver iodide complex-forming agent (compound No. 22). Accordingly, a 5% by weight solution of silver iodide complex-forming agent compound was prepared.

8) Preparations of Aqueous Solution of Mercapto Compound

<Preparation of Aqueous Solution of Mercapto Compound-1>

[0264] Mercapto compound-1 (1-(3-sulfophenyl)-5-mercaptotetrazole sodium salt) in an amount of 7 g was dissolved in 993 g of water to give a 0.7% by weight aqueous solution.

<Preparation of Aqueous Solution of Mercapto Compound-2>

[0265] Mercapto compound-2 (1-(3-methylureidophenyl)-5-mercaptotetrazole) in an amount of 20 g was dissolved in 980 g of water to give a 2.0% by weight aqueous solution.

9) Preparation of Pigment-1 Dispersion

[0266] C.I. Pigment Blue 60 in an amount of 64 g and 6.4 g of DEMOL N manufactured by Kao Corporation were added to 250 g of water and thoroughly mixed to give a slurry. Zirconia beads having the mean particle diameter of 0.5 mm were provided in an amount of 800 g, and charged in a vessel with the slurry. Dispersion was performed with a dispersing machine (1/4G sand grinder mill: manufactured by AIMEX Co., Ltd.) for 25 hours. Thereto was added water to adjust so that the concentration of the pigment became 5% by weight to obtain a pigment-1 dispersion. Particles of the pigment included in the resulting pigment dispersion had a mean particle diameter of 0.21 μm.

10) Preparations of Binder

<<Preparation of SBR Latex Solution (Comparative Latex)>>

[0267] SBR Latex (RP-1) was prepared as follows.

[0268] To a polymerization tank of a gas monomer reaction apparatus (manufactured by Taiatsu Techno Corporation, TAS-2J type), were charged 287 g of distilled water, 7.73 g of a surfactant (PIONIN A-43-S (manufactured by TAKE-MOTO OIL & FAT CO., LTD.): solid matter content of 48.5% by weight), 14.06 mL of 1 mol/L sodium hydroxide, 0.15 g of ethylenediamine tetraacetic acid tetrasodium salt, 255 g of styrene, 11.25 g of acrylic acid, and 3.0 g of tert-dodecyl mercaptan, followed by sealing of the reaction vessel and stirring at a stirring rate of 200 rpm. Degassing was conducted with a vacuum pump, followed by repeating nitrogen gas replacement several times. Thereto was injected 108.75 g of 1,3-butadiene, and the inner temperature is elevated to 60°C. Thereto was added a solution of 1.875 g of ammonium persulfate dissolved in 50 mL of water, and the mixture was stirred for 5 hours as it stands.

[0269] The temperature was further elevated to 90°C, followed by stirring for 3 hours. After completing the reaction, the inner temperature was lowered to reach to the room temperature, and thereafter the mixture was treated by adding

1 mol/L sodium hydroxide and ammonium hydroxide to give the molar ratio of Na⁺ ion : NH₄⁺ ion = 1 : 5.3, and thus, the pH of the mixture was adjusted to 8.4. Thereafter, filtration with a polypropylene filter having the pore size of 1.0 μm was conducted to remove foreign substances such as dust followed by storage. Accordingly, SBR latex RP-1 was obtained in an amount of 774.7 g. Upon the measurement of halogen ion by ion chromatography, concentration of chloride ion was revealed to be 3 ppm. As a result of the measurement of the concentration of the chelating agent by high performance liquid chromatography, it was revealed to be 145 ppm.

[0270] The aforementioned latex had a mean particle diameter of 90 nm, T_g of 17°C, solid matter concentration of 44% by weight, the equilibrium moisture content at 25°C and 60%RH of 0.6% by weight, ionic conductance of 4.80 mS/cm (measurement of the ionic conductance performed using a conductivity meter CM-30S manufactured by Toa Electronics Ltd. for the latex stock solution (44% by weight) at 25°C).

<<Preparations of Other Latex>>

[0271] Syntheses of latexes P-1, P-2, and P-4 of the present invention were conducted according to the synthetic example described above.

[0272] Further, syntheses of latexes P-17, P-19, and C-1 of the present invention and comparative latex C-2 were conducted similar to the synthetic example described above.

2-2. Preparations of Coating Solution

1) Preparations of Coating Solution for Image Forming Layer-1 to -8

[0273] To the dispersion A of silver salt of fatty acid obtained as described above in an amount of 1000 g were serially added water, the organic polyhalogen compound-1 dispersion, the organic polyhalogen compound-2 dispersion, the silver iodide complex-forming agent (compound No. 22) solution, the latex binder solution shown in Table 1, the reducing agent-1 dispersion, the reducing agent-2 dispersion, the hydrogen bonding compound-1 dispersion, the development accelerator-1 dispersion, the development accelerator-2 dispersion, the color-tone-adjusting agent-1 dispersion, the mercapto compound-1 aqueous solution, and the mercapto compound-2 aqueous solution. The coating solution for the image forming layer prepared by adding the mixed emulsion for coating solution thereto followed by thorough mixing just prior to the coating was fed directly to a coating die, and was coated.

