

- (54) Silver halide light-sensitive color photographic material.
- (57) A silver halide light-sensitive color photographic material is disclosed. The material comprises a hydrophillic colloidal layer containing a white pigment a yellow dye image-forming silver halide emulsion layer containing converted silver amount of 0.48 g/m<sup>2</sup> or less. The material is suitable for preparing color proof image.

#### **Field of the Invention**

The present invention relates to a silver halide light-sensitive color photographic material suitable for producing a color image for proofing from a plurality of black-and-white dot images obtainable by color separating and converting the color-separated images into dot images.

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Heretofore in the step of plate-making or printing, as a method of producing a color proof, which is obtainable from a plurality of dot images obtained by color-separating a color original and converting the separated images into dot images, overlay method and surprinting method are well known.

The overlay method has advantages that it is very simple, that the manufacturing cost is low and that the color image for proofing can be used by simply piling four color-separated film sheets, which are formed of three primary colors and black used in subtraction color image-forming process, however, it has a defect that it tends to give an observer an impression that the produced image has a different image quality.

Surprint method, on the other hand, consists of piling colored images on a single support, and a method of obtaining a color image by toner development, making the use of adhesion power of photopolymerizable materials. Such a method is disclosed in, for example, U.S. Patents No.3,582,327, No.3,607,264 and No. 3,620,726.

Further, a method of producing a color proof image by transferring a color image produced on a lightsensitive colored sheet on to a substratum an by repeating the same process, is disclosed in Japanese patent Publication No.47-27441(1972) and Japanese Patent O.P.I. publication No.56-50121(1981).

20 Still further, a method of producing a proof image on a support using a light-sensitive colored sheet by transferring respective color images, which are obtained by transferring the respective colored images, is disclosed in Japanese Patent Publication No. 59-97140(1984) obtained by exposure and development of a colored material. As for the toner and the coloring agent used for producing these color images, since the color tone of the color proof thus obtained there is an advantage that a coloring material is that of the printing ink, similar

to the printing ink can be used, color tone of the thus obtained color proof tends to be close to that of the printing material.

However, these methods, since the images have to be superimposed or transferred during the step of preparing the color proof, and thus there are disadvantages that more time is required for the operation and that the manufacturing cost is relatively high.

As for the technique by which these disadvantages can be overcome, a method of producing a color proof by the use of a silver halide light-sensitive color photographic material has been proposed in Japanese Patent O.P.I. Publications No.56-113139(1981), No.56-104335(1981), No.62-280746(1987),No.62-280747(1987), No.62-280748(1987), No.62-280749(1987), No.62-280750(1987) and No.62-280849(1987),etc.

In this method, a color image formed of dyes, which are produced imagewise from dye-forming couplers, is used as the image for proofing.

For the color image thus obtained, improvement in the final image quality and, especially, sharpness of the image and the improvement in the solid white portion are requested.

In order to improve these characteristics, in the negative-type light-sensitive color photographic material, a method of incorporating a water-soluble dye to absorb unnecessary ambient light has been known and, recently, a method of incorporating the water-soluble dye in the form of fin powder has been known. I the positivetype light-sensitive color photographic material, on the other hand, a method of providing an anti-halation layer containing black colloidal silver and a yellow filter layer containing yellow colloidal silver, and a method of using these and the above-mentioned water-soluble dye in combination have been known.

In these methods, however, in the case of incorporating a water-soluble dye, for example, there is a defect that sensitivity of a light-sensitive silver halide emulsion, which has sensitivity in the similar optical region as that of the dye, is lowered when a large quantity is incorporated for the purpose of improving sharpness. Further in the case of providing a layer containing colloidal silver, there is a defect that the white background is degraded due to incomplete removal of the colloidal silver during the process.

Especially in the case of a light-sensitive color photographic material used for a color proof, lack in the sharpness of the image often leads to deterioration in the reproduction of dot image, and deterioration of the white background due to incomplete removal of the colloidal silver can be a serious problem in the light of good final qualities. Recently, a color proof using a direct positive-type light-sensitive color photographic material has become popular, and in this respect demands for the final image quality by the user has become stricter. Thus still further improvement in the reproduction of the dot image and quality of the white background

55 is demanded.

Still further, as another method of improving reproduction of the dot, a method of providing a white pigmentcontaining layer has been known in, for example, Japanese Patent O.P.I. Publications No.58-60738(1983), No.62-187846(1987), etc.

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#### Summary of the Invention

In this method, although reproduction of the dot may be improved, however there has been a problem that the minimum density of the yellow portion tends to rise.

Accordingly, the object of the present invention is to provide a silver halide light-sensitive color photographic material having excellent reproduction property of dot and white background in the yellow image portion.

The silver halide light-sensitive color photographic material of the invention comprises a hydrophilic colloidal layer containing a white pigment provided on a support, and provided further thereon, a yellow dye imageforming silver halide emulsion layer, a green dye image-forming silver halide emulsion layer and a cyan dye image-forming silver halide emulsion layer; wherein amount of silver contained in the yellow dye image-forming silver halide emulsion layer is 0.48 g/m<sup>2</sup> or less.

The silver halide light-sensitive color photographic material of the invention preferably comprises a yellow dye-forming coupler represented by the following formula (Y-1) in the yellow dye image-forming layer.



In the formura, R represents an alkyl group or a cycloalkyl group; R2 represents an alkyl group, a cycloalkyl group or an aryl group; R3 represents a group which is capable of being substituted on the benzene ring and m represents an integer from zero to four; provided that when m is two or more, R3's may be either the same or different and z represents a hydrogen atom or a group which is capable of being split-off upon reaction with an oxidation product of a developing agent.

The other yellow dye-forming coupler preferably used in the invention is represented by the following formula (Y-II).



In the formula R<sub>1</sub> represents an alkyl group or a cycloalkyl group; R<sub>2</sub> represents an alkyl group, a cycloalkyl group, or an aryl group; R<sub>3</sub> represents an unsubstituted straight chain alkyl group and z represents a hydrogen atom or a group which is capable of being split-off upon reaction with an oxidation product of a developing agent.

 $\mathbb{Z}_1$ 

The silver halide light-sensitive color photographic material preferably comprises a compound represented by the formula (III) in the image-forming silver halide emulsion layer or the hydrophilic colloidal layer.

(III)

с́ с́— SM

OR<sub>2</sub>

NHCOR<sub>3</sub>

In the formula, M represents a hydrogen atom, an alkali metal atom, an ammonium group or a protective group for a mercapto group and z represents a group of non-metal atoms necessary to form a heterocycle.

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## **Detailed Description of the Invention**

In the present invention the amount of silver contained in the yellow dye image-forming silver halide emulsion layer is 0.48 g/m<sup>2</sup> or less. In the case where a hydrophilic colloidal layer containing a white pigment is provided, and when the amount of silver 0.48 g/m<sup>2</sup> or less, the white background will be sufficient for the use of a color proof. Preferably it is 0.25 g/m<sup>2</sup> or less and more preferably, 0.10 g/m<sup>2</sup> or less.

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Herein, the term "amount of silver" is used in terms of the total amount of silver when the color photographic material of the present invention comprises a plurality of yellow dye image-forming layers,

As the white pigment used in the present invention, for example, rutile-type titanate dioxide, anatase-type titan dioxide, barium sulfate, barium stearate, silica, alumina, zirconium oxide, caoline, etc. can be mentioned, however, for various reasons, titanium dioxide is preferable. The white pigment is dispersed in an aqueous solution such as aqueous gelatin solution. Coated amount of the white pigment is not less than one gram square meter and not more than 50 g/m<sup>2</sup> and especially, not more than 20 g/m<sup>2</sup>.

It is preferable that the hydrophilic colloidal layer containing the white pigment is provided between the support and a silver halide emulsion layer located nearest the support. Between the support and the silver halide emulsion layer located closest to the support, another appropriate layer such as a subbing layer or other non-light-sensitive intermediate hydrophilic layer may optionally be provided in addition to the layer containing the white pigment,

As for the reflective support used in the present invention, one, which comprises a raw paper as a basis and laminated thereon a polyolefin layer is preferable.

A white pigment such as titan oxide may be incorporated in the polyolefin resin.

In the present invention, it is preferable to comprises a high boiling point organic compound, of which boiling point is 150°C or more, and which is immiscible with water. The compound is contained in a hydrophilic colloidal layer containing the white pigment and/or a non-light-sensitive hydrophilic layer, which is located closest to the hydrophilic layer containing the white pigment on the same side of the support,

It may be a compound which is capable of being decomposed at the time of measurement of the boiling point, however it is advantageous that the compound is an organic solvent of which boiling point is higher than 300°C. Herein the term "boiling point" denotes that under one atomospheric pressure. Also, an organic high boiling point solvent, of which vapor pressure at 100°C is 0.5 mmHg or less, is preferable.

- 30 Examples of the high boiling point organic solvent which is immiscible with water, are phthalates, phosphates, aliphatic acid esters, organic acid amides, ketones, hydrocarbon compounds. Also, those organic compounds H-1 through H-20 disclosed on page 34 Of Japanese Patent O.P.I. Publication No.1-156748(1989) may be used.
- As the high boiling point organic compounds which are applicable in the present invention, are preferably those having 20 or more carbon atoms, which may be of branched or substituted by a substituent, and, more preferably, organic compounds having 24 or more carbon atoms, which may be either branched or substituted by a substituent,

Still more preferably, they are saturated hydrocarbon compounds, which may be either branched or substituted by a substituent.

Most advantageously, they are parafins.

Specific examples of the organic compounds preferably used in the present invention are herein below.

## Examples:

- 45 O-1: Di-n-octylphthalate
  - O-2: Di-i-decylphthalate
  - O-3: Tri-n-nonylphosphate
  - O-4: Di(ω-butyl-di(ethyleneoxy))adipate
  - o-5: Di-n-octylsebatate
- 50 O-6: Glycerin acetate
  - o-7; Di-n-octylfumarate
  - O-8: Trioctyl-trimellitate
  - O-9: Tridodecylphosphate
  - O-10: Trioctyl-phosphineoxide
- 55 0-11: n-hexadecane
  - O-12: n-eicosane
  - O-13: n-Docosane
  - O-14: n-tetracosane

O-15: n-hexacosane

O-16: Sansosizer E-200(Product of Shin-Nihon Rika, Co.,Ltd.

O-17: Sansosizer P-1500A(Product of Shin-Nihon Rika Co.,Ltd.

O-18 Fluid parafin No150S(product of Sanko Chemical Industries Co.,Ltd.)

Above-mentioned high boiling point organic compounds may be used either singly or in combination.

The above-mentioned high boiling point organic compound is added to the hydrophilic colloidal layer, after dispersing in , for example, an aqueous solution containing a hydrophilic binder such as gelatin together with an appropriate surface active agent, low boiling point organic solvent and/or water-soluble organic solvent, by the use of a stirring machine, a homogenizer, a flow-jet mixer, an ultrasonic mixing apparatus, etc. in accordance with necessity.

In the case when it is incorporated in the non-light-sensitive hydrophilic colloidal layer located near the support, gelatin is preferably used as the hydrophilic binder.

