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

(57) Disclosed is a tabular internal-latent-image-type direct positive silver halide emulsion that comprises core/shell-type silver halide particles in which the average particle diameter is 0.3 μm or more, the average ratio of the particle diameter/particle thickness of each particle is 2 or more and the ratio (in area) occupied by tabular particles (the ratio of the particle diameter/the particle thickness is from 2 to 100) is 50% or more, wherein at least one metal complex of the formula (I) is contained as a localized phase in a region containing 0.1 to 90 mol% of the amount of silver contained in the shell portion:



wherein N is Fe, Ru, Ir, Co, Cr, Mn, Rh, Re or Os, a is 0, 1 or 2, L is a ligand other than CN, and n is 2, 3 or 4. The silver halide emulsion is high in sensitivity, allows the low-density portion on an reversal characteristic curve to be high in contrast and is low in re-reversal negative sensitivity. A color diffusion transfer light-sensitive material using the silver halide emulsion is also disclosed.

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DescriptionFIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

- 10 **[0002]** Photographs using a silver halide are superior in sensitivity and gradation characteristics to those obtained by other photographic methods, such as an electrophotographic method and a diazo photographic method, and the former have been widely used. Among these methods using a silver halide, a method of forming a direct positive image is known. In this method, as disclosed, for example, in U.S. Patent No. 3,761,276 and JP-B-60-55821 ("JP-B" means examined Japanese patent publication), when an internal-latent-image-type direct positive silver halide photographic
15 emulsion is used to develop silver halide particles, formed with an internal latent image, by using a surface developer (a developer that allows a latent-image-formed portion within the silver halide particles to remain substantially undeveloped), uniform exposure is performed, or a nucleating agent is used, to thereby obtain a positive image.

- [0003]** A transition metal compound is added in some stages of producing a silver halide emulsion, to thereby sensitize the silver halide emulsion, as described in U.S. Patent No. 2,448,060. It is known that there is a significant difference in the photographic effect of a transition metal compound in a silver halide emulsion, between the case where the
20 transition metal compound is added during the formation of silver halide particles, and the case where the transition metal compound is added after silver halide particles are precipitated. In the former case, the metal is called a metal dopant. The information concerned is explained in Research Disclosure, Vol. 176, issued in December 1978, Item 17643.

- 25 **[0004]** It is known that, in an internal-latent-image-type direct positive silver halide photographic emulsion (autopositive emulsion), the lower density part on an reversal characteristic curve is increased in gradation hardness (made high in contrast) by doping the silver halide emulsion with a metal ion. This is described, for example, in U.S. Patents No. 3,271,157, No. 3,367,778, No. 3,447,927, No. 3,531,291, No. 3,761,267, No. 3,761,276, No. 3,850,637, No. 3,923,513, No. 4,035,185, No. 4,444,874, No. 4,444,865, No. 4,433,047, and No. 4,395,478, and GB Patents No. 1,151,782 and No. 1,529,011. However, a known result of doping with a metal ion is that the gradation hardening in the
30 lower density part on an reversal characteristic curve does not reach a well-sufficient level, and it also causes the drawback of the maximum density to decrease. Particularly, U.S. Patent No. 4,395,478 describes the effect of decreasing a re-reversal negative image by doping a shell portion with a polyvalent metal ion. This patent, however, does not give a definition concerning a ligand of a metal ion, or a definition concerning the doping of the shell portion to form a localized
35 phase, nor does it describe the effects obtained by these definitions.

- [0005]** On the other hand, in each of European Patents No. 0,336,425 and No. 0,336,426, and in JP-A-2-20853 ("JP-A" means unexamined published Japanese patent application) and JP-A-2-20854, there is a description concerning a silver halide emulsion that has high stability of sensitivity and gradation with the lapse of time and is improved in low-intensity failure, in the presence of a complex of a six-coordination metal, e.g., rhenium, ruthenium, osmium, or iridium, which has at least four cyano ligands. Here, the view in these publications differs from the conventional general
40 view that the six-coordination transition metal complex is incorporated into silver halide particles as a single halide ion or atom in the inside of the crystal structure. However, in these patent publications, the type of transition metal is limited to rhenium, ruthenium, osmium, or iridium, and there is no description concerning iron. Also, these publications do not describe an internal-latent-image-type direct positive silver halide emulsion.

- 45 **[0006]** In JP-A-2-259,749 and U.S. Patent No. 5,112,732, there is a description that a direct positive silver halide photographic light-sensitive material is obtained that is high in maximum density and low in minimum density and that is reduced in the occurrence of a rereversal negative image in a high-intensity exposure, by using an internal-latent-image-type direct positive silver halide emulsion containing, particularly, a hexacyanoiron complex, among iron complexes. However, there is no description concerning the effect of hexacyano complexes of metals other than iron, and
50 also no description concerning the tabular autopsitive emulsion and the effect produced by the doped localized phase of the shell portion with respect to the hexacyanoiron complexes.

- [0007]** In JP-A-6-51,423, there is a description concerning an internal-latent-image-type direct positive silver halide emulsion containing a hexacyano complex. JP-A-6-51,423 describes, in the examples of this publication, that the sensitivity in both the center and lower density portions is higher in the case of using iridium, cobalt, or ruthenium, than in
55 the case of using iron as the center metal of the hexacyano metal complex, and the former case has the effect of increasing in gradation hardness in a low density part. However, this publication does not describe the effect produced by the doping in a localized phase of the shell portion in an autopsitive emulsion of the hexacyano metal complex. A direct positive silver halide photographic light-sensitive material that is high in sensitivity and allows the lower density

part on an reversal characteristic curve to be high in contrast, is obtained by doping the shell portion of a tabular auto-positive emulsion with a hexacyano metal complex. However, it has been clarified, from the studies of the present invention, that this doping has the drawback that, if the doping reaches the surface of the shell, a re-reversal negative image is significantly increased.

[0008] Further, JP-A-7-333,767 describes that a tabular internal-latent-image-type direct positive silver halide emulsion containing lead in the core and shell portions, enables the preparation of a direct positive silver halide photographic light-sensitive material that is high in sensitivity and has high storage stability. However, JP-A-7-333,767 does not disclose, in particular, the effect produced by the doping in a localized phase of the shell portion in a tabular auto-positive emulsion of the hexacyano metal complex.

SUMMARY OF THE INVENTION

[0009] An object of the present invention is to provide a tabular internal-latent-image-type direct positive silver halide emulsion that is high in sensitivity, that allows the low density portion on an reversal characteristic curve to be high in contrast, and that is decreased in re-reversal negative sensitivity. Another object of the present invention is to provide a color diffusion transfer photographic film unit (light-sensitive material) using the silver halide emulsion.

[0010] Other and further objects, features, and advantages of the invention will appear more fully from the following description.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The objects of the present invention are attained by the internal-latent-image-type direct positive silver halide emulsions and the color diffusion transfer photographic light-sensitive materials using the silver halide emulsion, as described in the following (1), (2), (3) and (4).

(1) A tabular internal-latent-image-type direct positive silver halide emulsion, comprising core/shell-type silver halide particles in which the average particle diameter is 0.3 μm or more, the average value of the ratio of the particle diameter/particle thickness of each particle is 2 or more, and the ratio (in area) occupied by tabular particles (the ratio of the particle diameter/the particle thickness is from 2 to 100) is 50% or more, wherein at least one metal complex represented by the following formula (I) is contained as a localized phase in a region containing 0.1 to 90 mol% of the amount of silver contained in the shell portion:



wherein M represents Fe, Ru, Ir, Co, Cr, Mn, Rh, Re, or Os;

a is 0, 1, or 2;

L represents a ligand other than CN; and

n is 2, 3, or 4.

(2) The tabular internal-latent-image-type direct positive silver halide emulsion according to the above (1), wherein the amount of the metal complex to be added is 1.0×10^{-7} mol/mol Ag or more, but 1.0×10^{-4} mol/mol Ag or less.

(3) The tabular internal-latent-image-type direct positive silver halide emulsion according to the above (1) or (2), wherein the type of metal complex is a hexacyanoiron complex.

(4) A color diffusion transfer light-sensitive material, having at least one light-sensitive silver halide emulsion layer combined with a dye image-forming substance on a support, the dye image-forming substance being a compound represented by the following formula (II), the compound being a nondiffusion compound releasing a diffusive dye or its precursor in association with silver development, or a compound that is changed in its diffusibility, wherein at least one layer of the silver halide emulsion layers contains the tabular internal-latent-image-type direct positive silver halide photographic emulsion as stated in any one of the above (1), (2) and (3):



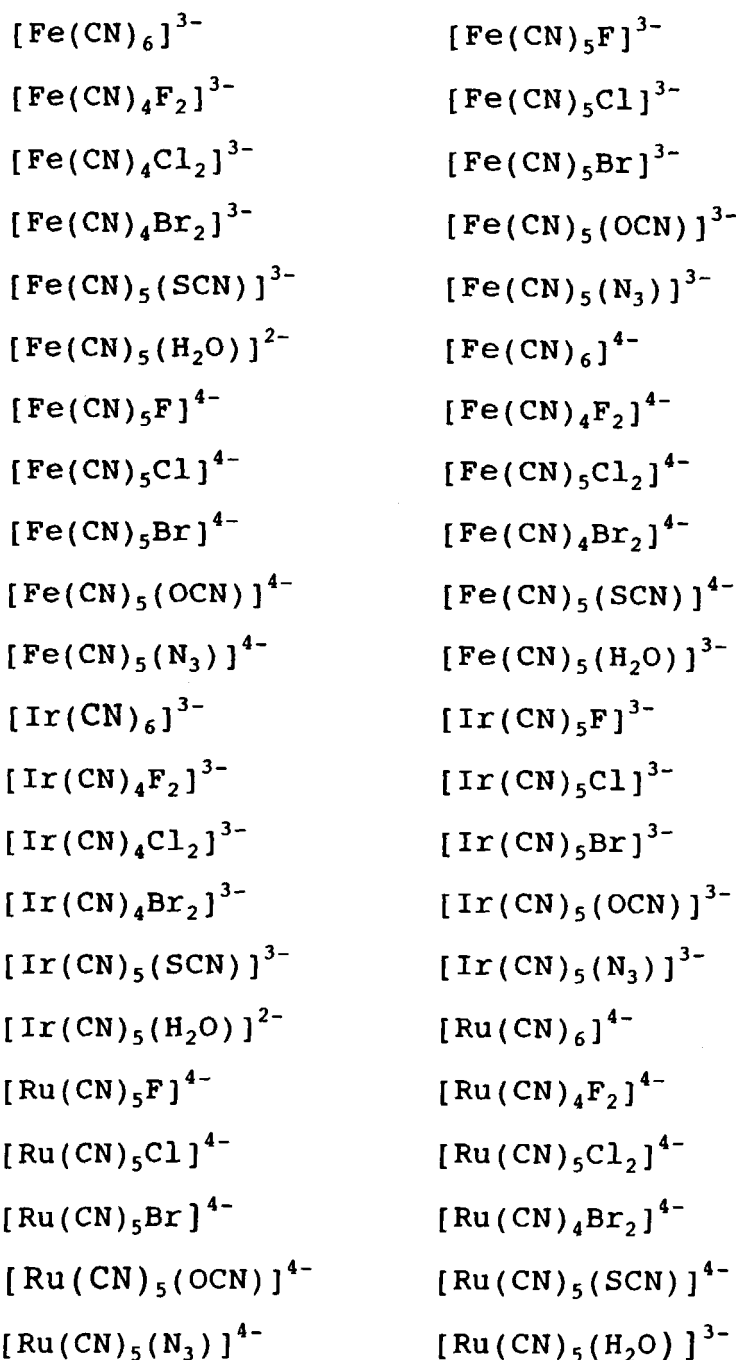
wherein DYE represents a dye group, a dye group that is temporarily short-waved, or a dye-precursor group; Y represents a simple bond or a linking group, Z represents a group having a property to release a diffusive dye or its precursor in association with silver development, or to produce a difference in diffusibility between the compounds represented by $(\text{DYE-Y})_n\text{-Z}$, and n is 1 or 2, and two (DYE-Y) groups may be the same or different when n is 2.

[0012] Here, the phrase "a metal complex is contained in a region containing 0.1 to 90 mol% of the amount of silver contained in the shell portion" means that the ratio of the amount of silver in a shell laminate layers (the amount of silver in a shell laminate portion containing a metal complex) to the total amount of silver in a shell after formation (namely the amount of silver in a shell portion) is set to be 0.1 to 90 mol%, that is, the surface layer exceeding 90% and up to 100% of the shell is made to be a layer containing no metal complex represented by formula (I).

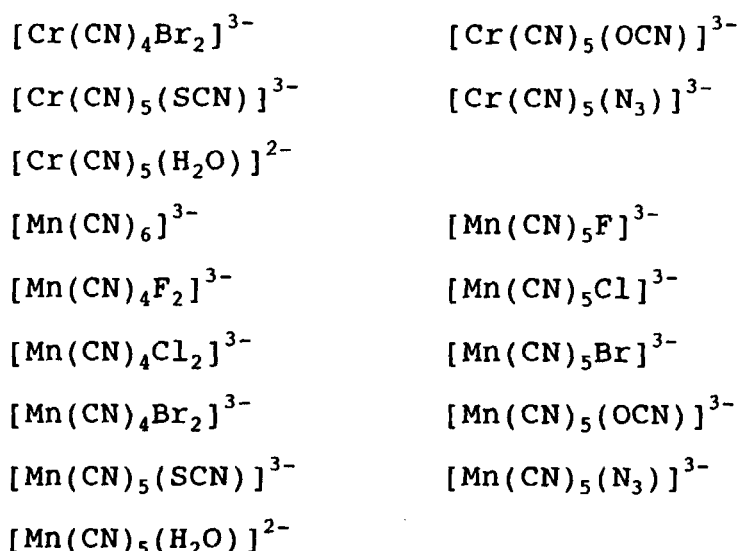
[0013] The present invention will be hereinafter explained in more detail.

[0014] Specific examples of a ligand, other than CN, represented by L in the formula (I) include F, Cl, Br, N₃, OCN, SCN and H₂O.

[0015] Specific examples of a metal complex having at least four cyano ligands, which complex is used in the present invention, are shown below.