2) Preparation of Coating Solution for Intermediate Layer

[0274] To 1000 g of polyvinyl alcohol PVA-205 (manufactured by Kuraray Co., Ltd.), 272 g of the pigment-1 dispersion, and 4200 mL of a 19% by weight solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (weight ratio of the copolymerization of 64/ 9/ 20/ 5/ 2) latex, were added 27 mL of a 5% by weight aqueous solution of aerosol OT (manufactured by American Cyanamid Co.), 135 mL of a 20% by weight aqueous solution of ammonium secondary phthalate and water to give total amount of 10000 g. The mixture was adjusted with sodium hydroxide to give the pH of 7.5. Accordingly, the coating solution for the intermediate layer was prepared, and was fed to a coating die to provide 9.1 mL/m².

[0275] Viscosity of the coating solution was 58 [mPa·s] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

3) Preparation of Coating Solution for First Layer of Surface Protective Layers

[0276] In water was dissolved 64 g of inert gelatin, and thereto were added 112 g of a 19% by weight solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (weight ratio of the copolymerization of 64/ 9/ 20/ 5/ 2) latex, 30 mL of a 15 % by weight methanol solution of phthalic acid, 23 mL of a 10% by weight aqueous solution of 4-methyl phthalic acid, 28 mL of 0.5 mol/L sulfuric acid, 5 mL of a 5% by weight aqueous solution of aerosol OT (manufactured by American Cyanamid Co.), 0.5 g of phenoxyethyl alcohol, and 0.1 g of benzoisothiazolinone. Water was added to give total amount of 750 g. Immediately before coating, 26 mL of a 4% by weight chrome alum which had been mixed with a static mixer was fed to a coating die so that the amount of the coating solution became 18.6 mL/m².

[0277] Viscosity of the coating solution was 20 [mPa·s] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

EP 1 584 978 A1

4) Preparation of Coating Solution for Second Layer of Surface Protective Layers

[0278] In water was dissolved 80 g of inert gelatin and thereto were added 102 g of a 27.5 % by weight solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (weight ratio of the copolymerization of 64/ 9/ 20/ 5/ 2) latex, 5.4 mL of a 2% by weight solution of a fluorocarbon surfactant (F-1), 5.4 mL of a 2% by weight aqueous solution of another fluorocarbon surfactant (F-2), 23 mL of a 5% by weight aqueous solution of aerosol OT (manufactured by American Cyanamid Co.), 25 g of polymethyl methacrylate fine particles (mean particle diameter of 8.0 μm , distribution of volume weighted average of 20%), 1.6 g of 4-methyl phthalic acid, 4.8 g of phthalic acid, 44 mL of 0.5 mol/L sulfuric acid, and 10 mg of benzoisothiazolinone. Water was added to give total amount of 650 g. Immediately before coating, 445 mL of a aqueous solution containing 4% by weight chrome alum and 0.67% by weight phthalic acid was mixed to give a coating solution for the second layer of the surface protective layers, which was fed to a coating die so that 8.3 mL/m² could be provided.

[0279] Viscosity of the coating solution was 19 [mPa·s] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

3. Preparations of Photothermographic Material-1 to -8

[0280] Simultaneous overlaying coating by a slide bead coating method was subjected, on both sides of the support, in order of the image forming layer, intermediate layer, first layer of the surface protective layers and second layer of the surface protective layers, and thus samples of the photothermographic material were produced. In this method, the temperature of the coating solution was adjusted to 31°C for the image forming layer and intermediate layer, to 36°C for the first layer of the surface protective layers, and to 37°C for the second layer of the surface protective layers. The amount of coated silver in the image forming layer was 0.821 g/m² per one side, with respect to the sum of the amounts of silver salt of fatty acid and silver halide. This was coated on both sides of the support.

[0281] The coating amount of each compound (g/m²) for the image forming layer per one side is as follows. The thickness of the image forming layer was 10 μm . The coating amount of silver salt of fatty acid was 0.00625 mol/m².

Silver salt of fatty acid A	
Organic polyhalogen compound-1	0.028
Organic polyhalogen compound-2	0.094
Silver iodide complex-forming agent	0.46
Latex binder (see Table 1)	5.20
Reducing agent-1	0.33
Reducing agent-2	0.13
Hydrogen bonding compound-1	0.15
Development accelerator-1	0.005
Development accelerator-2	0.035
Color-tone-adjusting agent-1	0.002
Mercapto compound-1	0.001
Mercapto compound-2	0.003
Silver halide (on the basis of Ag content)	0.146

[0282] Conditions for coating and drying were as follows.

[0283] The support was decharged by ionic wind. Coating was performed at the speed of 160 m/min. Conditions for coating and drying were adjusted within the range described below, and conditions were set to obtain the most stable surface state.