Amount of addition of the high boiling point organic compound is preferably in the proportion between 5 and 200 % by weight and, more preferably, between 10% and 100% by weight with respect to that of the binder incorporated in the hydrophilic colloidal layer.

Next, the compound represented by the formula (Y-I) is explained:



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 $R_1$  represents an alkyl group or a cycloalkyl group;  $R_2$  represents an alkyl group, a cycloalkyl group or an aryl group;  $R_3$  represents a group which is capable of being substituted on the benzene ring and m represents an integer from zero to four; provided that when m is two or more,  $R_3$ 's may be either the same or different and Z represents a hydrogen atom or a group which is capable of being split-off upon coupling reaction with an oxidation product of a developing agent.

In the Formula Y-I, as the alkyl group represented by  $R_1$ , it may be either of straight chained or branched, including ,for example, methyl group, ethyl group, i-propyl group, t-butyl group, n-dodecyl group and 1-hexyl-nonyl group. As the cycloalkyl group represented by  $R_1$ ,

for example, cyclopropyl group, cyclohexyl group, adamantyl group, etc. can be mentioned.

- 35 These alkyl group and cycloalkyl group may have a substituent, including, for example, a halogen atom such as chlorine atom, bromine atom, etc., a cyan group, a nitro group an aryl group such as phenyl group, pt-octylphenyl group, 2,4-di-t-amylphenyl group, etc.; a hydroxyl group, an alkoxyl group such as methoxy group, 2-ethoxyethoxy group, etc.; an aryloxy group such as phenoxy group, 2,4-di-t-amylphenoxy group, 4-(4-(hydroxyphenylsulfonyl)phenoxy group; a heterocyclicoxy group, such as 4-pyridyloxy group, 2-hexahydrophenyl-
- 40 pyranyloxy group, etc., a carbonyloxy group such as alkylcarbonyloxy group like acetyloxy group, pivaloyloxy group, etc.; aryloxy group like benzoyloxy group;etc.; sulfonyloxy group such as alkylsulfonyloxy group like methanesulfonyloxy group, trifluoromethanesulfonyloxy group, n-dodecanesulfonyloxy group, etc.;arylsulfonyloxy group like benzenesulfonyloxy group, p-toluenesulfonyloxy group, etc.; carbonyl group such as alkylcarbonyl group like acetyl group, pivaloyl group, etc.,;arylcarbonyl group like benzoyl group, 3,5-di-t-butyl-4-
- 45 hydroxybenzoyl group, etc.;; oxycarbonyl group such as alkoxycarbonyl group like methoxycarbonyl group, cyclohexyloxycabonyl group, dodecyloxycarbonyl group, etc.; aryloxycarbonyl group like 2,4-di-t-amylphenoxycarbonyl group; etc.; heterocyclicoxycarbonyl group like 2-pyridyloxycarbonyl group, 1-phenylpyrazolyl-5-oxycarbonyl group, etc.; carbamoyl group such as alkylcarbamoyl group like dimethylcarbamoyl group, 4-(2,4-dit-amylphenoxy)butylaminocarbonyl group, etc.; arylcarbamoyl group like phenylcarbamoyl group, 1-naphthyl-
- 50 carbamoyl group, etc.; sulfonyl group such as alkylsulfonyl group like methanesulfonyl group, trifluoromethanesulfonyl group, etc.; arylsulfonyl group like p-toluenesulfonyl group, etc.; sulfamoyl group such as alkylsulfamoyl group like dimethylsulfamoyl group,; arylsulfamoyl group like phenylsulfamoyl group, etc.; acylsulfamoyl group like acetylsulfamoyl group, ethylcarbonylaminosulfamoyl group, etc.; amino group such as alkylamino group like dimethylamino group, cyclohexylamino group, n-dodecylamino group, etc.; arylamino group
- <sup>55</sup> like anilino group, p-t-octylanilino group,; sulfonylamino group such as alkylsulfonylamino group like methanesulfonylamino group, heptafluoropropanesulfonylamino group, n-hexadecylsulfonylamino group, etc.; arylsulfonylamino group like p-toluenesulfonylamino group, pentafluorobenzenesulfonylamino group, etc.; acylamino group such as acetylamino group, myristoylamino group, etc.; arylcarbonylamino group such as benzoy-

lamino group, etc.; alkylthio group such as methylthio group, t-octylthio group, etc.; arylthio group such as phenylthio group, etc.; heterocyclicthio group such as 1-phenyltetrazole-5-thienylthio group, 5-methyl-1,3,4-oxadiazole-2-thio group, etc. can be mentioned.

R<sub>1</sub> is preferably an alkyl group, more preferably, an unsubstituted alkyl group and, most advantageously, methyl group.

As the alkyl group or the cycloalkyl group represented by  $R_2$  in the above-mentioned formula Y-I, for example, the same alkyl group and cycloalkyl group defined for  $R_1$  can be mentioned. Further as the aryl group represented by  $R_2$  in the formula Y-I, for example, phenyl group, 1-naphthyl group, etc. can be mentioned. These alkyl group, cycloalkyl group and aryl group represented by  $R_1$  in the formula Y-I, can have a substituent,

and as for the substituent, for example, the same alkyl or cycloalkyl group defined for  $R_1$  in the formula Y-I and the same substituents which are enumerated as the substituent for the alkyl and cycloalkyl groups for  $R_1$  can be mentioned.

R<sub>2</sub> is preferably an alkyl group, more preferably, an unsubstituted alkyl group and, most advantageously, methyl group.

As for the group which can be substituted on the benzene ring represented by  $R_3$  in the formula Y-I, for example the same groups enumerated as the substituent defined for  $R_2$  in formula (Y-I) can be mentioned.  $R_3$  is preferably an acylamino group, a sulfonylamino group, an oxycarbonyl group or a sulfamoyl group.

In the above-mentioned formula Y-I, m represents an integer from zero to four and when m is two or more  $R_3$ 's may be either same or different. m is preferably one.

In the formula Y-I, Z represents a group which is capable of being split off upon coupling reaction with a oxydation product of a developing agent and ,for example, represents the groups represented by the following formulae (12), (13) and (14):



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In the formulae (12) and (13),  $R_4$  represents an alkyl group, a cycloalkyl group, an aryl group or an aryl group.

As for the alkyl group, the cycloalkyl group and the aryl group represented by  $R_4$ , for example, the same alkyl, cycloalkyl and aryl groups defined for  $R_2$  in the above-mentioned formula Y-I can be mentioned. Further as for the heterocyclic group represented by the above-mentioned  $R^4$  in the formulae (12) and (13), 4-pyridyl group, 2-hexahydropyranyl group, etc. can be mentioned. These alkyl, cycloalkyl, aryl and heterocyclic groups represented by  $R^4$  in the above-mentioned formulae (12) and (13), 4-pyridyl group, 2-hexahydropyranyl group, etc. can be mentioned. These alkyl, cycloalkyl, aryl and heterocyclic groups represented by  $R^4$  in the above-mentioned formulae (12) and (13), can have a substituent, including, for example the same substituents, which are mentioned as substituents for the alkyl, cycloalkyl, aryl and hetero-

cyclic groups for defined for R<sub>2</sub>.in the formula Y-I.

Among those alkyl, cycloalkyl, aryl and heterocyclic groups represented by R<sub>4</sub>, aryl group is preferable.

Further as for the substituent for R<sub>4</sub>, an electron withdrawing group, for example, an oxycarbonyl group such as carboxyl group, methoxycarbonyl group or i-propyloxycarbonyl group, etc.; acyl group such as acetyl group, benzoyl group, etc.,; sulfonyl group such as trifluoromethanesulfonyl group, 4-hydroxyphenylsulfonyl group, etc.;nitro group; cyan group; halogen atom; sulfamoyl group such as dimethylsulfamoyl group; acylamino group such as acetylamino group, pentafluorobenzoylamino group; sulfonylamino group such as methanesulfonylamino group, etc. are preferable.

<sup>55</sup> In the above-mentioned formula (14), Z<sub>1</sub> represents a group of non-metal atoms necessary to form a fivemembered or a six-membered ring. Herein as for the group of atoms necessary to form the non-metal atomic group, for example, methylene, methine, -C(O)-, -N(R<sub>5</sub>)-,wherein R<sub>5</sub> represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group, -N=, -O-, -S(O)u, wherein, u represents an integer of zero, one or two, etc. can be mentioned.

(15)

Among those compounds represented by the above-mentioned formula Y-I, preferable one is a compound represented by the formula (15) shown below:

ORa



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In the above-mentioned formula (15),  $R_1$  and  $R_2$  independently represent the same groups defined for  $R_1$  and  $R_2$  in the above-mentioned formula (I).

R1COCHCONH

 $\mathbb{Z}_2$ 

In the above-mentioned formula (15), W is a group represented by the formula (16) given below: In the above-mentioned formula (15,  $Z_2$  represents the same group defined for Z represented by the abovementioned formula (Y-I).

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(16) -NH-X(L-Y) $\pi$ R<sub>6</sub>

In the above-mentioned formula (16), X represents a carbonyl group or a sulfonyl group and, preferably, it represents a carbonyl group.

In the above-mentioned formula (16), L represents an alkylene group or an arylene group, including, for example, straight-chain or branched alkylene group such as methylene group, ethylene group, 2,3-propylene group and 1,2-cyclohexylene group, 1,4-phenylene group, 1,2-naphthylene group, 9,10-anthranylene group, etc. can be mentioned. Among these groups, preferable ones are alkylene groups having one to six carbon

atoms.

In the above-mentioned formula (16), Y represents a divalent connecting group, including, for example, sulfinyl group, sulfenyl group, sulfonyl group, sulfamoyl group, carbonyl group, carbonyloxy group, carbamoyl

group, oxy group, oxycarbonyl group, amino group, acylamino group and sulfonylamino group, etc. can be mentioned. Among these connecting groups, preferable ones are sulfonyl group, sulfamoyl group, carbonyloxy group, carbamoyl group, oxy group, oxycarbonyl group and acylamino groups, and particularly preferable ones are sulfonyl group, oxy group, oxycarbonyl group, and carbamoyl group.

In the above-mentioned formula (16), n represents zero or one.

<sup>35</sup> In the above-mentioned formula (16),  $R_6$  represents an alkyl group, a cycloalkyl group or an aryl group. As for the alkyl, cycloalkyl and aryl groups, for example, the same alkyl, cycloalkyl and aryl groups defined for  $R_2$  in the above-mentioned formula (Y-I) can be mentioned. These alkyl, cycloalkyl and aryl group can have a substituent and as for the substituent, for example, the same groups defined as the substituent for the alkyl, cycloalkyl and aryl groups represented by  $R_2$  in the above-mentioned formula (Y-I).

In the above-mentioned formula (15), the substituent represented by  $Z_2$ , is, preferably, a substituent represented by the formula(17), (18), (19), (20),(21) and (22) shown below:





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In the above-mentioned formulae (17), (18), (19), (20).and (21),  $R_7$ ,  $R_8$  and  $R_9$  independently represent a group which is capable of being substituted on the azole ring and, for example, the same groups mentioned as the substituent for the alkyl, cycloalkyl and aryl groups represented by  $R_2$  in the above-mentioned formula (I) can be mentioned.