	$[\text{Co}(\text{CN})_6]^{3-}$	$[\text{Co}(\text{CN})_5\text{F}]^{3-}$
5	$[\text{Co}(\text{CN})_4\text{F}_2]^{3-}$	$[\text{Co}(\text{CN})_5\text{Cl}]^{3-}$
	$[\text{Co}(\text{CN})_4\text{Cl}_2]^{3-}$	$[\text{Co}(\text{CN})_5\text{Br}]^{3-}$
	$[\text{Co}(\text{CN})_4\text{Br}_2]^{3-}$	$[\text{Co}(\text{CN})_5(\text{OCN})]^{3-}$
10	$[\text{Co}(\text{CN})_5(\text{SCN})]^{3-}$	$[\text{Co}(\text{CN})_5(\text{N}_3)]^{3-}$
	$[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$	$[\text{Re}(\text{CN})_6]^{4-}$
15	$[\text{Re}(\text{CN})_5\text{F}]^{4-}$	$[\text{Re}(\text{CN})_4\text{F}_2]^{4-}$
	$[\text{Re}(\text{CN})_5\text{Cl}]^{4-}$	$[\text{Re}(\text{CN})_5\text{Cl}_2]^{4-}$
	$[\text{Re}(\text{CN})_5\text{Br}]^{4-}$	$[\text{Re}(\text{CN})_4\text{Br}_2]^{4-}$
20	$[\text{Re}(\text{CN})_5(\text{OCN})]^{4-}$	$[\text{Re}(\text{CN})_5(\text{SCN})]^{4-}$
	$[\text{Re}(\text{CN})_5(\text{N}_3)]^{4-}$	$[\text{Re}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$
25	$[\text{Rh}(\text{CN})_6]^{3-}$	$[\text{Rh}(\text{CN})_5\text{F}]^{3-}$
	$[\text{Rh}(\text{CN})_4\text{F}_2]^{3-}$	$[\text{Rh}(\text{CN})_5\text{Cl}]^{3-}$
	$[\text{Rh}(\text{CN})_4\text{Cl}_2]^{3-}$	$[\text{Rh}(\text{CN})_5\text{Br}]^{3-}$
30	$[\text{Rh}(\text{CN})_4\text{Br}_2]^{3-}$	$[\text{Rh}(\text{CN})_5(\text{OCN})]^{3-}$
	$[\text{Rh}(\text{CN})_5(\text{SCN})]^{3-}$	$[\text{Rh}(\text{CN})_5(\text{N}_3)]^{3-}$
	$[\text{Rh}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$	$[\text{Os}(\text{CN})_6]^{4-}$
35	$[\text{Os}(\text{CN})_5\text{F}]^{4-}$	$[\text{Os}(\text{CN})_4\text{F}_2]^{4-}$
	$[\text{Os}(\text{CN})_5\text{Cl}]^{4-}$	$[\text{Os}(\text{CN})_5\text{Cl}_2]^{4-}$
40	$[\text{Os}(\text{CN})_5\text{Br}]^{4-}$	$[\text{Os}(\text{CN})_4\text{Br}_2]^{4-}$
	$[\text{Os}(\text{CN})_5(\text{OCN})]^{4-}$	$[\text{Os}(\text{CN})_5(\text{SCN})]^{4-}$
45	$[\text{Os}(\text{CN})_5(\text{N}_3)]^{4-}$	$[\text{Os}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$
	$[\text{Cr}(\text{CN})_6]^{3-}$	$[\text{Cr}(\text{CN})_5\text{F}]^{3-}$
	$[\text{Cr}(\text{CN})_4\text{F}_2]^{3-}$	$[\text{Cr}(\text{CN})_5\text{Cl}]^{3-}$
50	$[\text{Cr}(\text{CN})_4\text{Cl}_2]^{3-}$	$[\text{Cr}(\text{CN})_5\text{Br}]^{3-}$



[0016] As the counter ion to these metal complexes, an ammonium ion or an alkali metal ion such as a sodium ion or potassium ion is preferably used.

[0017] The amount to be contained of the metal complex having at least four cyano ligands for use in the present invention is preferably 1.0×10^{-7} mol or more and 1.0×10^{-4} mol or less, and more preferably 1.0×10^{-6} mol or more and 5×10^{-5} mol or less, based on 1 mol of silver halide. The metal complex represented by formula (I) is preferably contained as a localized phase in a region containing 0.1 to 50 mol% of the amount of silver contained in the shell portion.

[0018] The term "localized phase" is used to mean that it includes an embodiment in which the region containing the metal complex forms a continuous layer and/or an embodiment in which the region forms a discontinuous part.

[0019] If the metal complex having at least four cyano ligands for use in the present invention can be localized in a region containing 90 mol% or less of the amount of silver of silver halide particles contained in the shell portion, it may be added and contained in any stage of the preparation of the shell. Also, the metal complex may be divided into several parts when it is added to contain. Two or more types of metal complex having each different center metal may be mixed and the mixture may be added to contain, and each metal complex may be divided when it is added to contain. In addition, the above metal complex may be contained further in the core portion.

[0020] When the metal complex, having at least four cyano ligands, which is used in the present invention is localized in the shell portion, for example, the core portion is coated with a silver halide containing the above metal complex and thereafter the silver halide is further coated with a silver halide free from the metal complex, to form the shell portion, thereby attaining the localization of the metal complex.

[0021] It is preferable to contain the metal complex in such a way that the metal complex is dissolved in water or another proper solvent, which is then added directly in a reaction solution when a silver halide in the shell portion is formed, or that the metal complex is added to an aqueous halide solution, aqueous silver salt solution or another solution that is used to form a silver halide in the shell portion, to form particles. Alternatively, a process is preferably performed in which silver halide fine particles containing the metal complex in advance are added and dissolved, and thereafter they are deposited on another silver halide particles, thereby containing these metal complexes.

[0022] The phrase "in a dispersion medium containing at least one of the metal complexes represented by the formula (I)" described in the present specification is used to mean that it includes the aforementioned embodiment.

[0023] The hydrogen ion concentration pH in a reaction solution when the metal complex is added is preferably 1 or more and 10 or less, and more preferably 3 or more and 7 or less.

[0024] The pBr during the formation of particles when the metal complex is added is preferably 2 to 4 and more preferably 2.42 to 3.29 at 75 °C.

[0025] The six-coordination metal complex used in the present invention may be used in combination with another metal ion. As the above another metal, Mg, Ca, Sr, Ba, Al, Sc, Y, La, Cr, Mn, Ni, Cu, Zn, Ga, Ru, Rh, Pd, Re, Os, Pt, Au, Cd, Hg, Tl, In, Sn, Pb or Bi may be used. These metals may be added as far as they have the form of a salt, e.g., an ammonium salt, acetate, nitrate, sulfate, phosphate, hydroxide, or six-coordination complex salt and four-coordination complex salt, which can be dissolved when particles are formed. Metal complexes other than the metal complexes represented by the formula (I) may be additionally used.

[0026] The internal-latent-image-type direct positive silver halide emulsion (hereinafter abbreviated as "internal-latent-image-type silver halide emulsion" as the case may be) of the present invention is such a silver halide emulsion as to form a latent image primarily in the inside of the silver halide particles when exposed image-wise. Specifically this is defined as those that ensure that the maximum density obtained when the silver halide emulsion is applied in a given amount onto a transparent support, exposed to light for a fixed time as long as 0.01 to 1 second, and subjected to development at 20°C for 5 minutes in the following developer A ("internal type" developer), is at least five times the maximum density obtained when a second sample that is exposed like the above is developed at 20°C for 5 minutes in the following developer B ("surface type" developer).

[0027] Here the maximum density is measured using the usual method of measuring photographic density.

Developer A

[0028]

N-methyl-p-aminophenol sulfite	2 g
Sodium sulfite (anhydride)	90 g
Hydroquinone	8 g
Sodium carbonate (mono hydrate)	52.5 g
Potassium bromide	5 g
Potassium iodide	0.5 g
Water is added to be	1 liter

Developer B

[0029]

N-methyl-p-aminophenol sulfite	2.5 g
L-ascorbic acid	10 g
Potassium methanitate	35 g
Potassium bromide	1 g
Water is added to be	1 liter

[0030] Examples of the internal-latent-image-type silver halide emulsion include conversion-type silver halide emulsions as described in U.S. Patents No. 2,456,953 and No. 2,592,250, laminate structure-type silver halide emulsions in which the halogen compositions of a first phase and a second phase differ from each other as disclosed in U.S. Patent No. 3,935,014, and core/shell-type silver halide emulsions prepared by applying a shell to each core particle that is doped with a metal ion or chemically sensitized. Among these silver halide emulsions, the core/shell-type silver halide emulsions are particularly preferable as the internal-latent-image-type silver halide emulsion used in the present invention. Examples of the core/shell-type silver halide emulsions include those described, for example, in U.S. Patents No. 3,206,313, No. 3,317,322, No. 3,761,266, No. 3,761,276, No. 3,850,637, No. 3,923,513, No. 4,035,185, No. 4,184,878, No. 4,395,478 and No. 4,504,570, JP-A-57-136641, JP-A-61-3137, JP-A-61-299155 and JP-A-62-208241.

[0031] In order to directly obtain a positive image, the front surface of the exposed layer is subjected to uniform second exposure before or after a developing process ("light-fog method", e.g., GB Patent No. 1,151,363) after the internal-latent-image-type silver halide emulsion is exposed image-wise, or a developing process is performed in the presence of a nucleating agent ("chemical-fog method", e.g., Research Disclosure, Vol. 151, No. 15162, pp.76-78). In the present invention, a method in which a positive image is directly obtained by the "chemical fog method" is preferred. The nucleating agent to be used in the present invention will be explained later.

[0032] As mentioned above, in order to directly obtain a positive image by using the internal-latent-image-type silver halide emulsion, the entire surface is exposed to uniform second exposure before or after a developing process after image-wise exposure is finished, or a developing process is performed in the presence of a nucleating agent. Examples of the nucleating agent used in the present invention include hydrazines described in U.S. Patents No. 2,563,785 and No. 2,588,982, hydrazides and hydrazones described in U.S. Patent No. 3,227,552, heterocyclic quaternary salt compounds described in GB Patent No. 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 No. 3,615,515, No. 3,719,494, No. 3,734,738, No. 4,094,683, No. 4,115,122, No. 4,306,016 and No. 4,471,044, sensitizing dyes having, in a dye molecule, a substituent with nucleation action, as described in U.S. Patent No. 3,718,470, thio-urea-bonded-type acylhydrazine-series compounds described in U.S. Patents No. 4,030,925, No. 4,031,127, No. 4,245,037, No. 4,255,511, No. 4,266,013 and No. 4,276,364 and GB Patent No. 2,012,443, and acylhydrazine-series compounds bound, as an adsorbing group, a thioamide ring or a heterocyclic group, such as triazole or tetrazole, as described in U.S. patents No. 4,080,270 and No. 4,278,748 and GB Patent No. 2,011,391B.

[0033] The amount of the nucleating agent to be used is desirably such an amount as to impart satisfactory maximum density when the internal-latent-image-type emulsion is developed using a surface developer. In practically, the amount differs depending upon the characteristics of the silver halide emulsion to be used, the chemical structure of the nucleating agent and development conditions, and hence an appropriate content varies in a wide range. Generally, the amount ranging from about 0.1 mg to 5 g per 1 mol of silver contained in the internal-latent-image-type silver halide emulsion is practically useful, and a preferable amount is about 0.5 mg to 2 g per 1 mol of silver. When the nucleating agent is contained in a hydrophilic colloid layer adjacent to the emulsion layer, it may be contained in an amount like the above, to the amount of silver contained in the internal-latent-image-type emulsion in the same area.

[0034] The average particle diameter of the silver halide emulsion (particles) of the present invention means the average diameter of a circle (circle-equivalent diameter) equivalent to the projected area of each particle, calculated for all the silver halide particles contained in the emulsion. It is necessary that the average particle diameter is 0.3 μm or more, with a preferable average particle diameter being 10 μm or less.

[0035] The average ratio (average aspect ratio) of the circle-equivalent diameter/thickness of each particle contained in the emulsion must be 2 or more, and it is preferably 5 to 8.

[0036] The shell constituting the core/shell type particles used in the present invention is a silver halide phase formed after silver halide particles forming the core are chemically sensitized, in the steps of the preparation of the emulsion.

[0037] A method for the production of the shell may refer to, for example, the examples of JP-A-63-151618 and U.S. Patents No. 3,206,316, No. 3,317,322, No. 3,761,276, No. 4,269,927 and No. 3,367,778. The mol ratio (mol ratio by weight) of core/shell in this case is preferably 1/30 to 5/1, more preferably 1/20 to 2/1, and further preferably 1/20 to 1/1.

[0038] The silver halide emulsion containing tabular particles according to the present invention may be prepared using each of the methods described in, for example, Gutoff, Photographic Science and Engineering, Vol. 14, pp.248-257 (1970); U.S. Patents No. 4,434,226, No. 4,414,310, No. 4,433,048 and No. 4,439,520 and GB Patent No. 2,112,157.

A method in which previously precipitated and formed silver halide grains are added to a reaction vessel for the preparation of an emulsion, and the methods described, for example, in U.S. Patent No. 4,334,012, No. 4,301,241, and No. 4,150,994, are preferable in some cases. These can be used as seed crystals, or they are effective when they are supplied as a silver halide for growth. In the latter case, it is preferable to add an emulsion having a small particle size. The method adopted to add the emulsion may be selected from a method in which entire amount of the emulsion is added at once, a method in which entire amount of the emulsion is divided and added in several times, and a method in which the emulsion is continuously added. Further, in some cases, it is also effective to add grains having different halogen compositions in order to modify the surface.

[0039] In addition to the method in which the grain growth is made by adding a soluble silver salt and a halogen salt at constant concentrations and at constant flow rates, grain formation methods wherein the concentration is changed or the flow rate is changed, as described in British Patent No. 1,469,480 and U.S. Patent No. 3,650,757 and No. 4,242,445, are preferable methods. By increasing the concentration or increasing the flow rate, the amount of the silver halide to be supplied can be changed as a linear function, a quadratic function, or a more complex function, of the addition time. It is preferable depending on the situation to reduce the amount of the silver halide to be supplied as required. Moreover, in the case of adding a plurality of soluble silver salts having different solution compositions, or adding a plurality of soluble halides having different solution compositions, an addition system in which one party is increased whereas another party is decreased is effective. A mixing vessel that is used when a solution of a soluble silver salt and a solution of a soluble halogen salt are reacted can be selected for use from methods described in U.S. Patent No. 2,996,287, No. 3,342,605, No. 3,415,650, and No. 3,785,777, and West German Publication Patent No. 2,556,885 and No. 2,555,364.

[0040] When an emulsion containing tabular particles is produced, a method is preferable in which the adding rate,

amount to be added, and addition concentration of a silver salt solution (e.g., an aqueous AgNO₃ solution) and halide solution (e.g., an aqueous KBr solution) are increased to accelerate the growth of particles. For example, descriptions in GB Patent No. 1,335,925, U.S. Patents No. 3,672,900, No. 3,650,757 and No. 4,242,445, JP-A-55-142329 and JP-A-55-158124 may serve as references for these methods.

[0041] In some cases, a method wherein a chalcogenide compound is added during the preparation of the emulsion, as described in U.S. Patent No. 3,772,031, is also useful. In addition to S, Se, and Te, a cyanate, a thiocyanate, a selenocyanate, a carbonate, a phosphate, or an acetate may be present.

[0042] These were described, for example, in U.S. Patent No. 2,448,060, No. 2,628,167, No. 3,737,313, No. 3,772,031, and in Research Disclosure, Vol. 134, Item 13452 (June 1975).

[0043] As the shape of an individual tabular particle contained in the silver halide emulsion of the present invention, a triangle, hexagon, circle or the like may be selected. An equilateral hexagonal form with six sides having almost the same length as described in U.S. Patent No. 4,996,137 is a preferable made.

[0044] The tabular particle in the present invention is a silver halide particle having an aspect ratio (the circle equivalent diameter/particle thickness of a silver halide particle) of 2 to 100, and 50% or more (in area) of all the silver halide particles in the emulsion used in the present invention is occupied by the tabular particles. The emulsion contains silver halide particles having an aspect ratio of preferably 5 or more, more preferably 5 to 8, in a content of generally 50% (in area) or more, preferably 70% or more, and particularly preferably 85% or more, of the total silver halide particles contained therein. Here, in the tabular particle, the circle equivalent diameter indicates the circle equivalent diameters of two facing principal planes which are parallel or close to parallel (the diameter of a circle having the same projected area as the principal planes), and the particle thickness indicates the distance between these principal planes. An aspect ratio exceeding 100 is undesirable because it gives rise to the problem that the emulsion is deformed or broken in the stage before the emulsion is completed as a coating product.

