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(54) **Internal latent image-type direct positive silver halide emulsion and color diffusion transfer light-sensitive material using the same**

(57) Disclosed is an internal latent image-type direct positive silver halide photographic emulsion having a core/shell structure comprising a chemically sensitized core and a chemically sensitized shell, wherein a compound having an adsorbing group to silver halide and a reducing group, or a precursor thereof is contained together with a gold sensitizer and a compound having C=X bond, P=X bond or R-XO₂X bond (wherein X represents sulfur, selenium or tellurium and R represents an aliphatic hydrocarbon group, an aryl group or a heterocyclic group) at the chemical sensitization of the core and/or shell. A color diffusion transfer light-sensitive material using the emulsion.

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Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to an internal latent image-type direct positive silver halide photographic emulsion and a color diffusion transfer light-sensitive material using the emulsion.

BACKGROUND OF THE INVENTION

10 **[0002]** Photographs using silver halide have been heretofore widely used because of its excellent sensitivity and gradation as compared with those obtained by other photographic processes such as electrophotographic process and diazo photographic process. In this connection, a method of directly forming a positive image is known. According to this method, as described, for example, in U.S. Patent 3,761,276 and JP-B-60-55821 (the term "JP-B" as used herein means an "examined Japanese patent publication"), an internal latent image-type direct positive silver halide photo-
 15 graphic emulsion is used and a silver halide grain having formed in the inside thereof a latent image is developed with a surface developer (developer which substantially does not develop but leaves the latent image-formed site inside the silver halide grain) while uniformly applying exposure or using a nucleating agent to obtain a positive image.

[0003] In recent years, demands for silver halide photographic materials having high sensitivity, excellent graininess, gradation, high sharpness and good storability and for rapid processing quickly proceeding in the development are more and more increasing. In particular, silver halide photographic materials having good storability and higher sensitivity with low suppressed fog are keenly demanded. For attaining higher sensitivity, studies of reduction sensitization have been long made. Heretofore, compounds such as stannous chloride (see, U.S. Patent 2,487,850), polyamine or cyclic amine compounds (see, U.S. Patents 2,518,698, 2,521,925 and 3,930,867), thiourea dioxide-based compounds (see, British Patent 789,823 and U.S. Patents 2,983,609 and 2,983,610), borane compounds (see, U.S. Patents
 25 3,779,777, 3,782,959 and 4,150,093) and ascorbic acid (see, EP-A-369491) have been disclosed as useful reduction sensitizers for silver halide emulsion. In Collier, Photographic Science and Engineering, Vol. 23, page 113 (1979), properties of silver nuclei prepared by various reduction sensitizing methods are compared and a method of dimethylamine borane, stannous chloride, hydrazine, high pH ripening and low pAg ripening is employed.

[0004] The reduction sensitizer in general readily generates conspicuous fogging when it is present together with a gold sensitizer. Also, the emulsion subjected to reduction sensitization is poor particularly in the storability. For overcoming these problems, not only the selection of reduction sensitizer but also the reduction sensitization method have been investigated. In most of the above-described patent publications, the reduction sensitization is performed after the formation of silver halide grains. The time when reduction sensitization is applied has been particularly studied and attempts of performing the reduction sensitization at the formation of silver halide grains have been heretofore made.
 30 This is described, for example, in JP-A-48-87825 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-50-3619, EP-A-348934, EP-A-369491, EP-A-371338 and EP-A-435355.

[0005] According to these methods, a commonly well-known reducing agents described above is used at the formation of silver halide grains, therefore, unnecessary fogged silver nuclei are readily produced at the same time. For preventing generation of fogged silver nuclei or improving the storability of emulsion, as described in some of those publications, an oxidizing agent such as thiosulfonic acid or iodine must be used in combination. However, if such a compound capable of oxidizing the silver nucleus is used in a large amount, the sensitization once obtained by the reduction sensitization is greatly reduced or if used in a small amount, the effect of improving storability or preventing fog is insufficient. Furthermore, the by-product or residue resulting from oxidation reaction of the oxidizing agent has adverse effect in many cases. Therefore, a reduction sensitization method requiring no use or a small amount of use of an oxidizing agent together while ensuring low fog and good storability, is being demanded.
 45

[0006] JP-A-8-272024 discloses a reduction sensitizing method of silver halide photographic emulsions, characterized in that a compound having an adsorbing group to silver halide and a reducing agent, or a precursor thereof is used. It is stated that by using this compound, a silver halide emulsion having low fog, high sensitivity and excellent storability can be obtained. However, an internal latent-image type direct positive silver halide is not specifically described therein and of course, the effect expected when the compound is applied to an emulsion for forming a direct positive image is not described at all. The reduction sensitization nucleus itself has heretofore been known to be useless in the internal latent image-type direct positive silver halide emulsion. The gold sensitization nucleus is an effective sensitization center in the internal latent image-type direct positive silver halide emulsion, particularly at the chemical sensitization of core, however, it has been heretofore known that the gold sensitizer used in excess disadvantageously causes formation of fog nucleus accompanied with the reduction of density affecting the reversal positive performance. Under these circumstances, development of a discriminative control method capable of forming high-sensitive gold sensitization centers while suppressing the formation of fog nuclei as much as possible is being keenly demanded.
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[0007] The present invention has been made to solve the above-described problems. An object of the present

invention is to provide an internal latent image-type direct positive silver halide emulsion having high sensitivity and giving high contrast in the low density area on the reversal characteristic curve, and another object of the present invention is to provide a color diffusion transfer photographic film unit using the emulsion.

5 SUMMARY OF THE INVENTION

[0008] These objects of the present invention can be attained by the internal latent image-type direct positive silver halide emulsion and the color diffusion transfer light-sensitive material using the emulsion, described in (1), (2), (3), (4) and (5) below:

10 (1) an internal latent image-type direct positive silver halide photographic emulsion having a core/shell structure comprising a chemically sensitized core and a chemically sensitized shell, wherein a compound having an adsorbing group to silver halide and a reducing group, represented by the following formula (I) or a precursor thereof is contained together with a gold sensitizer and a compound having C=X bond, P=X bond or R-XO₂X bond (wherein
15 X represents sulfur, selenium or tellurium and R represents an aliphatic hydrocarbon group, an aryl group or a heterocyclic group) at the chemical sensitization of the core and/or shell:



20 wherein A represents an atomic group containing a group capable of adsorbing to silver halide, W represents a divalent linking group, n represents 0 or 1, and R represents a reducing group;

(2) the internal latent image-type direct positive silver halide photographic emulsion as described in (1) above, wherein a compound having an adsorbing group to silver halide and a reducing group, represented by formula (I) or a precursor thereof is contained together with a gold sensitizer at the chemical sensitization of core;

25 (3) the internal latent image-type direct positive silver halide photographic emulsion as described in (1) or (2) above, wherein internal latent image-type direct positive silver halide photographic emulsion contains tabular silver halide grains having an average particle size of 0.3 μm or more and the average particle size/average particle thickness ratio of 2 or more in a proportion of 50% or more of all silver halide grains;

30 (4) the internal latent image-type direct positive silver halide photographic emulsion as described in any one of (1) to (3) above, wherein the precursor of the compound having an adsorbing group to silver halide and a reducing group, represented by formula (I) is a benzothiazolium compound;

35 (5) a color diffusion transfer light-sensitive material comprising a support having thereon at least one light-sensitive silver halide emulsion layer associated with a dye image-forming substance, wherein the dye image-forming substance is a non-diffusive compound capable of releasing a diffusive dye or a precursor thereof or a compound variable in the diffusibility of the compound itself in connection with the silver development, represented by the following formula (II), and at least one layer of the silver halide emulsion layers contains the internal latent image-type direct positive silver halide emulsion described in any one of (1) to (4) above:



40 wherein DYE represents a dye group, a dye group temporarily shifted to the short wave or a dye precursor group, Y represents a mere bond or a linking group, Z represents a group having property of imagewise releasing DYE-Y, or differentiating the diffusibility of the compound represented by (DYE-Y)_m-Z in correspondence or counter-correspondence with the light-sensitive silver salt having a latent image, m represents 1 or 2, and when m is 2, two DYE-Y moieties may be the same or different.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The present invention is described in detail below.

50 **[0010]** Formula (I) is described below.

[0011] Specific examples of the atomic group containing a group capable of adsorbing to silver halide represented by A in formula (I) include mercapto compounds (e.g., mercaptotetrazole, mercaptotriazole, mercaptoimidazole, mercaptothiadiazole, mercaptooxadiazole, mercaptobenzothiazole, mercaptobenzoxazole, mercaptobenzimidazole, mercaptotetrazaindene, mercaptopyridyl, mercaptoalkyl, mercaptophenyl), thione compounds (e.g., thiazoline-2-thione, imidazoline-2-thione, benzimidazoline-2-thione, benzothiazoline-2-thione, thiourea, thioamide) and imino silver-forming compounds (e.g., benzotriazole, tetrazole, hydroxytetrazaindene, benzimidazole). Among these, mercapto compounds and thione compounds are preferred.

[0012] The divalent linking group represented by W in formula (I) is a divalent linking group constituted by carbon

atom, hydrogen atom, oxygen atom, nitrogen atom and/or sulfur atom. Specific examples thereof include an alkylene group having from 1 to 20 carbon atoms (e.g., methylene, ethylene, trimethylene, tetramethylene, hexamethylene), an arylene group having from 6 to 20 carbon atoms (e.g., phenylene, naphthylene), -CONR¹-, -SO₂NR²-, -O-, -S-, -NR³-, -NR⁴CO-, -NR⁵SO₂-, -NR⁶CONR⁷-, -COO- and -OCO-, wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ each represents an aliphatic group or an aromatic group. Two of these groups may be appropriately combined to form a divalent linking group.

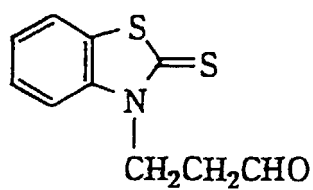
[0013] The aliphatic group represented by R¹, R², R³, R⁴, R⁵, R⁶ or R⁷ is preferably an aliphatic group having from 1 to 30 carbon atoms, more preferably a linear, branched or cyclic alkyl, alkenyl, alkynyl or aralkyl group having from 1 to 20 carbon atoms. Examples of the alkyl group, the alkenyl group, the alkynyl group and the aralkyl group include a methyl group, an ethyl group, an isopropyl group, a t-butyl group, an n-octyl group, an n-decyl group, an n-hexadecyl, a cyclopropyl group, a cyclopentyl group, a cyclohexyl group, an allyl group, a 2-butenyl group, a 3-pentenyl group, a propargyl group, a 3-pentynyl group and a benzyl group. The aromatic group represented by R¹, R², R³, R⁴, R⁵, R⁶ or R⁷ is preferably an aromatic group having from 6 to 30 carbon atoms, more preferably a monocyclic or condensed ring aryl group having from 6 to 20 carbon atoms. Examples thereof include a phenyl group and a naphthyl group.

[0014] The reducing group represented by R in formula (I) may be sufficient if it is a functional group capable of reducing silver halide. Specific examples thereof include a formyl group, an amino group, an acetylene group and a hydrazino group. Among these, a formyl group, an amino group and a hydrazino group are preferred.

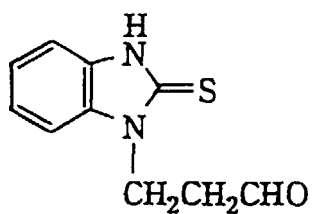
[0015] The precursor of a compound having a adsorbing group to silver halide and a reducing group is a compound which is subjected to chemical reaction when added to a silver halide emulsion, such as oxidation-reduction or hydrolysis, and releases the compound of formula (I). Examples thereof include compounds capable of producing a mercapto group as an adsorbing group and a formyl group as a reducing group by the hydrolysis reaction (for example, compound 13) such as thiazoliums (including benzothiazoliums and naphthothiazoliums), thiazolines and thiazolidines, and disulfide compounds having a reducing group capable of undergoing cleavage of the disulfide group and thereby producing a mercapto group as an adsorbing group.

[0016] Specific examples of the compound represented by formula (I) for use in the present invention are set forth below, however, the compound of the present invention is by no means limited thereto.

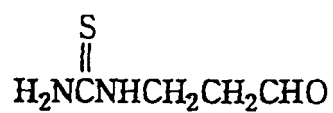
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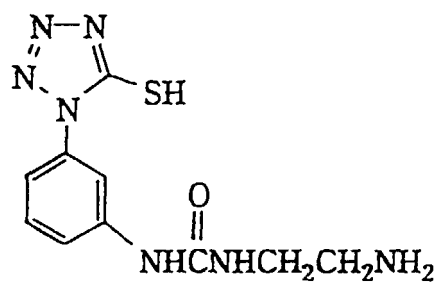
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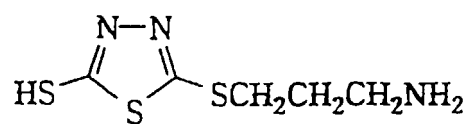
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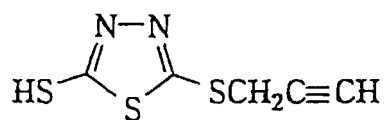
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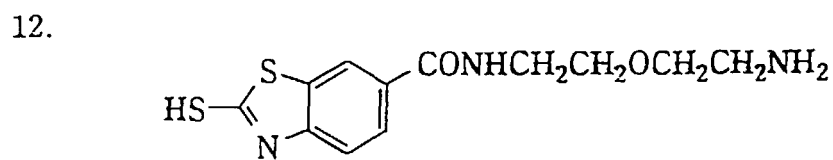
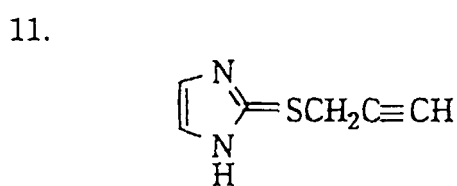
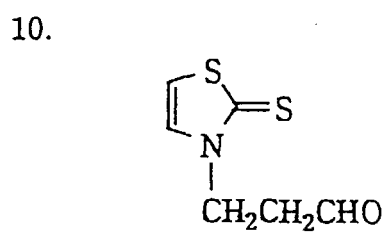
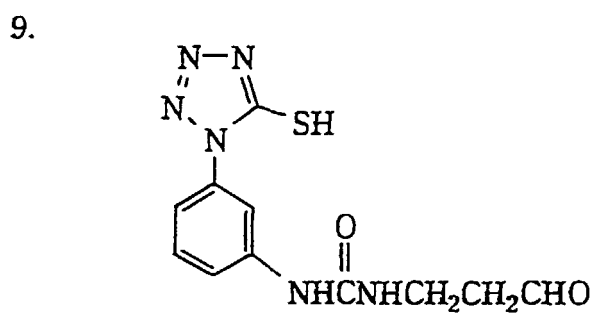
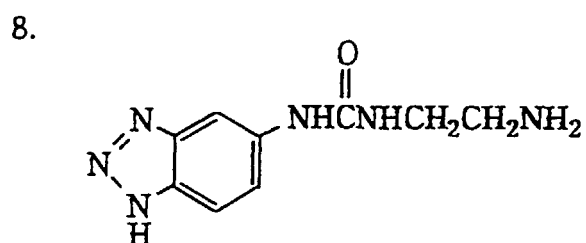
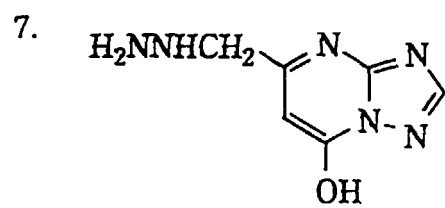


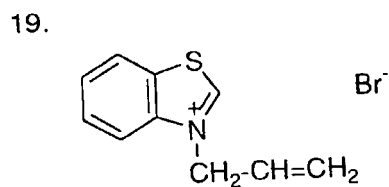
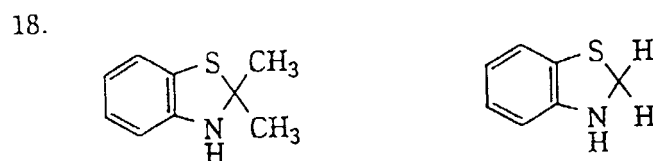
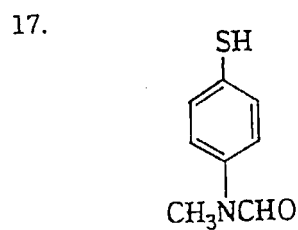
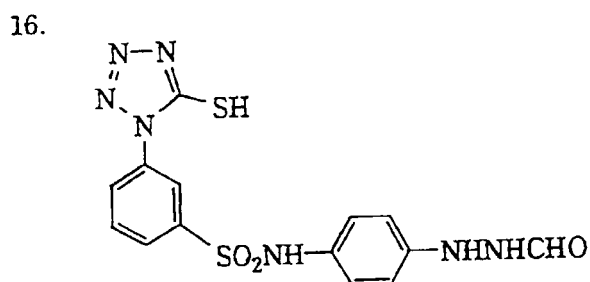
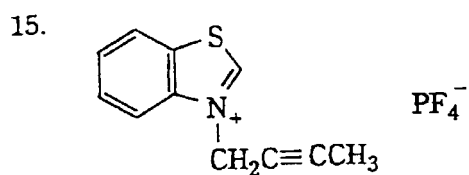
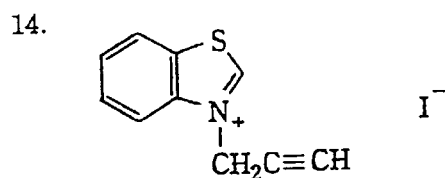
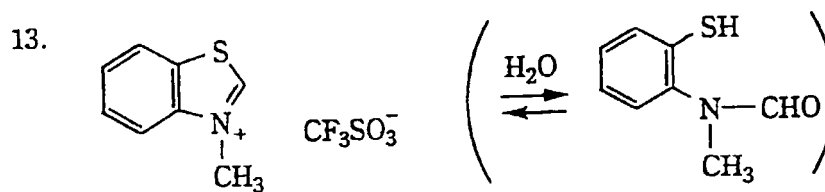
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6.







[0017] The internal latent image-type direct positive silver halide emulsion (hereinafter sometimes simply referred to as an "internal latent image-type silver halide emulsion") of the present invention is a silver halide emulsion mainly forming a latent image in the inside of a silver halide grain by the imagewise exposure. More specifically, the internal

latent image-type silver halide emulsion is defined as a silver halide emulsion such that when the silver halide emulsion is coated on a transparent support in a constant amount, exposed for a fixed time of from 0.01 to 1 second and then developed with the following Developer A ("internal" developer) at 20°C for 5 minutes, the maximum density obtained is at least 5 times larger than the maximum density obtained by developing a second sample at 20°C for 5 minutes after the same exposure with the following Developer B ("surface" developer).

[0018] The maximum density as used herein is determined by an ordinary photographic density measuring method.

Developer A:

[0019]

N-Methyl-p-aminophenol sulfite	2 g
Sodium sulfite (anhydrous)	90 g
Hydroquinone	8 g
Sodium carbonate (monohydrate)	52.5 g
Potassium bromide	5 g
Potassium iodide	0.5 g
Water to make	1 ℓ

Developer B:

[0020]

N-Methyl-p-aminophenol sulfite	2.5 g
1-Ascorbic acid	10 g
Potassium metantrate	35 g
Potassium bromide	1 g
Water to make	1 ℓ

[0021] In order to obtain a direct positive image, the internal latent image-type silver halide emulsion is imagewise exposed and before or during the subsequent development, the front surface of the exposed layer is subjected to uniform second exposure (called "light fogging method", see, for example, British Patent 1,151,363) or the silver halide emulsion is developed in the presence of a nucleating agent (called "chemical fogging method", see, for example, Research Disclosure, Vol. 151, No. 15162, pp. 76-78). In the present invention, the direct positive image is preferably obtained by the "chemical fogging method".