[0284] The clearance between the leading end of the coating die and the support was 0.10 mm to 0.30 mm.

[0285] The pressure in the vacuum chamber was set to be lower than atmospheric pressure by 196 Pa to 882 Pa.

[0286] In the subsequent cooling zone, the coating solution was cooled by wind having the dry-bulb temperature of 10°C to 20°C.

[0287] Transportation with no contact was carried out, and the coated support was dried with an air of the dry-bulb of 23°C to 45°C and the wet-bulb of 15°C to 21°C in a helical type contactless drying apparatus.

[0288] After drying, moisture conditioning was performed at 25°C in the humidity of 40%RH to 60%RH.

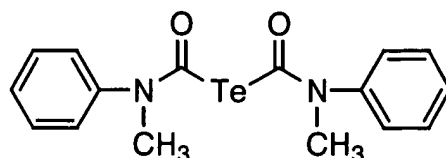
[0289] Then, the film surface was heated to be 70°C to 90°C, and after heating, the film surface was cooled to 25°C.

[0290] Thus prepared photothermographic material had a matt degree of 120 seconds as Beck's smoothness. In addition, measurement of the pH of the film surface gave the result of 6.0.

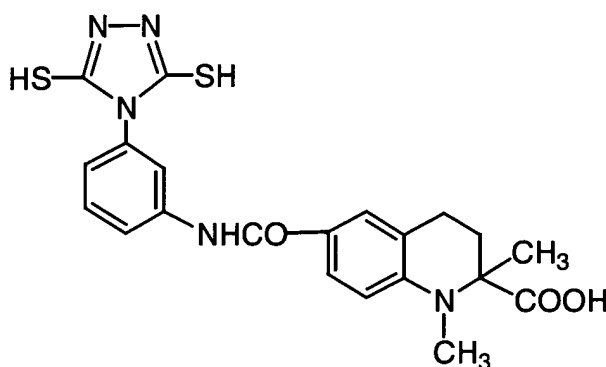
[0291] Chemical structures of the compounds used in Examples of the invention are shown below.

Tellurium sensitizer C

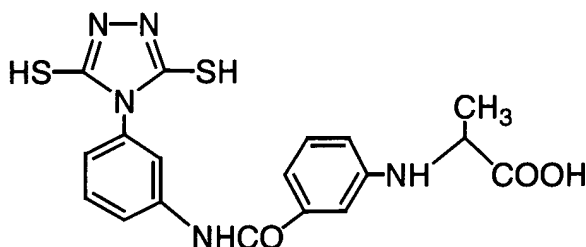
[0292]



[0293] Compound 1 that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons



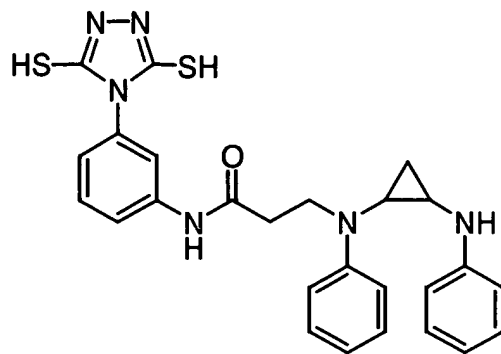
[0294] Compound 2 that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons



[0295] Compound 3 that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons

5

10

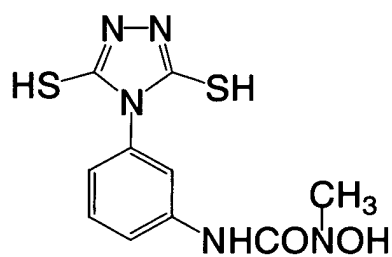


15

[0296] Compound 1 having adsorptive group and reducible group

20

25

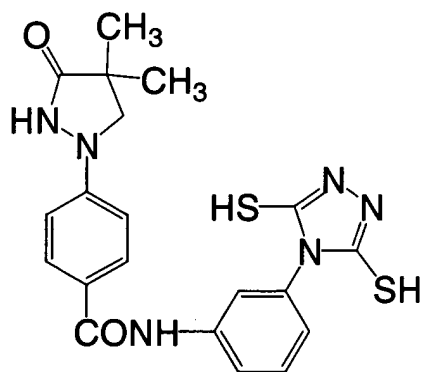


30

[0297] Compound 2 having adsorptive group and reducible group

35

40



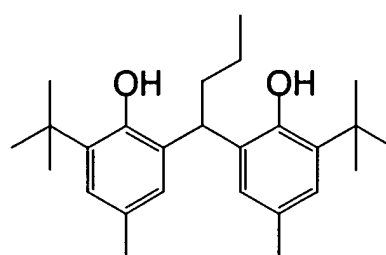
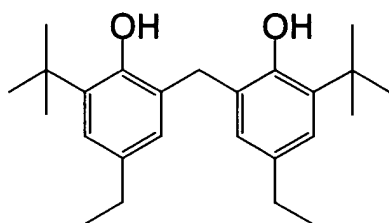
45