In the above-mentioned formula (21).  $R_{10}$  represents, for example, the same alkyl, cycloalkyl and aryl groups defined for  $R_4$  in the above-mentioned formulae (12) and (13).

In the above-mentioned formulae (20) and (21), Z3 represents the same group defined for  $R_5$  in the abovementioned formula (16), -O- and  $-S(0)_v$ -, wherein v represents an integer of zero, one or two.

In the above-identified formula (22), Y<sub>1</sub> represents -(R<sub>12</sub>)-,wherein R<sub>12</sub> represents the same group defined for R<sub>5</sub> in the above-identified formula (16), -o-, or a hetero atom represented by -S(O)<sub>r</sub>-,wherein r represents an integer of zero, one or two, etc., -C(O)-, -C(R<sub>13</sub>) (R<sub>14</sub>)-,wherein R<sub>13</sub> and R14 independently represent a hydrogen atom, or the same group defined as a substituent for the alkyl, cycloalkyl and aryl groups represented by R<sub>2</sub> in the above-identified formula (Y-I), or -C(R<sub>15</sub>)-,wherein R<sub>15</sub> represents a hydrogen atom or the same group as a substituent the alkyl, cycloalkyl and aryl groups represented by R<sub>2</sub> in the above-identified formula (Y-I).

(Y-I), etc.

In the above-identified formula (22),  $Z_4$  represents a group of non-metal atoms necessary to form a fivemember or sic-member ring in cooperation with -Y<sub>1</sub>-N-CO-. Herein, as for the atomic group necessary to form

a non-metal atom group, for example, the same atomic group defined for one represented by Z1 in the aboveidentified formula (16) can be mentioned.

Hereinbelow, representative examples of the yellow dye-forming coupler used in the present invention are given:

Next, yellow dye-forming coupler represented by the formula (Y-II) is explained:

OR<sub>2</sub> 10 R1COCHCONH  $\mathbf{Z}_1$  $R_3$ 15 20 25 30 35 40 45 50 55

EP 0 671 657 A2

	No.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Z
	(Y-I-1)	t-C₄H <sub>9</sub>	CH₃	(d)	(A)
5	(Y-I-2)	t-C₄H <sub>9</sub>	CH₃	(c)	(A)
	(Y-I-3)	t-C₄H <sub>9</sub>	CH₃	(d)	(B)
	(Y-I-4)	t-C₄H <sub>9</sub>	CH₃	(d)	(D)
10	(Y-I-5)	t-C₄H <sub>9</sub>	CH₃	(f)	(E)
	(Y-I-6)	t-C₄H <sub>9</sub>	CH₃	(d)	(G)
	(Y-I-7)	t-C₄H <sub>9</sub>	CH₃	(k)	(H)
15	(Y-I-8)	t-C₄H <sub>9</sub>	CH₃	(c)	(L)
	(Y-I-9)	t-C₄H <sub>9</sub>	CH₃	(g)	(H)
	(Y-I-10)	t-C₄H <sub>9</sub>	CH₃	(t)	(H)
20	(Y-I-11)	t-C₄H <sub>9</sub>	CH₃	(h)	(H)
	(Y-I-12)	t-C₄H <sub>9</sub>	CH₃	(i)	(A)
	(Y-I-13)	t-C₄H <sub>9</sub>	CH₃	(i)	(A)
25	(Y-I-14)	t-C₄H <sub>9</sub>	CH₃	(I)	(A)
	(Y-I-15)	t-C₄H <sub>9</sub>	CH₃	(i)	(N)
	(Y-I-16)	t-C₄H <sub>9</sub>	CH₃	(h)	(N)
30	(Y-I-17)	t-C₄H <sub>9</sub>	CH₃	(u)	(L)
	(Y-I-18)	t-C₄H <sub>9</sub>	CH₃	(e)	(M)
	(Y-I-19)	t-C₄H <sub>9</sub>	CH₃	(j)	(J)
35	(Y-I-20)	t-C₄H <sub>9</sub>	CH₃	(m)	(A)
	(Y-I-21)	t-C₄H <sub>9</sub>	CH₃	(o)	(A)
	(Y-I-22)	t-C₄H <sub>9</sub>	CH₃	(p)	(P)
40	(Y-I-23)	t-C₄H <sub>9</sub>	CH₃	(d)	(P)
	(Y-I-24)	t-C₄H <sub>9</sub>	CH₃	(d)	(Q)
	(Y-I-25)	t-C₄H <sub>9</sub>	CH₃	(0)	(Q)
45	(Y-I-26)	t-C₄H <sub>9</sub>	CH₃	(r)	(K)
	(Y-I-27)	t-C₄H <sub>9</sub>	CH₃	(o)	(K)



	No.	$R_1$	R <sub>2</sub>	R <sub>3</sub>	Z
	(Y-I-28)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(a)	(S)
5	(Y-I-29)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(g)	(T)
	(Y-I-30)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(k)	(T)
	(Y-I-31)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(n)	(U)
10	(Y-I-32)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(g)	(W)
	(Y-I-33)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(1)	(W)
	(Y-I-34)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(i)	(X)
4 E	(Y-I-35)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(u)	(N)
15	(Y-I-36)	t-C4H9	CH <sub>3</sub>	(s)	(Y)
	(Y-I-37)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(0)	(Z)
	(Y-I-38)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(t)	(B)
20	(Y-I-39)	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	(w)	(R)
25	(Y-I-40)	t-C₄H9	$ CH_3$ $ C_5H_{11}(t)$	(h)	(A)
	(Y-I-41)	t−C₄H9	) C <sub>5</sub> H <sub>11</sub> (t)	(c)	(H)
30	(Y-I-42)	t-C <sub>4</sub> H <sub>9</sub>	$-CH_2COOC_{12}H_{25}(n)$	(g)	(Z)
	(Y-I-43)	t−C <sub>4</sub> H <sub>9</sub>	$\neg $	(d)	(À)
35	(Y-T-44)		CHa	(a)	(H)
	(Y - T - 45)	t-CAHo	C16H33	(q) (d)	$(\alpha)$
	(Y - T - 46)	t-C4H0	CH2	(c)	(α)
40	(Y - T - 47)		CHa	(v)	(107)
	(1 1 47)	C C4119	CIIS	(A)	(**)
45		O - CH <sub>3</sub>			0
	CH	3	$CH_3$ $CH_3$		CH <sub>3</sub>

(A:128)

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(B:128) (C:114)







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 $\begin{array}{c} -\text{NHCOC}_{11}\text{H}_{23}(n) & -\text{NHCOC}_{13}\text{H}_{27}(n) & -\text{NHCOC}_{15}\text{H}_{31}(n) \\ & (a) & (b) & (c) \end{array}$ 

 $-NHCOC_{17}H_{35}(n) -NHCOC_{19}H_{39}(n) -NHCOC_{21}H_{43}(n)$ 55 (d) (e) (f)





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R<sub>1</sub> represents an alkyl group or a cycloalkyl group; R<sub>2</sub> represents an alkyl group, a cycloalkyl group or an aryl group and R3 represents a straight-chain unsubstituted alkyl group; Z1 represents a hydrogen atom or a
 group which is capable of being split-off upon coupling reaction with an oxidation product of a developing agent provided that R<sub>1</sub>, R<sub>2</sub> and Z<sub>1</sub> may be substituted.

NHCOR<sub>3</sub>

As for the alkyl group represented by  $R_1$  in the formula (Y-II),for example, straight chain or branched alkyl group such as methyl group, ethyl group, i-propyl group, t-butyl group, dodecyl group, 1-hexylnonyl group, etc. can be mentioned. As for the cycloalkyl group represented by  $R_1$ , for example, cyclopropyl group, cyclohexyl group, adamantyl group, etc. can be mentioned.

These alkyl group and cycloalkyl group can have a substituent, and as for such substituent, for example, a halogen atom such as chlorine, bromine, etc.; cyan group, nitro group, aryl group such as phenyl, p-t-octyl-phenyl, 2,4-di-t-amylphenyl, etc.; hydroxyl group, alkoxy group such as methoxy, 2-ethoxyethoxy, etc.; aryloxy

group such as phenoxy, 2,4-di-t-amylphenoxy, 4-(4-hydroxyphenylsulfonyl) phenoxy, etc.; heterocyclicoxy group such as 4-pyridyloxy, 2-hexahydropyranyloxy, etc.; carbonyloxy group, such as alkylcarbonyloxy group like acetyloxy, pivaroyloxy, etc.; aryloxy group like benzoyloxy, etc.; sulfonyloxy group such as alkylsulfonyloxy group group like methanesulfonyloxy, trifluoromethanesulfonyloxy, dodecanesulfonyloxy, etc.; arylsulfonyloxy group

- 5 like benzenesulfonyloxy, p-toluenesulfonyloxy, etc.; carbonyl group such as alkylcarbonyl group like acetyl, pivaloyl, etc.; arylcarbonyl group like benzoyl, 3,5-di-t-butyl-4-hydroxybenzoyl, etc.; oxycarbonyl group such as alkoxycarbonyl group; like methoxycarbonyl, cyclohexyloxycarbonyl, dodecyloxycarbonyl, etc.; aryloxycarbonyl group like 2,4-di-t-amylphenoxycarbonyl, etc.; heterocyclicoxycarbonyl group like 2-pyridyloxycarbonyl, 1-phenylpyrazolyl-5-oxycarbonyl, etc.;carbamoyl group such as alkylcarbamoyl group like dimethylcarbamoyl,
- 10 4-(2,4-di-t-amylphenoxy) butylaminocarbonyl, etc.; arylcarbamoyl group like phenylcarbamoyl, 1-naphthylcarbamoyl, etc.; sulfonyl group such as alkylsulfonyl group like methanesulfonyl, trifluoromethanesulfonyl, etc.; arylsulfonyl group like p-toluenesulfonyl, etc.; sulfamoyl group such as alkylsulfamoyl group like dimethylsulfamoyl, 4-(2,4-di-t-amylphenoxy) butylaminosulfonyl, etc.; arylsulfamoyl group like phenylsulfamoyl, etc.; acylsulfamoyl group like acetylsulfamoyl, ethylcarbonylaminosulfonyl, etc.; amino group such as alkylamino group
- 15 like dimethylamino, cyclohexylamino, dodecylamino, etc.; arylamino group like anilino, p-t-octylanilino, etc.; sulfonamido group such as alkylsulfonamido group like methanesulfonamide, heptafluoropropanesulfonamido, hexadecylsulfonamido, etc.; arylsulfonamido like p-toluenesulfonamido, pentafluorobenzenesulfonamido, etc.; acylamino group such as alkylcarbonylamino group like acetylamino, myristoylamino, etc.; arylcarbony-lamino group like benzoylamino, etc.; alkylthio group such as methylthio, t-octylthio, etc.; arylthio group such
- 20 as phenylthio, etc.; heterocyclicthio group such as 1-phenyltetrazole-5-thio, 5-methyl-1,3,4-oxadiazole-2-thio, etc. can be mentioned.