[0045] The circle equivalent diameter of the tabular particle is 0.3 μm or more, preferably 0.3 to 10 μm , more preferably 0.5 to 5.0 μm , and further preferably 0.5 to 3.0 μm .

[0046] The thickness of the tabular particle is less than 1.5 μm and preferably 0.05 to 1.0 μm .

[0047] An emulsion in which the coefficient of variation of the particle thickness is 30% or less and which has highly uniform thickness is preferable. Moreover, particles in which the particle thickness and the plane-to-plane distance between the twin plane are defined as described in JP-A-63-163451 are preferable.

[0048] The particle diameter and particle thickness of the tabular particle can be measured by means of an electron micrograph of particles and determined like in the method described in U.S. Patent No. 4,434,226.

[0049] The distribution of particle size of the tabular particle is optional but preferably a monodispersion. Here the monodispersion is defined as a dispersion system in which 95% of the total weight or total number of silver halide particles contained therein has sizes falling in a range of $\pm 60\%$ and preferably $\pm 40\%$ of the number average particle size. Here, the number average particle size is a number average diameter of the projected area diameter of the silver halide particles.

[0050] The structure and method of production of the monodispersion tabular particle are described, for example, in JP-A-63-151618. These monodispersion emulsions may be used by mixing them.

[0051] As the composition of silver halide of these particles, any of silver bromoiodide, silver chlorobromoiodide and silver chloroiodide may be used, but the use of silver bromoiodide is preferable.

[0052] In the silver halide particle, the inside and the surface have different phases. The composition of silver halide in the inside of the particle may either be uniform or consist of different silver halide compositions. The surface phase may either be a discontinuous layer or form a continuous layer structure. Also, the silver halide particles may be those having a dislocation line.

[0053] It is important to control the halogen composition in the vicinity of the surface of the particle. When the halogen composition in the vicinity of the surface is altered, any one of the structure in which the halogen composition embraces an entire particle and the structure in which the halogen composition adheres only to a part of the particle may be selected. Such a control of the halogen composition is made, for example, in the case where the halogen composition of only one of the (100) plane and (111) plane constituting a tetradecahedron particle is altered or in the case where the halogen composition of one of the primary surface and side surface of a tabular particle is altered.

[0054] Two or more of these silver halides differing in crystal habit, halogen composition, particle size, or the distribution of particle size may be used together, and they may also be used respectively in different emulsion layers and/or in the same layer.

[0055] It is preferable that for the silver halide emulsion of the present invention, the surface of particles be chemically sensitized further after core particles provided with chemical sensitization are coated with a shell, to exhibit a good reverse performance with a high maximum density. When the surface of particles are chemically sensitized, a polymer as described in JP-A-57-13641 may be allowed to coexist.

[0056] The chemical sensitization may be carried out using an activated gelatin as described in T.H. James, The Theory of the Photographic Process, 4th ed., pp.67-76, Macmillan, 1977. It may also be carried out at a pAg of 5 to 10,

a pH of 4 to 8 and a temperature of 30 to 80°C by using sulfur, selenium, tellurium, gold, platinum, palladium, iridium, rhodium, osmium or rhenium, or a combination of two or more of these sensitizers, as described in Research Disclosure, Vol. 120, April 1974, 12008; Research Disclosure, Vol. 34, June 1975, 13452, U.S. Patents No. 2,642,361, No. 3,297,446, No. 3,772,031, No. 3,857,711, No. 3,901,714, No. 4,266,018 and No. 3,904,415 and U.K. Patent No. 1,315,755.

[0057] The chemical sensitization in the photographic emulsion of the present invention may be carried out using a metal material such as Fe, Cr, Mn, Ni, Mo or Ti, but it is more preferably performed in a non-metallic material obtained by coating the surface of a metal with a fluororesin. Given as examples of the fluororesin material may be Teflon (trade name, tetrafluoroethylene) coating materials PFA, TFE and FEP developed by DuPont.

[0058] The chemical sensitization can be carried out in the presence of a chemical sensitization auxiliary. As a chemical sensitization auxiliary, a compound is used that is known to suppress fogging and to increase the sensitivity in the process of chemical sensitization, such as azaindene, azapyridazine, and azapyrimidine. Examples of the chemical sensitization auxiliary are described in U.S. Patent No. 2,131,038, No. 3,411,914, and No. 3,554,757, JP-A-58-126526 and JP-A-62-253159, and by G. F. Duffin in "Photographic Emulsion Chemistry" mentioned above, pages 138 to 143, Forcal Press (1966).

[0059] As for silver halide emulsions, the inside of particles may be reduction-sensitized in a precipitate-producing step, as described in JP-B-58-1410 and Moiser et al., Journal of Photographic Science, Vol. 25, pp.19-27 (1977).

[0060] As the chemical sensitization, the following reduction sensitization may be utilized. For example, hydrogen is used to conduct reduction sensitization as described in U.S. Patents No. 3,891,446 and No. 3,984,249. Also, reduction sensitization may be carried out by using a reducing agent or by a treatment performed at a low pAg (e.g., less than 5) or at a high pH (e.g., greater than 8) as described in U.S. Patents No. 2,518,698, No. 2,743,182 and No. 2,743,183. As typical examples of the reduction sensitizer, stannous salts, ascorbic acid and its derivatives, amines and polyamines, hydrazine derivatives, formamidinesulfonic acid, silane compounds, borane compounds, and the like are known. For the reduction sensitization for use in the present invention, an appropriate sensitizer selected from these known reduction sensitizers may be used and also a combination of two or more of these may be used. As the reduction sensitizer, stannous chloride, thiourea dioxide, dimethylamineborane, and ascorbic acid and its derivatives are preferable compounds.

[0061] The chemical sensitizing methods described in U.S. Patents No. 3,917,485 and No. 3,966,476 may be applied in the present invention.

[0062] The sensitizing methods using an oxidizing agent as described in JP-A-61-3134 and JP-A-61-3136 may also be applied.

[0063] The oxidizing agent for silver refers to a compound that acts on metal silver to convert it to silver ions. Particularly useful is a compound that converts quite fine silver grains, which are concomitantly produced during the formation of silver halide grains and during the chemical sensitization, to silver ions. The thus produced silver ions may form a silver salt that is hardly soluble in water, such as a silver halide, silver sulfide, and silver selenide, or they may form a silver salt that is readily soluble in water, such as silver nitrate. The oxidizing agent for silver may be inorganic or organic. Example inorganic oxidizing agents include ozone, hydrogen peroxide and its adducts (e.g. $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$, $2\text{NaCO}_3 \cdot 3\text{H}_2\text{O}_2$, $\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$, and $2\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$); oxygen acid salts, such as peroxyacid salts (e.g. $\text{K}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{C}_2\text{O}_6$, and $\text{K}_2\text{P}_2\text{O}_8$), peroxycomplex compounds (e.g. $\text{K}_2[\text{Ti}(\text{O}_2)\text{C}_2\text{O}_4] \cdot 3\text{H}_2\text{O}$, $4\text{K}_2\text{SO}_4 \cdot \text{Ti}(\text{O}_2)\text{OH} \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$), permanganates (e.g. KMnO_4), and chromates (e.g. $\text{K}_2\text{Cr}_2\text{O}_7$); halogen elements, such as iodine and bromine; perhalates (e.g. potassium periodate), salts of metals having higher valences (e.g. potassium hexacyanoferrate (III)).

[0064] Examples of the organic oxidizing agents include quinones, such as p-quinone; organic peroxides, such as peracetic acid and perbenzoic acid; and compounds that can release active halogen (e.g. N-bromosuccinimide, chloramine T, and chloramine B).

[0065] Preferable oxidizing agent for use in the present invention is ozone, hydrogen peroxide and its adducts, halogen elements and organic oxidants of quinones. A combination of the reduction sensitization and an oxidizing agent for silver is used in a preferred embodiment. An appropriate method selected from a method in which reduction sensitization is carried out after the oxidizing agent is used, the reverse in terms of process and a method in which both of the reduction sensitizer and the oxidizing agent are allowed to coexist may be used. An appropriate method selected from these methods may be used also in a particle-forming process or in a chemical sensitizing process.

[0066] As a dispersion medium (protective colloid) used in the preparation of the emulsion according to the present invention, gelatin is used advantageously, but another hydrophilic colloid can also be used.

[0067] Use can be made of, for example, a gelatin derivative, a graft polymer of gelatin with another polymer, a protein, such as albumin and casein; a cellulose derivative, such as hydroxyethyl cellulose, carboxymethyl cellulose, and cellulose sulfates; a saccharide derivative, such as sodium alginate, a starch derivative; and many synthetic hydrophilic polymers, including homopolymers and copolymers, such as a polyvinyl alcohol, a polyvinyl alcohol partial acetal, a poly-N-vinylpyrrolidone, a polyacrylic acid, a polymethacrylic acid, a polyacrylamide, a polyvinylimidazole, and a poly-

vinylpyrazole.

[0068] As the gelatin, in addition to lime-processed gelatin, acid-processed gelatin, and enzyme-processed gelatin described in Bull. Soc. Sci. Photo. Japan, No. 16, page 30 (1966), can be used. Further a hydrolyzate or enzymolyzate of gelatin can also be used.

[0069] Many impurity ions are contained in a gelatin. So it is preferable to use a gelatin reduced in the amount of inorganic impurity ions by ion exchange treatment.

[0070] Preferably, the emulsion according to the present invention is washed with water for desalting and is dispersed in a freshly prepared protective colloid. The temperature at which the washing with water is carried out can be selected in accordance with the purpose, and preferably the temperature is selected in the range of 5 to 50 °C. The pH at which the washing is carried out can be selected in accordance with the purpose, and preferably the pH is selected in the range of 2 to 10, and more preferably in the range of 3 to 8. The pAg at which the washing is carried out can be selected in accordance with the purpose, and preferably the pAg is selected in the range of 5 to 10. As a method of washing with water, one can be selected from the noodle washing method, the dialysis method using a diaphragm, the centrifugation method, the coagulation settling method, and the ion exchange method. In the case of the coagulation settling method, selection can be made from, for example, the method wherein sulfuric acid salt is used, the method wherein an organic solvent is used, the method wherein a water-soluble polymer is used, and the method wherein a gelatin derivative is used.

[0071] In the present invention, spectral sensitization may be carried out using a sensitizing dye. Examples of the sensitizing dye to be used include cyanine dyes, merocyanine dyes, composite cyanine dyes, composite merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Specific examples include sensitizing dyes described, for example, in U.S. Patent No. 4,617,257, JP-A-59-180550, JP-A-60-140335, JP-A-61-160739, RD17029 (1978), pp.12-13, and RD17643 (1978), p23.

[0072] These sensitizing dyes can be used singly or in combination, and a combination of these sensitizing dyes is often used, particularly for the purpose of supersensitization. Typical examples thereof are described in U.S. Patent No. 2,688,545, No. 2,977,229, No. 3,397,060, No. 3,522,052, No. 3,527,641, No. 3,617,293, No. 3,628,964, No. 3,666,480, No. 3,672,898, No. 3,679,428, No. 3,703,377, No. 3,769,301, No. 3,814,609, No. 3,837,862, and No. 4,026,707, British Patent No. 1,344,218 and No. 1,507,803, JP-B-43-4936 and JP-B-53-12375, and JP-A-52-110618 and JP-B-52-109925.

[0073] Together with the sensitizing dye, a dye having no spectral sensitizing action itself, or a substance that does not substantially absorb visible light and that exhibits supersensitization, may be included in the emulsion. (Examples thereof are described in U.S. Patent No. 3,615,613, No. 3,615,641, No. 3,617,295, No. 3,635,721, No. 2,933,390, No. 3,743,510, and JP-A-63-23145.)

[0074] The timing when the sensitizing dye for spectral sensitization is added to the emulsion may be at any stage known to be useful in the preparation of emulsions. The addition is carried out most usually at a time after the completion of chemical sensitization and before coating, but it can be carried out at the same time as the addition of a chemical sensitizer, to carry out spectral sensitization and chemical sensitization simultaneously, as described in US, Patent No. 3,628,969 and No. 4,225,666; it can be carried out prior to chemical sensitization, as described in JP-A-58-113928; or it can be carried out before the completion of the formation of the precipitate of silver halide grains to start spectral sensitization. Further, as taught in U.S. Patent No. 4,255,666, these foregoing compounds may be added in portions, i.e., part of these compounds is added prior to chemical sensitization, and the rest is added after the chemical sensitization, and also the addition may be carried out at any time during the formation of silver halide grains, as disclosed, for example, in U.S. Patent No. 4,183,756. In view of attaining the object of the present invention, the spectral sensitizing dye is preferably added during the chemical sensitization step of the shell part, and particularly preferably near the completion of chemical sensitization.

[0075] Generally the amount of the sensitizing dye to be added can be 10^{-8} to 10^{-2} mol per mol of the silver halide, but when the silver halide grain size is 0.2 to 1.2 μm , which is more preferable, the amount of the sensitizing dye to be added is more effectively about 5×10^{-5} to 2×10^{-3} mol per mol of the silver halide.

[0076] The amount of the light-sensitive silver halide to be applied and used in the present invention is generally in a range of 1 mg to 10 g/m^2 in terms of silver.

[0077] In the present invention, various antifoggants and photographic stabilizers may be used for the purpose of preventing a reduction in sensitivity and the occurrences of a fog. Examples of antifoggants and photographic stabilizers include azoles and azaindenes described in RD17643 (1978), pp.24-25 and U.S. Patent No. 4,629,678, carboxylic acids and phosphoric acids containing nitrogen described in JP-A-59-168442, mercapto compounds and their metal salts described in JP-A-59-111636, and acetylene compounds described in JP-A-62-87957.

[0078] It is also preferable to add phenethyl alcohol and various antiseptics or mildew-proofing agents, e.g., 1,2-benzisothiazolin-3-one, n-butyl, p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol and 2-(4-thiazolyl)benzimidazole as described in JP-A-63-257747, JP-A-62-272248 and JP-A-1-80941. These additives are described in detail in European Patent No. 436,938A2, pp.150, line 25 to line 28.

[0079] These additives are described in more detail in Research Disclosure, Item 17643 (December 1978); Research Disclosure, Item 18176 (November 1979); and Research Disclosure, Item 307105 (November 1989), and the particular parts are given below in a table.

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	Kind of Additive	RD 17643 (December, 1978)	RD 18716 (November, 1979)	RD 307105 (November, 1989)
10	1. Chemical sensitizers	p.23	p.648 (right column)	p.866
	2. Sensitivity-enhancing agents	-	p.648 (right column)	-
15	3. Spectral sensitizers and Supersensitizers	pp. 23-24	pp.648 (right column)-649 (right column)	pp. 866-868
	4. Brightening agents	p.24	pp.647	p.868
	5. Antifogging agents and Stabilizers	pp.24-25	p.649 (right column)	pp.868-870
20	6. Light absorbers, Filter dyes, and UV Absorbers	pp.25-26	pp.649 (right column)-650 (left column)	p.873
	7. Anti-stain agent	p.25 (right column)	p.650 (left column)-(right column)	p.872
25	8. Image dye stabilizers	p.25	p.650 (left column)	p.872
	9. Hardeners	p.26	p.651 (left column)	pp.874-875
	10. Binders	p.26	p.651 (left column)	pp.873-874
30	11. Plasticizers and Lubricants	p.27	p.650 (right column)	p.876
	12. Coating aids and Surfactants	pp.26-27	p.650 (right column)	pp.875-876
35	13. Antistatic agents	p.27	p.650 (right column)	pp.876-877
	14. Matting agents	-	-	pp.878-879

[0080] The internal-latent-image-type direct positive silver halide emulsion of the present invention can also be used for conventional light-sensitive materials, and it is preferably used for color diffusion transfer light-sensitive materials.