[0022] As described above, for obtaining a direct positive image, the internal latent image-type silver halide emulsion is imagewise exposed and before or during the subsequent development, subjected to uniform second exposure of the entire surface or developed in the presence of a nucleating agent. Examples of the nucleating agent which can be used include hydrazines described in U.S. Patents 2,563,785 and 2,588,982, hydrazides and hydrazones described in U.S. Patent 3,227,552, heterocyclic quaternary salt compounds described in British Patent 1,283,835, JP-A-52-69613, JP-A-55-138742, JP-A-60-11837, JP-A-62-210451, JP-A-62-291637 and U.S. Patents 3,615,515, 3,719,494, 3,734,738, 4,094,683, 4,115,122, 4,306,016 and 4,471,044, sensitizing dyes containing a substituent having a nucleating activity within the dye molecule described in U.S. Patent 3,718,470, thiourea bonded acylhydrazine-based compounds described in U.S. Patents 4,030,925, 4,031,127, 4,245,037, 4,255,511, 4,266,013 and 4,276,364 and British Patent 2,012,443, and acylhydrazine-based compounds having bonded thereto a thioamide ring or a heterocyclic group such as triazole or tetrazole, as an adsorbing group described in U.S. Patents 4,080,270 and 4,278,748 and British Pat-

ent 2,011,391B.

[0023] The amount of the nucleating agent used here is preferably such an amount as giving a sufficiently high maximum density when the internal latent image-type emulsion is developed with a surface developer. In actual use, the proper amount varies over a wide range depending on the properties of silver halide emulsion used, the chemical structure of nucleating agent and the developing conditions. However, the amount useful in practice is from about 0.1 mg to 5 g, preferably from about 0.5 mg to 2 g, per mol of silver in the internal latent image-type silver halide emulsion. In the case of incorporating the nucleating agent into a hydrophilic colloid layer adjacent to an emulsion layer, the nucleating agent may be added in an amount within the above-described range based on the amount of silver contained in the internal latent image-type emulsion having the same area.

[0024] In the present invention, a core/shell internal latent image-type silver halide emulsion is used.

[0025] Examples of the core/shell internal latent image-type silver halide emulsion include a conversion-type silver halide emulsion described in U.S. Patents 2,456,953 and 2,592,250, a multi-layer structure-type silver halide emulsion different in the halogen composition between the first phase and the second phase described in U.S. Patent 3,935,014, and a silver halide emulsion having doped with a metal ion. Other examples of the core/shell type silver halide emulsion include those described in U.S. Patents 3,206,313, 3,317,322, 3,761,266, 3,761,276, 3,850,637, 3,923,513, 4,035,185, 4,184,878, 4,395,478 and 4,504,570, JP-A-57-136641, JP-A-61-3137, JP-A-61-299155 and JP-A-62-208241.

[0026] In the present invention, the shell means a silver halide phase formed after the chemical sensitization of a silver halide grain which works out to a core, in the process of preparing an emulsion. The shell may be formed by referring to JP-A-63-151618 (the Examples) and U.S. Patents 3,206,316, 3,317,322, 3,761,276, 4,269,927 and 3,367,778. The core/shell molar ratio (weight molar ratio) is preferably from 1/30 to 5/1, more preferably from 1/20 to 2/1, still more preferably from 1/20 to 1/1.

[0027] The present invention is preferably applied to a tabular core/shell internal latent image-type silver halide emulsion. The tabular grain may be prepared by the method described in Guttoff, Photographic Science and Engineering, Vol. 14, pp. 248-257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520, and British Patent 2,112,157.

[0028] In some cases, the method of adding silver halide grains previously formed by precipitation to the reaction vessel for preparing an emulsion described in U.S. Patents 4,334,012, 4,301,241 and 4,150,994 is preferred. This silver halide grain may be used as a seed crystal or as silver halide for growing. In the latter case, the emulsion grain added preferably has a small grain size. With respect to the adding method, the emulsion grains may be added in a whole amount at once, may be added in parts at a plurality of times or may be continuously added. Furthermore, it is also effective depending on the case to add grains having various halogen compositions so as to modify the surface.

[0029] Other than the method of adding a soluble silver salt and a halogen salt each in a constant concentration at a constant flow rate for growing grains, a method of forming grains by changing the concentration or flow rate described in British Patent 1,469,480 and U.S. Patents 3,650,757 and 4,242,455 is also preferred. By increasing the concentration or flow rate, the amount of silver halide supplied may be changed by the linear, secondary or more complicated function with respect to the addition time. Depending on the case, it is preferred, if desired, to reduce the amount of silver halide supplied. Furthermore, in the case where a plurality of soluble silver salts different in the solution composition are added or a plurality of soluble halogen salts different in the solution composition are added, a method of adding these by increasing one and decreasing the other is also effective.

[0030] The mixing vessel for use in the reaction of a soluble silver salt solution with a soluble halogen salt solution may be selected from those used in the methods described in U.S. Patents 2,996,287, 3,342,605, 3,415,650 and 3,785,777 and German Patent Publication (OLS) Nos. 2,556,885 and 2,555,364.

[0031] At the time of producing an emulsion containing tabular grains, the silver salt solution (for example, AgNO_3 aqueous solution) and the halide solution (for example, KBr aqueous solution) are preferably added by increasing the addition rate, addition amount and the addition concentration so as to speed up the growth of grains. This method is described, for example, in British Patent 1,335,925, U.S. Patents 3,672,900, 3,650,757 and 4,242,445, JP-A-55-142329 and JP-A-55-158124.

[0032] At the time of preparing the emulsion of the present invention, a metal ion salt is preferably allowed to present according to the purpose, for example, during the grain formation, desalting or chemical sensitization or before the coating. By allowing a metal ion salt to be present, the amount of excess exposure for causing no generation of re-reversal may be increased or the minimum density may be decreased. In the case where the metal ion salt is doped to a grain, the metal ion salt is preferably added after the formation of grain or before the completion of chemical sensitization. The metal ion salt may be doped to the entire grain, only to the core part of grain, only to the shell part, only to the epitaxial part or only to the base grain (in the present invention, the grain may contain an epitaxial growth part in addition to the shell). Examples of the metal which can be used include Mg, Ca, Sr, Ba, Al, Sc, Y, La, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ru, Rh, Pd, Re, Os, Ir, Pt, Au, Cd, Hg, Tl, In, Sn, Pb and Bi. Among these, Fe, Co, Ru, Ir, Pt, Au and Pb are preferred, and Fe, Ru, Ir and Pb are more preferred.

[0033] These metals can be added as far as it is in the form of an ammonium salt, an acetate, a nitrate, a sulfate,

a phosphate, a hydroxyl salt or a salt capable of dissolving at the grain formation such as 6-coordinated complex salt or 4-coordinated complex salt. Examples thereof include CdBr_2 , CdCl_2 , $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Pb}(\text{CH}_3\text{COO})_2$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, $(\text{NH}_4)_4[\text{Fe}(\text{CN})_6]$, K_3IrCl_6 , NH_4RhCl_6 and $\text{K}_4\text{Ru}(\text{CN})_6$. The ligand of the coordination compound can be selected from halide, H_2O , cyano, cyanate, nitrosyl, thionitrosyl, oxo and carbonyl. These metal compounds may be used individually or in combination of two or more thereof.

[0034] The metal compound is preferably added after dissolving it in water or an appropriate solvent such as methanol or acetone. In order to stabilize the solution, a method of adding an aqueous hydrogen halogenide solution (e.g., HCl , HBr) or an alkali halogenide (e.g., KCl , NaCl , KBr , NaBr) may be used. If desired, an acid or an alkali may be added. The metal compound may be added to the reaction vessel either before grain formation or during grain formation. Furthermore, the metal compound may be added to a water-soluble silver salt (e.g., AgNO_3) or an aqueous alkali halogenide solution (e.g., NaCl , KBr , KI) and then continuously added during the formation of silver halide grains. Also, a solution may be prepared independently of the water-soluble silver salt or alkali halogenide and continuously added at an appropriate time during the grain formation. A combination of various methods is also preferred.

[0035] A method of adding a chalcogenide compound during the preparation of an emulsion described in U.S. Patent 3,772,031 is also useful in some cases. Other than S, Se and Te, a cyanate, a thiocyanate, a selenocyanate, a carbonate, a phosphate or an acetate may also be allowed to be present.

[0036] These are described in U.S. Patents 2,448,060, 2,628,167, 3,737,313 and 3,772,031, and Research Disclosure, Vol. 134, 13452 (June, 1975).

[0037] The silver halide grain for use in the present invention may be a regular grain having a cubic, octahedral or tetradecahedral form. In the case of a tabular grain, the shape thereof may be selected from triangle, hexagon and circle. An equilateral hexagon consisting of six sides having almost the same length described in U.S. Patent 4,996,137 is a preferred embodiment.

[0038] The tabular emulsion which is preferably used in the present invention means an emulsion where silver halide grains having an aspect ratio (circle-equivalent diameter of a silver halide grain/thickness of the grain) of from 2 to 100 occupy 50% (area) or more of all silver halide grains in the emulsion, preferably an emulsion where silver halide grains having an aspect ratio of 5 or more, more preferably 8 or more, occupy 50% (area) or more, preferably 70% or more, more preferably 85% or more, of all silver halide grains in the emulsion. Incidentally, the circle-equivalent diameter of the tabular silver halide grain means a circle-equivalent diameter of two opposing main planes running in parallel or nearly in parallel (namely, a diameter of a circle having the same projected area as the main plane), and the thickness of the grain means the distance between the main planes. If the aspect ratio exceeds 100, the emulsion may be disadvantageously deformed or ruptured during the process until the emulsion is completed as a coated material.

[0039] The circle-equivalent diameter of the tabular grain is $0.3\text{ }\mu\text{m}$ or more, preferably from 0.3 to $10\text{ }\mu\text{m}$, more preferably from 0.5 to $5.0\text{ }\mu\text{m}$, still more preferably from 0.5 to $3.0\text{ }\mu\text{m}$. The grain thickness is less than $1.5\text{ }\mu\text{m}$, preferably from 0.05 to $1.0\text{ }\mu\text{m}$.

[0040] Furthermore, an emulsion having high uniformity in the thickness such that the coefficient of variation of the grain thickness is 30% or less is also preferred. In addition, a grain having a specific grain thickness and a specific plane-to-plane distance described in JP-A-63-163451 is preferred.

[0041] The diameter and the thickness of a tabular grain can be determined by an electron microphotograph of the grain according to the method described in U.S. Patent 4,434,226.

[0042] The grain size of the emulsion for use in the present invention can be evaluated by the diameter of a circle having the projected area determined using an electron microscope, the diameter of a sphere having the volume of a grain calculated from the projected area and the grain thickness or the diameter of a sphere having the volume determined according to the Coulter counter method. The grain may be selected over the range of from an ultrafine grain having a sphere-equivalent diameter of $0.05\text{ }\mu\text{m}$ or less to a coarse grain having a sphere-equivalent diameter in excess of $10\text{ }\mu\text{m}$. Grains having a sphere-equivalent diameter of from 0.1 to $3\text{ }\mu\text{m}$ are preferred.

[0043] The silver halide grains may have any grain size distribution but preferably has a monodisperse distribution. The monodisperse distribution as used herein is defined as a dispersion system where 95% by weight or number of grains in all silver halide grains contained have a grain size falling within $\pm 60\%$, preferably within 40%, of the number average grain size. The number average grain size as used herein means a number average diameter, in terms of the projected area diameter, of silver halide grains.

[0044] The structure and the production method of monodisperse tabular grains are described, for example, in JP-A-63-151618, and a mixture of those monodisperse emulsions may also be used.

[0045] With respect to the silver halide composition of the grain, any silver halide of silver iodobromide, silver iodo-chlorobromide or silver chloriodide may be used but silver iodobromide is preferred.

[0046] The silver halide grain for use in the present invention has different phases between the inside and the surface. The silver halide composition inside the grain may be homogeneous or may comprise a heterogeneous silver halide composition. The surface phase may be a discontinuous layer or may form a continuous layer structure. Also, the grain may have a dislocation line.

[0047] It is important to control the halogen composition in the vicinity of the surface of a grain. In the case of changing the halogen composition in the vicinity of the surface, either a structure of entirely embracing the grain or a structure of adhering only to a part of the grain may be selected. For example, only one part face of a tetradecahedral grain comprising a (100) face and a (111) face may be changed in the halogen composition or one of the main plane and the lateral plane of a tabular grain may be changed in the halogen composition.

[0048] Two or more kinds of silver halides different in the crystal habit, halogen composition, grain size, grain size distribution or the like may be used in combination and these may be used in different emulsion layers and/or in the same emulsion layer.

[0049] After a shell is covered on a core grain subjected to chemical sensitization, the silver halide emulsion of the present invention is preferably further subjected to chemical sensitization of the grain surface, because in general, superior reversal performance with a high maximum density is attained when the grain surface is chemically sensitized. In the case of applying chemical sensitization to the grain surface, a polymer described in JP-A-57-13641 may be allowed to be present together.

[0050] In the present invention, at least one of the chemical sensitization of core and the chemical sensitization of shell is performed using a compound of formula (I) and a gold sensitizer in combination preferably at a pAg of from 5 to 10, a pH of from 4 to 8 and a temperature of from 30 to 80°C. Representative examples of the gold sensitizer include chlorauric acid and an alkali salt thereof. Together with a compound of formula (I) and a gold sensitizer, other chemical sensitizers may also be used in combination. The chemical sensitization of core is preferably performed using the compound of formula (I) and a gold sensitizer in combination.

[0051] It is not necessary that both of core and shell are chemically sensitized using a compound of formula (I) and a gold sensitizer in combination. In this case, the chemical sensitization is performed using a compound of formula (I) or a gold sensitizer alone or other chemical sensitizers may be applied.

[0052] More specifically, the chemical sensitization may be performed using an active gelatin as described in T.H. James. The Theory of the Photographic Process, 4th ed., pp. 67-76, Macmillan (1977) or may be performed using sulfur, selenium, tellurium, platinum, palladium, iridium, rhodium, osmium, rhenium or a combination of a plurality of these sensitizing agents as described in Research Disclosure, Vol. 120, 12008 (April, 1974), Research Disclosure, Vol. 34, 13452 (June, 1975), U.S. Patents 2,642,361, 3,297,446, 3,772,031, 3,857,711, 3,901,714, 4,266,018 and 3,904,415, and British Patent 1,315,755.

[0053] The gold sensitizer is preferably used in a ratio of from 5×10^{-5} to 1×10^{-7} mol, more preferably from 1×10^{-5} to 1×10^{-6} mol, per mol of silver halide of the core grain. The compound of formula (I) used in combination with the gold sensitizer is preferably used in a molar ratio of from 10 to 1/10 times, most preferably almost equimolar amount, based on the gold sensitizer. In the case of chemically sensitizing the shell grain, the sensitizer is preferably used in the above-described amount based on silver halide of the shell grain.

[0054] The chemical sensitization of the photographic emulsion of the present invention may be performed in a metal material such as Fe, Cr, Mn, Ni, Mo and Ti, but is preferably performed in a non-metallic material obtained by coating a fluororesin on the surface of a metal. Examples of the fluororesin material include Teflon-coated materials PFA, TFE and FEP produced by Du Pont.

[0055] The chemical sensitization may also be performed in the presence of a chemical sensitization aid. As the chemical sensitization aid, compounds known to prevent fogging and increase sensitivity during the process of chemical sensitization, such as azaindene, azapyridazine and azapyrimidine, are used. Examples of the chemical sensitization aid are described in U.S. Patents 2,131,038, 3,411,914 and 3,554,757, JP-A-58-126536, JP-A-62-253159, and Duffin, Photographic Emulsion Chemistry, pp. 138-143, The Focal Press (1966).

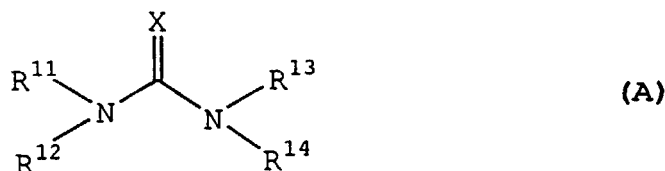
[0056] A sensitization method using an oxidizing agent described in JP-A-61-3134 and JP-A-61-3136 may also be used.

[0057] The oxidizing agent for silver means a compound having an activity of acting on a silver metal to convert it into silver ion. In particular, a compound capable of converting very fine silver grains generated as a by-product during the formation or chemical sensitization of silver halide grains into silver ion is effective. The silver ion produced may form a sparingly water-soluble silver salt such as silver halide, silver sulfide and silver selenide, or may form an easily water-soluble silver salt such as silver nitrate. The oxidizing agent for silver may be either an inorganic material or an organic material. Examples of the inorganic oxidizing agent include oxyacid salts such as ozone, hydrogen peroxide and an adduct thereof (e.g., $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O} \cdot 2\text{NaCO}_3 \cdot 3\text{H}_2\text{O}_2$, $\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$, $2\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$), peroxy acid salt (e.g., $\text{K}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{C}_2\text{O}_6$, $\text{K}_2\text{P}_2\text{O}_8$), a peroxy complex compound (e.g., $\text{K}_2[\text{Ti}(\text{O}_2)\text{C}_2\text{O}_4] \cdot 3\text{H}_2\text{O}$, $4\text{K}_2\text{SO}_4 \cdot \text{Ti}(\text{O}_2)\text{OH} \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$), a permanganate (e.g., KMnO_4) and a chromate (e.g., $\text{K}_2\text{Cr}_2\text{O}_7$); halogen elements such as iodine and bromine; perhalogen acid salts (e.g., potassium periodate); and salts of a high valence metal (e.g., potassium hexacyanoferrate).

[0058] Examples of the organic oxidizing agent include quinones such as p-quinone, organic peroxides such as peracetic acid and perbenzoic acid, and active halogen-releasing compounds (e.g., N-bromosuccinimide, chloramine T, chloramine B).

[0059] The oxidizing agent preferably used in the present invention is ozone, hydrogen peroxide or an adduct thereof, a halogen element or an organic oxidizing agent such as quinones. In a preferred embodiment, the above-described reduction sensitization and the oxidizing agent for silver are used in combination. A method of using an oxidizing agent and then performing reduction sensitization, a method reversed thereto, or a method of allowing both to be present together may be selected and used. These methods may be used during the grain formation or the chemical sensitization.

[0060] In the present invention, the compound having a C=X bond used at the chemical sensitization is preferably a compound represented by the following formula (A):



wherein X represents a sulfur atom, a selenium atom or a tellurium atom, R^{11} , R^{12} , R^{13} and R^{14} each represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, a heterocyclic group, an acyl group, an amino group, an alkoxy group, a hydroxy group or carbamoyl group, and R^{11} , R^{12} , R^{13} and/or R^{14} may be combined to form a ring.

[0061] Examples of the aliphatic hydrocarbon group represented by R^{11} , R^{12} , R^{13} or R^{14} in formula (A) include a substituted or unsubstituted, linear or branched alkyl group having from 1 to 30 carbon atoms (e.g., methyl, ethyl, isopropyl, n-propyl, n-butyl, t-butyl, 2-pentyl, n-hexyl, n-octyl, t-octyl, 2-ethylhexyl, 1,5-dimethylhexyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, hydroxyethyl, hydroxypropyl, 2,3-dihydroxypropyl, carboxymethyl, carboxyethyl, sodium sulfocethyl, diethylaminoethyl, diethylaminopropyl, butoxypropyl, ethoxyethoxyethyl, n-hexyloxypropyl), a substituted or unsubstituted cyclic alkyl group having from 3 to 18 carbon atoms (e.g., cyclopropyl, cyclopentyl, cyclohexyl, cyclooctyl, adamantyl, cyclododecyl), an alkenyl group having from 2 to 16 carbon atoms (e.g., allyl, 2-butenyl, 3-pentenyl), an alkynyl group having from 2 to 10 carbon atoms (e.g., propargyl, 3-pentynyl) and an aralkyl group having from 6 to 16 carbon atoms (e.g., benzyl). Examples of the aryl group include a substituted or unsubstituted phenyl group having from 6 to 20 carbon atoms and a substituted or unsubstituted naphthyl group having from 6 to 20 carbon atoms, such as unsubstituted phenyl group, unsubstituted naphthyl group, 3,5-dimethylphenyl, 4-butoxyphenyl and 4-dimethylaminophenyl. Examples of the heterocyclic group include a pyridyl group, a furyl group, an imidazolyl group, a piperidyl group and a morpholyl group. Examples of the acyl group include an acetyl group, a formyl group, a benzoyl group, a pivaloyl group, a caproyl group and n-nonanoyl group. Examples of the amino group include unsubstituted amino group, a methylamino group, a hydroxyethylamino group, a n-octylamino group, a dibenzylamino group, a dimethylamino group and a diethylamino group. Examples of the alkoxy group include a methoxy group, an ethoxy group, an n-butyloxy group, a cyclohexyloxy group, an n-octyloxy group and an n-decyloxy group. Examples of the carbamoyl group include an unsubstituted carbamoyl group, an N,N-diethylcarbamoyl group and an N-phenylcarbamoyl group. R^{11} , R^{12} , R^{13} and/or R^{14} may be combined to form a ring.