Reducing agent-1

Reducing agent-2

50

55

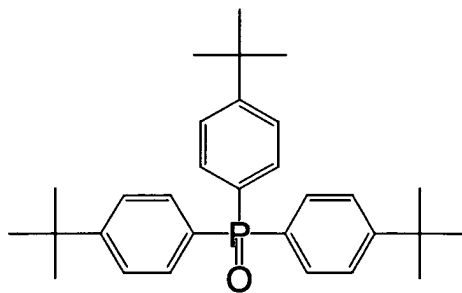


Hydrogen bonding compound-1

5

10

15

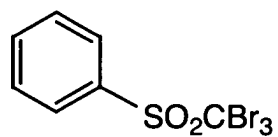


Organic polyhalogen
compound-1

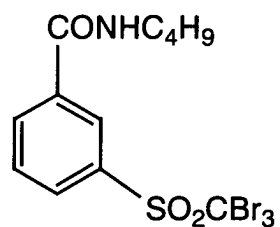
20

25

30



Organic polyhalogen
compound-2

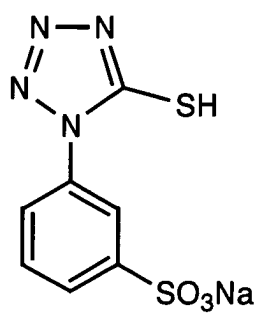


Mercapto compound-1

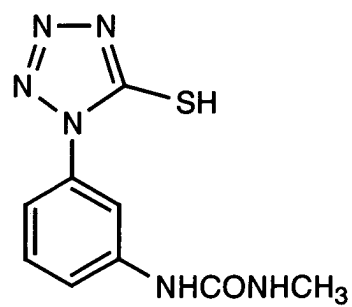
35

40

45



Mercapto compound-2



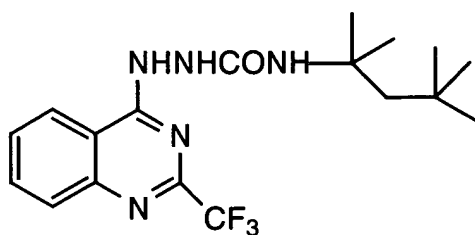
50

55

Development accelerator-1

5

10

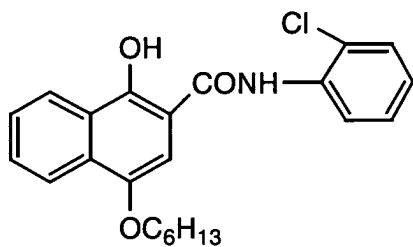


15

Development accelerator-2

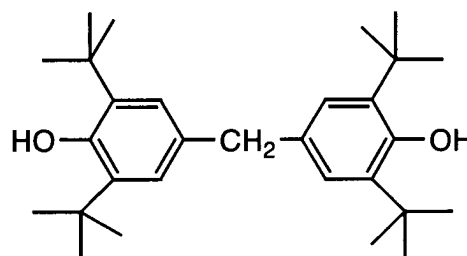
20

25



30

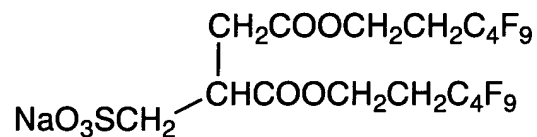
Color-tone-adjusting agent-1



35

(F-1)

40

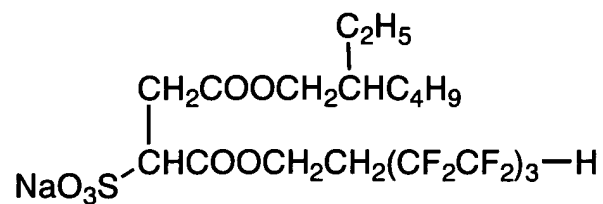


45

(F-2)

50

55



4. Evaluation of Photographic Properties

1) Preparation

5 **[0298]** The resulting sample was cut into a half-cut size, and was wrapped with the following packaging material under an environment of 25°C and 50%RH, and stored for 2 weeks at an ambient temperature.

<Packaging Material>

10 **[0299]** A film laminated with PET 10 μm/ PE 12 μm/ aluminum foil 9 μm/ Ny 15 μm/ polyethylene 50 μm containing carbon at 3% by weight:

oxygen permeability at 25°C: 0.02 mL·atm⁻¹m⁻²day⁻¹,
vapor permeability at 25°C: 0.10 g·atm⁻¹m⁻²day⁻¹.