[0081] Next, the color diffusion transfer light-sensitive material of the present invention will be explained.

[0082] A most typical form of the color diffusion transfer material is a color diffusion transfer film unit. A most typical form of the color diffusion transfer film unit is those, in which an image-receiving element and a light-sensitive element are laminated on one transparent support and it is unnecessary to peel the light-sensitive element from the image-receiving element after a transferred image is completed. To state in more detail, the image-receiving element comprises at least one mordant layer; and the light-sensitive element, in its preferred embodiment, 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 light-sensitive emulsion layer, or a combination of a blue-sensitive emulsion layer, a red-sensitive emulsion layer and an infrared light-sensitive emulsion layer, wherein each emulsion layer is combined with a yellow dye image-forming compound, a magenta dye image-forming compound and a cyan dye image-forming compound (here, the "infrared light-sensitive emulsion layer" means an emulsion layer having a maximum spectral sensitivity for light with a wavelength of 700 nm or more, and particularly 740 nm or more). Further, a white reflecting layer containing a solid pigment such as titanium oxide is disposed between the mordant layer and the light-sensitive layer or the dye image-forming compound-containing layer, to be able to view the transferred image through a transparent support.

[0083] A shading layer may be further disposed between the white reflecting layer and the light-sensitive layer, to carry out development under light. Also, a peelable layer may be disposed at a proper position, to be able to peel all or

a part of the light-sensitive element from the image-receiving element as desired. Such an embodiment is described, for example, in JP-A-56-67840 and Canadian Patent No. 674,082.

[0084] Examples of another embodiment which is a laminate and peelable type include a color diffusion transfer photographic film unit as described in JP-A-63-226649. The unit comprises a light-sensitive element provided with at least (a) a layer having a neutralizing function, (b) a dye image-receiving layer, (c) a peelable layer and (d) at least one silver halide emulsion layer combined with a dye image-forming compound, in this order; an alkali-processing composition containing a shading agent, and a transparent cover sheet, on a white support, the unit further comprising a layer having a shading function on the emulsion layer on the side opposite to the surface on which the processing composition is developed (applied).

[0085] In a further embodiment requiring no peeling, the light-sensitive element is applied to be formed on one transparent support, a white reflecting layer is applied to be formed on the light-sensitive element, and an image-receiving layer further laminated on the light-sensitive element. U.S. Patent No. 3,730,718 describes an embodiment in which an image-receiving element, a white reflecting layer, a peelable layer and a light-sensitive element are laminated on the same support, wherein the light-sensitive element is intentionally peeled from the image-receiving element.

[0086] On the other hand, the typical forms in which a light-sensitive element and an image-receiving element are separately applied to be formed on two supports are roughly classified into two categories. One is of the peelable type and another is of the peeling-needless type. To state these types in more detail, in a preferred embodiment of the peelable type film unit, at least one image-receiving layer is applied to be formed on one support, and a light-sensitive element is applied to be formed on a support having a shading layer, the embodiment having a devised structure, in which the coated surface of the light-sensitive layer is not facing the coated surface of the image-receiving layer (mordant layer) before exposure is finished, but the coated surface of the light-sensitive layer turns over in an image-forming apparatus so that it is brought into contact with the coated surface of the image-receiving layer after the exposure is finished (e.g. during development). The light-sensitive element is peeled-off from the image-receiving element, immediately after the formation of a transfer image on the mordant layer is completed.

[0087] In a preferred embodiment of the peeling-needless type film unit, at least one mordant layer is applied to be formed on a transparent support, and a light-sensitive element is applied to be formed on a support which is transparent or has a shading layer, wherein the light-sensitive layer and the mordant layer are overlapped on each other such that the coated surfaces of these layers face each other.

[0088] A container (processing element) which contains an alkaline process solution and can be ruptured by pressure, may further be combined with the modes. In a peeling-needless type film unit, in which an image-receiving element and a light-sensitive element are laminated on one support, in particular, this processing element is preferably disposed between the light-sensitive element and a cover sheet to be overlapped on the light-sensitive element. Also, in the form in which the light-sensitive element and the image-receiving element are separately formed by application on two supports, the processing element is preferably disposed between the light-sensitive element and the image-receiving element during developing at the latest. Preferably the processing element contains either one or both of a shading agent (e.g., carbon black or dyes which vary in color depending on pH) and a white pigment (such as titanium oxide), according to the mode of film unit. Further, in the color diffusion transfer type film unit, preferably a neutralizing timing mechanism comprising a combination of a neutralizing layer and a neutralization timing layer is incorporated into a cover sheet, an image-receiving element or a light-sensitive element.

[0089] The dye image-forming substance used in the present invention is a nondiffusion compound that releases a diffusive dye (this may be a dye precursor), or a compound that is changed in its diffusibility, in association with silver development, and it is described in "The Theory of the Photographic Process", the Fourth edition. These compounds each may be represented by the following formula (II):



wherein DYE represents a dye group, a dye group that is temporarily short-waved, or a dye-precursor group, Y represents a simple bond or a linking group, Z represents a group having a property to produce a difference in diffusibility between the compounds represented by $(DYE-Y)_n-Z$, or to release a DYE (a diffusive dye or its precursor) to produce a difference in diffusibility between the released DYE and the $(DYE-Y)_n-Z$, in association with silver development (specifically, corresponding to or inversely corresponding to a light-sensitive silver salt having a latent image image-wise); and, n is 1 or 2, in which two $(DYE-Y)$ groups may be the same or different when n is 2.

[0090] Depending on the function of the Z group, these compounds are roughly classified into negative type compounds that are changed to a diffusible one in a silver developed section, and positive type compounds that are changed to a diffusible one in an undeveloped section.

[0091] Given as specific examples of the negative type Z include those oxidized and cleft to release a diffusible dye as a result of development.

[0092] Specific examples of Z are described, for example, in U.S. Patents No. 3,928,312, No. 3,993,638, No.

4,076,529, No. 4,152,153, No. 4,055,428, No. 4,053,312, No. 4,198,235, No. 4,179,291, No. 4,149,892, No. 3,844,785, No. 3,443,943, No. 3,751,406, No. 3,443,939, No. 3,443,940, No. 3,628,952, No. 3,980,479, No. 4,183,753, No. 4,142,891, No. 4,278,750, No. 4,139,379, No. 4,218,368, No. 3,421,964, No. 4,199,355, No. 4,199,354, No. 4,135,929, No. 4,336,322 and No. 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.

[0093] Examples of the particularly preferable group among Z of the negative type dye-releasable redox compounds include N-substituted sulfamoyl groups (the N-substituent include groups derived from aromatic hydrocarbon rings and heterocycles). Examples of typical groups of Z are shown below, but not limited to the following groups.

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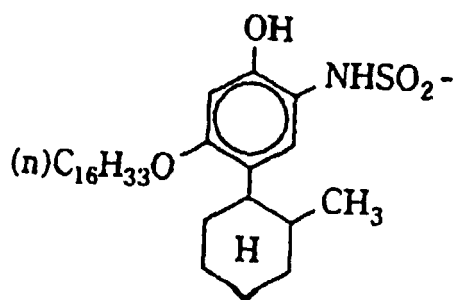
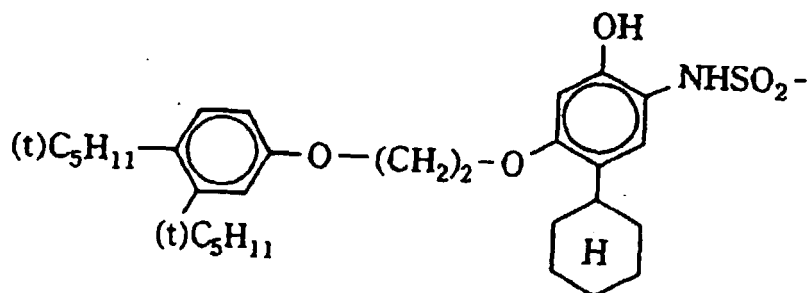
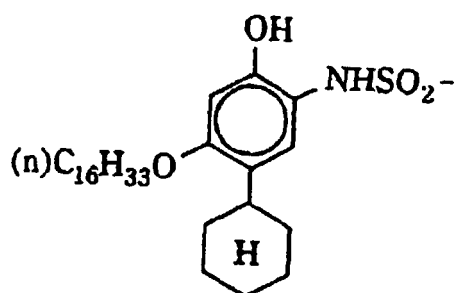
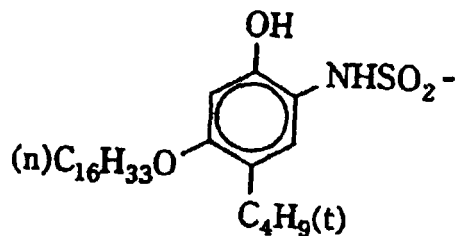
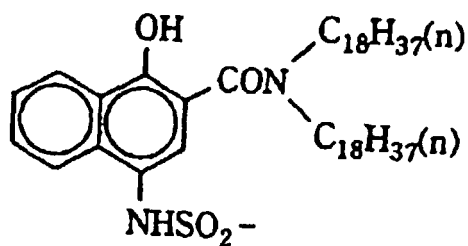
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[0094] The positive type compounds are described in "Angew. Chem. Int. Ed. Engl., 22, 191 (1982)".

[0095] As specific examples of the positive type compounds, compounds (dye developing agents) that are diffusible at the start in an alkaline condition and are oxidized by development to become non-diffusible, are given. Typical examples of Z useful for compounds of this type are given in U.S. Patent No. 2983606.

[0096] Another type is those that release a diffusible dye by, for example, self-ring-closing in an alkaline condition, but that substantially stop the release of the dye when being oxidized along with development. Specific examples of Z

having such a function are described, for example, in U.S. Patent No. 3,980,479, JP-A-53-69033, JP-A-54-130927 and U.S. Patents No. 3,421,964 and No. 4,199,355.

[0097] A further type includes those that themselves do not release any dye but release a dye when being reduced. Compounds of this type are used in combination with an electron-donor, thereby they can release a diffusible dye image-wise by the reaction with the remainder electron-donor oxidized image-wise by silver development. Examples of atomic groups having such a function are described, for example, in U.S. Patents No. 4,183,753, No. 4,142,891, No. 4,278,750, No. 4,139,379 and No. 4,218,368, JP-A-53-110827, U.S. Patents No. 4,278,750, No. 4,356,249 and No. 4,358,535, JP-A-53-110827, JP-A-54-130927, JP-A-56-164342, Published Technical report ("Kokai-Giho") 87-6199, and European Patent Application Laid-open No. 220746A2.

[0098] Specific examples of the group Z are shown below, but not limited to the following groups.

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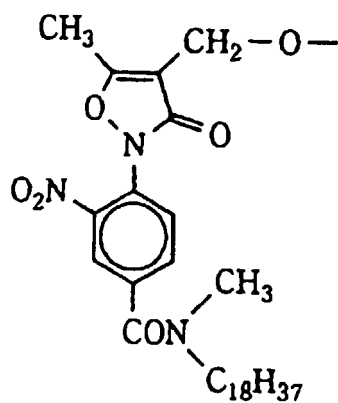
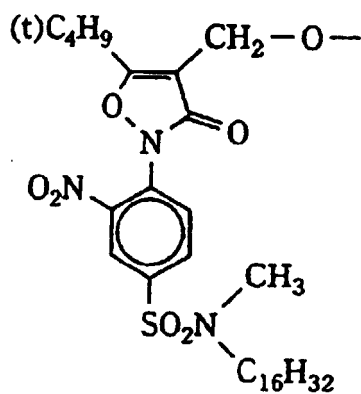
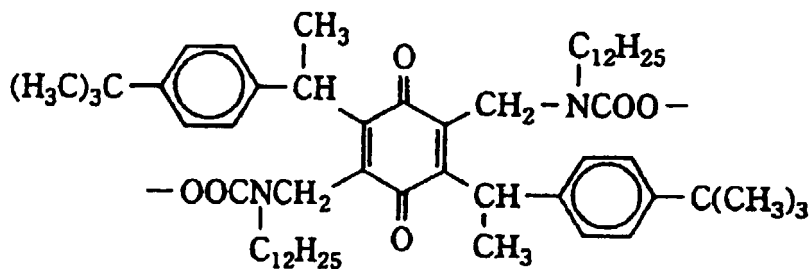
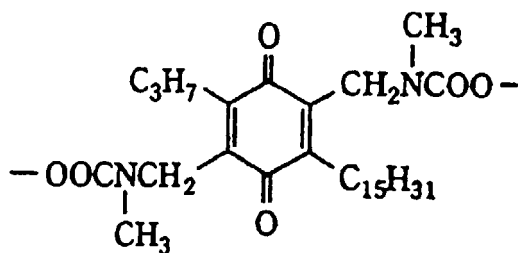
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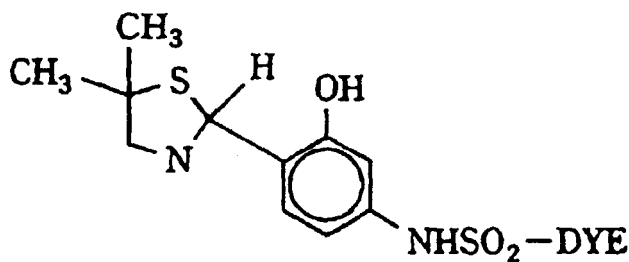
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[0099] When a compound of this type is used, preferably it is used in combination with an anti-diffusible electron-donating compound (well-known as an ED compound) or a precursor thereof. Examples of the ED compound are described, for example, in U.S. Patents No. 4,263,393 and No. 4,278,750 and JP-A-56-138736.

[0100] As specific examples of further another type of dye image-forming substance, the following compounds may also be used.



[0101] The details of this dye image-forming substance are described in U.S. Patents No. 3,719,489 and No. 4,098,783.

[0102] On the other hand, specific examples of the dye represented by the formula, "DYE", are described in the following literatures.

Examples of yellow dyes:

[0103] Those described in U.S. Patents No. 3,597,200, No. 3,309,199, No. 4,013,633, No. 4,245,028, No. 4,156,609, No. 4,139,383, No. 4,195,992, No. 4,148,641, No. 4,148,643, No. 4,336,322; JP-A-51-114930, JP-A-56-71072; Research Disclosures No. 17630 (1978), No. 16475 (1977).

Examples of magenta dyes:

[0104] Those described in U.S. Patents No. 3,453,107, No. 3,544,545, No. 3,932,380, No. 3,931,144, No. 3,932,308, No. 3,954,476, No. 4,233,237, No. 4,255,509, No. 4,250,246, No. 4,142,891, No. 4,207,104, No. 4,287,292; JP-A-52-106727, JP-A-53-23628, JP-A-55-36804, JP-A-56-73057, JP-A-56-71060, JP-A-55-134.