[0062] In formula (A), R^{11} , R^{12} , R^{13} and R^{14} each may have a substituent, if possible. Examples of the substituent include a halogen atom (e.g., fluorine, chlorine, bromine), an aliphatic hydrocarbon group (e.g., methyl, ethyl, isopropyl, n-propyl, t-butyl, n-octyl, cyclopentyl, cyclohexyl), an alkenyl group (e.g., allyl, 2-butenyl, 3-pentenyl), an alkynyl group (e.g., propargyl, 3-pentynyl), an aralkyl group (e.g., benzyl, phenethyl), an aryl group (e.g., phenyl, naphthyl, 4-methylphenyl), a heterocyclic group (e.g., pyridyl, furyl, imidazolyl, piperidinyl, morpholyl), an alkoxy group (e.g., methoxy, ethoxy, butoxy, 2-ethylhexyloxy, ethoxyethoxy, methoxymethoxy), an aryloxy group (e.g., phenoxy, 2-naphthyloxy), an amino group (e.g., unsubstituted amino, dimethylamino, diethylamino, dipropylamino, dibutylamino, ethylamino, dibenzylamino, anilino), an acylamino group (e.g., acetylamino, benzoylamino), a ureido group (e.g., unsubstituted ureido, N-methylureido, N-phenylureido), a thioureido group (e.g., unsubstituted thioureido, N-methylthioureido, N-phenylthioureido), a urethane group (e.g., methoxycarbonylamino, phenoxycarbonylamino), a sulfonylamino group (e.g., methylsulfonylamino, phenylsulfonylamino), a sulfamoyl group (e.g., unsubstituted sulfamoyl group, N,N-dimethylsulfamoyl, N-phenylsulfamoyl), a carbamoyl group (e.g., unsubstituted carbamoyl, N,N-diethylcarbamoyl, N-phenylcarbamoyl), a sulfonyl group (e.g., mesyl, tosyl), a sulfinyl group (e.g., methylsulfinyl, phenylsulfinyl), an alkyloxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl), an acyl group (e.g., acetyl, benzoyl, formyl, pivaloyl), an acyloxy group (e.g., acetoxyl, benzoyloxy), a phosphoric acid amide group (e.g., N,N-diethylphosphoric acid amide), an alkylthio group (e.g., methylthio, ethylthio), an arylthio group (e.g., phenylthio), a cyano group, a sulfo group, a thiosulfonic acid group, a sulfinic acid group, a carboxy group, a hydroxy group, a mercapto group, a phosphono group, a nitro group, a sulfinio group, an ammonio group (e.g., trimethylammonio), a phosphonio group, a hydrazino group, a thiazolino group and a silyloxy group (e.g., t-butyltrimethylsilyloxy, t-butylphenylsilyloxy).

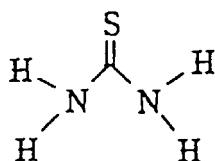
When two or more substituents are present, they may be the same or different.

[0063] In a preferred embodiment of the compound represented by formula (A), R^{11} , R^{12} , R^{13} and R^{14} each is a hydrogen atom, a substituted or unsubstituted, linear or branched alkyl group having from 1 to 6 carbon atoms, a substituted or unsubstituted cyclic alkyl group having from 3 to 6 carbon atoms, an alkenyl group having from 2 to 6 carbon atoms, a substituted or unsubstituted phenyl group having from 6 to 10 carbon atoms, a heterocyclic group or an acyl group, more preferably a hydrogen atom, a substituted or unsubstituted, linear or branched alkyl group having from 1 to 4 carbon atoms, a substituted or unsubstituted phenyl group having from 6 to 10 carbon atoms or an acyl group.

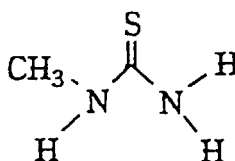
[0064] In a more preferred embodiment of the compound represented by formula (A), Z is a selenium atom or a tellurium atom, at least one of R^{11} , R^{12} , R^{13} and R^{14} has a water-soluble group, and the water-soluble group is preferably a sulfo group, a carboxy group, a hydroxy group, an ammonium group or an amino group, more preferably a sulfo group, a carboxy group or a hydroxy group.

[0065] Specific examples of the compound represented by formula (A) are set forth below, however, the present invention is by no means limited thereto.

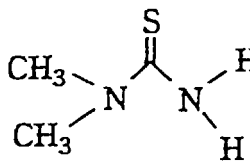
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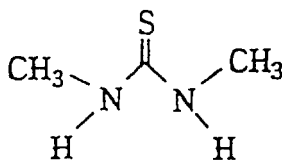
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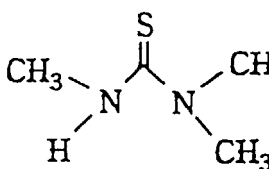
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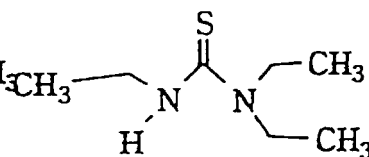
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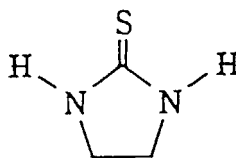
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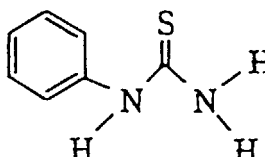
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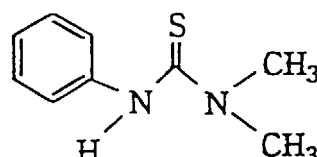
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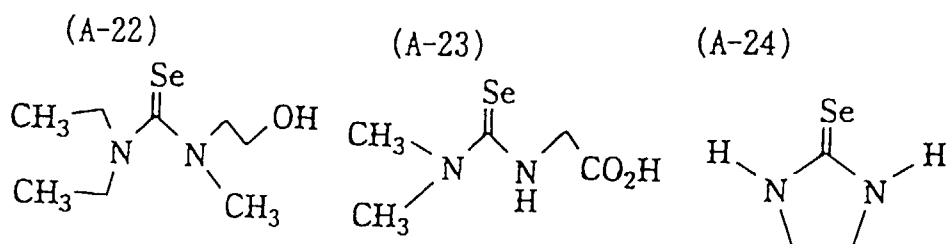
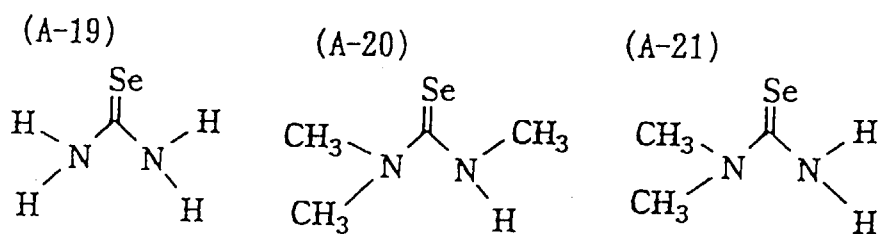
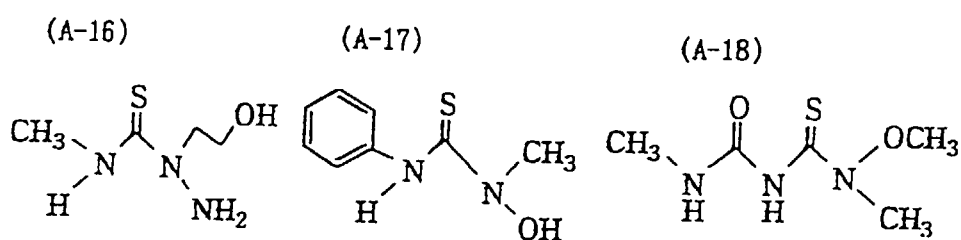
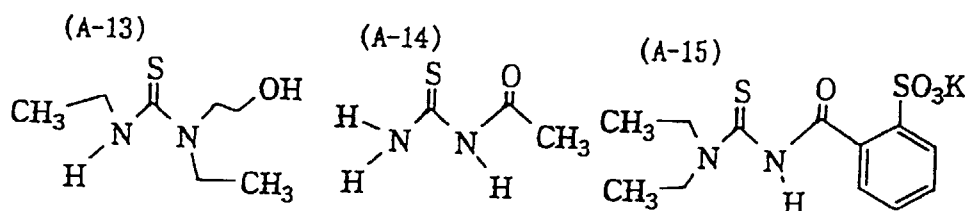
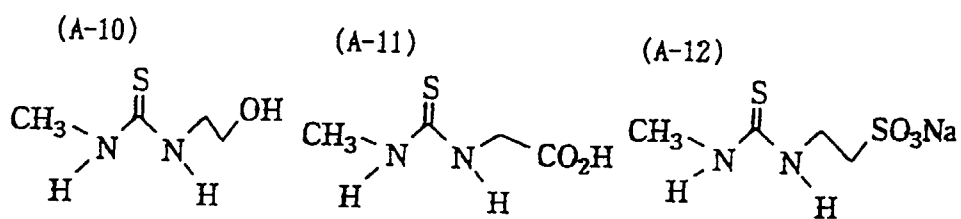


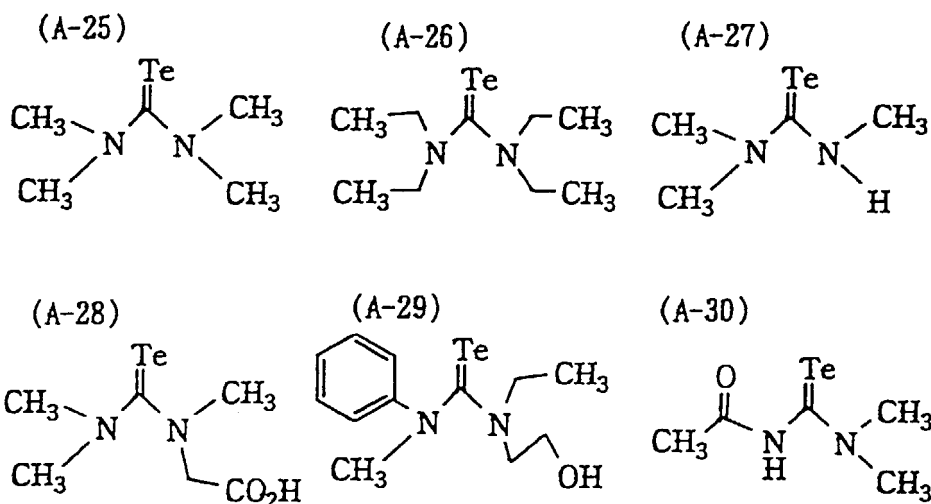
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(A-9)







[0066] The compound represented by formula (A) of the present invention can be synthesized by a known method, for example, by referring to *Chem. Rev.*, 55, 181-228 (1955), *J. Org. Chem.*, 24, 470-473 (1959), *J. Heterocycl. Chem.*, 4, 605-609 (1967), *Yakushi (Journal of Drugs)*, 82, 36-45 (1962), JP-B-39-26203, JP-A-63-229449 and OLS 2,043,944.

[0067] Specific examples of the synthesis are described below.

Synthesis of Compound (A-10)

[0068] In an acetonitrile (1.2 L) solution of methyl isothiocyanate (239.4 ml, 3.5 mol), a methanol (1.2 L) solution of ethanolamine (211 ml, 3.5 mol) was added dropwise while keeping the temperature at 50°C or less. After stirring the reaction mixture at 40°C for 1 hour, the solution was distilled under reduced pressure by an evaporator. The crystal-like residue obtained was recrystallized from acetonitrile, then, Compound (A-10) (413 g, 3.1 mol, yield: 88%) was obtained.

[0069] The compound having a P=X bond used at the chemical sensitization is preferably a phosphorus compound represented by the following formula (B):



wherein R²¹, R²² and R²³ each represent an aliphatic group, an aromatic group, or a heterocyclic group.

[0070] In formula (B), the aliphatic group represented by R²¹, R²² or R²³ is preferably an aliphatic group having from 1 to 30 carbon atoms, more preferably a linear, branched or cyclic alkyl group, an alkenyl group, an alkynyl group or an aralkyl group. Examples of the alkyl group, the alkenyl group, the alkynyl group and the aralkyl group include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, a t-butyl group, an n-octyl group, an n-decyl group, an n-hexadecyl group, a cyclopentyl group, a cyclohexyl group, an allyl group, a 2-butenyl group, a 3-pentenyl group, a propargyl group, a 3-pentynyl group, a benzyl group and a phenethyl group.

[0071] In formula (B), the aromatic group represented by R²¹, R²² or R²³ is preferably an aromatic group having from 6 to 30 carbon atoms, more preferably a monocyclic or condensed aromatic group having from 6 to 20 carbon atoms, such as phenyl group and naphthyl group.

[0072] In formula (B), the heterocyclic group represented by R²¹, R²² or R²³ is preferably a 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-membered ring saturated or unsaturated heterocyclic group containing at least one of nitrogen atom, oxygen atom and sulfur atom. The heterocyclic group may be a monocyclic ring or may form a condensed ring with another aromatic ring or heterocyclic ring. The heterocyclic group is preferably a 5- or 6-membered aromatic heterocyclic group and examples thereof include a pyridyl group, a furyl group, a thienyl group, a thiazolyl group, an imidazolyl group and a benzimidazolyl group.

5 [0073] These aliphatic group, aromatic group and heterocyclic group each may be substituted. Representative examples of the substituent include an alkyl group, an aralkyl group, an alkenyl group, an alkynyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group, an acylamino group, a ureido group, a urethane group, a sulfo-nylamino group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, a sulfinyl group, an alkyloxycarbonyl group, an aryloxycarbonyl group, an acyl group, an acyloxy group, a phosphoric acid amide group, a diacylamino group, an imido group, an alkylthio group, an arylthio group, a halogen atom, a cyano group, a sulfo group, a carboxyl group, a hydroxy group, a phosphono group, a nitro group, a phosphintelluroyl group and a heterocyclic group. These groups each may be further substituted. When two or more substituents are present, they may be the same or different. R²¹, R²² and R²³ may be combined to each other to form a ring together with a phosphorus atom (including an N,P-alkyl diazadipho-
10 phetizine ring).

[0074] Specific examples of the compound represented by formula (B) of the present invention are set forth below, however, the present invention is by no means limited thereto.

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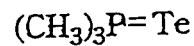
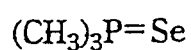
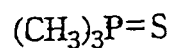
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(B-2)

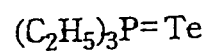
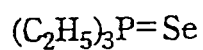
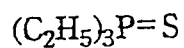
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(B-4)

(B-5)

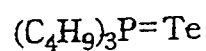
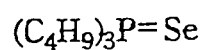
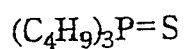
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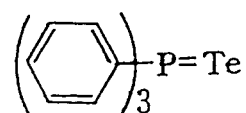
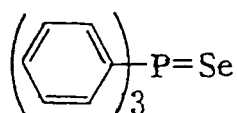
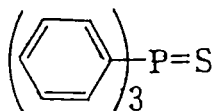
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(B-11)

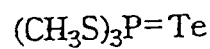
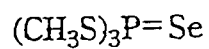
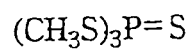
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(B-14)

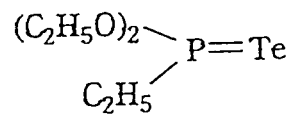
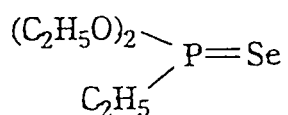
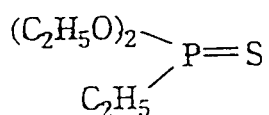
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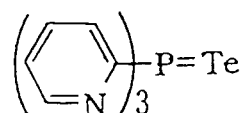
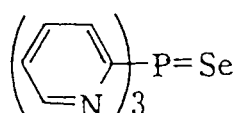
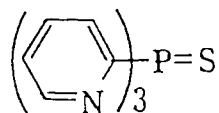
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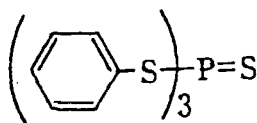
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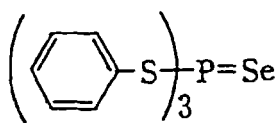
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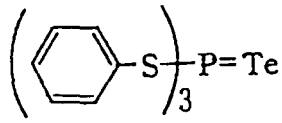
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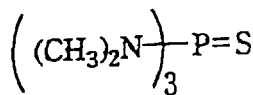
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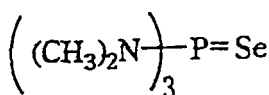
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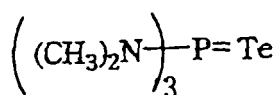
(B-25)



(B-26)



(B-27)



[0075] The compound represented by formula (B) of the present invention can be synthesized by referring to publications, for example, Organic Phosphorus Compounds, Vol. 4, pp. 1-73, J. Chem. Soc. (B), 1416 (1968), J. Org. Chem., Vol. 32, 1717 (1967), ibid., Vol. 32, 2999 (1967), Tetrahedron, 20, 449 (1964), and J. Am. Chem. Soc., Vol. 91, 2915 (1969).

[0076] The compound having an R-XO₂X bond used at the chemical sensitization is preferably a compound represented by the following formula (C), (D) or (E):



wherein R⁴⁰, R⁴¹ and R⁴² each represents an aliphatic group, an aromatic group, or a heterocyclic group.

[0077] When R⁴⁰, R⁴¹ and R⁴² each is an aliphatic group, the aliphatic group is a saturated or unsaturated, linear, branched or cyclic aliphatic hydrocarbon group, preferably an alkyl group having from 1 to 22 carbon atoms which may have a substituent, an alkenyl group having from 2 to 22 carbon atoms which may have a substituent or an alkynyl group which may have a substituent. Examples of the alkyl group include methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, 2-ethylhexyl, decyl, dodecyl, hexadecyl, octadecyl, cyclohexyl, isopropyl and t-butyl.

[0078] Examples of the alkenyl group include allyl and butenyl.

[0079] Examples of the alkynyl group include propargyl and butynyl.

[0080] The aromatic group represented by R⁴⁰, R⁴¹ or R⁴² includes a monocyclic or condensed ring aromatic group and preferably has from 6 to 20 carbon atoms. Examples thereof include a phenyl group which may be substituted and a naphthyl group which may be substituted.

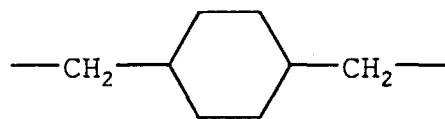
[0081] The heterocyclic group represented by R⁴⁰, R⁴¹ or R⁴² is a 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14- or 15-membered ring, preferably a 3-, 4-, 5- or 6-membered ring, containing at least one element selected from nitrogen, oxygen, sulfur, selenium and tellurium and having at least one carbon atom. Examples thereof include a pyrrolidine ring, a piperidine ring, a pyridine ring, a tetrahydrofuran ring, a thiophene ring, an oxazole ring, a thiazole ring, an imidazole ring, a benzothiazole ring, a benzoxazole ring, a benzimidazole ring, a selenazole ring, a benzoselenazole ring, a tellurazole ring, a triazole ring, a benzotriazole ring, a tetrazole ring, an oxadiazole ring and a thiadiazole ring.

[0082] Examples of R⁴⁰, R⁴¹ or R⁴² include an alkyl group (e.g., methyl, ethyl, hexyl), an alkoxy group (e.g., methoxy, ethoxy, octyl), an aryl group (e.g., phenyl, naphthyl, tolyl), a hydroxy group, a halogen atom (e.g., fluorine, chlorine, bromine, iodine), an aryloxy group (e.g., phenoxy), an alkylthio group (e.g., methylthio, butylthio), an arylthio group (e.g., phenylthio), an acyl group (e.g., acetyl, propionyl, butyl, valeryl), a sulfonyl group (e.g., methylsulfonyl, phenylsulfonyl), an acylamino group (e.g., acetylamino, benzoylamino), a sulfonylamino group (e.g., methanesulfonylamino, benzenesulfonylamino), an acyloxy group (e.g., acetoxy, benzoxy), a carboxyl group, a cyano group, a sulfo group, an amino group, a -SO₂SM group (wherein M represents a monovalent cation) and a -SO₂R¹ group.