R<sub>1</sub> is preferably an alkyl group and, more preferably, a branched alkyl group and, especially t-butylalkyl group.

As for the alkyl group or the cycloalkyl group represented by R<sub>2</sub>, for example, the same alkyl and cycloalkyl groups defined for R1 can be mentioned. Further as for the aryl group represented by R<sub>2</sub>, for example, phenyl group, 1-naphthyl group, etc. can be mentioned. These alkyl group, cycloalkyl group and aryl group represented by R1 can have a substituent, which includes, for example, the same groups enumerated for the alkyl and the cycloalkyl groups represented by R1 and the same groups enumerated for the substituent for the alkyl or the cycloalkyl group represented R<sub>1</sub>.

 $R_2$  is preferably an alkyl group and, especially, methyl group.

As for the atom or the group represented by  $Z_1$ , which is capable of being split-off upon coupling reaction with the oxidation product of the developing agent, for example, a nitrogen-containing heterocyclic group, an aryloxy group, an arylthio group, a heterocyclicoxy group. a heterocyclicthio group, an acyloxy group, a carbamoyloxy group, an alkylthio group or a halogen atom can be mentioned.

<sup>35</sup> When  $Z_1$  represents the nitrogen-containing heterocyclic group, in which  $Z_1$  is connected with the coupling position through the nitrogen atom, this nitrogen-containing heterocyclic group of a five membered or six-membered, saturated or unsaturated, monocyclic or polycyclic group having 1 - 15, and, more preferably, 1 - 10 carbon atoms.

As for the hetero atom, it may contain an oxygen atom or a sulfur atom other than the nitrogen atom..

As for preferable specific compound, for example, 1-pyrazolyl group, 1-imidazolyl group, pyrrolino group, 1, 2, 3-triazole-2-il group, 1.2.3-triazole-1-il group, benztriazolyl group, benzimidazolyl group, imidazolidine2,4-dione-3-il group, oxazolydine-2,4-dione-3-il group, 1,2,4-triazolidine-3.5-dione-4-il group, imidazolydine-2,4,5-trione-3-il group, 2-imidazolinone-2,4,5-trione-3-il group, 2-imidazolinone-1-il group, 3,5-dioxomorpholino- or 1-indazolyl group can be mentioned. When these heterocyclic group have a substituent, there

- 45 is no specific limitation as to the substituent, however, as the preferable substituent, at least one of the substituents includes, for example, an alkyl group, an alkoxy group, a halogen atom, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkylthio group, an acylamino group, a sufonamido group, an aryl group, a nitro group, a carbamoyl group, a cyano group or a sulfonyl group.
- When Z1 represents an aryloxy group, it is preferably a substituted or an unsubstituted aryloxy group( con taining 6-10 carbon atoms, and, more specifically, substituted or unsubstituted phenoxy group. When it has a substituent, it preferably has at least one electron withdrawing substituent such as a sulfonyl group, an al koxycarbonyl group, a sulfamoyl group, a halogen atom, a carbamoyl group, a nitro group, a cyano group or an acyl group.

When Z<sub>1</sub> represents an arylthio group, it preferably is a substituted or unsubstituted arylthio group containing six to ten carbon atoms, particularly preferably, it is a substituted or unsubstituted phenylthio group. When it has a substituent, it preferably has, as the substituent at least one alkyl group, alkoxy group, sulfonyl group, alkoxycarbonyl group, sulfamoyl group, a halogen atom, carbamoyl group or a nitro group.

When Z<sub>1</sub> represents a heterocyclicoxy group, it preferably has one to 20 and, more preferably, one to ten

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carbon atoms.

It contains as a hetero atom, at least one nitrogen, oxygen or sulfur atom. The heterocyclic ring preferably consists of three to 12 and, more preferably five or six members. The heterocyclic ring may be one which is either substituted or unsubstituted and which is of monocyclic, polycyclic or a fused cyclic group.

- As for the example of such heterocyclicoxy group, for example, pyridyloxy group, pyrazolyloxy group and furyloxy group can be mentioned. When it has a substituent, at least one of the substituent is an alkyl group, an aryl group, a carboxyl group, an alkoxy group, a halogen atom, a carboxycarbonyl group, an aryloxycarbonyl group, an alkylthio group, an acylamino group, a sulfonamide group, a nitro group, a carbamoyl group or a sulfonyl group.
- 10 When Z<sub>1</sub> represents an acyloxy group, this acyloxy group is a monocyclic or fused cyclic group, containing six to ten carbon atoms. Further, it may be either substituted, or unsubstituted, and either of an aromatic or of an aliphatic

When  $Z_1$  represents a carbamoyloxy group, thiocarbamoyloxy carbamoyloxy group is preferably one which contains one to 30 and, more preferably, one to 20 carbon atoms, is of an aliphatic or aromatic, and is substituted or unsubstituted carbamoyloxy group, which may further have a substituent.

For example, N,N-diethylcarbamoyloxy group, N-phenylcarbamoyloxy group, 1-imidazolylcarbonyloxy group, tc. can be mentioned.

When Z<sub>1</sub> represents an alkylthio group, this alkylthio group is one, which contains one to 30 and, more preferably one to 20 carbon atoms, is of an aliphatic or aromatic, and is substituted or unsubstituted alkylthio group, which may further have a substituent.

Among those groups represented by  $Z_1$ , preferable ones are those represented by the following formulae (26), (27) and (28):



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In the formulae(26) and(27), R<sub>4</sub> represents an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group. As for the alkyl group, cycloalkyl group and aryl groups represented by R<sub>4</sub>, for example, the same groups defined as alkyl, cycloalkyl and aryl groups represented by R<sub>2</sub> in the above-identified formula (Y-II) can be mentioned. As for the heterocyclic group represented by R<sub>4</sub>, 4-pyridyl group, 2-hexahydropyranyl group, etc. can be mentioned. These alkyl, cycloalkyl, aryl and heterocyclic groups may have a substituent and as for the substituent, for example, the same groups mentioned as the substituent for the alkyl, cycloalkyl and aryl groups represented by R<sub>2</sub> in the above-identified formula (Y-II) can be mentioned.

Among these alkyl, cycloalkyl aryl and heterocyclic groups, represented as R<sub>4</sub>, aryl group is preferable. Further as for the substituent for R<sub>4</sub>, an electron withdrawing group such as carboxyl group, oxycarbonyl group like methoxycarbonyl, i-propyloxycarbonyl group, etc.; an acyl group like acetyl or benzoyl, etc.; a sulfonyl group like trifluoromethanesulfonyl, 4-hydroxyphenylsulfonyl, etc.; a nitro group; a cyano group; a halogen atom; a sulfamoyl group like dimethylsulfamoyl; an acylamino group like acetylamino, pentafluorobenzoyla-

mino, etc. and a sulfonamide group like methanesulfonamide; etc. are preferable.

In the above-identified formula (28), X2, represents a group of non-metal atoms necessary to form a fivemembered or six-membered ring. Herein as for the group of non-metal atoms necessary to form a non-metal atom group, for example, methylene, methine, substituted methine, -CO-,  $N(R_5)$ -,wherein  $R_5$  is a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, -N=, -O- and-S(O)u-, wherein u represents an integer

50 atom, an alkyl group, an aryl group, a heterocyclic group, -N=, -O- and-S(O)u-, wherein u represents of zero, one or two, can be mentioned.

particularly preferable group as  $Z_1$  is a group represented by the following formula (29):

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- In the above-identified formula (29),Y<sub>1</sub> represents a hetero atom represented by-N(R<sub>6</sub>)-,wherein R<sub>6</sub> represents the same group defined as R<sub>6</sub> in the above-identified formula (28), -O-, or -S(O)<sub>r</sub>-, wherein r represents an integer of zero one or two; -C(O)-, -C(R<sub>7</sub>)(R<sub>8</sub>),wherein R<sub>7</sub> and R<sub>6</sub> independently represent a hydrogen atom, or the same groups defined for the substituent of alkyl, cycloalkyl and aryl groups for R<sub>7</sub> in R<sub>2</sub> in the aboveidentified formula (26) and -CR<sub>9</sub>)-(R<sub>9</sub>), wherein R<sub>9</sub> represents a hydrogen atom, or the same groups as the substituent for the alkyl, cycloalkyl and aryl group represented by R<sub>2</sub> in the above-identified formula (Y-II).
- <sup>15</sup> Further X<sub>3</sub> represents a group of non-metal atoms necessary to form a five-membered or six-membered cyclic ring together with a  $-Y_1$ -N-CO- group. Herein, as the group of atoms necessary to form the non-metal atoms, for example, the same atomic group defined for the group represented by X<sub>2</sub>.
- R<sub>3</sub> represents an alkyl group and, preferably, a straight chain alkyl group containing 11 to 21 carbon atoms.
   Representative examples of the yellow dye-forming coupler represented by the formula (Y-II) are shown
   below:



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	No.	R <sub>1</sub>	R <sub>2</sub> F	R <sub>3</sub>	Z <sub>1</sub>
5	Y-II-9	t-C4H9	CH <sub>3</sub>	C <sub>19</sub> H <sub>39</sub>	
10 15	Y-II-10	t-C₄H9	CH3	C <sub>15</sub> H <sub>31</sub>	-0-     SO2-     *       *OCH2-     *
20	Y-II-11	t-C₄H9	C <sub>16</sub> H <sub>33</sub>	C <sub>15</sub> H <sub>31</sub>	$N \rightarrow N$ $N \rightarrow N \rightarrow CH_3$
	Y-II-12	t-C₄H9	CH2COOC12H2	5 C <sub>15</sub> H <sub>31</sub>	
25	Y-II-13	t-C₄H9		C <sub>17</sub> H <sub>31</sub>	
30	Y-II-14	t-C₄H9	CH <sub>3</sub>	C <sub>17</sub> H <sub>31</sub>	-0-COOC <sub>3</sub> H <sub>7</sub> (i)
35	Y-II-15	$\square$	CH3	C <sub>13</sub> H <sub>27</sub>	$C_{4H_9} - N - CH_3$

40 Next, the compound represented by the formula (III) is explained:

(III)

<u>,</u>È−SM

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Herein, m represents an alkaline metal atom, an ammonium group or a protective group for mercapto group;
Z represents a group of non-metal atoms necessary to form a heterocyclic ring. Of course, the heterocyclic ring may have a substituent and it may be fused.) As for the protective group for the mercapto group, for example, a group which opens the ring with alkali and form a mercapto group and, more specifically, acyl group, arkoxycarbonyl group, alkylsulfonyl group, etc. can be mentioned.

As for the nitrogen-containing heterocyclic group, it may also contain in the ring a carbon atom, a nitrogen atom, an oxygen atom, a sulfur atom, a selenium atom as a constituent for the ring, and a five-member or sixmember ring is preferable.

As for the specific examples for the nitrogen-containing heterocyclic group, imidazole, benzimidazole, naphthoimidazole, thiazole, thiazole, benzthiazole, naphthothiazole, oxazole, benzoxazole, naphthoxazole,

selenazole, benzselenazole, naphthoselenazole, triazole, benztriazole, tetrazole, oxadiazole, thiadiazole, pyridine, pyrimidine, triazine, purine, azaindene, etc. can be mentioned.