Examples of cyan dyes:

[0105] Those described in U.S. Patents No. 3,482,972, No. 3,929,760, No. 4,013,635, No. 4,268,625, No. 4,171,220, No. 4,242,435, No. 4,142,891, No. 4,195,994, No. 4,147,544, No. 4,148,642; U.K. Patent No. 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) No. 53,037, No. 53,040; Research Disclosures No. 17,630 (1978), No. 16,475 (1977).

[0106] These compounds can be dispersed using the method described in JP-A-62-215,272, pp.144-146. In these dispersions, the compound described in JP-A-62-215,272, pp.137-144 may be contained.

[0107] The internal-latent-image-type direct positive silver halide emulsion of the present invention may be used for conventional light-sensitive materials. Applicable examples of the light-sensitive material include light-sensitive materials for color or black-and-white printing paper, light-sensitive materials for color slide, and light-sensitive materials for microfilm.

[0108] The light-sensitive material of the present invention has not only a function as photographing materials but also a function as appreciation materials. An image can be written in the light-sensitive material not only by photographing using a camera but also by exposing the light-sensitive material directly to image information (analogue information and digital information) by using various light sources. The resulting image can be utilized and appreciated as various information media besides the so-called photography. The light-sensitive material of the present invention is developed (spread) in the apparatus after the image is written, thereby an image can be obtained in a short time, which indicates

that the light-sensitive material has properties suitable, particularly, to the above use (applications).

[0109] Any one of light sources may be used as the light source used for the writing of an image as far as it can modulate emission strength and emission time, depending on the image information. For example, CRTs, LEDs, LED arrays, VFPHs or organic ELs may be used. Also when a color image is written using three colors of blue(B), green(G) and red(R), the above light-source may be combined with filters to carry out exposure three times, or three independent light sources of B, G and R may be used to carry out exposure.

[0110] The light-sensitive material of the present invention may be utilized for printer materials and the like in applications in addition to photographing materials. The light-sensitive material of the present invention is preferably used as materials for portable printers described in, for example, JP-A-11-344772, Japanese Patent Applications No. 2000-67532 and No. 2000-67535, and JP-A-11-352595.

[0111] When the light-sensitive material is used as the aforementioned materials, it is sometimes used in the applications which need the secrecy and inhibition to falsification of authorized information. There are various methods to provide such a function, for example, a method of printing a security pattern on an image-receiving material is preferably used. As this method, those described in U. S. Patent No. 4653775, and Japanese Patent Applications No. 2000-147050 and No. 2000-147060 are preferably applied for the light-sensitive material of the present invention.

[0112] The present invention can provide a tabular internal-latent-image-type direct positive silver halide emulsion that is high in sensitive and that allows the low density portion on an reversal characteristic curve to be high in contrast and that is decreased in re-reversal negative sensitivity. The present invention can also provide a color diffusion transfer photographic film unit using the silver halide emulsion.

[0113] The present invention will be explained in more detail with reference to the following examples, which are not intended to limit the present invention.

EXAMPLE

Example-1

[0114] Firstly, a method for the preparation of a silver halide emulsion will be explained.

[0115] The following ten types of silver halide emulsion particles (Emulsion-A-1 to Emulsion-G, Emulsion-T-2, Emulsion U-2, and Emulsion X) were prepared, according to the method for the preparation of emulsion particles shown below. Preparation of Emulsion-A-1 (octahedron internal-latent-image-type direct positive emulsion):

[0116] To 1000 ml of an aqueous gelatin solution containing 0.05 M of potassium bromide, 1 g of 3,6-dithia-1,8-octanediol, 0.034 mg of lead acetate, and 60 g of deionized gelatin with a Ca content of 100 ppm or less, were added a 0.4 M aqueous silver nitrate solution and a 0.4 M aqueous potassium bromide solution, while the temperature was kept at 75°C and the rate of addition of the aqueous potassium bromide solution was controlled by a control double jet method such that the pBr would be 1.60, thereby 300 ml of the aqueous silver nitrate solution was added over 40 min.

[0117] The completion of the addition resulted in the formation of octahedron silver bromide crystals (hereinafter referred to as core particles) with a uniform particle size having an average particle diameter (sphere-equivalent diameter that was the diameter of a sphere whose volume was equivalent to an individual particle) of about 0.7 μm.

[0118] Then, chemical sensitization of the core was performed using the following container and formulation.

1. Tank: a type produced by Teflon-coating the surface of a metal with a fluororesin material FEP developed by Du Pont in a thickness of 120 μm and having a hemispherical bottom.
2. Stirring blade: a seamless integrated and propeller type produced by Teflon-coating the surface of a metal.
3. Formulation:

[0119] 3 ml of an aqueous solution obtained by dissolving 1 mg of sodium thiosulfate, 90 μg of potassium tetrachloroaurate and 1.2 g of potassium bromide in 1000 ml of water was added to a preparative solution of the aforementioned octahedron direct positive emulsion, and the mixture was heated to 75°C for 80 minutes to carry out chemical sensitization. After 0.15 M of potassium bromide was added to the emulsion solution that was chemically sensitized in the above manner, a 0.9 M aqueous silver nitrate solution and a 0.9 M aqueous potassium bromide solution were added to the resulting mixture, while the temperature was kept at 75°C and the rate of addition of the aqueous potassium bromide solution was controlled by a controlled double jet method such that pBr would be 1.30, thereby 670 ml of the aqueous silver nitrate solution was added over 70 min, in the similar manner as in the preparation of the core particles.

[0120] This emulsion was washed with water using a usual flocculation method, and the aforementioned gelatin, 2-phenoxyethanol and methyl p-hydroxybenzoate were added thereto, to obtain octahedron silver bromide crystals (hereinafter referred to as internal-latent-image-type core/shell particles) with a uniform particle size having an average particle diameter (a sphere-equivalent diameter) of about 1.4 μm.

[0121] Then, 3 ml of an aqueous solution obtained by dissolving 100 mg of sodium thiosulfate and 40 mg of sodium

tetraborate in 1000 ml of water was added to the internal-latent-image-type core/shell emulsion, to which 14 mg of poly(N-vinylpyrrolidone) was further added, and the mixture was ripened under heating to 60°C, followed by adding 0.005 M of potassium bromide, to prepare an octahedron internal-latent-image-type direct positive emulsion.

5 Preparation of Emulsion-B to Emulsion-G (octahedron internal-latent-image-type direct positive emulsions):

[0122] In the preparation of the Emulsion-A-1, the time required to add the aqueous silver nitrate solution and the aqueous potassium bromide solution was altered and the amount of chemicals to be added was changed, to obtain octahedron internal-latent-image-type direct positive silver halide emulsions having a uniform particle size with the average particle diameter (sphere-equivalent diameter) shown in Table 1.

Table 1

Name of emulsion	Average particle diameter/ μm
B	1.20
C	0.93
D	1.20
E	0.94
F	0.74
G	0.66

Preparation of Emulsion-T-2 (hexagonal tabular internal-latent-image-type direct positive emulsion):

[0123] To 1.2 liter of an aqueous gelatin solution containing 0.05 M of potassium bromide and 0.7 wt% of a gelatin having an average molecular weight of 100,000 or less, were added 33 ml of a 1.4 M aqueous silver nitrate solution containing the above gelatin and 33 ml of a 2M aqueous potassium bromide solution, at the same time, with vigorous stirring for one minute by a double jet method. During this period of time, the aqueous gelatin solution was kept at 30°C. Further, 300 ml of a gelatin solution containing 10 wt% of a deionized gelatin with a Ca content of 100 ppm or less was added to the mixture, which was then heated to 75°C.

[0124] Then, to the resulting mixture were added 40 ml of a 0.9 M aqueous silver nitrate solution over 3 minutes and a further 25 wt% aqueous ammonia solution, followed by ripening at 75°C. After the ripening was completed, ammonia was neutralized and thereafter 5 mg of lead acetate (as an aqueous solution) was added. Further thereto, a 1 M aqueous silver nitrate solution and a 1 M aqueous potassium bromide solution were added at an accelerated flow rate (the flow rate at the end was 6 times that at the start) while the pBr was kept at 2.5 by a double jet method (the amount of the aqueous silver nitrate solution to be used was 500 ml).

[0125] The particles (hereinafter referred to as core particles) thus formed were washed with water by a usual flocculation method, and a gelatin, 2-phenoxyethanol and methyl p-hydroxybenzoate were added to the particles, to obtain 750 g of hexagonal tabular core particles.

[0126] The resulting hexagonal tabular core particles had an average projected area-circle equivalent diameter of 0.9 μm and an average thickness of 0.20 μm , and 95% of all the projected area of the particles was occupied by the hexagonal tabular particles.

[0127] Then, chemical sensitization of the core was performed using the following container and formulation.

1. Tank: a type produced by Teflon-coating the surface of a metal with a fluororesin material FEP developed by Du Pont in a thickness of 120 μm and having a hemispherical bottom.

2. Stirring blade: a seamless integrated and propeller type produced by Teflon-coating the surface of a metal.

3. Formulation:

1300 ml of water, 0.11 M of potassium bromide and 40 g of a deionized gelatin were added to 200 g of the aforementioned hexagonal tabular core emulsion, and the resultant mixture was then heated to 75°C. Thereafter, 2.4 ml of an aqueous solution obtained by dissolving 10 mg of sodium benzene thiosulfate, 66 μg of N-methylbenzothiazolium iodide, 90 μg of potassium tetrachloroaurate and 1.2 g of potassium bromide in 1000 ml of water was added thereto, and the resulting mixture was heated to 75°C for 90 minutes to carry out chemical sensitization. To the thus chemically sensitized core particles, an aqueous solution containing 15 mg of lead acetate was accelerat-

ingly added at the same flow rate as that of the following aqueous silver nitrate solution in the same manner as in the preparation of the core particles, and a 2 M aqueous silver nitrate solution and a 2.5 M aqueous potassium bromide solution were added, at an accelerated flow rate (the flow rate at the end was 3 times that at the start), while the rate of addition of the aqueous potassium bromide solution was controlled such that the pBr would be 2.71 by a double jet method (the amount of the aqueous silver nitrate solution to be used was 810 ml).

[0128] After 0.3 M of potassium bromide was added, the resulting emulsion was washed with water by a usual flocculation method and a gelatin was added to the washed emulsion. A hexagonal tabular internal-latent-image-type core/shell emulsion was thus obtained. The resulting hexagonal tabular particles had an average projected area-circle equivalent diameter of 2.0 μm and an average volumetric size of 1.3 (μm)³, and 88% of all the projected area of the particles was occupied by the hexagonal tabular particles.

[0129] Then, to the hexagonal tabular internal-latent-image-type core/shell emulsion, were added 15 ml of an aqueous solution obtained by dissolving 100 mg of sodium thiosulfate and 40 mg of sodium tetraborate in 1000 ml of water, and further 20 mg of poly(N-vinylpyrrolidone) was added, and the mixture was heated to 70°C for 100 minutes, to carry out the chemical sensitization of the surface of the particles, thereby a hexagonal tabular internal-latent-image-type direct positive emulsion T-2 was thus prepared.

Preparation of Emulsion-X (Agl fine particle emulsion):

[0130] 0.5 g of potassium iodide and 26 g of gelatin were added in water. To the solution kept at 35°C, were added 80 ml of an aqueous solution containing 40 g of silver nitrate and 80 ml of an aqueous solution containing 39 g of potassium iodide, for 5 minutes with stirring. At this time, each flow rate of the aqueous silver nitrate solution and the aqueous potassium iodide solution to be added was set to 8 ml/min at the start of addition, and it was linearly accelerated such that an addition of each solution in an amount of 80 ml was completed in 5 minutes.

[0131] After the formation of particles were completed as above, soluble salts were removed at 35°C by a sedimentation method. Then, the temperature was raised to 40°C, and 10.5 g of a gelatin and 2.56 g of phenoxyethanol were added thereto, and caustic soda was added to regulate the pH to 6.8. The resulting emulsion was obtained finally in an amount of 730 g and was found to be monodispersion Agl fine particles with an average diameter of 0.015 μm .

Preparation of Emulsion-U-2 (hexagonal tabular internal-latent-image-type direct positive emulsion):

[0132] When the outer shell of the Emulsion-T-2 was formed, it was allowed to contain 0.15 mol% of iodine uniformly to further increase the amount of the outer shell to be formed. The resulting particles had an average projected area-circle equivalent diameter of 2.5 μm and an average volumetric size of 1.7 (μm)³, and 88% of all the projected area of the particles was occupied by the hexagonal tabular particles. 0.12 mol% of the Emulsion-X was added prior to the chemical sensitization of the shell, and the obtained particles were physically ripened for 5 minutes.

[0133] Then, the chemical sensitization of the shell was carried out in the same manner as in the Emulsion-T-2, to prepare a hexagonal tabular internal-latent-image-type direct positive emulsion.

[0134] The type, amount to be added, and position to be added of metal dopants to the Emulsions A-1, T-2 and U-2 for comparison were changed as in Table 2, to prepare Emulsions A-2 to A-9, T-1, T-3 to T-9, U-1, and U-3 to U-9.

Table 2

Samples varied in the type, addition amount and added position of metal dopants in the shell portion			
Name of emulsion	Dopant type	Amount to be added	Added position (shell silver amount %)
A-1(For comparison)	None	0	0
A-2(For comparison)	Pb(CH ₃ COO) ₂	15.0mg	0.1~100
A-3(For comparison)	Pb(CH ₃ COO) ₂	15.0mg	0.1~90
A-4(For comparison)	K ₄ [Fe(CN) ₆]	16.8mg	0.1~100
A-5(For comparison)	K ₄ [Fe(CN) ₆]	16.8mg	0.1~90
A-6(For comparison)	K ₄ [Ru(CN) ₆]	18.6mg	0.1~90

Table 2 (continued)

Samples varied in the type, addition amount and added position of metal dopants in the shell portion			
Name of emulsion	Dopant type	Amount to be added	Added position (shell silver amount %)
A-7(For comparison)	$K_4[Fe(CN)_6]/K_4[Ru(CN)_6]$ (8.4mg in 0.1~45%)/(9.3mg in 45~90%)	8.4mg/9.3mg	0.1~45/45~90
A-8(For comparison)	$K_4[Fe(CN)_6]$	16.8mg	0.1~50
A-9(For comparison)	$K_4[Fe(CN)_6]$	16.8mg	50~100
T-1(For comparison)	None	0	0
T-2(For comparison)	$Pb(CH_3COO)_2$	15.0mg	0.1~100
T-3(For comparison)	$Pb(CH_3COO)_2$	15.0mg	0.1~90
T-4(For comparison)	$K_4[Fe(CN)_6]$	16.8mg	0.1~100
T-5(This invention)	$K_4[Fe(CN)_6]$	16.8mg	0.1~90
T-6(This invention)	$K_4[Ru(CN)_6]$	18.6mg	0.1~90
T-7(This invention)	$K_4[Fe(CN)_6]/K_4[Ru(CN)_6]$ (8.4mg in 0.1~45%)/(9.3mg in 45~90%)	8.4mg/9.3mg	0.1~45/45~90
T-8(This invention)	$K_4[Fe(CN)_6]$	16.8mg	0.1~50
T-9(For comparison)	$K_4[Fe(CN)_6]$	16.8mg	50~100
U-1(For comparison)	None	0	0
U-2(For comparison)	$Pb(CH_3COO)_2$	15.0mg	0.1~100
U-3(For comparison)	$Pb(CH_3COO)_2$	15.0mg	0.1~90
U-4(For comparison)	$K_4[Fe(CN)_6]$	16.8mg	0.1~100
U-5(This invention)	$K_4[Fe(CN)_6]$	16.8mg	0.1~90
U-6(This invention)	$K_4[Ru(CN)_6]$	18.6mg	0.1~90
U-7(This invention)	$K_4[Fe(CN)_6]/K_4[Ru(CN)_6]$ (8.4mg in 0.1~45%)(9.3mg in 45~90%)	8.4mg/9.3mg	0.1~45/45~90
U-8(This invention)	$K_4[Fe(CN)_6]$	16.8mg	0.1~50
U-9(For comparison)	$K_4[Fe(CN)_6]$	16.8mg	50~100
Molecular weight; $Pb(CH_3COO)_2$; 325.34 $K_4[Fe(CN)_6]$; 422.39 $K_4[Ru(CN)_6]$; 467.61 Note) The ratio of the silver amount in the shell laminate layer to the total silver amount grown in the shell is defined as the shell silver amount %.			