[0083] The divalent linking group represented by L is an atom or atomic group containing at least one selected from C, N, S and O. Specific examples thereof include an alkylene group, an alkenylene group, an alkynylene group, an

arylene group, -O-, -S-, -NH-, -CO-, -SO₂- and a combination thereof.

[0084] L is preferably a divalent aliphatic group or a divalent aromatic group. Examples of the divalent aliphatic group represented by L include the followings: $\{\text{CH}_2\}_n$ (n=1 to 12, -CH₂-CH=CH-CH₂-, —CH₂C≡CCH₂—,



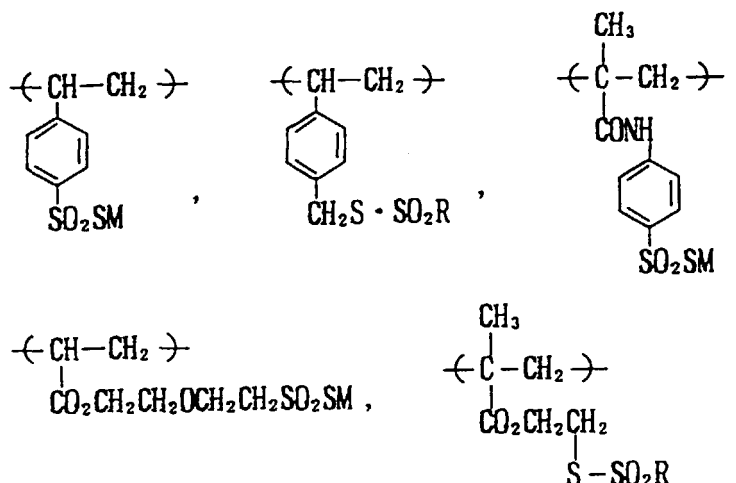
and xylylene group

[0085] Examples of the divalent group represented by L include a phenylene group and a naphthylene group.

[0086] These substituents each may be further substituted by a substituent described above.

[0087] M is preferably metal ion or organic cation. Examples of the metal ion include lithium ion, sodium ion and potassium ion. Examples of the organic cation include ammonium ion (e.g., ammonium, tetramethylammonium, tetrabutylammonium), phosphonium ion (e.g., tetraphenylphosphonium) and a guanidyl group.

[0088] When the compound represented by formula (C), (D) or (E) is a polymer, examples of the repeating unit thereof include the followings.



[0089] These polymers may be a homopolymer or may be a copolymer with another copolymerizable monomer.

[0090] The compounds represented by formulae (C), (D) and (E) may be easily synthesized by the method described or referred to in JP-A-54-1019, British Patent 972,211, *Journal of Organic Chemistry*, Vol. 53, page 396 (1988), and *Chemical Abstracts*, Vol. 59, 9776e.

[0091] The compound represented by formula (C), (D) or (E) is preferably added in an amount of from 10^{-7} to 10^{-1} mol, more preferably from 10^{-7} to 10^{-3} mol, still more preferably from 10^{-6} to 10^{-4} mol, per mol of silver halide.

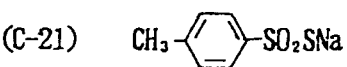
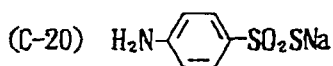
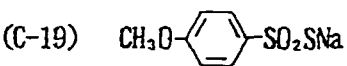
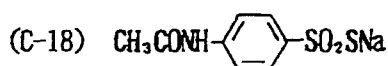
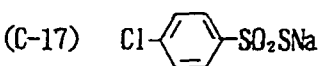
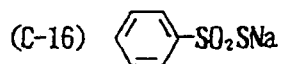
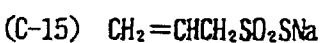
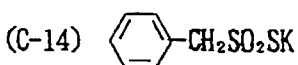
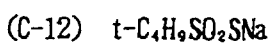
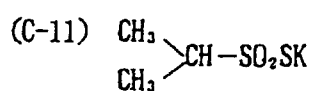
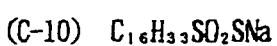
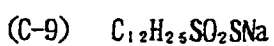
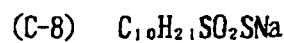
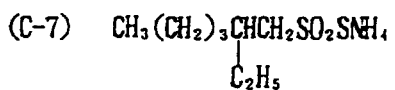
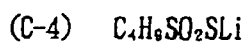
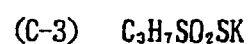
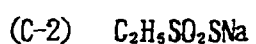
[0092] The compound represented by formula (C), (D) or (E) is added during the production process by a method commonly used for adding additives to a photographic emulsion. For example, a water-soluble compound is formed into an aqueous solution in an appropriate concentration. A water-soluble or sparingly water-soluble compound may be added as a solution by dissolving it in a solvent having no adverse effect on the photographic properties among solvents such as alcohols, glycols, ketones, esters and amides.

[0093] The compound represented by formula (C), (D) or (E) is necessary to be present at the chemical sensitization of core grains. As long as it is a stage of grain formation before the chemical sensitization of core grains, the compound may be added in any stage of the production process. It is also possible to previously add the compound (C), (D) or (E) to an aqueous solution of water-soluble silver salt or water-soluble alkali halide and form core grains using the aqueous solution. Also, a method of adding the solution of compound (C), (D) or (E) in parts or continuously over a long period of time during the chemical sensitization of core grains is also preferred.

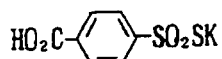
[0094] Among those compounds, the compound represented by formula (C) is most preferred.

[0095] Specific examples of the compounds represented by formulae (C), (D) and (E) are set forth below, however,

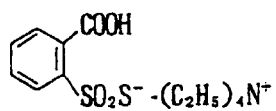
the effect of the present invention is obtained not only by these compounds.



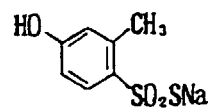
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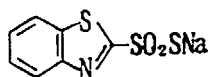
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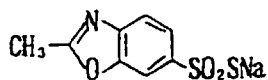
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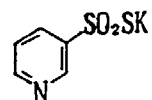
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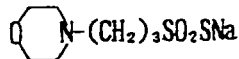
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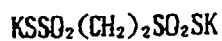
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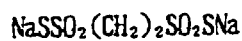
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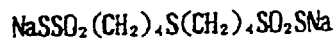
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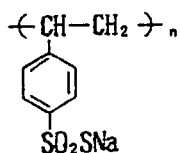
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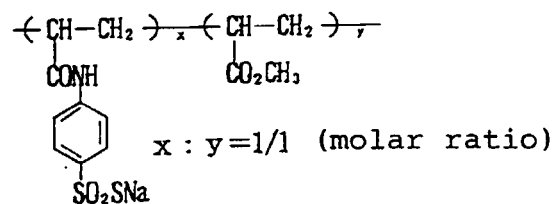
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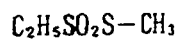
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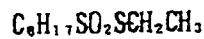
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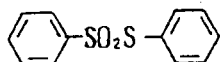
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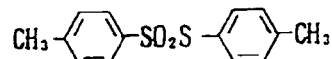
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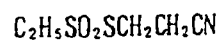
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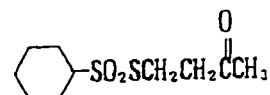
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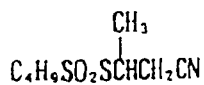
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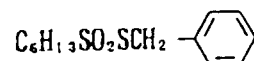
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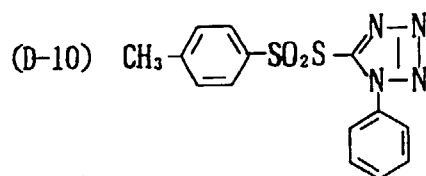
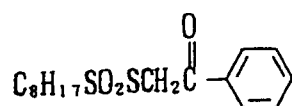
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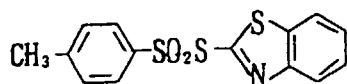
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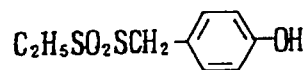
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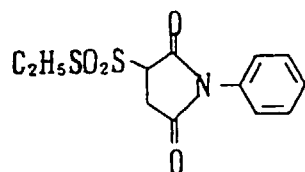
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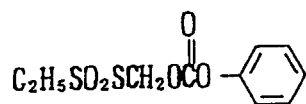
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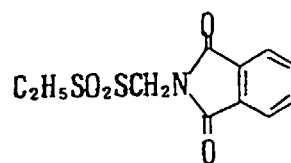
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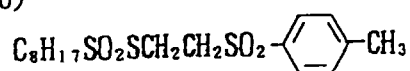
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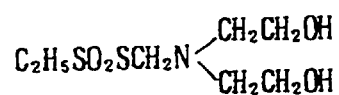
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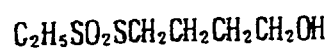
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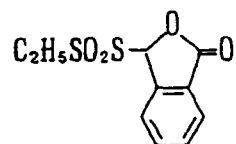
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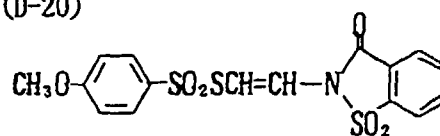
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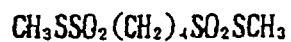
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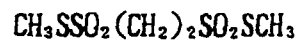
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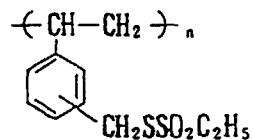
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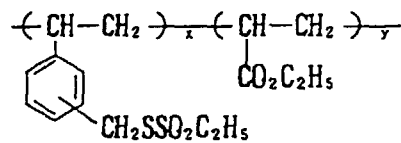
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(D-23)

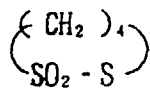


(D-24)

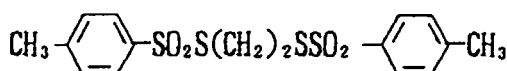


$x : y = 2/1$ (molar ratio)

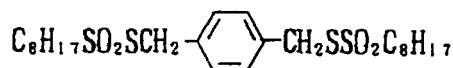
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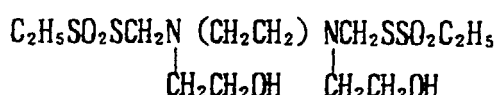
(E-1)

(E-2) $\text{C}_2\text{H}_5\text{SO}_2\text{SCH}_2\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{SSO}_2\text{C}_2\text{H}_5$

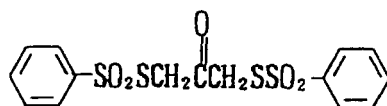
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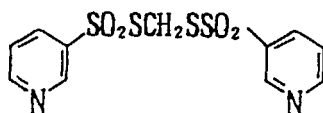
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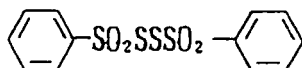
(E-5)



(E-6)

(E-7) $\text{C}_2\text{H}_5\text{SO}_2\text{SSSO}_2\text{C}_2\text{H}_5$ (E-8) $(n)\text{C}_3\text{H}_7\text{SO}_2\text{SSSO}_2\text{C}_3\text{H}_7(n)$

(E-9)



[0096] In the present invention, the compound represented by formula (C), (D) or (E) is preferably added at the chemical sensitization of core grains.

[0097] In the present invention, the chemical sensitization of core grains is preferably performed under the condition such that thiosulfate ion commonly used in the sulfur sensitization is substantially absent. The condition that thiosulfate ion is substantially absent means that the concentration of thiosulfate ion is 1 ppm or less.

[0098] Gelatin is advantageous as a protective colloid for use in the preparation of an emulsion for use in the present invention, however, other hydrophilic colloids may also be used.

[0099] Examples of the hydrophilic colloid which can be used include proteins such as gelatin derivatives, graft polymers of gelatin to other polymer, albumin and casein; saccharide derivatives such as cellulose derivatives (e.g., hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulfate), sodium arginates and starch derivatives; and various synthetic hydrophilic polymer materials such as homopolymers and copolymers of polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole or polyvinyl pyrazole.

[0100] The gelatin may be a lime-processed gelatin, an acid-processed gelatin or an enzyme-processed gelatin described in *Bull. Soc. Photo. Japan*, No. 16, p. 30 (1966). Furthermore, a hydrolysate or enzymolysate of gelatin may also be used.

[0101] Gelatin contains many impurity ions but use of a gelatin subjected to an ion exchange treatment and thereby reduced in the inorganic impurity ion amount is also preferred.

[0102] The emulsion of the present invention is preferably washed with water and dispersed in a newly prepared protective colloid for the purpose of desalting. The temperature at the water washing may be selected according to the purpose but it is preferably from 5 to 50°C. The pH at the water washing may also be selected according to the purpose

but it is preferably from 2 to 10, more preferably from 3 to 8. Furthermore, the pAg at the water washing may be selected according to the purpose but it is preferably from 5 to 10. The water washing may be performed by a method selected from a noodle washing method, a dialysis method using a semipermeable membrane, a centrifugal separation method, a coagulating precipitation method and an ion exchange method. In the case of the coagulating precipitation method, a method of using a sulfate, a method of using an organic solvent, a method of using a water-soluble polymer or a method of using a gelatin derivative may be selected.

[0103] In the present invention, the spectral sensitization may be performed using a sensitizing dye. The sensitizing dye used to this purpose is a cyanine dye, a merocyanine dye, a complex cyanine dye, a complex merocyanine dye, a holopolar cyanine dye, a hemicyanine dye, a styryl dye or a hemioxonol dye. Specific examples thereof include the sensitizing dyes described in U.S. Patent 4,617,257, JP-A-59-180550, JP-A-60-140335, JP-A-61-160739, RD17029, pp. 12-13 (1978), and RD17643; page 23 (1978).

[0104] These sensitizing dyes may be used either individually or in combination and the combination of sensitizing dyes is often used for the purpose of supersensitization. Representative examples thereof are described in U.S. Patents 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862 and 4,026,707, British Patents 1,344,281 and 1,507,803, JP-B-43-4936, JP-B-53-12375, JP-A-52-110618 and JP-A-52-109925.

[0105] In combination with the sensitizing dye, a dye which does not have a spectral sensitization activity by itself or a material which does not substantially absorb a visible light, but which exhibits supersensitization may be contained in the emulsion (for example, those described in U.S. Patents 3,615,613, 3,615,641, 3,617,295, 3,635,721, 2,933,390 and 3,743,510, and JP-A-63-23145).

[0106] The time when the sensitizing dye for spectral sensitization is added to the emulsion may be any stage heretofore known to be useful in the process of preparing the emulsion. Most commonly, the sensitizing dye is added after the completion of chemical sensitization and prior to the coating, but the sensitizing dye may be added at the same time with the chemical sensitizing dye to effect spectral sensitization and chemical sensitization simultaneously as described in U.S. Patents 3,628,969 and 4,225,666, the sensitizing dye may be added in advance of the chemical sensitization as described in JP-A-58-113928, or the sensitizing dye may be added before the completion of formation by precipitation of the silver halide grains to initiate the spectral sensitization. Furthermore, the above-described compound may be added in parts, more specifically, a part of the compound may be added in advance of the chemical sensitization and the remaining may be added after the chemical sensitization as described in U.S. Patent 4,225,666. Thus, the sensitizing dye may be added at any stage during the formation of silver halide grains as in the method described in U.S. Patent 4,183,756.

[0107] The amount of sensitizing dye added may be from 10^{-8} to 10^{-2} mol per mol of silver halide but in the case of a silver halide grain having a grain size of from 0.2 to 1.2 μm , which is preferred in the present invention, it is more effective to add the sensitizing dye in an amount of from about 5×10^{-5} to 2×10^{-3} mol per mol of silver halide.

[0108] The light-sensitive silver halide for use in the present invention is coated in an amount of from 1 mg to 10 g/m² in terms of silver.

[0109] In the present invention, various kinds of antifoggants and photographic stabilizers may be used for the purpose of preventing reduction in the sensitivity or generation of fogging. Examples thereof include azoles and azaindenes described in RD17643, pp. 24-25 (1978) and U.S. Patent 4,629,678, nitrogen-containing carboxylic acids and phosphoric acids described in JP-A-59-168442, mercapto compounds and metal salts thereof described in JP-A-59-111636 and acetylene compounds described in JP-A-62-87957.

[0110] Furthermore, an antiseptic or antifungal of various types is preferably added, such as phenethyl alcohol and additionally, 1,2-benzisothiazolin-3-one, n-butyl, p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethyl phenol, 2-phenox-yethanol and 2-(4-thiazolyl)benzimidazole described in JP-A-63-257747, JP-A-62-272248 and JP-A-1-80941. These are described in detail in EP-A-436938, page 150, lines 25 to 28. These additives are described in more detail in Research Disclosure, Item 17643 (1978), ibid., item 18716 (November, 1979) and ibid., Item 307105 (November, 1989). The pertinent portions thereof are summarized in the table below.

	Kind of Additives	RD17643 (Dec., 1978)	RD18716 (Nov., 1979)	RD307105 (Nov., 1989)
1	Chemical sensitizer	p. 23	p. 648, right column	p. 866
2	Sensitivity increasing agent		p. 648, right column	
3	Spectral sensitizer, super-sensitizer	pp. 23-24	p.648, right column to p. 649, right column	pp. 866-868

(continued)

	Kind of Additives	RD17643 (Dec., 1978)	RD18716 (Nov., 1979)	RD307105 (Nov., 1989)
5	4 Brightening agent	p. 24	p. 647, right column	p. 868
	5 Antifoggant, stabilizer	pp. 24-25	p. 649, right column	pp. 868-870
	6 Light absorbent, filter dye, UV absorbent	pp. 25-26	p. 649, right column to p. 650, left column	p. 873
10	7 Stain inhibitor	p. 25, right column	p. 650, left to light columns	p. 872
	8 Dye image stabilizer	p. 25	p. 650, left column	p. 872
	9 Hardener	p. 26	p. 651, left column	pp. 874-875
	10 Binder	p. 26	ditto	pp. 873-874
15	11 Plasticizer, lubricant	p. 27	p. 650, right column	p. 876
	12 Coating aid, surfactant	pp. 26-27	ditto	pp. 875-876
	13 Antistatic agent	p. 27	ditto	pp. 876-877
20	14 Matting agent			pp. 878-879

[0111] The color diffusion transfer light-sensitive material of the present invention is described below.

[0112] A most representative form of the color diffusion transfer material is a color diffusion transfer film unit. One representative form thereof is a film unit of such a type that an image-receiving element and a light-sensitive element are stacked on one transparent support and after the completion of a transfer image, the light-sensitive element need not be stripped off from the image-receiving element. To speak more specifically, the image-receiving element comprises at least one mordanting layer. The light-sensitive element preferably comprises a combination of a blue-sensitive emulsion layer, a green-sensitive emulsion layer and a red-sensitive emulsion layer, a combination of a green-sensitive emulsion layer, a red-sensitive emulsion layer and an infrared-sensitive emulsion layer, or a combination of a blue-sensitive emulsion layer, a red-sensitive emulsion layer and an infrared-sensitive emulsion layer (the term "infrared-sensitive emulsion layer" as used herein means an emulsion layer having a spectral sensitivity maximum to the light at 700 nm or more, particularly 740 nm or more), each emulsion layer being combined with a yellow dye image-forming compound, a magenta dye image-forming compound or a cyan dye image-forming compound. Between the mordanting layer and the light-sensitive layer or the dye image-forming compound-containing layer, a white reflective layer containing a solid pigment such as titanium oxide is provided so that the transferred image can be viewed through the transparent support.

[0113] Between the white reflective layer and the light-sensitive layer, a light-shielding layer may further be provided so as to accomplish the development in a bright place. Furthermore, if desired, a release layer may be provided at an appropriate site so that the light-sensitive layer can be wholly or partly stripped off from the image-receiving element. Such an embodiment is described, for example, in JP-A-56-67840 and Canadian Patent 674,082.

[0114] As the stacked layer type film unit where the element is stripped off, JP-A-63-226649 describes a color diffusion transfer photographic film unit comprising a white support having thereon a light-sensitive element consisting sequentially of at least (a) a layer having a neutralizing function, (b) a dye image-receiving layer, (c) a release layer and (d) at least one silver halide emulsion layer combined with a dye image-forming compound, an alkali processing composition containing a light-shielding agent and a transparent cover sheet, and further comprising a layer having a light-shielding function on the side of the emulsion layer opposite to the side on which the processing composition is spread.