15

2) Exposure and Thermal Development

<Exposure>

20 **[0300]** Two sheets of X-ray regular screen HI-SCREEN-B3 (CaWO₄ was used as fluorescent substance, the emission peak wavelength of 425 nm) produced by Fuji Photo Film Co., Ltd. were used, and the assembly for image formation was provided by inserting the sample between them. This assembly was subjected to X-ray exposure for 0.05 seconds, and then X-ray sensitometry was performed. The X-ray apparatus used was DRX-3724HD (trade name) produced by
25 Toshiba Corp., and a tungsten target tube was used. X-ray emitted by a pulse generator operated at three phase voltage of 80 kVp and penetrated through a filter comprising 7 cm thickness of water having the absorption ability almost the same as human body was used as the light source. By the method of distance, varying the exposure value of X-ray, the sample was subjected to exposure with a step wedge tablet having a width of 0.15 in terms of log E.

25

<Thermal Development>

30

[0301] The thermal developing portion of Fuji Medical Dry Laser Imager FM-DP L was modified so that it can heat from both sides, and by another modification the transportation rollers in the thermal developing portion were changed to the heating drum so that the sheet of film could be conveyed. The temperature of four panel heaters were set to 112°C- 118°C- 120°C-120°C, and the temperature of the heating drum was set to 120°C. By increasing the speed of
35 transportation, the total time period for thermal development was set to be 14 seconds.

35

3) Method for Evaluation and Results

<Terms for Evaluation>

40

[0302]

- Fog: Fog is an optical density (D_{min}) of an unexposed part.
- Haze after Thermal Development:

45

Concerning haze after thermal development, an unexposed part of the sample was measured using a haze measuring apparatus Model 1001DP produced by Nippon Denshoku Co., Ltd.. The measured haze is an index which represents the transparency of the membrane and correlates with the light scattering properties caused by the incorporated fine particles and the disturbance of the boundary. The ratio of the scattered light is expressed by percent. The smaller is the value, the higher is the transparency of the film. The ratio is expressed by a relative value based on the value of Sample No.1, which was taken as 100.

50

- Evaluation of Membrane Cracking during Thermal Development

A scratch test was carried out at a linear speed of 5 cm/second by using a stainless steel stylus having a point diameter of 0.4 mm, while applying a load which weights in a range of from 0 g to 20 g by increasing 2 grams and making the stylus perpendicular contact with the surface of the sample. Thereafter the sample was subjected to
55 the thermal developing process. Thereby some samples may result in a membrane cracking on the surface of an image forming layer where the scratch test described above was performed. The load under which the cracking starts is an index for the pressure resistance, and the value is expressed by a relative value based on the value for Sample No.1, which was taken as 100. The bigger is the value, the superior is the cracking resistance of the

55

material.

<Results of Evaluation>

5 **[0303]** The obtained results are shown in Table 1 below.

[0304] The photothermographic materials of the present invention attain excellent results in fog, haze, and membrane cracking after processing. However, Sample No.6, where C-1 was used as the binder, results in a small improvement in membrane cracking.

10 TABLE 1

Sample No.	Polymer Latex	Fog	Haze after Development	Membrane Cracking	Note
1	P-1 (Tg :17°C)	0.16	100	100	Invention
2	P-2 (Tg : 20°C)	0.17	102	95	Invention
3	P-4 (Tg : 13°C)	0.16	104	120	Invention
4	P-7 (Tg : 8°C)	0.16	98	110	Invention
5	P-19 (Tg : 18°C)	0.17	99	100	Invention
6	C-1	0.18	110	80	Invention
7	C-2	0.18	125	25	Comparative
8	RP-1 (Tg : 17°C)	0.19	128	35	Comparative
C-1 : methyl methacrylate/isoprene/itaconic acid (weight ratio: 47. 5/47. 5/5, Tg: 0°C) C-2 : methyl methacrylate/butadiene/itaconic acid (weight ratio: 45/45/10, Tg: -2°C)					

EXAMPLE 2

30 **[0305]** Preparations of silver halide emulsion E, G, and I were conducted in a similar manner to the process in the preparation of the silver halide emulsion A except that adequately changing the addition amount of a 5% by weight methanol solution of 2,2'-(ethylene dithio)diethanol, the temperature at grain formation step, and the time for adding the solution A.

35 **[0306]** Preparations of silver halide emulsion F, H, and J were conducted using the emulsion E, G, and H, in a similar manner to the process in the preparation of silver halide emulsion B. Thereby, silver halide emulsion F, H, and J containing 10 mol% of epitaxial silver bromide, respectively, were prepared (Table 2).

40 TABLE 2

Silver Halide Emulsion	Mean Projected Area Equivalent Diameter	Variation Coefficient	Mean Thickness (μm)	Mean Aspect Ratio	Equivalent Spherical Diameter (μm)
A	0.93	17.7%	0.057	16.3	0.42
C	1.369	19.7%	0.130	11.1	0.71
F	0.621	18.5%	0.062	10.0	0.33
H	0.655	18.0%	0.180	3.6	0.34
J	0.602	17.2%	0.330	1.8	0.30

50 **[0307]** Photothermographic material-11 to -16 were prepared as shown in Table 3, using silver halide emulsion F, H, or J instead of silver halide emulsion B, which was used in Sample Nos. 1 and 8 prepared in the Example.