 $R^{21}-Ar-N$  N  $N \sim N$   $N \sim N$ 

SM

As for the substuent which these heterocyclic group can have, for example, a halogen atom, a hydroxyl group, an amino group, a nitro group, a mercapto group, a carboxyl group or a salt thereof, a sulfo group or a 5 salt thereof, an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an alkylthio group, an arylthio group, an acylamino group, a sulfonamide group, a carbamoyl group, a sulfamoyl group, etc.. can be mentioned. Among those compounds shown as the formula (III), those which t are particularly preferably used in the present invention can be given in the following formulae (31), (32) and (33):

(31)

(32)

(33)

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In the formulae (31) through (33), M has the same definition as M in the formula (III): R<sub>21</sub> and R<sub>22</sub> independently represent an atom or a group which is capable of being substituted on the benzene ring: Ar represents a phenyl group: R23 represents an atom or a group selected from the group consisting of halogen atoms, a hydroxyl group, an amino group, a nitro group, a mercapto group, a carboxyl group or a salt thereof, an alkyl

35 group, an alkoxy group, an aryl group, an aryloxy group, an alkylthio group, an arylthio group, an acylamino group, a sulfonamino group, a sulfonamide group and a carbamoyl group, etc. and Z<sub>21</sub> and Z22 independently represent an oxygen atom, a sulfur atom ore an -NH- group.

As for the specific examples of the compound represented by the formula (III), for example those exemplified compounds (1) through (39) on pages 11 through 15 of Japanese Patent O.P.I.. Publication No.64-73338(1989) can be mentioned.

These compounds may be synthesized according to the manner, which is conventionally well-known in the art. For example, they may be prepared according to the methods disclosed in U.S. Patents No. 2,403,927 and No.3,476,310; Japanese Patent O.P.I. Publication No. 55-59463(1980), description on page 4237 in The Journal of Chemical Society (1952), etc. can be mentioned. Further, some of the compounds may be available

as products on the market. 45

> The compound represented by the formula (III) can be incorporated in the light-sensitive material by dissolving in water or in an organic solvent which is soluble or miscible with water such as methanol, acetone, etc., or dissolving in a weak alkaline or weak acid solution. Quantity of addition of the compound may be varied depending on the nature of the compound or the layer, to which the compound is to be incorporated and, in general, within a range between 1 x 10-8 and  $1 \times 10^{-2}$  mols a mol of silver halide and, more preferably, not

less than  $1 \times 10^{-6}$  and not more than  $1 \times 10^{-3}$  mols.

As for the silver halide emulsion used in the present invention, a so-called surface latent image-type silver halide emulsion, in which a latent image is formed on the surface of the silver halide grains by exposure and a negative image is formed by development, may be used.

Also, it is possible to use so-called an internal latent image-type silver halide emulsion, with which a positive-type image is formed using silver halide emulsion containing so-called an internal latent image-type silver halide grains, the surface of the silver halide crystals is not fogged beforehand, undergoing fogging process, or nucleation process, and, after imagewise exposure, carrying out surface development, while undergoing

the fogging process, thus to form a positive image directly, may also be used.

The above-mentioned fogging process may be carried out either by giving an overall exposure, or it may be done using a chemical process by the use of a fogging agent. Herein the term "the emulsion containing internal latent image-type silver halide grains" is used in terms of a silver halide emulsion containing silver halide crystals which have light-sensitive specs mainly inside the silver halide crystals, and a latent image is

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formed inside the crystal by exposure. In the technical field of this internal latent image-type direct positive silver halide emulsion, various techniques have been heretofore known. For example, methods disclosed in U.S. Patents No.2,592,250, No.2.466,957, No.2,497.875, No.2,588,982, No.3,761,276, No.3,796,577 and British Patent No.1,151,363, etc.

10 are known.

Mechanism of the positive image-formation is not necessarily clear, however, for example, on page 158, Vol. 20(1976) of "The Photographic Science and Engineering" it is described as follows:

"Photo-electrons which are generated inside the silver halide crystal are selectively trapped inside the crystal and thus the internal latent image is formed. Since this internal latent image works as effective trapping center for the electrons present in the conduction band and, therefore, in the exposed grains, electrons which are injected thereafter are trapped within the crystal and intensify the latent image. In this case since the latent image is inside the crystal, it is not developed by the surface development. In the crystals which were not subjected to exposure, at least a part of electrons are trapped on the surface of the crystal and forms a latent image is formed there, and thus the crystal is developed by the surface development.

20 The internal latent image-type silver halide emulsion containing silver halide crystals, which are not subjected to fogging beforehand and is used in the present invention, is a type of emulsion, in which a latent image is formed mainly inside the silver halide crystal and has most of sensitive specks inside the grain. This type of silver halide emulsion includes optional types of silver halide, for example, silver bromide, silver chloride, silver chlorobromide, silver iodochloride, silver iodobromide, silver iodochlorobromide, etc.

25 Particularly, when a portion of a sample, which was prepared so that the total amount of silver coated on a transparent support is not less than one gram and not more than 3.5 grams a square meter is exposed for a predetermined period of time, not shorter than 0.1 seconds and not longer than one second. through an optical wedge and then developed with a surface developing solution A, which does not substantially contain a silver halide solvent and whose composition is given hereinbelow, at 20°C for four minutes, gives the maximum

30 density not exceeding one tenth that of the another portion of the same sample. The silver halide emulsion which is particularly advantageously applicable to the present invention is such an emulsion, which gives the maximum density not exceeding one tenth that of the another portion of the same sample, when it is exposed for a predetermined period of time, not shorter than 0.1 seconds and not longer than one second through an optical wegde and then developed with an internal developing solution B at 20°C for four minutes still more

35 preferably.

r		
	Metol	2.5 g
	L-ascorbic acid	10.0 g
	Sodium metaborate tetrahydrate	35.0 g
	Potassium bromide	1.0 g
	Add water to make the total volume	1000 ml

## (Surface Developing Agent A)

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(Internal Developing Solution B)

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Metol	2.0 g
Sodium sulfate unhydrite	90.0 g
Hydroquinone	8.0 g
Sodium carbonate unhydrite	52.5 g
potassium bromide monohydrite	5.0 g
Potassium iodide	0.5 g
Add water to make the total volume	1000 ml

- <sup>15</sup> Further the internal latent image-type silver halide emulsion includes those prepared in a variety of methods, including, for example, a conversion-type silver halide emulsion disclosed in U.S. Patent No. 2,592,250; silver halide emulsion containing silver halide grains which are internally sensitized; as disclosed in U.S. Patents No. 3,206.316; No.3,317,322 and No.3,367,778; a silver halide emulsion containing silver halide grains containing a polyvalent metal ion; as disclosed in U.S. Patent No.3,271,157; No.3,447,927 and No.3, 20
- <sup>20</sup> 53,53,291; silver halide emulsion containing silver halide grains containing a doping agent as disclosed in U.S. Patent No.3,761,276; a silver halide emulsion containing silver halide grains, consisting of laminated layers as disclosed in Japanese Patent O.P.I. publications No.50-8524(1975), No.52-156614(1977), No.53-2408(1978),etc. and those silver halide emulsions disclosed in Japanese Patent O.P.I. publications No.50-8524(1975), No.52-156614(1977), No.53-156614(1977), No.55-127549(1980), etc.

The internal latent image-type silver halide grain may be made of any optional silver halide compositions, for example, silver bromide, silver chloride, silver chlorobromide, silver iodochloride, silver iodobromide and silver chloroiodobromide.

Among theses, one containing silver chloride has superior in the developmental performance, and is more suitable for rapid processing.

The shape of the silver halide grain used in the present invention is optional, including cubic, octahedral, tetradecahedral which consists of a mixture of (100) planes and (111) planes, a shape containing (110) plane, spherical and tabular. Average grain size of the silver halide grain is preferably between 0.05 and 3 microns. As regards grain size distribution, it my be either so-called a mono disperse emulsion, in which size and shape of the grain is uniform or vice-versa. In the present invention the former is preferable. In the present invention

- <sup>35</sup> the term "mono-disperse silver halide emulsion" denotes one in which more than 60%, more preferably more than 70% and, still more preferably, more than 80% by weight of the total weight of the silver halide grains contained in the silver halide emulsion has its grain size 20 % around. Herein, the average grain size r<sub>m</sub> is defined as the grain size r<sub>i</sub>, when the product of frequency ni of a gain having the grain size ri and the third power
- thereof, ni x r<sub>i</sub><sup>3</sup> becomes the maximum value, wherein, the significant figure is given in three digits and the figure at the minimum digit is rounded off. The term "grain size" is given as the diameter of the grain, when the silver halide grain has a spherical shape. When the silver halide crystal has a shape other than spherical, it is given as the diameter of a circle, when the grain is projected and the projected image is converted into a circle having equivalent projection area. The grain size can be obtained by actually measuring the diameter or the area of the projected image of a grain when it is photographed with the use of an electron microscope
- <sup>45</sup> and, then, printed at a magnification rate of 10,000 to 50,000. Herein the number of grains to be measured are indiscriminately 1000 or more.
  - Particularly preferable mono-disperse emulsion is one having a coefficient of variation, which is given in the following equation, of 20% or less.

(Standard Deviation of Grain Size)/(Average Grain Size) x 100 = Coefficient of variation(%). Herein the average grain size and the standard deviation are obtainable from above-defined  $r_i$ .

The mono-disperse emulsion can be obtained by adding an aqueous solution containing silver salt and an aqueous solution containing halide into an aqueous gelatin solution containing seed grains by double-jet mixing process, while controlling pAg and pH of the solution, for example, descriptions in Japanese Patent O.P.I.. Publication No.54-48521(1984) and, No.58-49938(1983)can be referred

As a method of obtaining a mono-disperse emulsion having higher mono-dispersity, for example, techniques disclosed in Japanese Patent O.P.I. Publication No.60-122935(1985), in which development of the silver halide crystal is performed in the presence of a tetrazaindene compound.

Next gelatin used in the present invention is explained:

Gelatin usually comprises various kinds of heavy metals such as iron, copper, zinc, mangan, etc. as impurities, and, generally it comprises 5 to 20 ppm of iron ion.

The iron content of iron and iron ion contained in the gelatin contained in the light-sensitive material of the present invention, is preferably less than 5 ppm and, more preferably, less than 3 ppm.

The iron content of the gelatin used in the present invention is the content of iron and iron ion contained in the gelatin, and is measured based on the method described in the "Baggy's method" published by the Joint Counsel for Measurements of the Photographic Gelatin", Vol. 6 (published in October 1987).

When a plurality of different kinds of gelatin is incorporated in the light-sensitive material of the present invention, average value of the total iron content contained in the light-sensitive material, i.e., weight ratio of iron contained in the total gelatin against the total weight of gelatin contained in the light-sensitive material.

As a method of reducing metal ions contained in gelatin, an ion-exchange treatment with an ion-exchange resin is usually carried out, however, this method is not necessarily effective for the removal of a very small quantity of iron present in gelatin, Therefore, the use of a chelating resin, a solvent extraction, babbling separation, etc. may also be employed.