[0115] In another form of the non-stripping type film unit, the above-described light-sensitive element is provided on one transparent support, a white reflective layer is provided on the light-sensitive element, and an image layer is further stacked on the white reflective layer. Also, a film unit of such a type that an image-receiving element, a white reflective layer, a release layer and a light-sensitive element are stacked on the same support and the light-sensitive element is intentionally stripped off from the image-receiving element is described in U.S. Patent 3,730,718.

[0116] On the other hand, the form of the film unit where the light-sensitive element and the image-receiving element are separately provided on respective two supports is roughly classified into two groups. One is a stripping type film unit and another is a non-stripping type film unit. These film units are described in detail below. In a preferred embodiment of the stripping type film unit, at least one image-receiving layer is provided on one support and the light-sensitive element is provided on a support having thereon a light-shielding layer, where the light-sensitive layer-coated surface and the mordanting layer-coated surface do not face each other before the completion of exposure, however, it is designed so that after the completion of exposure (for example, during the development), the light-sensitive layer-

coated surface can be reversed within an image forming apparatus and contact the image-receiving layer-coated surface. After a transfer image is completed on the mordanting layer, the light-sensitive element is swiftly stripped off from the image-receiving element.

[0117] In a preferred embodiment of the non-stripping type film unit, at least one mordanting layer is provided on a transparent support, the light-sensitive element is provided on a transparent support or a support having thereon a light-shielding layer, and these supports are superposed one on another such that the light-sensitive layer-coated surface and the mordanting layer-coated surface face each other.

[0118] These film units each may be further combined with a container (processing element) containing an alkaline processing solution and capable of rupturing under a pressure. Particularly, in the case of a non-stripping type film unit where the image-receiving element and the light-sensitive element are stacked on one support, the processing element is preferably disposed between the light-sensitive element and the cover sheet superposed thereon. In the case of a film unit where the light-sensitive element and the image-receiving element are separately provided on two supports, the processing element is preferably disposed between the light-sensitive element and the image-receiving element at the latest at the development processing. The processing element preferably contains one or both of a light-shielding agent (e.g., carbon black or a dye of which color is variable by the pH) and a white pigment (e.g., titanium oxide) according to the form of film unit. Furthermore, in the case of a color diffusion transfer system film unit, a neutralization timing mechanism comprising a combination of a neutralizing layer and a neutralization timing layer is preferably integrated into the cover sheet, the image-receiving element or the light-sensitive element.

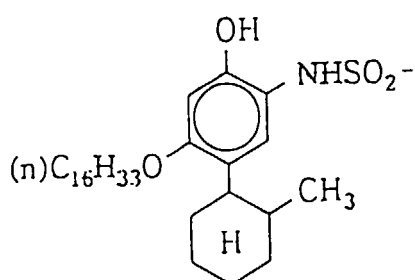
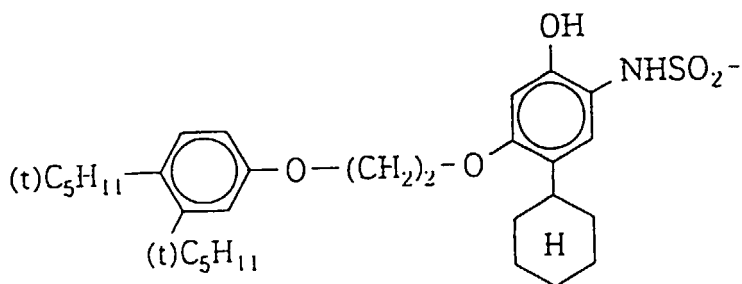
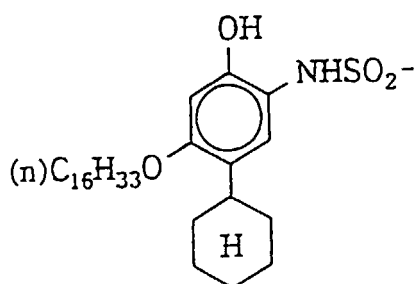
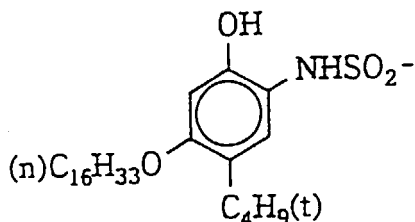
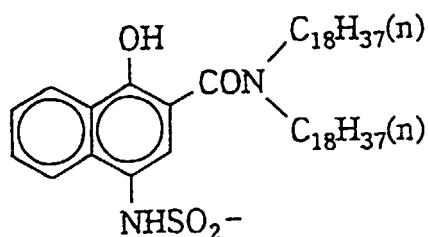
[0119] The dye image-forming substance for use in the present invention is a non-diffusive compound which releases a diffusive dye (or a dye precursor) in connection with the silver development, or a compound of which diffusibility itself changes, and this is described in The Theory of the Photographic Process, 4th ed. These compounds both may be represented by the following formula (II):

[0120] By the function of Z in formula (II), the compounds are roughly classified into a negative compound which becomes diffusive in the silver developed area, and a positive compound which becomes diffusive in the undeveloped area.

[0121] Z in the negative type compound is oxidized as a result of development and cleaved to release a diffusive dye.

[0122] Specific examples of Z include those described in U.S. Patents 3,928,312, 3,993,638, 4,076,529, 4,152,153, 4,055,428, 4,053,312, 4,198,235, 4,179,291, 4,149,892, 3,844,785, 3,443,943, 3,751,406, 3,443,939, 3,443,940, 3,628,952, 3,980,479, 4,183,753, 4,142,891, 4,278,750, 4,139,379, 4,218,368, 3,421,964, 4,199,355, 4,199,354, 4,135,929, 4,336,322 and 4,139,389, JP-A-53-50736, JP-A-51-104343, JP-A-54-130122, JP-A-53-110827, JP-A-56-12642, JP-A-56-16131, JP-A-57-4043, JP-A-57-650, JP-A-57-20735, JP-A-53-69033, JP-A-54-130927, JP-A-56-164342 and JP-A-57-119345.

[0123] Among the groups for Z in the negative dye releasing redox compound, particularly preferred is an N-substituted sulfamoyl group (the N-substituent is a group derived from an aromatic hydrocarbon ring or a heterocyclic ring) Representative examples of this group for Z are set forth below, however, the present invention is by no means limited thereto.



[0124] With respect to the positive compound, *Angev. Chem. Int. Ed. Engl.*, 22, 191 (1982) describes the compound.

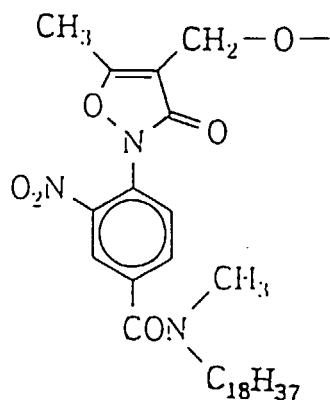
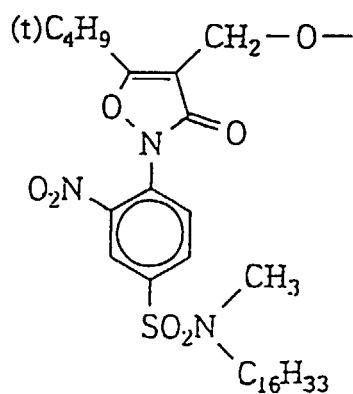
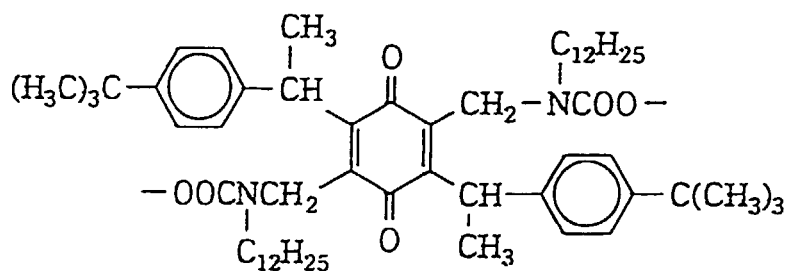
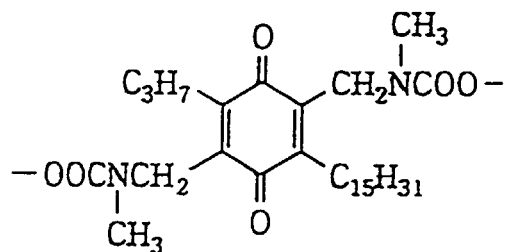
[0125] More specifically, the positive compound includes a compound which is initially diffusive under alkali conditions but is oxidized by the development and becomes non-diffusive (dye developer). Representative examples of Z effective for the compound of this type include those described in U.S. Patent 2,983,606.

[0126] The positive compound also includes a compound where self ring closing or the like takes place under alkaline conditions and a diffusive dye is released but when the compound is oxidized, the dye is not substantially released. Specific examples of Z having such a function include those described in U.S. Patent 3,980,479, JP-A-53-69033, JP-A-

54-130927, and U.S. Patents 3,421,964 and 4,199,355.

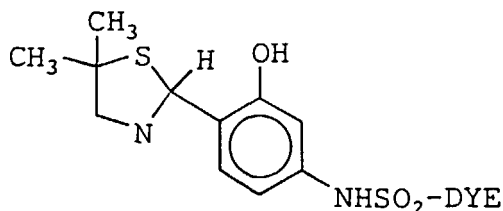
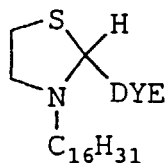
[0127] Furthermore, the positive compound includes a compound which does not release a dye by itself but when the compound is reduced, releases a dye. When a compound of this type is used in combination with an electron donor, the compound reacts with the residual electron donor which is imagewise oxidized by the silver development, and thereby the diffusive dye can be imagewise released. The atomic group having such a function is described, for example, in U.S. Patents 4,183,753, 4,142,891, 4,278,750, 4,139,379 and 4,218,368, JP-A-53-110827, U.S. Patents 4,278,750, 4,356,249 and 4,358,535, JP-A-53-110827, JP-A-54-130927, JP-A-56-164342, JIII Journal of Technical Disclosure No. 87-6199, and EP-A-220746.

[0128] Specific examples of Z in the compound of this type are set forth below, however, the present invention is by no means limited thereto.



[0129] The compound of this type is preferably used in combination with a non-diffusive electron donating compound (well known as ED compound) or a precursor thereof. Examples of the ED compound include those described, for example, in U.S. Patents 4,263,393 and 4,278,750 and JP-A-56-138736.

[0130] Another type of dye image-forming substance may be used and specific examples thereof are set forth below.



[0131] These compounds are described in detail in U.S. Patents 3,719,489 and 4,098,783.

[0132] Specific examples of the dye represented by DYE in the formulae are described in the following publications:

Examples of Yellow Dye:

[0133] U.S. Patents 3,597,200, 3,309,199, 4,013,633, 4,245,028, 4,156,609, 4,139,383, 4,195,992, 4,148,641, 4,148,643 and 4,336,322, JP-A-51-114930, JP-A-56-71072, Research Disclosure, No. 17630 (1978), and ibid., No. 16475 (1977).

Examples of Magenta Dye:

[0134] U.S. Patents 3,453,107, 3,544,545, 3,932,380, 3,931,144, 3,932,308, 3,954,476, 4,233,237, 4,255,509, 4,250,246, 4,142,891, 4,207,104 and 4,287, 292, JP-A-52-106727, JP-A-53-23628, JP-A-55-36804, JP-A-56-73057, JP-A-56-71060 and JP-A-55-134.

Examples of Cyan Dye:

[0135] U.S. Patents 3,482,972, 3,929,760, 4,013,635, 4,268,625, 4,171,220, 4,242,435, 4,142,891, 4,195,994, 4,147,544 and 4,148,642, British Patent 1,551,138, JP-A-54-99431, JP-A-52-8827, JP-A-53-47823, JP-A-53-143323, JP-A-54-99431, JP-A-56-71061, European Patents (EP) 53,037 and 53,040, Research Disclosure, No. 17630 (1978), and ibid., No. 16475 (1977).

[0136] These compounds each may be dispersed by the method described in JP-A-62-215272, pp. 144-146. Furthermore, the dispersion may contain the compounds described in JP-A-62-215272, pp. 137-144.

[0137] The present invention is described in greater detail below by referring to the Examples, however, the present invention should not be construed as being limited thereto.

Example 1:

[0138] The preparation method of silver halide emulsion is described below.

[0139] Ten kinds of silver halide emulsion grains (Emulsions A to G and Emulsions T, U and X) were prepared according to the preparation methods of emulsion described below.

Preparation of Emulsion A (octahedral internal latent image-type direct positive emulsion)

[0140] To 1,000 ml of an aqueous gelatin solution containing 0.05 M potassium bromide, 1 g of 3,6-dithia-1,8-octanediol, 0.034 mg of lead acetate and 60 g of deionized gelatin having a Ca content of 100 ppm or less, a 0.4M aqueous silver nitrate solution and a 0.4M aqueous potassium bromide solution were added while keeping the temperature at 75°C by a controlled double jet method such that 300 ml of the aqueous silver nitrate solution was added over

40 minutes while controlling the addition rate of the aqueous potassium bromide solution so as to have a pBr of 1.60.

[0141] After the completion of addition, octahedral silver bromide crystals (hereinafter called a core grain) having a uniform grain size of about 0.7 μm in terms of the average grain size (sphere-equivalent diameter) were produced.

[0142] Thereafter, the chemical sensitization of core was performed in a vessel described below according to the following formulation.

1. Tank:

A tank having a hemispherical bottom obtained by teflon-coating the surface of a metal with a fluororesin material FEP produced by Du Pont to have a thickness of 120 μm .

2. Stirring blade:

A seamless and integrated propeller type blade made of a metal of which surface was teflon-coated.

3. Formulation:

To a solution of the octahedral direct positive emulsion prepared above, 3 ml of an aqueous solution obtained by dissolving 10 mg of sodium benzenethiosulfate, 90 μg of potassium aurate tetrachloride and 1.2 g of potassium bromide in 1,000 ml of water was added. The mixed solution was heated at 75°C for 80 minutes to perform chemical sensitization. To the emulsion solution thus subjected to chemical sensitization, 0.15 M potassium bromide was added. Thereafter, in the same manner as in the preparation of the core grain, a 0.9M aqueous silver nitrate solution and a 0.9M aqueous silver potassium bromide solution were added while keeping the temperature at 75°C by a controlled double jet method such that 670 ml of the aqueous silver nitrate solution was added over 70 minutes while controlling the addition rate of the aqueous potassium bromide solution so as to have a pBr of 1.30.

[0143] The emulsion obtained was washed with water by an ordinary flocculation method and thereto, the gelatin described above, 2-phenoxyethanol and methyl p-hydroxybenzoate were added. As a result, octahedral silver bromide crystals (hereinafter called an "internal latent image-type core/shell grain") having a uniform crystal size of about 1.4 μm in terms of the average grain size (sphere-equivalent diameter) were obtained.

[0144] To the thus-obtained internal latent image-type core/shell emulsion, 3 ml of an aqueous solution obtained by dissolving 100 mg of sodium thiosulfate and 40 mg of sodium tetraborate in 1,000 ml of water was added and further 14 mg of poly(N-vinylpyrrolidone) was added. The resulting emulsion solution was ripened under heating at 60°C and thereto 0.005 M potassium bromide was added, thereby preparing an octahedral internal latent image-type direct positive emulsion.

Preparation of Emulsions B to G (octahedral internal latent image-type direct positive emulsion):

[0145] Octahedral internal latent image-type direct positive silver halide emulsions each having a uniform grain size shown in Table 1 below in terms of the average grain size (sphere-equivalent diameter) were prepared by changing the addition time of the aqueous silver nitrate solution or the aqueous potassium bromide solution and also changing the amount of chemicals added, in the preparation of Emulsion A.

TABLE 1

Emulsion Name	Average Grain Size, μm
B	1.20
C	0.93
D	1.20
E	0.94
F	0.74
G	0.66

Preparation of Emulsion T (hexagonal tabular internal latent image-type direct positive emulsion):

[0146] Into 1.2 ℓ of an aqueous gelatin solution containing 0.05 M potassium bromide and 0.7 wt% of gelatin having an average molecular weight of 100,000 or less, a 1.4M aqueous silver nitrate solution containing the same gelatin used above and 2M potassium bromide were simultaneously mixed each in an amount of 33 ml over 1 minute under vigorous stirring by a double jet method. During the mixing, the aqueous gelatin solution was kept at 30°C. Furthermore, 300 ml

of an aqueous gelatin solution containing 10 wt% of deionized gelatin having a Ca content of 100 ppm or less was added. Then, the temperature of the mixed solution was elevated to 75°C.

[0147] Subsequently, 40 ml of a 0.9M aqueous silver nitrate solution was added over 3 minutes and also a 25 wt% aqueous ammonia solution was added. The resulting solution was ripened at 75°C. After the completion of ripening, the ammonia was neutralized, 5 mg of lead acetate was added (added in the form of an aqueous solution), and then a 1M aqueous silver nitrate solution and a 1M aqueous potassium bromide solution were added at an accelerated flow rate (the flow rate at the end was 6 times the flow rate at the start) by a double jet method while keeping the pBr at 2.5 (the amount of the aqueous silver nitrate solution used was 500 ml).

[0148] The thus-formed grains (hereinafter called a core grain) were washed with water by an ordinary flocculation method and thereto gelatin, 2-phenoxyethanol and methyl p-hydroxybenzoate were added to obtain 750 g of hexagonal tabular core grains.

[0149] The thus-obtained hexagonal tabular core grain had an average diameter of 0.9 μm in terms of the diameter of a circle having the same projected area and an average thickness of 0.20 μm , and 95% of the entire projected area of all grains was occupied by hexagonal tabular grains.

[0150] Thereafter, the chemical sensitization of core was performed using a vessel described below according to the following formulation.

1. Tank:

A tank having a hemispherical bottom obtained by teflon-coating the surface of a metal with a fluororesin material FEP produced by Du Pont to have a thickness of 120 μm .

2. Stirring blade:

A seamless and integrated propeller type blade made of a metal of which surface was teflon-coated.

3. Formulation:

To 200 g of the hexagonal tabular core emulsion, 1,300 ml of water, 0.11M potassium bromide and 40 g of deionized gelatin were added. After elevating the temperature to 75°C, 2.4 ml of an aqueous solution obtained by dissolving 10 mg of sodium benzenethiosulfate, 90 μg of potassium aurate tetrachloride and 1.2 g of potassium bromide in 1,000 ml of water, and 15 mg of lead acetate (added in the form of an aqueous solution) were added. The solution obtained was heated at 75°C for 90 minutes to perform the chemical sensitization. To the core grain thus subjected to chemical sensitization, similarly to the preparation of core grains, a 2M aqueous silver nitrate solution and a 2.5M aqueous potassium bromide solution were added at an accelerated flow rate (the flow rate at the end was 3 times the flow rate at the start) by a double jet method while controlling the addition rate of the aqueous potassium bromide solution so as to have pBr of 2.2 (the amount of the aqueous silver nitrate solution used was 810 ml).

[0151] After adding thereto 0.3M potassium bromide, the emulsion obtained was washed with water by an ordinary flocculation method and thereto gelatin was added to obtain a hexagonal tabular internal latent image-type core/shell emulsion. The thus-obtained hexagonal tabular grain had an average diameter of 2.0 μm in terms of the diameter of a circle having the same projected area, an average thickness of 0.38 μm and an average volume size of 1.3 (μm)³, and 88% of the entire projected area of all grains was occupied by hexagonal tabular grains.

[0152] Thereafter, to this hexagonal tabular internal latent image-type core/shell emulsion, 15 ml of an aqueous solution obtained by dissolving 100 mg of sodium thiosulfate and 40 mg of sodium tetraborate in 1,000 ml of water was added and further 20 mg of poly (N-vinylpyrrolidone) was added. The resulting solution was heated at 70°C for 100 minutes to perform the chemical sensitization of grain surface, thereby preparing a hexagonal tabular internal latent image-type direct positive emulsion.