[0308] These photothermographic materials were evaluated similar to Example 1. Results are shown in Table 3.

55 **[0309]** When a tabular silver halide emulsion having as aspect ratio of 2 or more of the present invention was used, a photothermographic material which has low haze after processing and low fog can be provided.

TABLE 3

Sample No.	Polymer Latex	Silver Halide Emulsion (Aspect Ratio)	Fog	Haze after Development	Membrane Cracking	Note Note
1	P-1	B (16.3)	0.16	100	100	Invention
8	RP-1	B (16.3)	0.19	128	35	Comparative
11	P-1	F (10)	0.16	102	105	Invention
12	RP-1	F (10)	0.22	130	40	Comparative
13	P-1	H (3.6)	0.16	103	110	Invention
14	RP-1	H (3.6)	0.22	131	39	Comparative
15	P-1	J (1.8)	0.23	133	125	Comparative
16	RP-1	J (1.8)	0.23	135	122	Comparative

EXAMPLE 3

[0310] Latex P-1b was prepared in a similar manner to the preparation of latex P-1 used for Sample No.1 in Example 1 except that using "SANDET BL" (trade name, available from Sanyo Kasei K.K.) instead of the surfactant "PIONIN A-43-S" (trade name, available from Takemoto Oil & Fat Co., Ltd.) used in the synthesis of latex P-1. Chloride ion concentration of this latex was 553 ppm.

[0311] Sample No.21 was prepared where latex P-1 used for Sample No.1 was changed for latex P-1b by same weight. The processed photothermographic materials were stored under an environment of 1000 Lux (25°C and 60%RH) for one day and thereafter fog was measured, in addition to the evaluation terms carried out in Example 1.

[0312] The obtained results are shown in Table 4.

[0313] The photothermographic materials containing the polymer latex having a high chloride ion concentration exhibit unfavorable increase in fog after exposure to light.

TABLE 4

Sample No.	Polymer Latex	Fog	Haze after Development	Membrane Cracking	Note
1	P-1	0.16	100	100	Invention
21	P-1b	0.19	128	35	Invention

EXAMPLE 4

1. Preparations of Silver Halide Emulsion

<<Preparation of Silver Halide Emulsion K>>

[0314] 1 mol of the tabular silver iodide emulsion prepared similar to the silver halide emulsion A was added to the reaction vessel. The pAg measured at 38°C was 10.2. 0.5 mol/L potassium bromide solution and 0.5 mol/L silver nitrate solution were added at an addition speed of 10 mL/min over 20 minutes by the method of double jet addition at 40°C, to precipitate substantially a 10 mol% of silver bromide on the silver iodide host emulsion in an epitaxial. During the operation, the pAg was kept at 10.2. Furthermore, the mixture was adjusted to the pH of 3.8 with 0.5 mol/L sulfuric acid. After stopping stirring, the mixture was subjected to precipitation/ desalting/ water washing steps. The mixture was adjusted to the pH of 5.9 with 1 mol/L sodium hydroxide to produce a silver halide dispersion having the pAg of 11.0.

[0315] The above-mentioned silver halide dispersion was kept at 38°C with stirring, and thereto was added 5 mL of a 0.34% by weight methanol solution of 1,2-benzisothiazoline-3-one, and after 40 minutes the temperature was elevated to 60°C. At 20 minutes after elevating the temperature, sodium benzene thiosulfonate in a methanol solution was added in an amount of 7.6×10^{-5} mol per 1 mol of silver. At additional 5 minutes later, an aqueous solution of sodium thiosulfate pentahydrate was added in an amount of 7.5×10^{-5} mol per 1 mol of silver, and then after 10 minutes, an aqueous solution of aurichloric acid and an aqueous solution of potassium thiocyanate were added in an amount of 9×10^{-6} mol per 1 mol of silver and 8×10^{-3} mol per 1 mol of silver respectively, and subjected to ripening

for 90 minutes. And then, 1.3 mL of a 0.8% by weight N,N'-dihydroxy-N'',N''-diethylmelamine in methanol was added thereto, and at additional 4 minutes thereafter, 5-methyl-2-mercaptobenzimidazole in a methanol solution at 4.8×10^{-3} mol per 1 mol of silver, 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole in a methanol solution at 5.4×10^{-3} mol per 1 mol of silver, and 1-(3-methylureido phenyl)-5-mercaptotetrazole in an aqueous solution at 8.5×10^{-3} mol per 1 mol of silver were added to produce silver halide emulsion K.

<<Preparation of Silver Halide Emulsion L>>

[0316] A silver halide dispersion containing 10 mol% of epitaxial silver bromide was prepared in a similar manner to the process in the preparation of silver halide emulsion K, except that using silver halide emulsion C of Example 1 instead of using silver halide emulsion A.