Further, it is also effective to lower the iron content in gelatin to manufacture gelatin with raw materials of reduced iron content. Still further, prevention of iron contamination of the apparatus used for manufacturing gelatin during manufacturing steps thereof and removal of iron by the use of magnetic effect are also effective for lowering the iron content in gelatin.

Particularly, gelatin having improved and preferable transmittance may be obtained by, for example, using gelatin manufactured from raw bones having less color, by extracting gelatin from ossein which has been treated with hydrogen peroxide, treating the gelatin extract solution with hydrogen peroxide, and so forth.

Gelatin used in the present invention may be either one of an alkaline-treated ossein gelatin, acid treated gelatin, a gelatin derivative or a modified gelatin, and alkaline-treated ossein gelatin is particularly preferable.

The light transmittance of the gelatin used for the silver halide light-sensitive photographic material of the present invention is preferably not less than 70% when it is manufactured as a 10% solution and the transmittance is measured by the use of a spectrophotometer at 420 nm.

Although the manner of eliminating coloring ingredients from gelatin and enhancing the transmittance has been mentioned herein-above, a method in which treatment with hydrogen peroxide is carried out during the step of processing of ossein, a method of reacting with ossein during liming step by adding hydrogen peroxide to a liming bath, or a method of using it in the gelatin extract solution is preferable.

The gelly strength of the gelatin used in the present invention by Paggy method is ,preferably, not less than 250 g and, more preferably, not less than 270 g.

Calcium content of the gelatin used in the present invention according to Paggy's method is preferably not more than 1000 ppm and, particularly preferably, not more than 500 ppm. In order to reduce the calcium content in the gelatin, treatment with an ion exchange column is generally preferable.

There is no specific limitation as to the molecular weight of the gelatin used in the present invention, however, it preferably is in the range between 10,000 and 100,000.

The total amount of gelatin contained in the light-sensitive material of the present invention is preferably not more than 11.0 g/m<sup>2</sup>. There is no specific limitation as to the lowest limit, however, it is preferably not less than 3.0 g/m<sup>2</sup> in view of physical properties or photographic characteristics.

The amount of gelatin is obtained in terms of the weight of gelatin, which contains 11.0% by weight of water measured by the description on Paggy's method converting into the weight

Gelatin which is incorporated in the light-sensitive material of the present invention is preferably hardened with a hardener. There is no limitation as to the nature of the hardener applicable to the present invention, any hardener which is known in the photographic industry, for example, an aldehyde-type, an active vinyl-type, an active halogen- type, an epoxy-type, an ethyleneimine-type, a methanesulfonate-type, a carbo-di-imide type, an iso-oxazole type and a carboxyl-activated-type hardener such as carbamoyl pyridinium salt, etc.. can be mentioned.

- <sup>50</sup> Hardeners which are particularly preferably applicable to the present invention are vinylsulfon-type hardeners, for example, Compounds H-1 through h-24, and/or Compounds II-1 through II-13, III-1 through III-10, etc.; which are disclosed on pages 13 and 14 in Japanese Patent O.P.I. Publication No.2-188753(1990); and/or chlorotriazine-type hardeners, for example, Compounds II-1 through II-13, III-1 through III-10, etc. disclosed on pages 20 and 21 in Japanese Patent O.P.I. Publication No.2-216340(1989) or carboxyl-activated-type hard-
- eners disclosed in Japanese Patent O.P.I. Publications No.2-82237(1990) and No.1-129245(1989). The swelling rate of the light-sensitive material of the present invention expressed in terms of thickness of the hydrophilic colloidal ;layer in the processing solution./ thickness of the same in the dry state is, preferably between 1.5 and 4.0 and, more preferably, between 2.0 and 3.0.

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The silver halide used in the present invention can be spectrally sensitized with one or more spectral sensitizing dyes which are conventionally used in the art. It is also effective with respect to the silver halide emulsion used in the present invention to use sensitizing dyes in combination with a sensitizing dye used for supersensitization of a internal latent image-type silver halide emulsion or a negative-type silver halide emulsion, etc. As regards the sensitizing dyes, for example, Research Disclosure No.15,162 and 17,643 may be referred

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to.

Fogging treatment of the internal latent image-type direct positive-image formation, can be performed by uniformly exposing the light-sensitive material to light or by the use of a fogging agent which is capable of producing fog specs.

Overall uniform exposure may be carried out by uniformely exposing the light-sensitive material to light after the light-sensitive material is dipped in the developing solution or by dipping the light-sensitive material in the developing solution or in other aqueous solution. As for light source used herein, any kind of light source can be used as far as it is cable of emitting light in the same spectral range of the light-sensitive material of the present invention. Moreover it is possible for the light-sensitive material to be exposed to light of high lu-

- 15 minous intensity for a short period of time, or, alternatively, to light of small luminous intensity for a long period of time. The period of the overall exposure may be varied to a great extent depending on the nature of the light-sensitive material, conditions of the development, kind of the light-source to be applied, etc. so that a best direct-positive image can finally be obtained. Moreover, the amount of exposure may preferably be determined within pre-determined range in the light of a combination of the light-sensitive material may be used. Usually
- 20 when excess amount of exposure causes increase of the minimum density or desensitization , and, accordingly, image quality is inclined to be deteriorated.
  Next the facting exect which is preferably used in the present invention is explained.

Next, the fogging agent which is preferably used in the present invention is explained.

As for the fogging agent used in the present invention, for example, hydrazine compounds disclosed in the U.S. Patents No.2,563,785 and No.2,588,982; hydrazide or hydrazine compounds disclosed in U.S. Patent No.3,227,552; quaternary nitrogen-containing heterocyclic compounds disclosed in U.S. Patents No.3,615,615, 3,718,479,3,719,494, 3,734,738 and No.3,759,901; and a compound having an adsorbing group to the surface of the silver halide such as acylhydrazinophenylthioureas disclosed in U.S. Patent No.4,030,925 can be mentioned. These fogging agents can be used in combination. For example, combined use of the nonadsorptive type fogging agent with an adsorptive-type fogging agent is disclosed in the above-mentioned Re-

30 search Disclosure No.15,162, and this technique is also effective in the present invention. As for the fogging agent used in the present invention either the adsorptive-type or the non-adsorptive type can be used either singly or in combination.

Further, the silver halide light-sensitive material of the present invention may comprise, in addition to the above-mentioned yellow dye image-forming layer, magenta dye image-forming layer and cyan dye image-forming layer, a black image-forming layer.

In the present invention, it is preferable that the black image-forming layer has spectral sensitivity common with the above-mentioned yellow dye image-forming layer, magenta dye image-forming layer and cyan dye image-forming layer. That is to say, the black image-forming layer of the light-sensitive material of the present invention has spectral sensitivity in the common portion of that of the yellow dye image-forming layer, the magenta dye-image-forming layer and the cyan dye image-forming layer.

According to one of the preferable embodiments of the present invention, for example, the yellow dye image-forming layer comprises a blue-sensitive emulsion; the magenta dye image-forming layer comprises a green-sensitive emulsion and the cyan dye image-forming layer comprises a red-sensitive emulsion.

The emulsion of this kind can be realized by appropriately selecting spectral sensitizing dyes. For example, the emulsion which has sensitivity to any of blue light, green-light and red-light, may be prepared by, for example, by using a green-sensitizing dye and a red-sensitizing dye in combination in the emulsion sensitive to blue light.

The silver halide light-sensitive color photographic material of the present invention can be prepared by coating the yellow dye image-forming layer, the magenta dye image-forming layer, tssible to arrange, from the side of the support, a cyan image-forming layer, a magenta image-forming layer, a yellow image-forming layer and a black image-forming layer in order. In addition, if necessary, an intermediate layer, a filter he cyan dye image-forming layer and the black image-forming emulsion layer on a support. The order of coating these layers may be optional. In accordance with one of the preferable embodiments of the present invention, for example, it is polayer, protective layer, etc. may be arranged.

<sup>55</sup> As for the developing agent which can be used for the development of the silver halide light-sensitive color photographic material of the present invention, those developing agents which are used for the development of the silver halide photographic material can be mentioned. For example, polyhydroxybenzenes such as hydroquinone; aminophenols, 3-pyrazolidones; ascorbic acid and derivatives thereof; reductones; phenylenedia-

mines; etc. and a mixture thereof are included. Specifically, hydroquinone, aminophenol, N-methylaminophenol, 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3pyrazolidone, ascorbic acid, N.N-diethyl-p-phenylenediamine, diethylamino-o-toluizine, 4-amino-3-methyl-Nethyl-N-( $\beta$ -methanesulfonamidoethyl)aniline, 4-amino-3-methyl-N-ethyl-N-( $\beta$ -hydroxyethyl)aniline, 4-amino-N-ethyl-N-( $\beta$ -hydroxyethyl)aniline, etc. can be mentioned. These developing agents may be incorporated in

5 N-ethyl-N-(β-hydroxyethyl)aniline, etc. can be mentioned. These developing agents may be incorporated the emulsion beforehand and, then is dipped into a high pH solution, thereby to act on the silver halide.

These developing solutions can contain an anti-foggant and development restricting agent and these additives may also optionally be incorporated in the constituent layer of the light-sensitive material of the present invention.

10 In the silver halide light-sensitive color photographic material of the present invention, any photographic additives which are known in the art can optionally be incorporated.

Such photographic additives, which are known in the art include those compounds shown in the table below, and those disclosed in the Research Disclosures No. 17,643 and No.18,716:

	Additives	<u>RD_17,643</u>		<u>RD 18,716</u>	
20		Page	Class	Page	Class
20	Chemical Sensitizer	23	III	648	right-up
	Sensitizing Dye	23	IV	648	right-up
25	Development Accelerator	29	XXI	648	right-up
	Anti-Foggant	24	VI	649	right-down
	Stabilizer	ditto.		Ditto.	
30	Anti-Color Staining Agent	25	VII	650	left-right
	<u>Dye Image-Stabilizer</u>	25	VII		
	UV Absorbent	25-26	VII	649 ri	lght - 650 left
35	Filtering Dye	25-26	VII	649 ri	lght - 650 left
	Whitening Agent	24	V		
10	Hardener	26	Х	651 ri	lght
40	Coating Aid	26-27	XI	650 ri	lght
45	<u>Surfactant</u>	26-27	XI	650 ri	lght
	<u>Plasticizer</u>	27	XII	650 ri	lght

50	Lubricant	Ditto.		Ditto.
	Anti-Static Agent	Ditto.		Ditto.
	Matting Agent	28	XVI	650 right
55	<u>Binder</u>	29	IX	651 right

In the emulsion layer of the silver halide light-sensitive color photographic layer of the present invention, it is possible to incorporate a dye-forming coupler, which is capable of forming a dye upon reaction with an oxidation product of a color developing agent. Said dye-forming coupler is usually selected so that it may produce a dye which absorbs spectral light to which respective emulsion layers are sensitive, and accordingly, a

yellow dye-forming coupler is usually used in the blue-sensitive emulsion layer, a magenta dye-forming coupler in the green-sensitive layer and a cyan dye-forming coupler in the red-sensitive layer, respectively.