[0135] Using the Emulsions A-1 to G, a light-sensitive element (Sample 101) for comparison having the structure as described in the following Table 3 was prepared. In addition, each sensitizing dye was added when the chemical sensitization of the shell was finished. The type, dispersion form, temperature and amount of the dye to be added at this time are shown in the following Table 4.

Table 3 Constitution of Light-Sensitive Element 101 for Comparison

Number of layer	Name of layer	Additive	Coated amount (g/m ²)
22th layer	Protective layer	Matting agent(1) Gelatin Surfactant(1) Surfactant(2) Surfactant(3) Additive(1) Additive(5)	0.15 0.25 5.3×10^{-3} 4.1×10^{-3} 3.9×10^{-3} 8.0×10^{-3} 0.009
21th layer	Ultraviolet absorbing layer	Ultraviolet absorber(1) Ultraviolet absorber(2) Ultraviolet absorber(3) Additive(2) Surfactant(3) Surfactant(4) Additive(1) Additive(5) Hardener(1) Hardener(2) Gelatin	0.09 0.05 0.01 0.17 0.013 0.019 8.0×10^{-3} 0.023 0.050 0.017 0.052
20th layer	Blue-light-sensitive layer (high speed)	Internal-latent-image-type direct positive emulsion :A-1 Nucleating agent(1) Additive(3) Additive(4) Additive(5) Additive(1) Surfactant(5) Gelatin	In terms of Ag 0.38 2.9×10^{-6} 4.0×10^{-3} 0.013 3.8×10^{-3} 9.0×10^{-3} 9.0×10^{-3} 0.042
19th layer	Blue-light-sensitive layer (low speed)	Internal-latent-image-type direct positive emulsion :B Internal-latent-image-type direct positive emulsion :C Nucleating agent(1) Additive(3) Additive(5) Additive(1) Surfactant(5) Gelatin	In terms of Ag 0.07 In terms of Ag 0.10 2.5×10^{-6} 0.022 9.0×10^{-3} 0.013 9.0×10^{-3} 0.35
18th layer	White reflection layer	Titanium dioxide Additive(1) Surfactant(1) Additive(5) Additive(8) Gelatin	0.30 9.0×10^{-3} 9.0×10^{-3} 0.011 9.0×10^{-3} 0.37

Table 3 (continued)

Number of layer	Name of layer	Additive	Coated amount (g/m ²)
17th layer	Yellow colored material layer	Yellow-dye-releasing compound(1) High-boiling organic solvent(1) Additive(6) Additive(7) Surfactant(4) Surfactant(5) Additive(9) Additive(1) Gelatin	0.62 0.27 0.18 0.09 0.062 0.030 0.031 6.0×10^{-3} 0.087
16th layer	Intermediate layer	Additive(10) Surfactant(1) Additive(1) Gelatin	0.013 4.0×10^{-4} 7.3×10^{-3} 0.42
15th layer	Color-mixing preventing layer	Additive(11) High-boiling organic solvent(2) Poly(methyl methacrylate) Surfactant(5) Additive(1) Additive(12) Gelatin	0.47 0.23 0.81 0.019 2.0×10^{-3} 0.61 0.81
14th layer	Green-light-sensitive layer (high speed)	Internal-latent-image-type direct positive emulsion :A-1 Nucleating agent(1) Additive(3) Additive(5) Additive(1) Additive(2) High-boiling organic solvent(2) Surfactant(5) Gelatin	In terms of Ag 0.69 2.2×10^{-6} 0.12 0.014 3.0×10^{-3} 0.015 0.07 0.06 0.97
13th layer	Green-light-sensitive layer (low speed)	Internal-latent-image-type direct positive emulsion :D Internal-latent-image-type direct positive emulsion :E Nucleating agent(1) Additive(3) Additive(4) Additive(5) Additive(1) Surfactant(5) Gelatin	In terms of Ag 0.11 In terms of Ag 0.08 2.7×10^{-6} 0.011 0.033 1.5×10^{-3} 0.010 0.024 0.26
12th layer	Intermediate layer	Additive(1) Surfactant(1) Surfactant(3) Additive(5) Gelatin	0.014 0.038 4.0×10^{-3} 0.014 0.033

Table 3 (continued)

Number of layer	Name of layer	Additive	Coated amount (g/m ²)
11th layer	Magenta colored material layer	Magenta-dye-releasing compound(1) High-boiling organic solvent(1) Additive(13) Additive(5) Surfactant(4) Additive(14) Additive(1) Gelatin	0.56 0.18 9.3×10^{-4} 0.02 0.04 0.02 7.0×10^{-3} 0.045
10th layer	Intermediate layer	Additive(10) Surfactant(1) Additive(1) Gelatin	0.014 3.0×10^{-4} 9.0×10^{-3} 0.36
9th layer	Color-mix preventing layer	Additive(11) High-boiling organic solvent(2) Poly(methyl methacrylate) Surfactant(5) Additive(1) Additive(12) Gelatin	0.38 0.19 0.66 0.016 2.0×10^{-3} 0.49 0.65
8th layer	Red-light-sensitive layer (high speed)	Internal-latent-image-type direct positive emulsion :A-1 Nucleating agent(1) Additive(3) Additive(5) Additive(1) Additive(2) High-boiling organic solvent(2) Surfactant(5) Gelatin	In terms of Ag 0.33 6.1×10^{-6} 0.04 0.01 1.0×10^{-3} 0.08 0.04 0.02 0.33
7th layer	Red-light-sensitive layer (low speed)	Internal-latent-image-type direct positive emulsion :F Internal-latent-image-type direct positive emulsion :G Nucleating agent(1) Additive(3) Additive(5) Additive(1) Surfactant(5) Gelatin	In terms of Ag 0.10 In terms of Ag 0.11 2.5×10^{-5} 0.047 0.016 8.0×10^{-3} 0.02 0.57
6th layer	White reflection layer	Titanium dioxide Additive(1) Surfactant(1) Additive(5) Additive(8) Gelatin	1.87 7.0×10^{-3} 4.0×10^{-4} 0.02 0.016 0.73

Table 3 (continued)

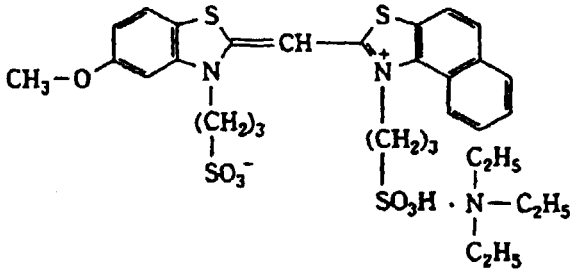
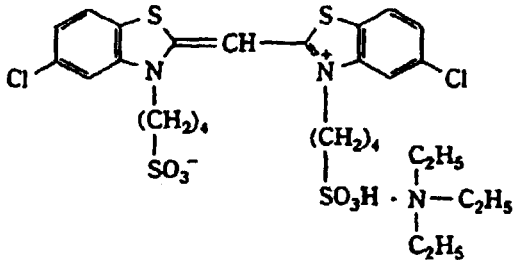
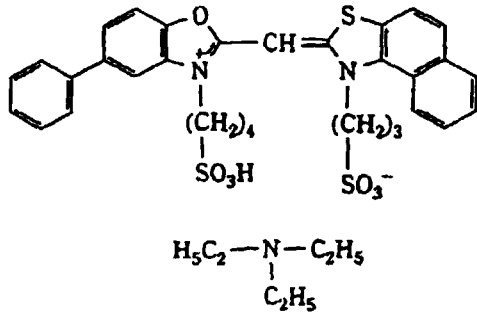
Number of layer	Name of layer	Additive	Coated amount (g/m ²)
5th layer	Cyan colored material layer	Cyan-dye-releasing compound(1) Cyan-dye-releasing compound(2) High-boiling organic solvent(1) Additive(3) Additive(5) Surfactant(4) Additive(9) Additive(1) Hardener(3) Gelatin	0.25 0.14 0.05 0.06 0.01 0.05 0.05 4.0×10^{-3} 0.014 0.40
4th layer	Shading layer	Carbon black Surfactant(1) Additive(1) Additive(5) Additive(12) Gelatin	1.50 0.08 0.06 0.06 0.15 1.43
Third layer	Intermediate layer	Surfactant(1) Additive(1) Additive(5) Gelatin	6.0×10^{-4} 9.0×10^{-3} 0.013 0.29
Second layer	White reflection layer	Titanium dioxide Additive(15) Additive(16) Surfactant(6) Additive(8) Hardener(1) Hardener(2) Gelatin	19.8 0.378 0.094 0.019 0.16 0.02 0.007 2.45
First layer	Image-receiving layer	Polymer mordant(1) Additive(17) Surfactant(7) Additive(5) Hardener(1) Hardener(2) Gelatin	2.22 0.26 0.04 0.11 0.03 0.01 3.25
Base(90 μ m of polyethylene terephthalate undercoated and containing titanium dioxide for preventing light piping)			
Backing layer	Curl controlling layer	Ultraviolet absorber(4) Ultraviolet absorber(5) Diacetylcellulose (Acetylation degree...51%) Additive(18) Barium stearate Hardener(4)	0.40 0.10 4.20 0.25 0.11 0.50

Table 4 Content of sensitizing dyes per 1 kg of the emulsion

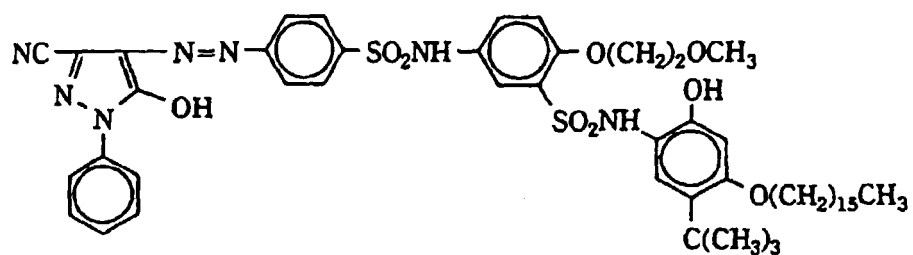
Number of layer	Name of emulsion	Sensitizing dye type	Dye dispersion form	Temperature when added	Amount of dye g/kg emulsion
20	A-1	(9)	Aqueous solution	70°C	9.38×10^{-2}
		(8)	Aqueous solution		1.19×10^{-1}
19	B	(9)	Aqueous solution	60°C	6.50×10^{-2}
		(8)	Aqueous solution		1.47×10^{-1}
19	C	(9)	Aqueous solution	60°C	7.31×10^{-2}
		(8)	Aqueous solution		1.66×10^{-1}
14	A-1	(7)	Gelatin dispersion	60°C	1.18×10^{-1}
		(4)	Gelatin dispersion		2.94×10^{-3}
		(6)	Dispersion of water/organic solvent with surfactant		9.23×10^{-2}
13	D	(7)	Gelatin dispersion	40°C	6.49×10^{-2}
		(4)	Gelatin dispersion		1.62×10^{-3}
		(6)	Dispersion of water/organic solvent with surfactant		4.85×10^{-2}
13	E	(7)	Gelatin dispersion	40°C	7.34×10^{-2}
		(4)	Gelatin dispersion		1.83×10^{-3}
		(6)	Dispersion of water/organic solvent with surfactant		5.69×10^{-2}
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}

	Molecular weight : 728.77 Molecular formula : $C_{25}H_{26}Cl_2N_2O_6S_4 \cdot C_5H_5N_1$ Sensitizing dye (1)
	Molecular weight : 686.24 Molecular formula : $C_{30}H_{31}Cl_1N_2O_7S_3 \cdot Na_1$ Sensitizing dye (3)
	Molecular weight : 782.09 Molecular formula : $C_{33}H_{32}N_2O_6S_4 \cdot C_8H_{15}N_1$ Sensitizing dye (2)

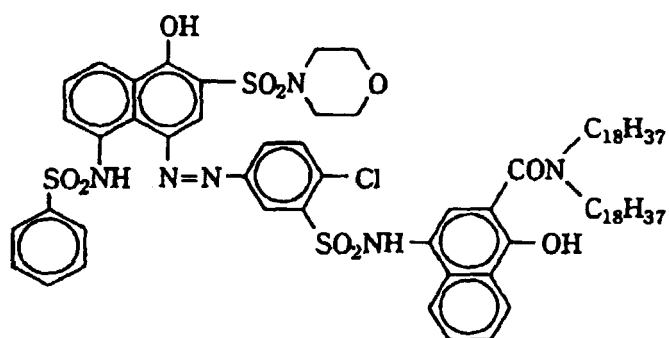
5 10	Molecular weight : 751.89 Molecular formula : $C_{35}H_{32}N_2O_8S_2$ C_5H_5N Sensitizing dye (7)
15 20	Molecular weight : 707.96 Molecular formula : $C_{33}H_{36}N_2O_7S_3 \cdot K_1$ Sensitizing dye (4)
25 30	Molecular weight : 742.57 Molecular formula : $C_{30}H_{28}Cl_2F_7N_5O_3$ S_1 Sensitizing dye (6)

	Molecular weight : 707.96 Molecular formula : $C_{26}H_{26}N_2O_7S_4$ $C_6H_5N_1$ Sensitizing dye (9)
	Molecular weight : 724.83 Molecular formula : $C_{23}H_{24}Cl_2N_2O_6S_4$ $C_6H_{15}N_1$ Sensitizing dye (5)
	Molecular weight : 752.00 Molecular formula : $C_{32}H_{30}N_2O_7S_3$ $C_6H_{15}N_1$ Sensitizing dye (8)

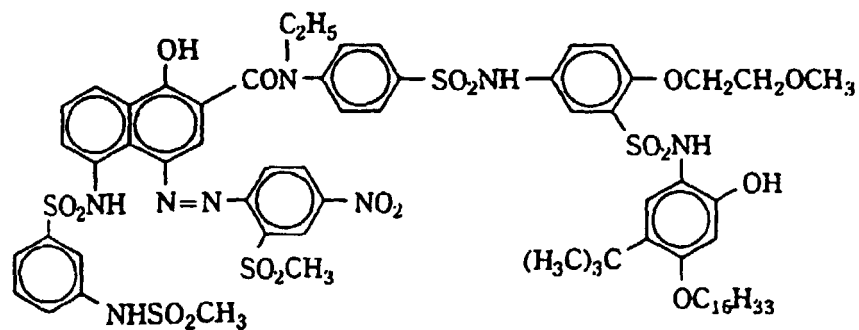
Yellow-dye-releasing compound (1)