[0317] The above-mentioned silver halide dispersion was kept at 38°C with stirring, and thereto was added 5 mL of a 0.34% by weight methanol solution of 1,2-benzisothiazoline-3-one, and after 20 minutes the temperature was elevated to 50°C. At 20 minutes after elevating the temperature, sodium benzene thiosulfonate in a methanol solution was added in an amount of 7.6×10^{-5} mol per 1 mol of silver. At additional 5 minutes later, a methanol solution of 4-oxo-3-benzyl-oxazolizine-2-thione as a sulfur sensitizer was added thereto in an amount of 4.5×10^{-5} mol per 1 mol of silver, and after 10 minutes, an aqueous solution of aurichloric acid and an aqueous solution of potassium thiocyanate were added in an amount of 6×10^{-6} mol per 1 mol of silver and 5×10^{-3} mol per 1 mol of silver respectively, followed by ripening for 60 minutes. And then, 1.3 mL of a 0.8% by weight N,N'-dihydroxy-N'',N''-diethylmelamine in methanol was added thereto, and at additional 4 minutes thereafter, 5-methyl-2-mercaptobenzimidazole in a methanol solution at 4.8×10^{-3} mol per 1 mol of silver, 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole in a methanol solution at 5.4×10^{-3} mol per 1 mol of silver, and 1-(3-methylureido phenyl)-5-mercaptotetrazole in an aqueous solution at 8.5×10^{-3} mol per 1 mol of silver were added to produce silver halide emulsion L.

<<Preparation of Mixed Emulsion 2 for Coating Solution>

[0318] The silver halide emulsion K and the silver halide emulsion L at the rate of (silver halide emulsion K : silver halide emulsion L =) 3.5 : 2 by mole of silver were dissolved, and thereto was added benzothiazolium iodide at 1.5×10^{-2} mol per 1 mol of silver with a 1% by weight aqueous solution. Further, as "a compound that can be one-electron-oxidized to provide a one-electron oxidation product, which releases one or more electrons", the compounds Nos. 1, 2, and 3 were added respectively in an amount of 4×10^{-3} mol per 1 mol of silver in silver halide.

[0319] Thereafter, as "a compound having an adsorptive group and a reducible group", the compound Nos. 1 and 2 were added respectively in an amount of 4×10^{-3} mol per 1 mol of silver halide.

[0320] Further, water was added thereto to give the content of silver halide of 15.6 g in terms of silver, per 1 liter of the mixed emulsion for a coating solution.

2. Preparations of Coated Sample

[0321] Photothermographic materials were prepared similar to Example 1, except that using the mixed emulsion 2 for coating solution instead of the mixed emulsion for coating solution used in Example 1.

3. Evaluation of Photographic Properties

[0322] The obtained samples were evaluated similar to Example 1. The photothermographic materials of the present invention attain excellent results in fog, haze, and membrane cracking after processing.

Claims

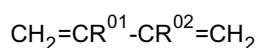
1. A photothermographic material comprising, on at least one side of a support, an image forming layer including at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent, and a binder, wherein:

the photosensitive silver halide has an average silver iodide content of 40 mol% or higher and at least 50% of a projected area of total grains of the photosensitive silver halide is occupied by tabular grains having an aspect ratio of 2 or more; and

50% by weight or more of the binder is formed by a polymer latex containing a monomer component shown below within a range of from 10% by weight to 70% by weight:

EP 1 584 978 A1

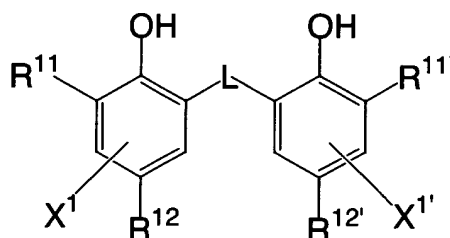
Formula (M)



wherein R⁰¹ and R⁰² each independently represent one selected from a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a halogen atom, and a cyano group, provided that both of R⁰¹ and R⁰² are not hydrogen atoms simultaneously.

2. The photothermographic material according to claim 1, wherein the photosensitive silver halide has an average silver iodide content of 80 mol% or higher.
3. The photothermographic material according to claim 2, wherein the photosensitive silver halide has an average silver iodide content of 90 mol% or higher.
4. The photothermographic material according to claim 1, wherein the photosensitive silver halide tabular grains have a mean equivalent spherical diameter of 0.3 μm to 8.0 μm.
5. The photothermographic material according to claim 1, wherein the photosensitive silver halide tabular grains have a mean thickness of 0.3 μm or less.
6. The photothermographic material according to claim 1, wherein the polymer latex comprises a monomer component having an acidic group within a range of from 1% by weight to 20% by weight.
7. The photothermographic material according to claim 1, wherein the polymer latex has a glass transition temperature (T_g) of -10°C to 70°C.
8. The photothermographic material according to claim 1, wherein the polymer latex has a glass transition temperature (T_g) of 5°C to 35°C.
9. The photothermographic material according to claim 1, wherein the polymer latex has a halogen ion content of 500 ppm or less per latex liquid.
10. The photothermographic material according to claim 1, wherein the polymer latex has styrene in a range of from 30% by weight to 90% by weight as the monomer component.
11. The photothermographic material according to claim 1, wherein the reducing agent is a compound represented by the following formula (R):

Formula (R)



wherein: R¹¹ and R^{11'} each independently represent an alkyl group having 1 to 20 carbon atoms; R¹² and R^{12'} each independently represent a hydrogen atom or a substituent capable of substituting for a hydrogen atom on a benzene ring; L represents an -S- group or a -CHR¹³- group; R¹³ represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms; and X¹ and X^{1'} each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring.