Preparation of Emulsion X (fine grain AgI emulsion):

[0153] To a solution obtained by adding 0.5 g of potassium iodide and 26 g of gelatin to water and kept at 35°C, 80 ml of an aqueous silver nitrate solution containing 40 g of silver nitrate and 80 ml of an aqueous solution containing 39 g of potassium iodide were added over 5 minutes. At this time, the aqueous silver nitrate solution and the aqueous potassium iodide solution each was added at a flow rate of 8 ml/min at the initiation of addition, and the flow rate was linearly accelerated so that the addition of 80 ml of each solution could be completed within 5 minutes.

[0154] After the completion of grain formation, soluble salts were removed by precipitation at 35°C and then the temperature was elevated to 40°C. Thereafter, 10.5 g of gelatin and 2.56 g of phenoxyethanol were added and the pH of the resulting solution was adjusted to 6.8 by sodium hydroxide. The emulsion obtained in a finished amount of 730 g was a monodisperse fine grain AgI having an average diameter of 0.015 μm .

Preparation of Emulsion U (hexagonal tabular internal latent image-type direct positive emulsion):

[0155] At the formation of outer shell in the preparation of Emulsion T, 0.15 mol% of iodide was uniformly incorporated into the outer shell and furthermore, the amount of the outer shell formed was increased. The thus-obtained emulsion grain had an average diameter of 2.5 μm in terms of the diameter of a circle having the same projected area, an average grain thickness of 0.45 μm and an average volume size of 1.7 (μm)³, and 88% of the entire projected area of all grains was occupied by hexagonal tabular grains.

[0156] Thereafter, the chemical sensitization of shell was performed in the same manner as in Emulsion T to prepare a hexagonal tabular internal latent image-type direct positive emulsion.

[0157] At the same time with the addition of potassium aurate tetrachloride in the chemical sensitization of core, a reducing substance shown in Tables 2 to 4 was added to prepare Emulsions A-1 to A-7, A-12 to A-13, T-1 to T-7, T-12 to T-13, U-1 to U-7, and U-12 to U-13 for comparison, and Emulsions A-8 to A-11, T-8 to T-11, and U-8 to U-11 of the present invention.

[Table 2]

Name of Emulsion	Original Emulsion	Amount of Potassium Aurate Tetrachloride, mol/mol-Ag	Kind of Reduction Sensitizer	Amount Added, mol/mol-Ag	Kind of Sulfur Sensitizer
A-1 (Comparison)	A	2.5×10^{-6}	none	0	sodium benzenethiosulfate
A-2 (Comparison)	A	0	none	0	ditto
A-3 (Comparison)	A	2.5×10^{-6}	thiourea dioxide	2.5×10^{-6}	ditto
A-4 (Comparison)	A	2.5×10^{-6}	thiourea dioxide	1.3×10^{-5}	ditto
A-5 (Comparison)	A	0	thiourea dioxide	2.5×10^{-6}	ditto
A-6 (Comparison)	A	0	Compound 6	2.5×10^{-6}	ditto
A-7 (Comparison)	A	0	Compound 13	2.5×10^{-6}	ditto
A-8 (Invention)	A	2.5×10^{-6}	Compound 6	2.5×10^{-6}	ditto
A-9 (Invention)	A	2.5×10^{-6}	Compound 6	1.3×10^{-5}	ditto
A-10 (Invention)	A	2.5×10^{-6}	Compound 13	2.5×10^{-6}	ditto
A-11 (Invention)	A	2.5×10^{-6}	Compound 13	1.3×10^{-5}	ditto
A-12 (Comparison)	A	2.5×10^{-6}	Compound 13	2.5×10^{-6}	sodium thiosulfate
A-13 (Comparison)	A	2.5×10^{-6}	Compound 13	1.3×10^{-5}	ditto

Sulfur sensitizer was added in an amount of 3.2×10^{-4} mol/mol-Ag.

[Table 3]

Name of Emulsion	Original Emulsion	Amount of Potassium Aurate Tetrachloride, mol/mol-Ag	Kind of Reduction Sensitizer	Amount Added, mol/mol-Ag	Kind of Sulfur Sensitizer
T-1 (Comparison)	T	2.5×10^{-6}	none	0	sodium benzenethiosulfate
T-2 (Comparison)	T	0	none	0	ditto
T-3 (Comparison)	T	2.5×10^{-6}	thiourea dioxide	2.5×10^{-6}	ditto
T-4 (Comparison)	T	2.5×10^{-6}	thiourea dioxide	1.3×10^{-5}	ditto
T-5 (Comparison)	T	0	thiourea dioxide	2.5×10^{-6}	ditto
T-6 (Comparison)	T	0	Compound 6	2.5×10^{-6}	ditto
T-7 (Comparison)	T	0	Compound 13	2.5×10^{-6}	ditto
T-8 (Invention)	T	2.5×10^{-6}	Compound 6	2.5×10^{-6}	ditto
T-9 (Invention)	T	2.5×10^{-6}	Compound 6	1.3×10^{-5}	ditto
T-10 (Invention)	T	2.5×10^{-6}	Compound 13	2.5×10^{-6}	ditto
T-11 (Invention)	T	2.5×10^{-6}	Compound 13	1.3×10^{-5}	ditto
T-12 (Comparison)	T	2.5×10^{-6}	Compound 13	2.5×10^{-6}	sodium thiosulfate
T-13 (Comparison)	T	2.5×10^{-6}	Compound 13	1.3×10^{-5}	ditto

[Table 4]

Name of Emulsion	Original Emulsion	Amount of Potassium Aurate Tetrachloride, mol/mol-Ag	Kind of Reduction Sensitizer	Amount Added, mol/mol-Ag	Kind of Sulfur Sensitizer
U-1 (Comparison)	U	2.5×10^{-6}	none	0	sodium benzenethiosulfate
U-2 (Comparison)	U	0	none	0	ditto
U-3 (Comparison)	U	2.5×10^{-6}	thiourea dioxide	2.5×10^{-6}	ditto
U-4 (Comparison)	U	2.5×10^{-6}	thiourea dioxide	1.3×10^{-5}	ditto
U-5 (Comparison)	U	0	thiourea dioxide	2.5×10^{-6}	ditto
U-6 (Comparison)	U	0	Compound 6	2.5×10^{-6}	ditto
U-7 (Comparison)	U	0	Compound 13	2.5×10^{-6}	ditto
U-8 (Invention)	U	2.5×10^{-6}	Compound 6	2.5×10^{-6}	ditto
U-9 (Invention)	U	2.5×10^{-6}	Compound 6	1.3×10^{-5}	ditto
U-10 (Invention)	U	2.5×10^{-6}	Compound 13	2.5×10^{-6}	ditto
U-11 (Invention)	U	2.5×10^{-6}	Compound 13	1.3×10^{-5}	ditto
U-12 (Comparison)	U	2.5×10^{-6}	Compound 13	2.5×10^{-6}	sodium thiosulfate
U-13 (Comparison)	U	2.5×10^{-6}	Compound 13	1.3×10^{-5}	ditto

[0158] Using Emulsions A to G, a comparative light-sensitive element (Sample 101) having a structure shown in Tables 5 to 8 below was prepared. The kind, dispersion form, addition temperature and amount of the sensitizing dyes

added at the end of chemical sensitization of the core are shown in Table 9 below.

[Table 5]

Structure of Light-Sensitive Element 101 for Comparison

<u>Layer No.</u>	<u>Name of Layer</u>	<u>Additive</u>	<u>Amount Coated</u> (g/m ²)
22nd Layer	Protective Layer	Matting Agent (1)	0.15
		Gelatin	0.25
		Surface Active Agent (1)	5.3×10^{-3}
		Surface Active Agent (2)	4.1×10^{-3}
		Surface Active Agent (3)	3.9×10^{-3}
		Additive (1)	8.0×10^{-3}
		Additive (5)	0.009
21st Layer	Ultraviolet Absorbing Layer	Ultraviolet Absorbent (1)	0.09
		Ultraviolet Absorbent (2)	0.05
		Ultraviolet Absorbent (3)	0.01
		Additive (2)	0.17
		Surface Active Agent (3)	0.013
		Surface Active Agent (4)	0.019
		Additive (1)	8.0×10^{-3}
		Additive (5)	0.023
		Hardening Agent (1)	0.050
		Hardening Agent (2)	0.017
		Gelatin	0.52

5	20th Layer	Blue-Sensitive Layer (high sensitivity)	Internal Latent Image-Type Direct Positive Emulsion: A-1	0.38 as silver
			Nucleating Agent (1)	2.9×10^{-6}
			Additive (3)	4.0×10^{-3}
10			Additive (4)	0.013
			Additive (5)	3.8×10^{-3}
			Additive (1)	9.0×10^{-3}
15			Surface Active Agent (5)	9.0×10^{-3}
			Gelatin	0.42
20	19th Layer	Blue-Sensitive Layer (low sensitivity)	Internal Latent Image-Type Direct Positive Emulsion: B	0.07 as silver
			Internal Latent Image-Type Direct Positive Emulsion: C	0.10 as silver
25			Nucleating Agent (1)	2.5×10^{-6}
			Additive (3)	0.022
			Additive (5)	9.0×10^{-3}
30			Additive (1)	0.013
			Surface Active Agent (5)	9.0×10^{-3}
			Gelatin	0.35
35	18th Layer	White Reflective Layer	Titanium dioxide	0.30
			Additive (1)	9.0×10^{-3}
			Surface Active Agent (1)	7.2×10^{-5}
40			Additive (5)	0.011
			Additive (8)	2.8×10^{-3}
			Gelatin	0.37

[Table 6]

Structure of Light-Sensitive Element 101
for Comparison (continued)

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<u>Layer No.</u>	<u>Name of Layer</u>	<u>Additive</u>	<u>Amount Coated</u> (g/m ²)
10	17th Layer	Yellow Color Material Layer	Yellow Dye Releasing Compound (1) 0.62
		High Boiling Point Organic Solvent (1)	0.27
15		Additive (6)	0.18
		Additive (7)	0.09
		Surface Active Agent (4)	0.062
20		Surface Active Agent (5)	0.030
		Additive (9)	0.031
		Additive (1)	6.0×10 ⁻³
25		Gelatin	0.87
	16th Layer	Interlayer	Additive (10) 0.013
		Surface Active Agent (1)	4.0×10 ⁻⁴
30		Additive (1)	7.0×10 ⁻³
		Gelatin	0.42
	15th Layer	Color Mixing Inhibiting Layer	Additive (11) 0.47
35		High Boiling Point Organic Solvent (2)	0.23
		Polymethyl methacrylate	0.81
		Surface Active Agent (5)	0.019
40		Additive (1)	2.0×10 ⁻³
		Additive (12)	0.61
		Gelatin	0.81
45	14th Layer	Green-Sensitive Layer (high sensitivity)	Internal Latent Image-Type Direct Positive Emulsion: as silver 0.69
		A-1	
		Nucleating agent (1)	2.2×10 ⁻⁶
50		Additive (3)	0.12

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		Additive (5)	0.014
5		Additive (1)	3.0×10^{-3}
		Additive (2)	0.15
		High Boiling Point Organic Solvent (2)	0.07
10		Surface Active Agent (5)	0.06
		Gelatin	0.97
	13th Layer	Green Sensitive Layer (low sensitivity)	Internal Latent Image-Type Direct Positive Emulsion: D
15			0.11 as silver
			Internal Latent Image-Type Direct Positive Emulsion: E
20			0.08 as silver
		Nucleating agent (1)	2.7×10^{-6}
		Additive (3)	0.011
25		Additive (4)	0.033
		Additive (5)	1.5×10^{-3}
		Additive (1)	0.010
30		Surface Active Agent (5)	0.024
		Gelatin	0.26
	12th Layer	Interlayer	Additive (1)
			0.014
		Surface Active Agent (1)	0.038
35		Surface Active Agent (3)	4.0×10^{-3}
		Additive (5)	0.014
40		Gelatin	0.33

[Table 7]

Structure of Light-Sensitive Element 101
for Comparison (continued)

	<u>Layer No.</u>	<u>Name of Layer</u>	<u>Additive</u>	<u>Amount Coated</u> (g/m ²)
10	11th Layer	Magenta Coloring Material Layer	Magenta Dye Releasing Compound(1)	0.56
			High Boiling Point Organic Solvent(1)	0.18
15			Additive (13)	9.3×10^{-4}
			Additive (5)	0.02
			Surface Active Agent (4)	0.04
20			Additive (14)	0.02
			Additive (1)	7.0×10^{-3}
			Gelatin	0.45
25	10th Layer	Interlayer	Additive (10)	0.014
			Surface Active Agent (1)	3.0×10^{-4}
			Additive (1)	9.0×10^{-3}
30			Gelatin	0.36
	9th Layer	Color Mixing Inhibiting Layer	Additive (11)	0.38
			High Boiling Point Organic Solvent(2)	0.19
35			Polymethyl methacrylate	0.66
			Surface Active Agent (5)	0.016
			Additive (1)	2.0×10^{-3}
40			Additive (12)	0.49
			Gelatin	0.65
	8th Layer	Red-Sensitive Layer (high sensitivity)	Internal Latent Image-Type Direct Positive Emulsion: A-1	0.33 as silver
45			Nucleating Agent (1)	6.1×10^{-6}
			Additive (3)	0.04
50			Additive (5)	0.01

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		Additive (1)	1.0×10^{-3}
5		Additive (2)	0.08
		High Boiling Point Organic Solvent (2)	0.04
10		Surface Active Agent (5)	0.02
		Gelatin	0.33
	7th Layer	Red-Sensitive Internal Latent Image-Type Direct Positive Emulsion: F	0.10 as silver
15		Internal Latent Image-Type Direct Positive Emulsion: G	0.11 as silver
20		Nucleating agent (1)	2.5×10^{-5}
		Additive (3)	0.047
		Additive (5)	0.016
25		Additive (1)	8.0×10^{-3}
		Surface Active Layer (5)	0.02
		Gelatin	0.57
30	6th Layer	White Reflective Layer	Titanium dioxide 1.87
		Additive (1)	7.0×10^{-3}
		Surface Active Agent (1)	4.0×10^{-4}
35		Additive (5)	0.02
		Additive (8)	0.015
		Gelatin	0.73

[Table 8]

Structure of Light-Sensitive Element 101
for Comparison (continued)

<u>Layer No.</u>	<u>Name of Layer</u>	<u>Additive</u>	<u>Amount Coated</u> (g/m ²)
10	5th Layer	Cyan Coloring Material Layer	Cyan Dye Releasing Compound (1) 0.25
			Cyan Dye Releasing Compound (2) 0.14
15			High Boiling Point Organic Solvent (1) 0.05
			Additive (3) 0.06
			Additive (5) 0.01
20			Surface Active Agent (4) 0.05
			Additive (9) 0.05
			Additive (1) 4.0×10^{-3}
25			Hardening Agent (3) 0.014
			Gelatin 0.40
30	4th Layer	Light-Shielding Layer	Carbon black 1.50
			Surface Active Agent (1) 0.08
			Additive (1) 0.06
			Additive (5) 0.06
35			Additive (12) 0.15
			Gelatin 1.43
	3rd Layer	Interlayer	Surface Active Agent (1) 6.0×10^{-4}
40			Additive (1) 9.0×10^{-3}
			Additive (5) 0.013
			Gelatin 0.29
45	2nd Layer	White Reflective Layer	Titanium dioxide 19.8
			Additive (15) 0.378
			Additive (16) 0.094
50			Surface Active Agent (6) 0.019

		Additive (8)	0.16	
5		Hardening Agent (1)	0.02	
		Hardening Agent (2)	0.007	
		Gelatin	2.45	
10	1st Layer	Image-Receiving Layer	Polymer Mordant (1)	2.22
			Additive (17)	0.26
			Surface Active Agent (7)	0.04
15			Additive (5)	0.11
			Hardening Agent (1)	0.03
			Hardening Agent (2)	0.01
20			Gelatin	3.25
	Support (90 μm-thick polyethylene terephthalate containing titanium dioxide for preventing light piping and subjected to undercoating)			
25	Back Layer	Curling Controlling Layer	Ultraviolet Absorbent (4)	0.40
			Ultraviolet Absorbent (5)	0.10
30			Diacetyl cellulose (acetylation degree: 51%)	4.20
			Additive (18)	0.25
			Barium stearate	0.11
35			Hardening Agent (4)	0.50

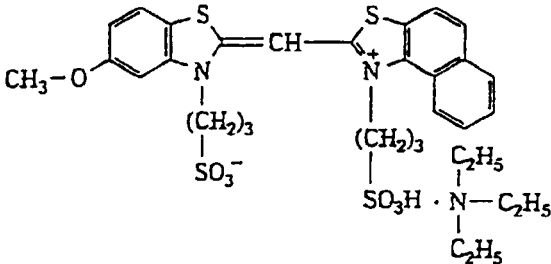
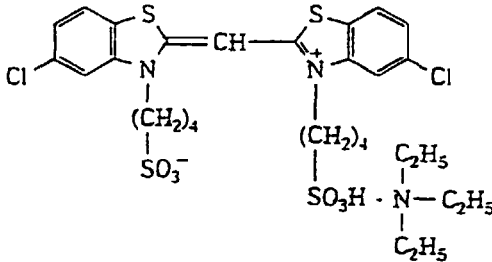
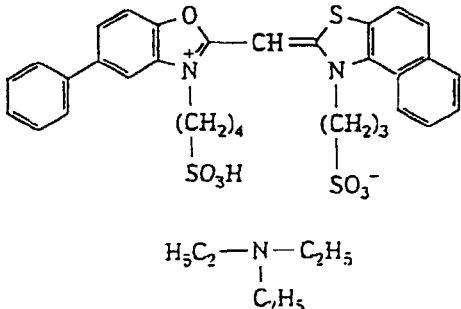
[Table 9]
Content of Sensitizing Dye per 1 Kg of Emulsion

Layer No.	Name of Emulsion	Kind of Sensitizing Dye	Dispersion Form of Dye	Addition Temperature	Dye Amount, g/kg of Emulsion
20	A-1	(9)	aqueous solution	70 °C	9.38×10^{-2}
19	B	(8)	aqueous solution	60 °C	1.19×10^{-1}
19	C	(9)	aqueous solution	60 °C	6.50×10^{-2}
14	A-1	(8)	aqueous solution	60 °C	1.47×10^{-1}
13	D	(7)	aqueous solution	60 °C	7.31×10^{-2}
13	E	(8)	aqueous solution	60 °C	1.66×10^{-1}
13		(7)	gelatin dispersion	60 °C	1.18×10^{-1}
13		(4)	gelatin dispersion	60 °C	2.94×10^{-3}
13		(6)	water/organic solvent dispersion by surface active agent	60 °C	9.23×10^{-2}
13		(7)	gelatin dispersion	40 °C	6.49×10^{-2}
13		(4)	gelatin dispersion	40 °C	1.62×10^{-3}
13		(6)	water/organic solvent dispersion by surface active agent	40 °C	4.85×10^{-2}
13		(7)	Gelatin dispersion	40 °C	7.34×10^{-2}
13		(4)	Gelatin dispersion	40 °C	1.83×10^{-3}
13		(6)	water/organic solvent dispersion by surface active agent	40 °C	5.69×10^{-2}

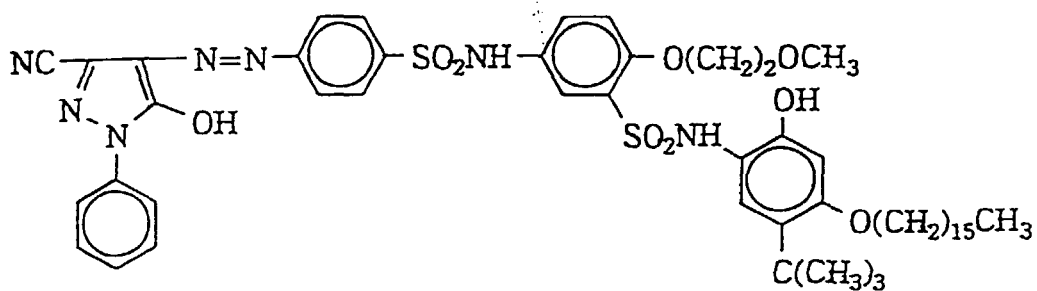
Layer No.	Name of Emulsion	Kind of Sensitizing Dye	Dispersion Form of Dye	Addition Temperature	Dye Amount, g/kg of Emulsion
8	A-1	(5)	aqueous solution	60 °C	3.10×10^{-2}
		(4)	gelatin dispersion		2.26×10^{-2}
		(3)	gelatin dispersion		2.26×10^{-2}
		(2)	gelatin dispersion		2.79×10^{-3}
		(1)	gelatin dispersion		9.20×10^{-2}
7	F	(5)	aqueous solution	60 °C	1.63×10^{-2}
		(4)	gelatin dispersion		1.34×10^{-2}
		(3)	gelatin dispersion		1.34×10^{-2}
		(2)	gelatin dispersion		1.91×10^{-3}
		(1)	gelatin dispersion		6.32×10^{-2}
7	G	(5)	aqueous solution	50 °C	1.17×10^{-2}
		(4)	gelatin dispersion		8.90×10^{-3}
		(3)	gelatin dispersion		8.90×10^{-3}
		(2)	gelatin dispersion		1.32×10^{-3}
		(1)	gelatin dispersion		4.37×10^{-2}