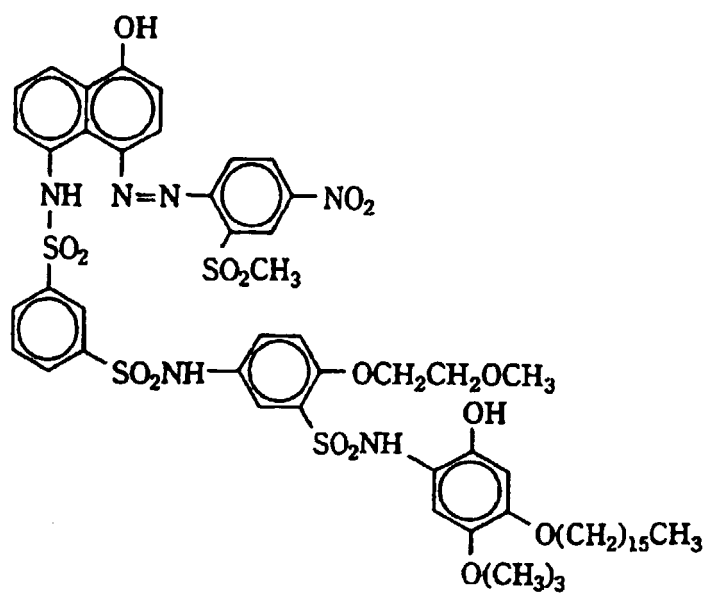
Magenta-dye-releasing compound (1)



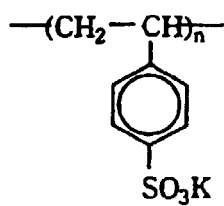
Cyan-dye-releasing compound (1)



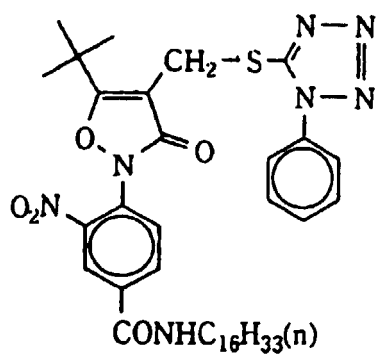
Cyan-dye-releasing compound (2)



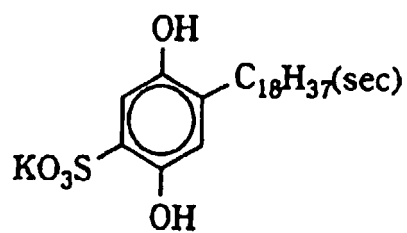
Additive (1)



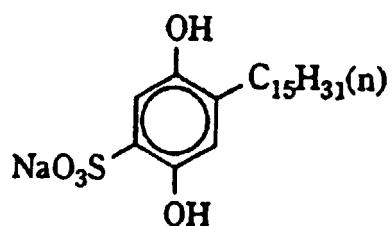
Additive (2)



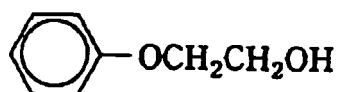
Additive (3)



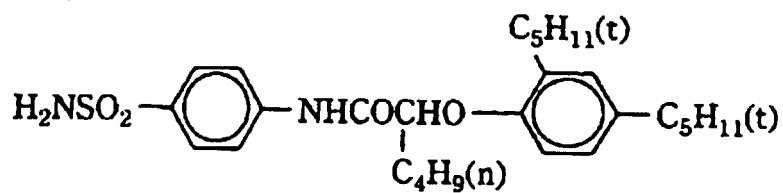
Additive (4)



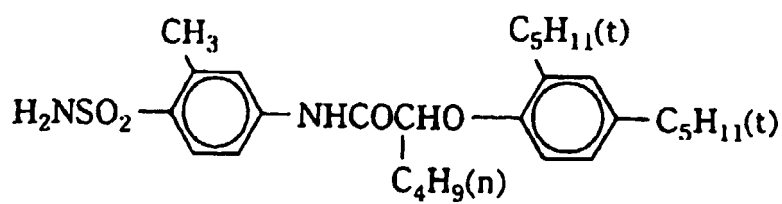
Additive (5)



Additive (6)



Additive (7)



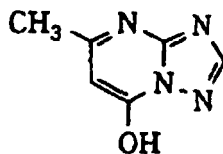
Additive (8)

Carboxymethyl cellulose
(CMC cellogen 6A, trade name, manufactured by
Dai-ichi Kogyo Seiyaku Co., Ltd)

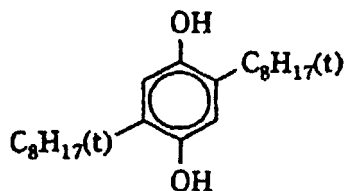
Additive (9)

Polyvinyl alcohol (PVA-220E)
Degree of polymerization, approximately 2000
Degree of saponification, 88%

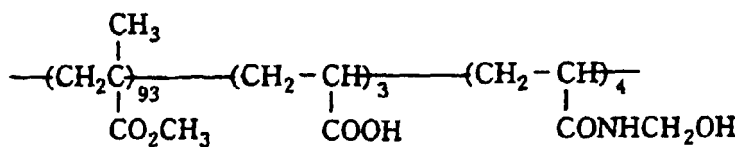
Additive (10)



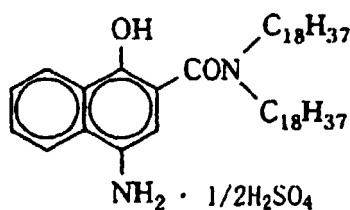
Additive (11)



Additive (12)



Additive (13)



$$\begin{array}{ccccccc} \text{CH}_3 & & & & \text{CH}_3 & & \\ | & & & & | & & \\ -(\text{CH}_2-\text{C})_{40}- & (\text{CH}_2\text{CH})_{47}- & (\text{CH}_2\text{CH})_{10}- & (\text{CH}_2\text{C})_3- & & & \\ | & | & | & | & & & \\ \text{CONH}(\text{CH}_2)_3\text{N}(\text{C}_4\text{H}_9)_2 & \text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 & \text{CONH}(\text{CH}_2)_{11}\text{COOH} & & & \\ & & | & & & & \\ & & -(\text{CH}-\text{CH}_2)- & & & & \end{array}$$
COc1cc(O)cc(C13CCCCCCCCC13)c1Cc1cc(C)c(O)c(C)c1C2CC(C)OC(C)(C)CCCC(C)CCC(C)CCC(C)CCCCc1cc(O)c2c(c1)O[C@H]3C(C)(C)[C@@H](OC4=CC=C(C)C4O)C5=CC(=C(C)C)C=C5O
$$\text{---}(\text{CH}_2\text{CH})_{50}\text{---}(\text{CHCH})_{50}\text{---}$$

COCH_3

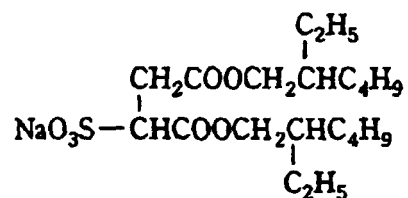
COOCH_3
 COOH

Matting agent (1)

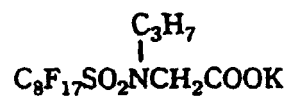
Spherical latex of poly(methyl methacrylate)

(Average particle diameter $3 \mu\text{m}$)

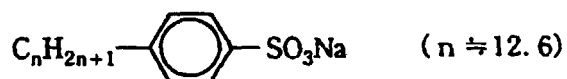
Surfactant(1)



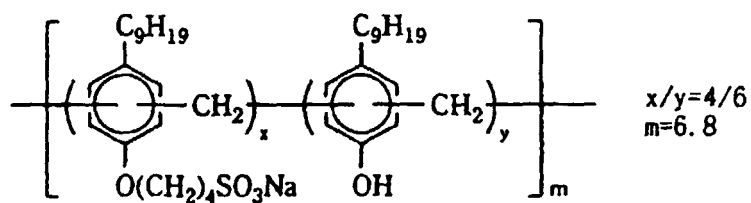
Surfactant(2)



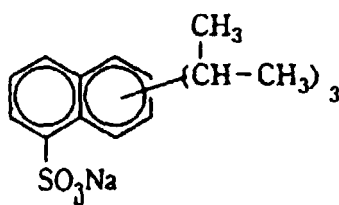
Surfactant(3)



Surfactant(4)



Surfactant(5)



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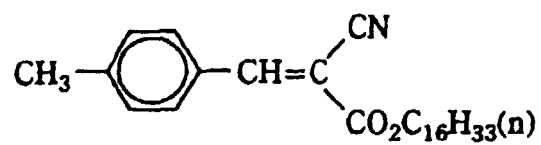
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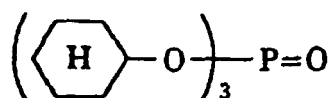
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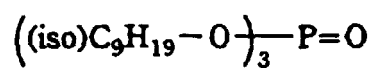
Ultraviolet absorber (3)



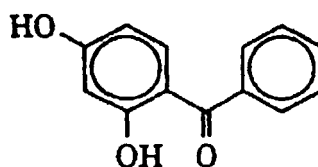
High-boiling organic solvent (1)



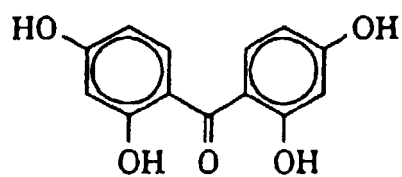
High-boiling organic solvent (2)



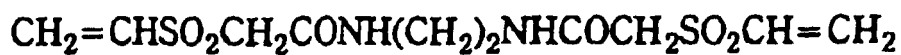
Ultraviolet absorber (4)



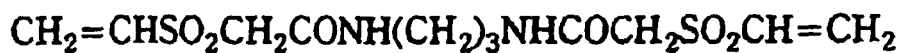
Ultraviolet absorber (5)



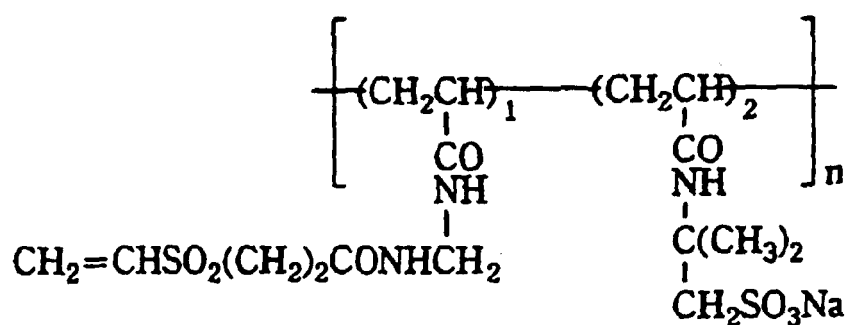
Hardener (1)



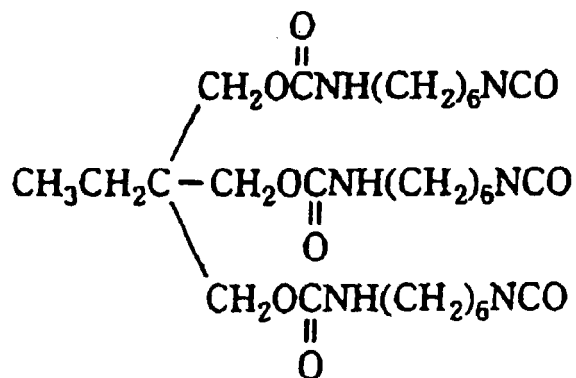
Hardener (2)



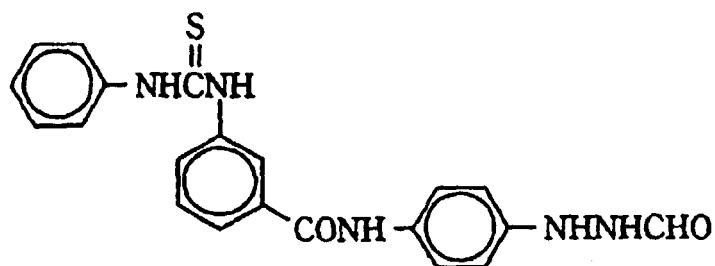
Hardener (3)



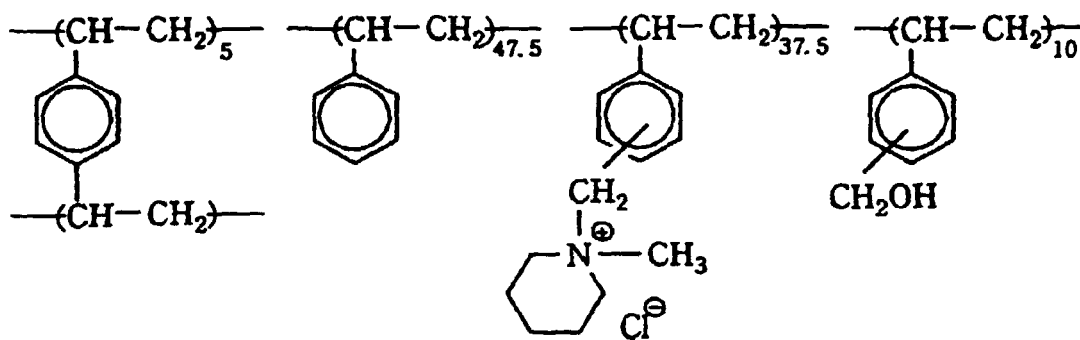
Hardener (4)



Nucleating agent (1)



Polymer mordant (1)



[0136] Then, the emulsions in the 8th layer, 14th layer and 20th layer were replaced by the Emulsions A-2 to A-9, T-1 to T-9, and U-1 to U-9, as shown in Table 5, to prepare Samples 102 to 109, 201 to 209, and 301 to 309.

Table 5

List of emulsions to be used			
Sample No.	8th layer	14th layer	20th layer
101(Comparative example)	A-1	A-1	A-1
102(Comparative example)	A-2	A-2	A-2
103(Comparative example)	A-3	A-3	A-3
104(Comparative example)	A-4	A-4	A-4
105(Comparative example)	A-5	A-5	A-5
106(Comparative example)	A-6	A-6	A-6
107(Comparative example)	A-7	A-7	A-7
108(Comparative example)	A-8	A-8	A-8
109(Comparative example)	A-9	A-9	A-9
201(Comparative example)	T-1	T-1	T-1
202(Comparative example)	T-2	T-2	T-2
203(Comparative example)	T-3	T-3	T-3
204(Comparative example)	T-4	T-4	T-4
205(This invention)	T-5	T-5	T-5

Table 5 (continued)

List of emulsions to be used			
Sample No.	8th layer	14th layer	20th layer
206(This invention)	T-6	T-6	T-6
207(This invention)	T-7	T-7	T-7
208(This invention)	T-8	T-8	T-8
209(Comparative example)	T-9	T-9	T-9
301(This invention)	T-8	T-8	U-1
302(This invention)	T-8	T-8	U-2
303(This invention)	T-8	T-8	U-3
304(This invention)	T-8	T-8	U-4
305(This invention)	T-8	T-8	U-5
306(This invention)	T-8	T-8	U-6
307(This invention)	T-8	T-8	U-7
308(This invention)	T-8	T-8	U-8
309(This invention)	T-8	T-8	U-9

[0137] The cover sheet was produced as follows.

[0138] The following layers were applied on a polyethylene terephthalate support that contained a light-piping-preventing dye and that was provided with a gelatin undercoat.