12. The photothermographic material according to claim 11, wherein, in the reducing agent represented by the formula (R), R¹¹ and R^{11'} each independently represent a secondary or tertiary alkyl group having 3 to 15 carbon atoms.

13. The photothermographic material according to claim 1, further comprising a development accelerator.

14. The photothermographic material according to claim 13, wherein the development accelerator is a compound represented by the following formula (A-1):

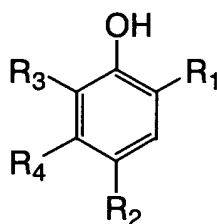
Formula (A-1)



wherein: Q₁ represents an aromatic group or a heterocyclic group which bonds to -NHNH-Q₂ at a carbon atom; and Q₂ represents one selected from a carbamoyl group, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a sulfonyl group, and a sulfamoyl group.

15. The photothermographic material according to claim 13, wherein the development accelerator is a compound represented by the following formula (A-2):

Formula (A-2)

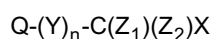


wherein: R₁ represents one selected from an alkyl group, an acyl group, an acylamino group, a sulfonamide group, an alkoxy carbonyl group, and a carbamoyl group; R₂ represents one selected from a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an acyloxy group, and a carbonate ester group; R₃ and R₄ each independently represent a group capable of substituting for a hydrogen atom on a benzene ring; and R₃ and R₄ may link together to form a condensed ring.

16. The photothermographic material according to claim 1, further comprising an organic polyhalogen compound as an antifoggant.

17. The photothermographic material according to claim 16, wherein the organic polyhalogen compound is a compound represented by the following formula (H):

Formula (H)



wherein: Q represents one selected from an alkyl group, an aryl group, and a heterocyclic group; Y represents a divalent linking group; n represents 0 or 1; Z₁ and Z₂ each independently represent a halogen atom; and X represents a hydrogen atom or an electron-attracting group.

18. The photothermographic material according to claim 1, further comprising a silver iodide complex-forming agent.

19. The photothermographic material according to claim 1 having the image forming layer on both sides of the support.

20. An image forming method utilizing a photothermographic material according to claim 1, comprising:

EP 1 584 978 A1

- (a) providing an assembly for forming an image by placing the photothermographic material between a pair of fluorescent intensifying screens;
- (b) putting an analyte between the assembly and an X-ray source;
- (c) applying exposure to the analyte using X-rays having an energy level in a range of 25 kVp to 125 kVp;
- (d) taking the photothermographic material out of the assembly; and
- (e) heating the photothermographic material at a temperature at which the material can be developed thermally.

5

10

15

20

25

30

35

40

45

50

55



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 2003/232288 A1 (OKA YUTAKA ET AL) 18 December 2003 (2003-12-18) * abstract * * paragraphs [0018] - [0023] * * paragraphs [0203], [1017] * * paragraphs [1529] - [1563] * * paragraphs [0743], [1412] * -----	1-20	G03C1/498 G03C5/17
A	US 2003/235795 A1 (NAKAGAWA HAJIME ET AL) 25 December 2003 (2003-12-25) * abstract * * paragraphs [0056], [0195] - [0216], [0386] * -----	1-20	
A	US 6 300 044 B1 (UYTTERHOEVEN HERMAN ET AL) 9 October 2001 (2001-10-09) * example 31 * -----	1-20	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			G03C
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 2005	Bolger, W
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

1
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 05 00 6628

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

06-07-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003232288 A1	18-12-2003	JP 2003140294 A	14-05-2003
		JP 2003295382 A	15-10-2003
		EP 1308776 A2	07-05-2003
		JP 2003207867 A	25-07-2003
		JP 2003207869 A	25-07-2003
		JP 2003228149 A	15-08-2003
		JP 2004184430 A	02-07-2004
US 2003235795 A1	25-12-2003	JP 2003066562 A	05-03-2003
		JP 2003066556 A	05-03-2003
		JP 2003084387 A	19-03-2003
		JP 2003140295 A	14-05-2003
US 6300044 B1	09-10-2001	WO 9748014 A1	18-12-1997
		DE 69633406 D1	21-10-2004
		EP 0904564 A1	31-03-1999
		JP 2001507468 T	05-06-2001