5 10	Molecular weight: 728.77 Molecular formula: $C_{25}H_{26}Cl_2N_2O_6S_4C_5H_5N_1$ Sensitizing Dye (1)
15 20	Molecular weight: 686.24 Molecular formula: $C_{30}H_{31}Cl_2N_2O_7S_3Na_1$ Sensitizing Dye (3)
25 30	Molecular weight: 782.09 Molecular formula: $C_{33}H_{32}N_2O_6S_4C_6H_{15}N_1$ Sensitizing Dye (2)

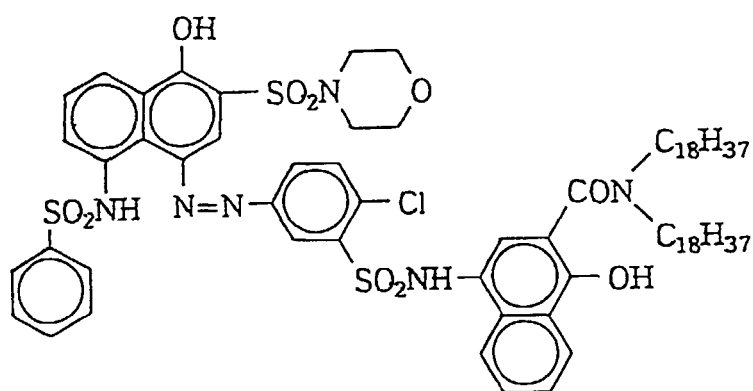
5 10	Molecular weight: 751.89 Molecular formula: $C_{35}H_{32}N_2O_8S_2C_5H_5N_1$ Sensitizing Dye (7)
15 20	Molecular weight: 707.96 Molecular formula: $C_{33}H_{36}N_2O_7S_3K_1$ Sensitizing Dye (4)
25 30 35	Molecular weight: 742.57 Molecular formula: $C_{30}H_{28}Cl_2F_7N_5O_3S_1$ Sensitizing Dye (6)

5  10	Molecular weight: 707.96 Molecular formula: $C_{26}H_{26}N_2O_7S_4C_6H_5N_1$ Sensitizing Dye (9)
15  20	Molecular weight: 724.83 Molecular formula: $C_{23}H_{24}Cl_2N_2O_6S_4C_6H_{15}N_1$ Sensitizing Dye (5)
25  30 35	Molecular weight: 752.00 Molecular formula: $C_{32}H_{30}N_2O_7S_3C_6H_{15}N_1$ Sensitizing Dye (8)

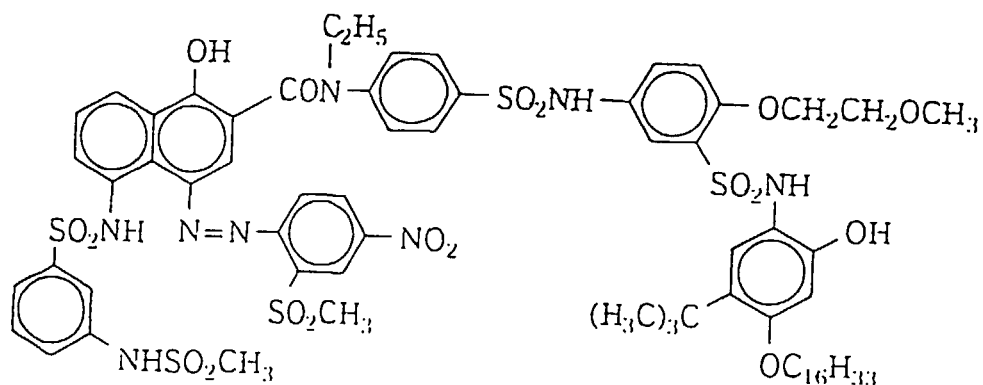
Yellow Dye Releasing Compound (1):



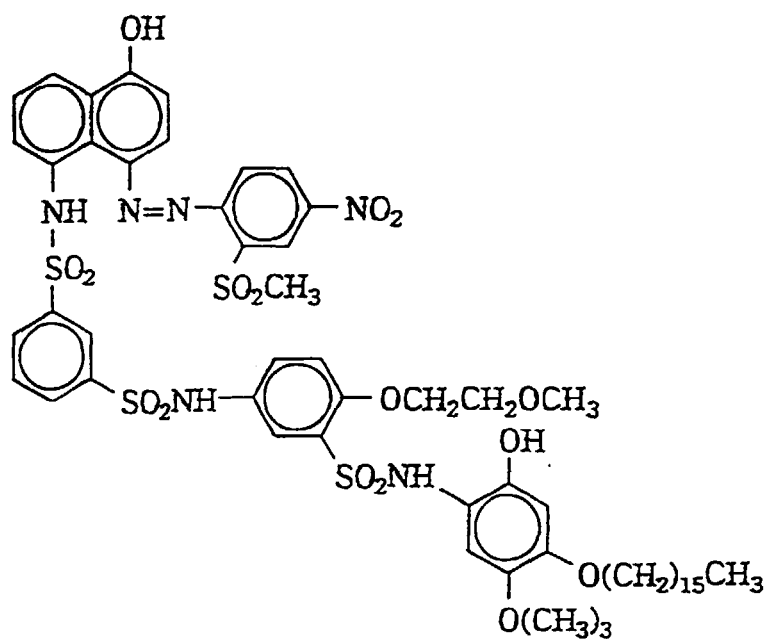
Magenta Dye Releasing Compound (1):



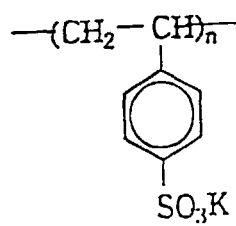
Cyan Dye Releasing Compound (1):



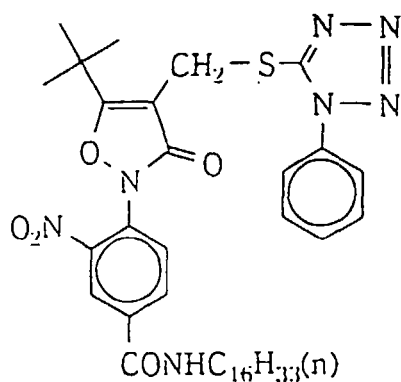
Cyan Dye Releasing Compound (2):



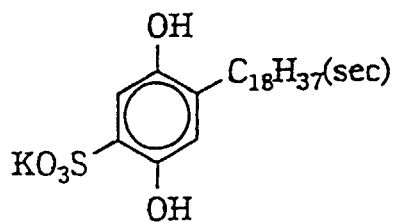
Additive (1):



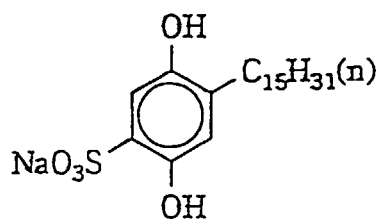
Additive (2):



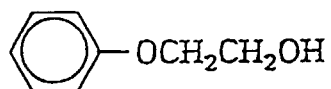
Additive (3):



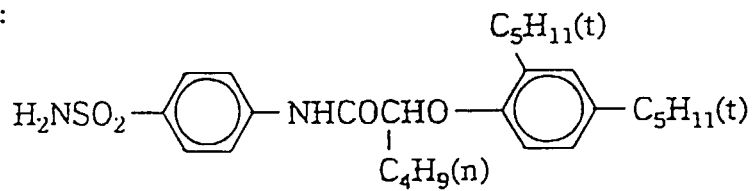
Additive (4):



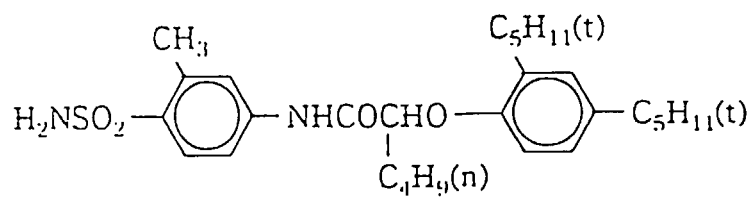
Additive (5):



Additive (6):



Additive (7)



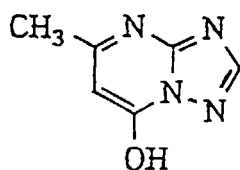
Additive (8):

Carboxymethyl cellulose
(CMC CELLOGEN 6A, produced by Daiichi Kogyo Seiyaku
K.K.)

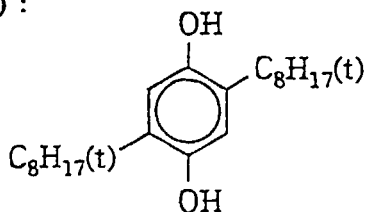
Additive (9):

Polyvinyl alcohol (PVA-220E)
Polymerization degree: about 2,000, saponification
degree: 88%

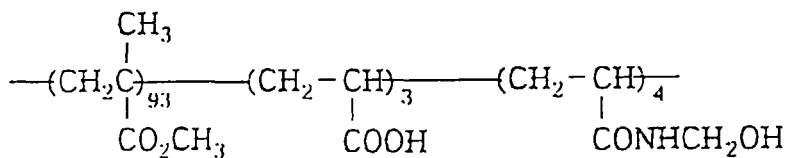
Additive (10):



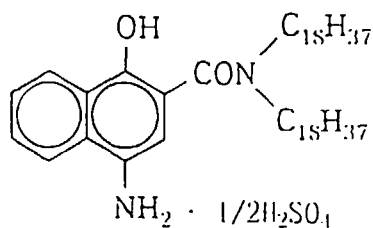
Additive (11):



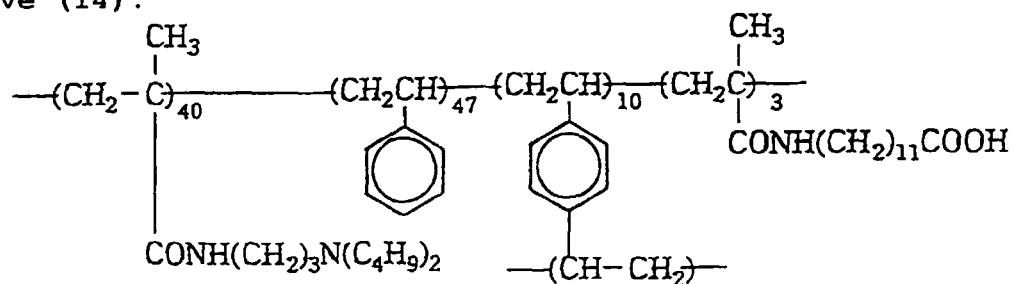
Additive (12):



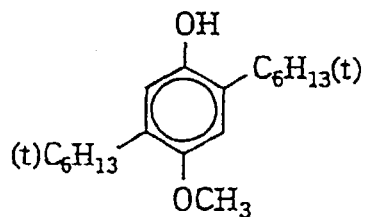
Additive (13):



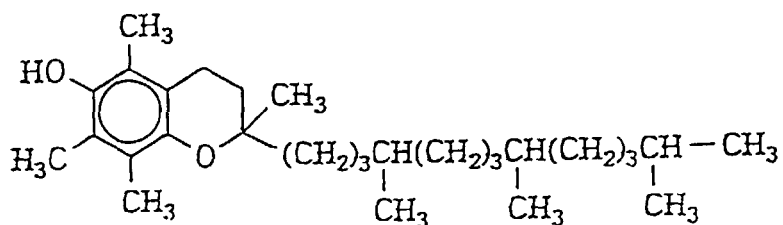
Additive (14):



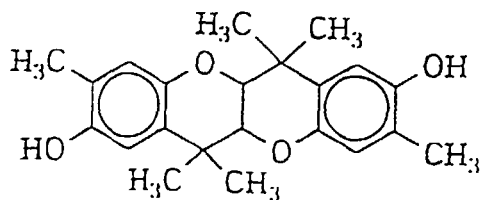
Additive (15):



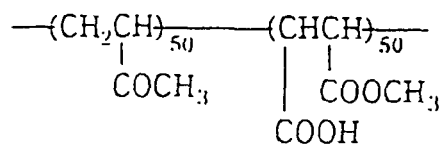
Additive (16):



Additive (17):



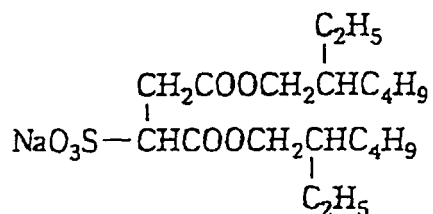
Additive (18):



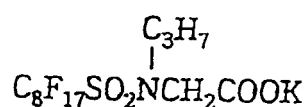
Matting Agent (1):

Polymethyl methacrylate spherical latex (average
particle size: 3 μm)

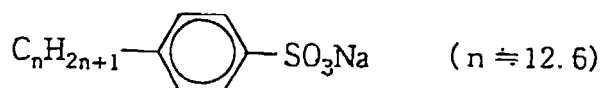
Surface Active Agent (1):



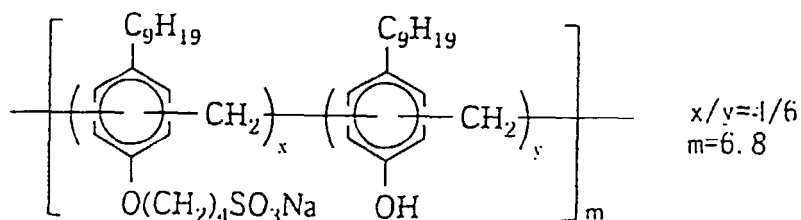
Surface Active Agent (2):



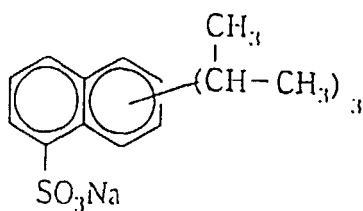
Surface Active Agent (3):



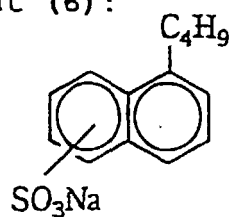
Surface Active Agent (4):



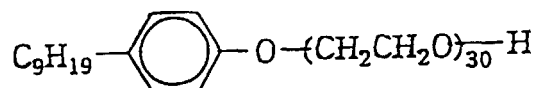
Surface Active Agent (5):



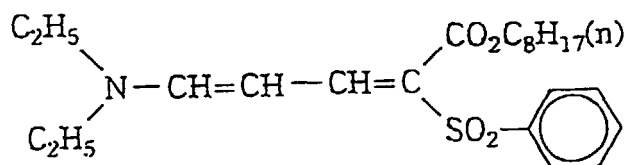
Surface Active Agent (6):



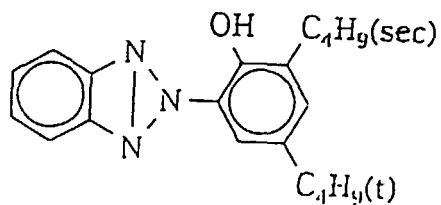
Surface Active Agent (7):



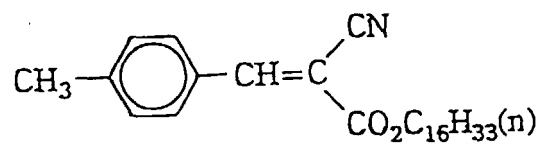
Ultraviolet Absorbent (1):



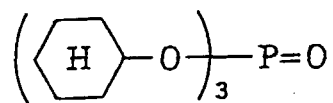
Ultraviolet Absorbent (2):



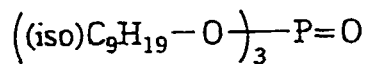
Ultraviolet Absorbent (3):



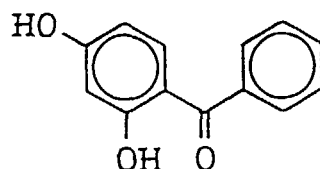
High Boiling Point Organic Solvent (1):



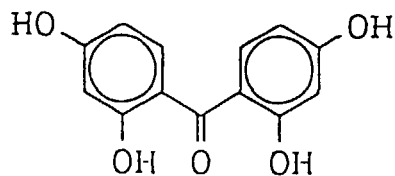
High Boiling Point Organic Solvent (2):



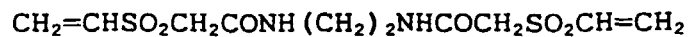
Ultraviolet Absorbent (4):



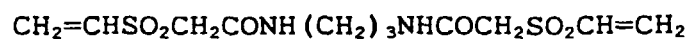
Ultraviolet Absorbent (5):



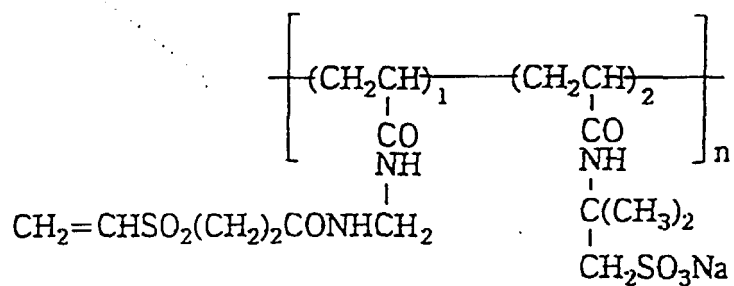
Hardening Agent (1):



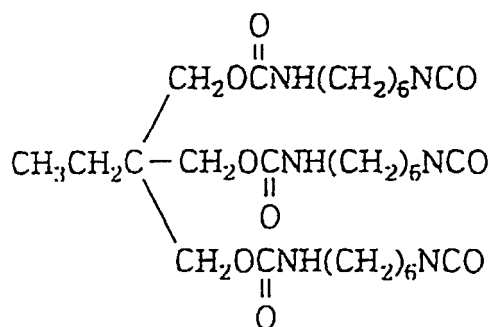
Ultraviolet Absorbent (2):



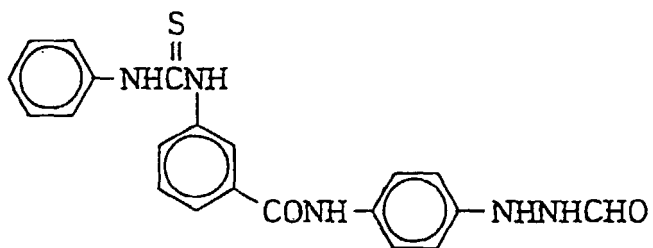
Hardening Agent (3):

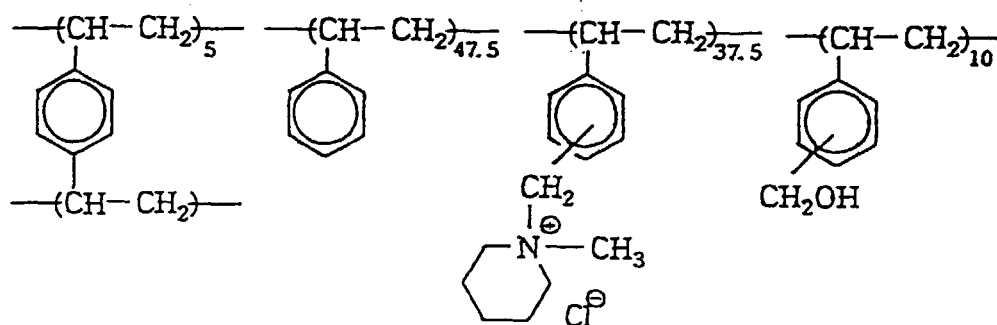


Hardening Agent (4):



Nucleating Agent (1):



Polymer Mordant (1):

[0159] Samples 102 to 113 and 201 to 213 were prepared using Emulsions A-2 to A-13 and T-1 to T-13, respectively, in place of the emulsions of the 8th layer, the 14th layer and the 20th layer, and Samples 301 to 313 were prepared using Emulsions U-1 to U-13, respectively, in place of the emulsion of the 20th Layer, as shown in Tables 10 and 11 below.