However, depending upon the objective, it is also possible to prepare a silver halide light-sensitive color photographic material using a different combination of the dye-forming coupler and the light-sensitive silver halide emulsion.

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It is preferable that these dye-forming couplers contain in their molecules so-called a ballasting group which comprises at least eight carbon atoms and is capable of conferring the produced dyes an anti-diffusing property.

Moreover, these dye-forming couplers may be either of a four-equivalent type, with which four silver ions are required to be reduced in order to form a mol of dye, or of a two-equivalent type, with which only two silver

- 15 ions are required to be reduced for the formation of a mol of dye. Further, it is also possible to use so-called a DIR coupler, which release a development inhibitor at the time of development and is capable of improving sharpness and graininess of the image or so-called a DIR compound which, upon coupling reaction with the oxidation product of the developing agent, is capable of releasing a colorless compound as well as a development inhibitor.
- 20 A development inhibitor is connected, either directly or through a divalent group with the DIR coupler or the DIR compound at the coupling position, and the DIR coupler and DIR compound include so-called a timing DIR coupler, in which the development inhibitor is released by nucleophilic reaction inside the released group and a timing DIR compound, in which the development inhibitor is released by the electron transportation reaction in the molecule.
- 25 It is also possible to use a colorless coupler or a competing coupler, which reacts with the oxidation product of an aromatic primary amine developing agent but does not produce a visible dye. in combination with a dyeforming coupler.

As for the yellow dye-forming coupler, in addition to the compounds represented by the above-identified formulae (Y-I) and (Y-II), conventional benzoylacetoanilide-type compounds and pivaloylacetanilide-type compounds may also be used.

As for the magenta dye-forming coupler, conventional 5-pyrazolone-type coupler, pyrazolobenzimidazoletype coupler, pyrzoloazole-type coupler, acylacetoniyrile-type coupler, indazolone-type coupler, etc. can be used.

As for the cyan dye-forming coupler, conventional phenol-type coupler, naphthol-type coupler, and imidazole-type coupler can be used.

For example, a phenol-type coupler, to which an alkyl group, an acylamino group or a ureido group is substituted; a naphthol-type coupler formed from 5-aminonaphthol structure.; a two-equivalent naphthol-type coupler to which an oxygen atom is introduced as a releasing group. etc. are representative.

In the magenta image-forming layer of the silver halide light-sensitive material of the present invention, in order to approximate the color ton of the printing ink it is preferable to use a magenta dye-forming coupler in combination with a yellow dye-forming coupler.

#### Examples

<sup>45</sup> The present invention is hereinbelow explained with reference to examples.

Example 1

#### (Preparation of emulsion EM-1)

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While controlling an aqueous solution containing ossein gelatin to be at 40°C, an aqueous solution containing ammonia and silver nitrate and an aqueous solution containing potassium bromide and sodium chloride (in a mol ratio of KBr:NaCl=95:5) were added thereto at the same time in a controlled double-jet method, so that a cubic-shaped silver chlorobromide core emulsion having a grain-size of  $0.30\mu m$  could be prepared. At

55 that time, the pH and pAg were controlled so that the grains could be in the cubic form. To the resulting core emulsion, an aqueous solution containing ammonia and silver nitrate and an aqueous solution containing potassium bromide and sodium chloride (in a mol ratio of KBr:NaCl=40:60) were added thereto at the same time in a controlled double-jet method, so that shells could be so formed as to have an average grain-size of 0.42µm.

At that time, the pH and pAg were controlled so that the grains could be in the cubic form.

After the resulting emulsion was washed with water and the water-soluble salts were removed therefrom, gelatin was added, so that emulsion EM-1 could be prepared. The distribution range of the resulting emulsion EM-1 was proved to be 8%.

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(Preparation of emulsion EM-2)

While controlling an aqueous solution containing ossein gelatin to be at 40°C, an aqueous solution containing ammonia and silver nitrate and an aqueous solution containing potassium bromide and sodium chloride (in a mol ratio of KBr:NaCl=95:5) were added thereto at the same time in a controlled double-jet method, so that a cubic-shaped silver chlorobromide core emulsion having a grain-size of 0.18µm could be prepared. At that time, the pH and pAg were controlled so that the grains could be in the cubic form. To the resulting core emulsion, an aqueous solution containing ammonia and silver nitrate and an aqueous solution containing potassium bromide and sodium chloride (in a mol ratio of KBr:NaCl=40:60) were added thereto at the same time in a controlled double-jet method, so that shells could be so formed as to have an average grain-size of 0.25µm.

At that time, the pH and pAg were controlled so that the grains could be in the cubic form.

After the resulting emulsion was washed with water and the water-soluble salts were removed therefrom, gelatin was added, so that emulsion EM-2 could be prepared. The distribution range of the resulting emulsion EM-2 was proved to be 8%.

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(Preparation of blue-sensitive emulsion EM-B)

Sensitizing dye D-1 was added to EM-1 so as to apply a color-sensitization to EM-1 and, thereafter, T-1 was added in an amount of 600 mg per mol of silver, so that blue-sensitive emulsion EM-B could be prepared.

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(Preparation of green-sensitive emulsion EM-G)

Green-sensitive emulsion EM-G was prepared in the same manner as in the blue-sensitive emulsion, except that sensitizing dye D-2 was added to EM-2 so as to apply a color-sensitization thereto.

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(Preparation of red-sensitive emulsion EM-R)

Red-sensitive emulsion EM-R was prepared in the same manner as in the blue-sensitive emulsion, except that sensitizing dyes D-3 and D-4 (amount D-3:56.6, D-4:14.2 mg/mol Ag) were added to EM-2 so as to apply a color-sensitization thereto.

(Preparation of panchromatic emulsion EM-P)

D-1

Panchromatically-sensitive emulsion EM-P was prepared in the same manner as in the blue-sensitive emulsion, except that sensitizing dyes D-1, D-2, D-3 and D-4 were added to EM-1 so as to apply a color-sensitization thereto.

T-1: 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene

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On both side of paper-made support whose basis weight is 80g/m<sup>2</sup>, corona discharge eas provided and then the front surface thereof was laminated with high density polyethylene containing anatase titanium oxide in an amount of 15 wt% to form 27 µm thickness of resincoating layer by means of extrusion coating, and, on the other side thereof, a double layer polyethylene resin coating layer was provided by means of co-extrusion coating process to obtain a photographic support. Each of layers 1 through 9 having the following compositions was coated on the front side thereof by making use of the above-mentioned EM-B, EM-G, EM-R and EM-P, and layer 10 was coated on the rear side thereof, so that multilayered color light-sensitive material was prepared. Also, therein, SA-1 and SA-2 were each used as a coating aid and H-1 and H-2 were each used as a layer hardener.

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SA-1: Sodium di(2-ethylhexyl) sulfosuccinate, SA-2: Sodium di(2,2,3,3,4,4,5,5-octafluoropentyl) sulfosuccinate, H-1: Sodium 2,4-dichloro-6-hydroxy-s-triazine, and

H-2: Tetrakis(vinyl sulfonylmethyl)methane.

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	Layer	Composition	Coating weigh	<u></u>
5			(g/m <sup>2</sup> )	
	Layer 9 (a UV a	bsorption layer)		
		Gelatin	0.78	
10		UV absorbent (UV-1)	0.065	
		UV absorbent (UV-2)	0.120	
		UV absorbent (UV-3)	0.160	
15		Solvent (SO-2)	0.1	
,0		Silica matting agent	0.03	
	Layer 8 (a blue	e-sensitive layer)		
20		Gelatin	1.43	
		Blue-sensitive emulsion EM- (coating weight of silve	B 0.52 r)	
		Yellow coupler (YC-1)	0.82	
25		Antistaining agent (AS-2)	0.025	
		Solvent (SO-1)	0.82	
		Inhibitors ST-1:	0.000	1
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00				
0.5				
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		ST-2:	0.00001
		T-1 :	0.0039
5	Layer 7	(an intermediate layer)	
		Gelatin	0.54
		Color-mixture preventive (AS-1)	0.055
10		Solvent (SO-2)	0.072
	Layer 6	(a yellow colloidal silver layer)	
		Gelatin	0.42
15		Yellow colloidal silver	0.03
		Color-mixture preventive (Mixture c same amounts of AS-1, 3, 4, 5, 6)	of 0.04
		Solvent (SO-2)	0.049
20		Polyvinyl pyrrolidone (PVP)	0.047
		Anti-irradiation dye (AI-3)	0.03
	Layer 5	(an intermediate layer)	
25		Gelatin	0.54
		Color-mixture preventive (Mixture of same amounts of AS-1, 3, 4, 5, 6)	of 0.055
20		Solvent (SO-2)	0.072
30	Layer 4	(a green-sensitive layer)	
		Gelatin	1.43
35		Green-sensitive emulsion EM-G (coating weight of silver)	0.40
		Panchromatically sensitive emulsion EM-P (coating weight of silver)	0.10
40		Magenta coupler (MC-1)	0.25
		Yellow coupler (YC-2)	0.06
		Antistaining agent (AS-2)	0.019
45		Solvent (SO-1)	0.31
τυ		Inhibitors ST-1:	0.0008
		ST-2:	0.00001
		T-1 :	0.0036

	Layer 3	(an intermediate layer)	
_		Gelatin	0.75
5		Color-mixture preventive (Mixture same amounts of AS-1, 3, 4, 5, 6)	of 0.055
		Solvent (SO-2)	0.072
		Anti-irradiation dye (AI-1)	0.01
10		Anti-irradiation dye (AI-2)	0.01
	Layer 2	(a red-sensitive layer)	
15		Gelatin	1.38
		Red-sensitive emulsion EM-R (coating weight of silver)	0.30
20	a a constant a succession	Panchromatically sensitive emulsion EM-P (coating weight of silver)	0.06
		Cyan coupler (CC-1)	0.44
		Solvent (SO-1)	0.31
		Antistaining agent (AS-2)	0.015
25		Inhibitors ST-1:	0.00007
		ST-2:	0.00001
		T-1. :	0.0019
30	Layer 1	(a white-pigment layer)	
		Gelatin	1.0
		Anatase type titanium dioxide	3.0
25	Layer 10	(a rear-surface layer)	
30		Gelatin	6.0
		Silica matting agent	0.65

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The silver amounts coated were obtained by converting them into the corresponding amounts of silver used.

 SO-1: Trioctyl phosphate, SO-2: Dioctyl phthalate,
 AS-1: 2,5-di-t-octyl hydroquinone, AS-2: 2,5-di-t-butyl hydroquinone, ST-1: 1-(3-acetamidophenyl)-5-mercaptotetrazole, and ST-2: N-benzyl adenine.

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(n)  $C_6H_{13}OOC - (H_2C)_3 - C - (CH_2)_3 - COOC_6H_{13}(n)$ (n)  $C_6H_{13}OOC - (H_2C)_3 - C - (CH_2)_3 - COOC_6H_{13}(n)$ 



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AS-5 (sec)H<sub>25</sub>C<sub>12</sub> OHOH AS-6



\_C<sub>14</sub>H<sub>29</sub>(sec)

Samples 101 was prepared in this way. Samples 102 to 109 were prepared by modifying the content shown in Table 1 shown below. (An oil-soluble dyes of the invention are represented by F-.)