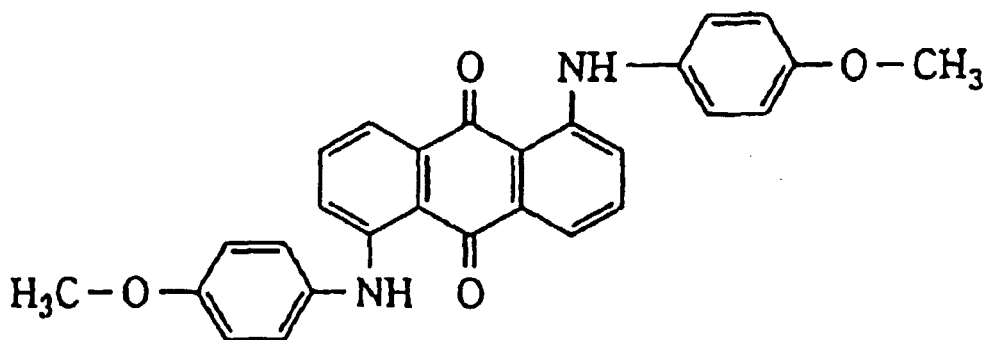
(a) A neutralizing layer containing 10.4 g/m² of an acrylic acid/n-butyl acrylate copolymer (80/20 (mol%)) having an average molecular weight of 50,000 and 0.1 g/m² of 1,4-bis(2,3-epoxypropoxy)-butane.

(b) A layer containing 4.3 g/m² of cellulose acetate having an acetylation degree of 55% and 0.2 g/m² of a methyl half ester of a methyl vinyl ether/maleic anhydride copolymer (50/50 (mol%)).

(c) A neutralization timing layer containing 0.3 g/m² of an 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 (66.1/28.4/5.5 (wt%)) having an average molecular weight of 40,000.

[0139] As the light-piping preventive dye, a combination of KAYASET GREEN A-G, trade name, manufactured by Nippon Kayaku Co., Ltd., and the following compound in a ratio of 3:1 was used.

< Light-piping preventive dye >



[0140] The alkaline processing composition was prepared by the following method.

[0141] 0.8 g of the processing solution having the following composition was filled in a container which could be ruptured by pressure.

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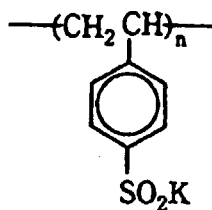
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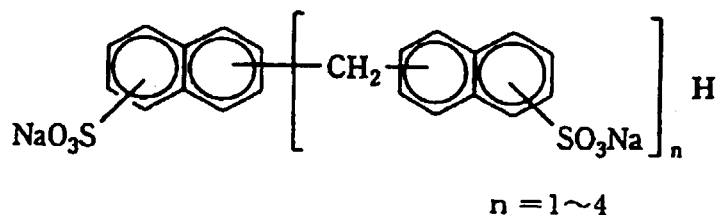
55

Water	695 g
1-p-tolyl-4-hydroxymethyl-4-methyl -3-pyrazolidin-1-one	7.00 g
1-phenyl-4-hydroxymethyl-4-methyl -3-pyrazolidin-1-one	9.85 g
Sulfinic acid polymer	2.10 g
5-methylbenzotriazole	2.50 g
Zinc nitrate hexahydrate	0.60 g
Potassium sulfite	1.90 g
Aluminum nitrate nonahydrate	0.60 g
Na salt of carboxymethyl cellulose	56.0 g
Potassium hydroxide	55.0 g
Carbon black	160 g
Anionic surfactant ①	8.60 g
Anionic surfactant ②	0.03 g
Alkyl-modified PVA (manufactured by Kuraray Co., Ltd.)	0.06 g
Cationic polymer	1.05 g

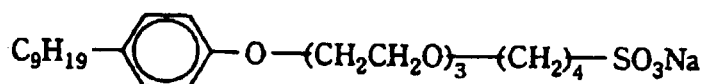
Sulfinic acid polymer



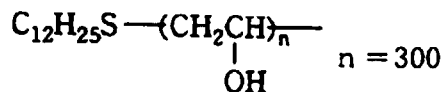
Anionic surfactant ①



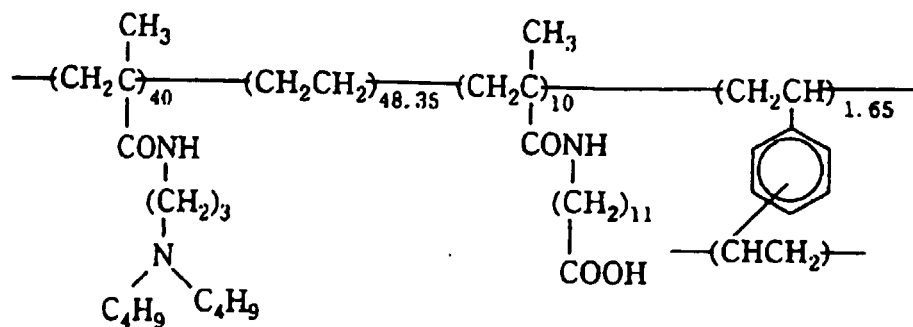
Anionic surfactant ②



Alkylmodified PVA



Cationic polymer



[0142] Each of the light-sensitive elements 101 to 109, 201 to 209 and 301 to 309 was exposed to light from the side of the emulsion layer through a gray continuous wedge, and it was then overlapped on the cover sheet. Then the above processing solution was extended (developed) between the both materials so that the thickness of the solution would be 62 μm , by using a pressure roller. The exposure to light was carried out for 1/100 seconds while controlling exposure intensity such that the exposure value would be constant. The process was carried out at 25°C, and ten minutes after, the transferred density was measured with a color-densitometer.

[0143] The results are shown in Table 6. The maximum density, minimum density, middle-point sensitivity, and toe

sensitivity, shown in Table 6, were determined in the following manner. Specifically, in a graph in which the abscissa indicates logarithmic exposure value and the ordinate indicates each developed color density, a characteristic curve was plotted. The developed color density at the unexposed portion was determined as the maximum density, and the developed color density in a region where the exposure amount was sufficiently large was determined as the minimum density. The middle-point sensitivity was defined as the sensitivity giving a middle density between the maximum density and the minimum density, and the toe sensitivity was defined as the sensitivity giving a density of 0.3, and the reversal negative sensitivity was defined as the sensitivity giving a density of 0.3 on a negative image formed by high intensity illumination exposure. The sensitivity of Sample 101 was designated to be 100.

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Table 6 Maximum density, Minimum density, Middle-point sensitivity, Toe sensitivity, Re-reversal negative sensitivity

Sample Number	Maximum density			Minimum density			Middle-point sensitivity			Toe sensitivity			Re-reversal negative sensitivity		
	Y	M	C	Y	M	C	Y	M	C	Y	M	C	Y	M	C
101(Comparative example)	2.10	2.30	2.40	0.17	0.16	0.24	100	100	100	100	100	100	100	100	100
102(Comparative example)	2.12	2.32	2.42	0.17	0.16	0.24	97	98	98	100	101	102	101	101	99
103(Comparative example)	2.11	2.32	2.41	0.17	0.16	0.24	98	99	97	101	99	99	99	100	99
104(Comparative example)	1.92	2.12	2.23	0.17	0.16	0.24	90	91	92	88	89	90	106	105	104
105(Comparative example)	1.93	2.13	2.23	0.17	0.16	0.24	91	90	90	89	90	90	102	102	101
106(Comparative example)	1.92	2.12	2.22	0.17	0.16	0.24	89	90	91	89	89	90	101	101	102
107(Comparative example)	1.92	2.12	2.23	0.17	0.16	0.24	90	89	89	90	91	90	102	102	102
108(Comparative example)	1.94	2.13	2.22	0.17	0.16	0.24	90	91	89	91	90	90	98	99	98
109(Comparative example)	1.86	2.07	2.16	0.17	0.16	0.24	86	84	85	87	85	86	104	103	103
201(Comparative example)	2.20	2.40	2.50	0.36	0.48	0.56	72	75	76	74	75	77	80	79	81
202(Comparative example)	2.12	2.34	2.41	0.16	0.15	0.23	114	116	117	116	118	120	80	80	81
203(Comparative example)	2.13	2.32	2.42	0.16	0.15	0.23	111	114	115	114	116	118	80	79	80
204(Comparative example)	2.15	2.34	2.45	0.16	0.15	0.23	128	129	132	131	132	141	92	89	91
205 (This Invention)	2.13	2.32	2.42	0.16	0.15	0.23	135	139	141	140	144	150	60	56	59
206 (This Invention)	2.13	2.33	2.43	0.16	0.15	0.23	136	138	140	141	145	151	59	55	58
207 (This Invention)	2.12	2.34	2.42	0.16	0.15	0.23	139	140	145	144	150	158	54	50	52
208 (This Invention)	2.07	2.24	2.33	0.16	0.15	0.23	148	149	150	150	151	151	40	36	38
209(Comparative example)	2.18	2.36	2.48	0.16	0.15	0.23	125	124	128	128	129	133	94	92	92
301 (This Invention)	2.16	2.24	2.33	0.35	0.15	0.23	96	149	150	94	151	150	122	36	38
302 (This Invention)	2.01	2.24	2.33	0.20	0.15	0.23	152	149	150	148	151	150	126	37	39
303 (This Invention)	2.00	2.24	2.33	0.20	0.15	0.23	150	149	150	146	151	151	124	38	38
304 (This Invention)	2.01	2.24	2.33	0.18	0.15	0.23	201	149	150	208	151	151	142	38	39
305 (This Invention)	2.01	2.24	2.33	0.18	0.15	0.23	211	149	150	216	151	151	97	38	39
306 (This Invention)	2.01	2.24	2.33	0.18	0.15	0.23	213	149	150	218	151	151	95	39	39
307 (This Invention)	2.01	2.24	2.33	0.18	0.15	0.23	215	149	150	220	151	151	93	39	40
308 (This Invention)	1.96	2.24	2.33	0.18	0.15	0.23	225	149	150	230	151	151	82	39	41
309 (This Invention)	2.04	2.24	2.33	0.20	0.15	0.23	196	149	150	202	151	151	148	40	41

[0144] It is understood that Samples 205 to 208 and 301 to 309 according to the present invention each were made higher in sensitivities of both the middle-point sensitivity and the toe sensitivity and had lower maximum density and lower re-reversal negative sensitivity, as compared to Samples 201 to 204 for comparison. Particularly Samples 205 to 208 and 305 to 308 were made higher in sensitivities of both the middle-point sensitivity and the toe sensitivity and had

lower maximum density and lower re-reversal negative sensitivity, as compared to the yellow-color-formig layer (Y) of the Samples 201 to 204 and 209, or 301 to 304 and 309, respectively. From these facts, it is understood that preferably the metal complex for use in the present invention is added not to extend to the surface of the shell but to be present as a localized phase that does not allow to exist in the surface of the shell.

- 5 **[0145]** Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

Claims

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1. A tabular internal-latent-image-type direct positive silver halide emulsion, comprising core/shell-type silver halide particles in which the average particle diameter is 0.3 μ m or more, the average value of the ratio of the particle diameter/particle thickness of each particle is 2 or more, and the ratio (in area) occupied by tabular particles (the ratio of the particle diameter/the particle thickness is from 2 to 100) is 50% or more, wherein at least one metal complex represented by the following formula (I) is contained as a localized phase in a region containing 0.1 to 90 mol% of the amount of silver contained in the shell portion:

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wherein M represents Fe, Ru, Ir, Co, Cr, Mn, Rh, Re, or Os;

a is 0, 1, or 2;

L represents a ligand other than CN; and

n is 2, 3, or 4.

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2. The tabular internal-latent-image-type direct positive silver halide emulsion according to claim 1, wherein the amount of the metal complex to be added is 1.0×10^{-7} mol/mol Ag or more, but 1.0×10^{-4} mol/mol Ag or less.
3. The tabular internal-latent-image-type direct positive silver halide emulsion according to claim 1 or 2, wherein the type of metal complex is a hexacyanoiron complex.
- 30 4. The tabular internal-latent-image-type direct positive silver halide emulsion according to any one of claims 1 to 3, wherein the metal complex represented by formula (I) is contained as a localized phase in a region containing 0.1 to 50 mol% of the amount of silver contained in the shell portion.
- 35 5. The tabular internal-latent-image-type direct positive silver halide emulsion according to any one of claims 1 to 4, wherein the shape of each tabular silver halide particle contained in the silver halide emulsion is a triangle, hexagon, or circle.
- 40 6. The tabular internal-latent-image-type direct positive silver halide emulsion according to any one of claims 1 to 5, wherein the silver halide composition of the silver halide particles is silver bromiodide, silver chlorobromiodide, or silver chloriodide.
- 45 7. The tabular internal-latent-image-type direct positive silver halide emulsion according to any one of claims 1 to 6, wherein the metal complex represented by formula (I) is contained further in the core portion.
8. The tabular internal-latent-image-type direct positive silver halide emulsion according to any one of claims 1 to 7, wherein the pBr during the formation of particles when the metal complex represented by formula (I) is added is 2 to 4 at 75 °C.
- 50 9. A color diffusion transfer light-sensitive material, having at least one light-sensitive silver halide emulsion layer combined with a dye image-forming substance on a support, with the dye image-forming substance being a compound represented by the following formula (II), with the compound being a nondiffusion compound releasing a diffusive dye or its precursor in association with silver development, or a compound that is changed in its diffusibility, wherein at least one layer of the silver halide emulsion layers contains the tabular internal-latent-image-type direct positive silver halide photographic emulsion as claimed in any one of claims 1 to 8:

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wherein DYE represents a dye group, a dye group that is temporarily short-waved, or a dye-precursor group; Y represents a simple bond or a linking group, Z represents a group having a property to release a diffusive dye or its precursor in association with silver development, or to produce a difference in diffusibility between the compounds represented by $(\text{DYE-Y})_n\text{-Z}$, and n is 1 or 2, and two (DYE-Y) groups may be the same or different when n is 2.

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EUROPEAN SEARCH REPORT

Application Number
EP 00 11 7314

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.7)		
Y	EP 0 573 066 A (FUJI) 8 December 1993 (1993-12-08) * page 2, line 52 - page 3, line 8 * * page 3, line 25 - line 48 * * page 4, line 24 - line 30 * * page 6, line 23 * * page 8, line 30 - line 33 * * page 12, line 54 - page 17, line 20 * * page 21, line 44 - line 50 * * page 22, line 3 - line 5 * * page 22, line 18 * * page 34, line 5 - line 47 * * page 35, line 12 *	1-9	G03C1/485 G03C8/08		
D	& JP 06 051423 A 25 February 1994 (1994-02-25) ----				
Y	JP 04 278940 A (FUJI) 5 October 1992 (1992-10-05) * page 13, paragraph 120 - paragraph 122 * * page 26, line 10 - line 12 * * page 69; table 1 * * claim 1 * -----	1-9	<table border="1"> <thead> <tr> <th>TECHNICAL FIELDS SEARCHED (Int.CI.7)</th> </tr> </thead> <tbody> <tr> <td>G03C</td> </tr> </tbody> </table>	TECHNICAL FIELDS SEARCHED (Int.CI.7)	G03C
TECHNICAL FIELDS SEARCHED (Int.CI.7)					
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The present search report has been drawn up for all claims					
Place of search THE HAGUE		Date of completion of the search 6 October 2000	Examiner Magrizos, S		
<table border="0"> <tr> <td> CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document </td> <td> T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document </td> </tr> </table>				CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document	T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document	T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document				

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