[Table 10]

List of Emulsions Used			
Sample No.	8th Layer	14th Layer	20th Layer
101 (Comparison)	A-1	A-1	A-1
102 (Comparison)	A-2	A-2	A-2
103 (Comparison)	A-3	A-3	A-3
104 (Comparison)	A-4	A-4	A-4
105 (Comparison)	A-5	A-5	A-5
106 (Comparison)	A-6	A-6	A-6
107 (Comparison)	A-7	A-7	A-7
108 (Invention)	A-8	A-8	A-8
109 (Invention)	A-9	A-9	A-9
110 (Invention)	A-10	A-10	A-10
111 (Invention)	A-11	A-11	A-11
112 (Comparison)	A-12	A-12	A-12
113 (Comparison)	A-13	A-13	A-13
201 (Comparison)	T-1	T-1	T-1
202 (Comparison)	T-2	T-2	T-2
203 (Comparison)	T-3	T-3	T-3
204 (Comparison)	T-4	T-4	T-4
205 (Comparison)	T-5	T-5	T-5
206 (Comparison)	T-6	T-6	T-6
207 (Comparison)	T-7	T-7	T-7

[Table 11]

List of Emulsions Used (continued)			
Sample No.	8th Layer	14th Layer	20th Layer
208 (Invention)	T-8	T-8	T-8
209 (Invention)	T-9	T-9	T-9
210 (Invention)	T-10	T-10	T-10
211 (Invention)	T-11	T-11	T-11
212 (Comparison)	T-12	T-12	T-12
213 (Comparison)	T-13	T-13	T-13
301 (Comparison)	T-1	T-1	U-1
302 (Comparison)	T-1	T-1	U-2
303 (Comparison)	T-1	T-1	U-3
304 (Comparison)	T-1	T-1	U-4
305 (Comparison)	T-1	T-1	U-5
306 (Comparison)	T-1	T-1	U-6
307 (Comparison)	T-1	T-1	U-7
308 (Invention)	T-1	T-1	U-8
309 (Invention)	T-1	T-1	U-9
310 (Invention)	T-1	T-1	U-10
311 (Invention)	T-1	T-1	U-11
312 (Comparison)	T-1	T-1	U-12
313 (Comparison)	T-1	T-1	U-13

[0160] The cover sheet was formed as follows.

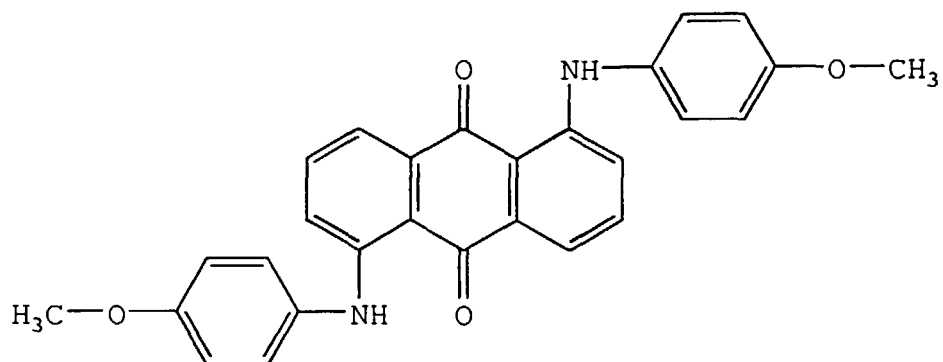
[0161] The following layers were coated on a polyethylene terephthalate support containing a dye for preventing light piping and having a gelatin undercoat:

- (a) a neutralizing layer containing 10.4 g/m² of an acrylic acid/n-butyl acrylate copolymer (80/20 (mol%)) having an average molecular weight of 50,000 and 0.1 g/m² of 1,4-bis(2,3-epoxypropoxy)butane;
- (b) a layer containing 4.3 g/m² of cellulose acetate having an acetylation degree of 55% and 0.2 g/m² of methyl half ester of a methyl vinyl ether/maleic acid anhydride copolymer (50/50 (mol%)); and
- (c) a neutralization timing layer containing 0.3 g/m² of a n-butyl methacrylate/2-hydroxyethyl methacrylate/acrylic acid copolymer (66.1/28.4/5.5 (wt%)) having an average molecular weight of 25,000 and 0.8 g/m² of an ethyl methacrylate/2-hydroxyethyl methacrylate/acrylic acid copolymer having an average molecular weight of 40,000 (66.1/28.4/5.5 (wt%)).

[0162] As the dye for preventing light piping, a 3:1 mixture of KAYASET GREEN A-G produced by Nippon Kayaku K.K. and the compound shown below was used.

Dye for Preventing Light Piping:

[0163]

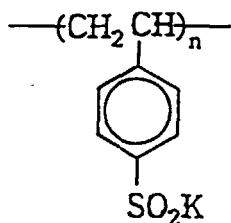


[0164] The alkali processing composition was prepared by the following method.

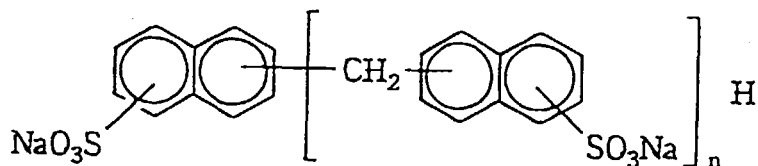
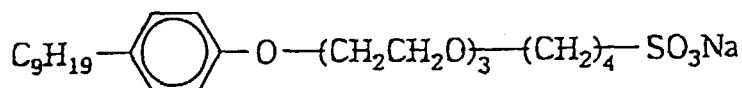
[0165] 0.8 g of the processing solution having the following composition was filled in a container capable of rupturing by a pressure.

	Water	695 g
5	1-p-Tolyl-4-hydroxymethyl-4-methyl-3-pyrazolidin-4-one	7.00 g
	1-Phenyl-4-hydroxymethyl-4-methyl-3-pyrazolidin-1-one	9.85 g
10	Sulfinic acid polymer	2.10 g
	5-Methylbenzotriazole	2.50 g
15	Zinc nitrate hexahydrate	0.60 g
	Potassium sulfite	1.90 g
20	Aluminum nitrate nonahydrate	0.60 g
	Carboxymethyl cellulose Na salt	56.0 g
25	Potassium hydroxide	55.0 g
	Carbon black	160 g
	Anionic surface active agent (1)	8.60 g
30	Anionic surface active agent (2)	0.03 g
	Alkyl-modified PVA (produced by Kuraray)	0.06 g
35	Cationic polymer	1.05 g

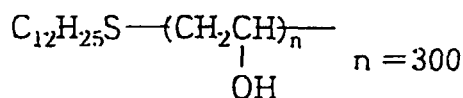
Sulfinic Acid Polymer:



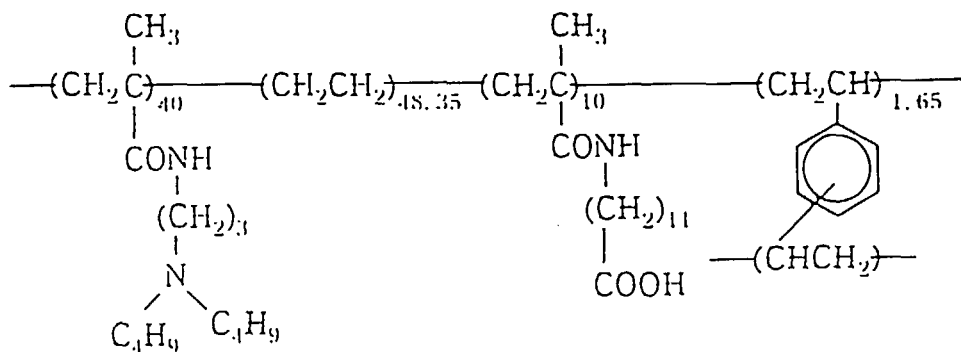
Anionic Surface Active Agent (1):

Anionic Surface Active Agent (2): $n = 1 \sim 4$ 

Alkyl-modified PVA:



Cationic Polymer:



[0166] Light-Sensitive Elements 101 to 113, 201 to 213 and 301 to 313 prepared above each was exposed through a gray continuous wedge from the emulsion layer side and superposed on the cover sheet prepared above, and the processing solution shown above was spread between these two materials using a pressure roller to have a thickness of 62 μm . The exposure was performed for 1/100 second by controlling the exposure illuminance to give a constant exposure amount. The processing was performed at 25°C and after 10 minutes, the transfer density was measured by a color densitometer.

[0167] The results obtained are shown in Tables 12 to 14. The maximum density, the minimum density, the midpoint sensitivity and the foot sensitivity in the Tables were determined as follows. A reversal characteristic curve was drawn such that the abscissa was the logarithm of exposure amount and the ordinate was the color density. The color density in the non-exposed area was defined as the maximum density, the color density in the region having a sufficiently large

exposure amount was defined as the minimum density, the sensitivity giving a medium density between the maximum density and the minimum density was defined as the midpoint sensitivity, and the sensitivity of giving a density of 0.3 was defined as the foot density. The sensitivity is a relative value of the reciprocal of exposure amount, assuming that Y, M and C of Sample 101 each is 100.

[Table 12]

Measurement Results of Photographic Properties												
Sample No.	Maximum Density			Minimum Density			Midpoint Sensitivity			Foot Sensitivity		
	Y	M	C	Y	M	C	Y	M	C	Y	M	C
101 (Comparison)	2.10	2.30	2.40	0.17	0.16	0.24	100	100	100	100	100	100
102 (Comparison)	2.25	2.50	2.70	2.25	2.50	2.70	U.D	U.D	U.D	U.D	U.D	U.D
103 (Comparison)	2.11	2.29	2.42	0.17	0.17	0.25	101	99	99	101	99	99
104 (Comparison)	2.11	2.31	2.43	0.18	0.17	0.24	99	98	101	101	100	99
105 (Comparison)	2.25	2.50	2.70	2.25	2.50	2.70	U.D	U.D	U.D	U.D	U.D	U.D
106 (Comparison)	2.25	2.50	2.70	2.25	2.50	2.70	U.D	U.D	U.D	U.D	U.D	U.D
107 (Comparison)	2.25	2.50	2.70	2.25	2.50	2.70	U.D	U.D	U.D	U.D	U.D	U.D
108 (Invention)	2.05	2.28	2.38	0.17	0.16	0.24	132	135	138	133	133	136
109 (Invention)	1.98	2.10	2.28	0.16	0.15	0.24	156	161	160	163	162	161
110 (Invention)	2.09	2.30	2.39	0.17	0.16	0.24	130	131	133	129	129	132
111 (Invention)	2.00	2.14	2.30	0.16	0.15	0.24	152	158	157	160	159	158
112 (Comparison)	2.10	2.30	2.40	0.17	0.16	0.24	101	102	101	100	101	99
113 (Comparison)	2.10	2.30	2.40	0.17	0.17	0.24	107	106	106	104	103	101

U.D: undetermined

[Table 13]

Sample No.	Maximum Density			Minimum Density			Midpoint Sensitivity			Foot Sensitivity		
	Y	M	C	Y	M	C	Y	M	C	Y	M	C
201 (Comparison)	2.12	2.32	2.42	0.17	0.16	0.24	122	130	133	118	125	126
202 (Comparison)	2.30	2.60	2.75	2.30	2.60	2.15	U.D	U.D	U.D	U.D	U.D	U.D
203 (Comparison)	2.14	2.33	2.45	0.17	0.17	0.25	121	129	132	115	128	129
204 (Comparison)	2.12	2.31	2.43	0.18	0.17	0.24	125	132	133	117	129	131
205 (Comparison)	2.30	2.60	2.75	2.30	2.60	2.75	U.D	U.D	U.D	U.D	U.D	U.D
206 (Comparison)	2.31	2.59	2.74	2.31	2.58	2.76	U.D	U.D	U.D	U.D	U.D	U.D
207 (Comparison)	2.31	2.58	2.74	2.30	2.58	2.75	U.D	U.D	U.D	U.D	U.D	U.D
208 (Invention)	2.09	2.30	2.40	0.17	0.16	0.24	172	185	188	173	183	186
209 (Invention)	2.02	2.13	2.31	0.16	0.15	0.24	196	201	200	203	202	201
210 (Invention)	2.12	2.32	2.41	0.17	0.16	0.24	169	181	173	169	179	180
211 (Invention)	2.05	2.18	2.36	0.16	0.15	0.24	192	198	197	200	199	198
212 (Comparison)	2.12	2.31	2.41	0.17	0.16	0.24	124	132	134	120	127	128
213 (Comparison)	2.10	2.30	2.40	0.17	0.16	0.24	129	135	138	129	136	140

U.D: undetermined

[Table 14]

Sample No.	Maximum Density			Minimum Density			Midpoint Sensitivity			Foot Sensitivity		
	Y	M	C	Y	M	C	Y	M	C	Y	M	C
301 (Comparison)	2.02	2.32	2.42	0.20	0.16	0.24	150	130	133	144	125	126
302 (Comparison)	2.30	2.32	2.42	2.30	0.16	0.24	U.D	130	132	U.D	124	124
303 (Comparison)	2.03	2.32	2.41	0.20	0.16	0.24	149	130	132	147	125	125
304 (Comparison)	2.01	2.32	2.42	0.20	0.16	0.24	151	130	132	145	125	124
305 (Comparison)	2.30	2.32	2.42	2.29	0.16	0.24	U.D	130	131	U.D	124	125
306 (Comparison)	2.29	2.32	2.43	2.28	0.16	0.24	U.D	130	132	U.D	125	126
307 (Comparison)	2.28	2.32	2.43	2.29	0.16	0.24	U.D	130	132	U.D	125	126
308 (Invention)	1.99	2.31	2.42	0.20	0.16	0.24	209	130	131	206	124	126
309 (Invention)	1.90	2.30	2.42	0.19	0.16	0.24	221	132	135	217	124	126
310 (Invention)	2.01	2.30	2.42	0.20	0.16	0.24	201	131	132	199	125	126
311 (Invention)	1.97	2.29	2.42	0.19	0.16	0.24	224	133	134	222	125	126
312 (Comparison)	2.01	2.32	2.42	0.20	0.16	0.24	153	130	133	150	125	126
313 (Comparison)	2.00	2.32	2.42	0.20	0.26	0.24	158	130	132	155	125	125

U.D: undetermined

[0168] It is seen that Samples 108 to 111, 208 to 211 and 308 to 311 of the present invention were increased both in the midpoint sensitivity and the foot sensitivity as compared with Comparative Samples 101, 201 and 301.

[0169] From the fact that Samples 108, 208 and 308 of the present invention are higher in the midpoint sensitivity and the foot sensitivity than the corresponding Comparative Samples 106, 206 and 306, it is seen that the effect of the reducing sensitizer of the present invention can be first obtained by using it in combination with a gold sensitizer.

[0170] Furthermore, from the fact that Samples 110, 111, 210, 211, 310 and 311 of the present invention is higher in the midpoint sensitivity and the foot sensitivity than the corresponding Comparative Samples 112, 113, 212, 213, 312 and 313, it is seen that the effect of the reducing sensitizer of the present invention can be first obtained by using it in combination with a specific kind of sulfur (chalcogen) sensitizer.

[0171] According to the present invention, an internal latent image-type direct positive silver halide emulsion having high sensitivity and being contrasted in the low density part on the reversal characteristic curve can be obtained. Furthermore, by producing a color diffusion transfer light-sensitive material using the emulsion, a reversal color image having excellent graininess can be obtained.

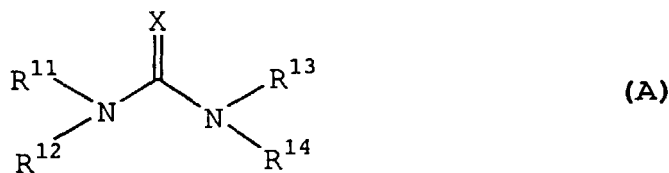
Claims

1. An internal latent image-type direct positive silver halide photographic emulsion having a core/shell structure comprising a chemically sensitized core and a chemically sensitized shell, wherein a compound having an adsorbing group to silver halide and a reducing group, represented by the following formula (I) or a precursor thereof is contained together with a gold sensitizer and a compound having C=X bond, P=X bond or R-XO₂X bond (wherein X represents sulfur, selenium or tellurium and R represents an aliphatic hydrocarbon group, an aryl group or a heterocyclic group) at the chemical sensitization of said core and/or shell:



wherein A represents an atomic group containing a group capable of adsorbing to silver halide, W represents a divalent linking group, n represents 0 or 1, and R represents a reducing group.

2. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 1, wherein a compound having an adsorbing group to silver halide and a reducing group, represented by formula (I) or a precursor thereof is contained together with a gold sensitizer at the chemical sensitization of core.
3. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 1 or 2, wherein internal latent image-type direct positive silver halide photographic emulsion contains tabular silver halide grains having an average particle size of 0.3 μ m or more and the average particle size/average particle thickness ratio of 2 or more in a proportion of 50% or more of all silver halide grains.
4. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 1, wherein the precursor of a compound having an adsorbing group to silver halide and a reducing group represented by formula (I) is a compound which is subjected to chemical reaction when added to a silver halide emulsion, and releases the compound of formula (I).
5. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 1, wherein the atomic group containing a group capable of adsorbing to silver halide represented by A in formula (I) is a mercapto compound, a thione compound or an imino silver-forming compound.
6. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 1, wherein the reducing group represented by R in formula (I) is a formyl group, an amino group, an acetylene group or a hydrazino group.
7. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 4, wherein the precursor of the compound having an adsorbing group to silver halide and a reducing group, represented by formula (I) is a benzothiazolium compound.
8. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 1, wherein the compound having a C=X bond is a compound represented by formula (A):



wherein X represents a sulfur atom, a selenium atom or a tellurium atom, R^{11} , R^{12} , R^{13} and R^{14} each represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, a heterocyclic group, an acyl group, an amino group, an alkoxy group, a hydroxy group or carbamoyl group, and R^{11} , R^{12} , R^{13} and/or R^{14} may be combined to form a ring.

9. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 1, wherein the compound having a $\text{P}=\text{X}$ bond is a compound represented by formula (B):



wherein R^{21} , R^{22} and R^{23} each represents an aliphatic group, an aromatic group, or a heterocyclic group.

10. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 1, wherein the compound having an $\text{R-XO}_2\text{X}$ bond is a compound represented by formula (C), (D) or (E):



wherein R^{40} , R^{41} and R^{42} each represents an aliphatic group, an aromatic group, or a heterocyclic group.

11. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 10, wherein the compound represented by formula (C), (D) or (E) is present at the chemical sensitization of core grains.

12. The internal latent image-type direct positive silver halide photographic emulsion as claimed in claim 1, wherein the chemical sensitization of core grains is performed under the condition that thiosulfate ion as sulfur sensitizer is substantially absent (the concentration of thiosulfate ion being 1 ppm or less).

13. A color diffusion transfer light-sensitive material comprising a support having thereon at least one light-sensitive silver halide emulsion layer associated with a dye image-forming substance, wherein said dye image-forming substance is a non-diffusive compound capable of releasing a diffusive dye or a precursor thereof or a compound variable in the diffusibility of the compound itself in connection with the silver development, represented by the following formula (II), and at least one layer of said silver halide emulsion layers contains the internal latent image-type direct positive silver halide emulsion described in any one of claims 1 to 12:



wherein DYE represents a dye group, a dye group temporarily shifted to the short wave or a dye precursor group, Y represents a mere bond or a linking group, Z represents a group having property of imagewise releasing DYE-Y, or differentiating the diffusibility of the compound represented by $(\text{DYE-Y})_m\text{---Z}$ in correspondence or counter-corre-

spondence with the light-sensitive silver salt having a latent image, m represents 1 or 2, and when m is 2, two DYE-Y moieties may be the same or different.

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