30	Sample	White pigment in Layer 1	Silver amount	Yellow Coupler in Layer 8	Compound of Formula III*
	101	Yes	0.52	YC-1	No
25	102	No	0.40	YC-1	No
30	103	Yes	0.40	YC-1	No
	104	Yes	0.24	Y-I-4	No
40	105	Yes	0.24	Y-II-7	No
	106	Yes	0.10	Y-I-10	Yes
	107	Yes	0.10	Y-II-7	Yes
45	108	No	0.52	YC-1	No
	109	No	0.10	Y-I-10	Yes

Compound of Formula III\*

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10 The Compound of Formula III was added into the Layer 8 in an amount of 2.0 × 10<sup>-4</sup> mol per one mol of silver.

Samples 101 through 109 were each brought into close contact with a black printer and a cyan printer out of the halftone-dot original document, and they were exposed to light under the following exposure conditions-1. Next, the black printer and the magenta printer were each brought into close contact therewith, and they were exposed to light under the following exposure conditions-2. Further, the black printer and the yellow printer

- were each brought into close contact therewith, and they were exposed to light under the following exposure conditions-3. Each of the samples 101 through 109 exposed to light in the above-mentioned manner was processed in the following development process, so that a dye image comprising halftone-dots could be obtained. In the density measurements at white area, a densitometer, Color Analyser 607 manufactured by Hitachi
- 20 Corp., was used.

# (Exposure conditions-1)

When exposing a light-sensitive material sample to white light through a red-filter (Wratten No. 26) and an ND filter, the exposure quantity was controlled by adjusting the density of the ND filter when exposing with while light so that the minimum red density can be obtained with minimum amount of exposure after the development, and the exposure is then made for 0.5 seconds.

### (Exposure conditions-2)

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When exposing a light-sensitive material sample to white light through a green-filter (Wratten No. 58) and an ND filter, the exposure quantity was controlled by adjusting the density of the ND filter when exposing with while light so that the minimum green density can be obtained with minimum amount of exposure after the development, and the exposure is then made for 0.5 seconds.

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(Exposure conditions-3)

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When exposing a light-sensitive material sample to white light through a blue-filter (Wratten No. 47B) and
an ND filter, the exposure quantity was controlled by adjusting the density of the ND filter when exposing with
while light so that the minimum blue density can be obtained with minimum amount of exposure after the de-
velopment, and the exposure is then made for 0.5 seconds.

Processing	step-1	Temperature	Time
Dipping (in a	a developer)	37°C	12sec.
Fogging exp	oosure	-	12sec.(1 lux)
Developing		37°C	95sec.
Bleach-fixin	g	35°C	45sec.
Stabilizing		25-30°C	90sec.
Drying		60-85°C	40sec.

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Each of the composition of the processing solutions was as follows.

	(Color developer)		
	Benzyl alcohol	15.0	ml
5	Ceric sulfate	0.0	15 g
	Ethylene glycol	8.0	ml
10	Potassium sulfite	2.5	g
	Potassium bromide	0.6	g
	Sodium chloride	0.2	g
15	Potassium carbonate	25.0	g
	T-1	0.1	g
20	Hydroxylamine sulfate	5.0	g

	Sodium diethylene triamine pentaacetate	2.0 g
5	4-amino-N-ethyl-N-(β-methane sulfonamidoethyl)metatoluidine 3/2 sulfate, monohydrate	4.5 g
10	Fluorescent whitening agent, (4,4'-diaminostilbene disulfonic acid derivative)	1.0 g
	Potassium hydroxide	2.0 g
45	Diethylene glycol	15.0 ml
15	Add water to make in total	1 liter
	Adjust pH to be	10.15
20	(Bleach-fixer)	
	Ferric ammonium diethylene	
	triamine pentaacetate	90.0 g
25	Diethylene triamine pentaacetic acid	3.0 g
	Ammonium thiosulfate, (in an aqueous 70% solution)	180 ml
30	Ammonium sulfite, (in an aqueous 40% solution)	27.5 ml
	3-mercapto-1,2,4-triazole	0.15 g
35	Adjust pH with potassium carbonate or glacial acetic acid to be	7.1
	Add water to make in total	1 liter
40	(Stabilizer)	
	o-phenyl phenol	0.3 g
45	Potassium sulfite, (in an aqueous 50% solution)	12 ml
	Ethylene glycol	10 g
50	1-hydroxy ethylidene-1,1- diphosphonic acid	2.5 g

	Bismuth chloride	0.2 g
-	Zinc sulfate, septihydrate	0.7 g
5	Ammonium hydroxide, (in an aqueous 28% solution)	2.0 g
	Polyvinyl pyrrolidone (K-17)	0.2 g
10	Fluorescent whitening agent, (4,4'-diaminostilbene disulfonic acid derivative)	2.0 g
15	Add water to make in total	1 liter
	Adjust pH with ammonium hydroxide	
	or sulfuric acid to be	7.5

The stabilizing photographic-processing was carried out in a double-tank counter-current system. The formula of the replenisher used in the running photographic-processing will be shown below.

25	(Color development replenisher)	
	Benzyl alcohol	18.5 ml
	Ceric sulfate	0.015 g
30	Ethylene glycol	10.0 ml
	Potassium sulfite	2.5 g
35	Potassium bromide	0.3 g
	Sodium chloride	0.2 g
	Potassium carbonate	25.0 g
40	т-1	0.1 g
	Hydroxylamine sulfate	5.0 g
45	Sodium diethylenetriamine pentaacetate	2.0 g

5	4-amino-N-ethyl-N-(β-methanesulfon- amidoethyl)metatoluidine 3/2 sulfate, monohydrate	5.4 g
	Fluorescent whitening agent, (4,4'-diaminostilbene disulfonic acid derivative)	1.0 g
10	Potassium hydroxide	2.0 g
	Diethylene glycol	18.0 ml
15	Add water to make in total	1 liter
	Adjust pH to be	10.35

(Replenisher for bleach-fixer)

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The same as the above-mentioned bleach-fixer.

(Replenisher for stabilizer)

25 The same as the above-mentioned stabilizer.

The amounts of the development replenisher, bleach-fixer and stabilizer replenished were each in an amount of 320 ml per m<sup>2</sup> of a light-sensitive material to be processed.

Density at 440 nm was measured to test the whiteness in the yellow image part and dot image reproduce ability was evaluated in the obtained samples. The result is summarized in Table 2.

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# Table 2

35	Sample No.	Whiteness (Density at 440 nm)	Dot Reproduce Ability
	101	0.130	А
	102	0.094	x
40	103	0.095	А
	104	0.092	А
45	105	0.090	A
	106	0.086	А
	107	0.085	А
50	108	0.093	х
	109	0.095	х
55	Standard	A: Reproduced 2% s	mall dot
		X: Not reproduced	3% small dot

As is obvious from the results shown above, the samples 103 to 107 of the invention are good in both of the whiteness in yellow area and dot reproduce ability. The Table also shows that the yellow coupler of the formulae (Y-I) and (Y-II) gives better whiteness at the yellow area.

5 Example 2

Light-sensitive material samples were prepared, respectively, in the same manner as in Samples 101 to 109 except that emulsion EM-B was replaced by a negative type blue-sensitive silver chlorobromide emulsion (in a ratio of AgBr:AgCl=4:96), EM-G was replaced by a negative type green-sensitive silver chlorobromide emulsion (in a ratio of AgBr:AgCl=4:96) and EM-R was replaced by a negative type red-sensitive silver chlorobromide emulsion (in a ratio of AgBr:AgCl=4:96), and EM-R was replaced by a negative type red-sensitive silver chlorobromide emulsion (in a ratio of AgBr:AgCl=4:96), and that each of emulsions EM-P contained in layers 4 and 6 was removed. The obtained samples were exposed and processed by using a proof making machine for negative material (Consensus, Product of Konica Corporation) to evalute the whiteness and dot image reproduce ability. The similar result was obtained.

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Example 3

Samples 103 to 107 were so modified that a water-immisscible high boiling poit organic compound O-18 was added to the white pigment containing layer at 30 wt % of gelatin coating amount to obtain new samples. The samples were evaluated and found that the similar result to Example 1 was given. Further, the hue at white area was evaluated to find better result than that of Samples 103 to 107 in Example 1.

## Example 4

- New emulsion EM-3 having an average grain size of 0.36 μm was prepared in the similar way to EM-1. A green sensitive emulsion EM-G was prepared in the similar way to EM-G using EM-3. Same test was repeated as in Example 1, but EM-G was replaced by EM-G2. Similar results were obtained with the new emulsion having different average grain size from those of Example 1. Further, another test was conducted by changing the exposure amount of light with three times of standard exposure amount of the exposure condition-3 in Example 30
  - The ratio of reduced maximum density of magenta image was less than
     1.

#### Example 5

<sup>35</sup> The same tests were repeated by using new red sensitive emulsions modified by changing the ratio of sensitizing dyes D-3 and D-4 to 9:1 and 5:5 respectively. The similar results were obtained to in Example 1.

## Claims

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  - 1. A silver halide light-sensitive color photographic material comprising a hydrophillic colloidal layer containing a white pigment provided on a support, and provided further thereon, a yellow dye image-forming silver halide emulsion layer, a green dye image-forming silver halide emulsion layer and a cyan dye image-forming silver halide emulsion layer; wherein amount of silver contained in the yellow dye image-forming silver halide emulsion layer is 0.48 g/m<sup>2</sup> or less.
  - 2. The silver halide light-sensitive color photographic material according to Claim 1, wherein said yellow dye image-forming layer comprises a yellow dye-forming coupler represented by Formula (Y-1);

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wherein R1 represents an alkyl group or a cycloalkyl group; R2 represents an alkyl group, a cy-

cloalkyl group or an aryl group; R3 represents a group which is capable of being substituted on the benzene ring and m represents an integer from zero to four; provided that when m is two or more, R3's may be either the same or different and z represents a hydrogen atom or a group which is capable of being split-off upon coupling reaction with an oxidation product of a developing agent.

3. The silver halide light-sensitive color photographic material according to Claim 1, wherein said yellow dye image-forming layer comprises a yellow dye-forming coupler represented by Formula (Y-II);

10 Formula (Y-II)  $R_1COCHCONH$   $I_2$  $I_3$  NHCOR<sub>3</sub>

wherein R<sub>1</sub> represents an alkyl group or a cycloalkyl group; R<sub>2</sub> represents an alkyl group, a cycloalkyl group, or an aryl group; R3 represents an unsubstituted straight chain alkyl group and z represents a hydrogen atom or a group which is capable of being split-off upon coupling reaction with an oxidation product of a developing agent.

4. The silver halide light-sensitive color photographic material suitable for making a color proof according to anyone of Claims 1 through 3, wherein the image-forming silver halide emulsion layer and/or the hydrophilic colloidal layer comprise a compound represented by Formula(III);



- wherein, M represents a hydrogen atom, an alkali metal atom, an ammonium group or a protective group for a mercapto group and z represents a group of non-metal atoms necessary to form a heterocycle.
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