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A silver halide colour photographic light-sensitive material.

There is disclosed a silver halide color photographic light-sensitive material improving in preservability and processing stability, and capable of providing a dye image having excellent sharpness, said light-sensitive material comprising a support and provided thereon, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a red-sensitive silver halide emulsion layer comprises a single layer and contains a yellow coupler having a molecular weight of 250 to 700 per coupling site of said yellow coupler.

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#### A SILVER HALIDE COLOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

#### FIELD OF THE INVENTION

The present invention relates to a silver halide color photographic light-sensitive material, and more particularly to a silver halide color photographic light-sensitive material having an excellent sharpness and improved preservability and processing stability.

#### **BACKGROUND OF THE INVENTION**

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It is well-known through Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) Nos. 72243/1986, 297845/1987 and 23153/1988 that the use of a low-molecular-weight yellow coupler in a negative silver halide color photographic light-sensitive material improves the sharpness and preservability of an image formed on the light-sensitive material.

A color photographic light-sensitive material to which the above technique is applied, however, has the problem that it has a poor preservability, an insufficient sharpness and an insufficient processing stability.

Accordingly, there has been a demand for improvements of the preservability, sharpness and processing stability of a color photographic light-sensitive material.

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#### SUMMARY OF THE INVENTION

It is an object of the invention to provide a silver halide color photographic light-sensitive material which is improved in the preservability as well as in the processing stability and excellent in the sharpness.

The above object of the invention is accomplished by a silver halide color photographic light-sensitive material which comprises a support and, provided thereon, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer is of a single-layer construction and contains a yellow coupler having a molecular weight of 250 to 700 per coupling site.

#### DETAILED DESCRIPTION OF THE INVENTION

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In the present invention, a single layer mentioned above includes also a plurality of emulsion layers provided as serial layers which are equal in the type of the coupler contained therein, the silver halide grain size, the silver halide composition and crystal habit, and the ratio of the coupler to the silver halide.

In the invention, preferably, each of the blue-sensitive and green-sensitive silver halide emulsion layers is of a single layer, and more preferably, each of the blue-sensitive, green-sensitive and red-sensitive emulsion layers is of a single layer.

In the emulsion layer of a single-layer construction, the number of layers on coated a light-sensitive material can be less than in that of multilayer construction, so that it is possible to make the total light-sensitive layers thinner, and therefore also possible to improve the graininess as well as the production efficiency and sharpness. The total dry thickness of the layers of a light-sensitive material is preferably 20 to 3  $\mu$ m, and more preferably 15 to 5  $\mu$ m.

A means to widen an exposure latitude of a silver halide emulsion layer of a single-layer construction to 3.0 or more includes a method of using a mixture of silver halide grains different in a sensitivity, more specifically, a method of using a mixture of silver halide grains different in a grain size and a method of incorporating a desensitizer into at least a part of silver halide grains.

A mixture of silver halide grains different in the grain size to be used in order to obtain a wide exposure latitude is preferably a combination of silver halide grains having the largest average grain size of 0.2 to 2.0µm and silver halide grains having the smallest average grain size of 0.05 to 1.0µm, and may also be a combination comprising one or more kinds of medium-average-grain-size silver halide grains.

The average grain size of the maximum-average-grain-size silver halide grains is preferably 1.5 to 40 times that of the above minimum-average-grain-size silver halide grains.

If silver halide grains containing a desensitizer are used instead of low-sensitive silver halide grains of a small grain size, in order to obtain a wide exposure latitude, it is possible to reduce the difference in the average grain sizes, without changing the sensitivity of the silver halide grains and also possible to use a mixture of silver halide grains equal in the average grain size but different in the sensitivity.

That is, by using silver halide grains containing a desensitizer, a wide exposure latitude can be obtained, even if a coefficient of variation of the whole grains is reduced,

Accordingly, such silver halide grains having a small coefficient of variation are advantageous since their photographic characteristics are stable to aging and fluctuation of processing conditions. Further, from the production technology point of view, it is also possible that silver halide grains different in the sensitivity in a mixture system be chemically sensitized in the same batch.

Compounds usable as the desensitizer, besides metallic ions, include various agents such as antifoggants, stabilizers, and desensitizing dyes. Especially, a metallic ion doping method is preferred.

Metallic ions for use in the doping method include ions of Cu, Cd, Zn, Pb, Fe, Tl, Rh, Bi, Ir, Au, Os and Pd. Of them, Cu, Rh and Os are preferable, and Rh is more preferable. These metal ions can be used also in a form of halogen complex, and can be used in combination. The pH of an AgX suspension in doping is preferably not more than 5.

The metallic ion's doping amount is normally  $10^{-17}$  to  $10^{-2}$  mole, and preferably  $10^{-16}$  to  $10^{-4}$  mole per mole of AgX.

Further, by selecting a type of metallic ions, a doping position and a doping amount, a large variety of sensitivity natures may be given to silver halide grains.

As the doped amount of not more than  $10^{-2}$  mol per mol of AgX less effects the growth of the silver halide grains, there can be prepared the silver halide grains with narrower grain size distribution in the same growth conditions as well as in the same batch.

After the silver halide grains doped in the different conditions are treated conventionally, they may be mixed in a prescribed ratio to the same batch and chemically sensitized.

Each silver halide grain can have a sensitizing effect based on its property, and the emulsion having a wide latitude can be prepared depending upon a sensitivity difference and a mixing ratio of the silver halide grains.

The aforementioned antifoggant or stabilizer includes azoles such as benzotriazolium salts, indazoles, triazoles, benzotriazoles, and benzimidazoles; mercapto substituted-heterocyclic compounds such as mercaptotetrazoles, mercaptothiazoles, mercaptothiadiazoles, and mercaptobenzimidazoles, and mercaptopyrimidines; azaindenes such as tetraazaindenes, and pentaazaindenes; nucleic acid decomposition products such as adenine and guanine; benzenethiosulfonic acids; and thioketo compounds.

The foregoing desensitizing dye includes cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolacyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes.

A desensitizer is preferably contained in a silver halide grain from the viewpoint of preservability of light-sensitive materials and aging stability of coating solutions. The desensitizer may distribute evenly; or may distribute locally in the center or the middle of the grain; or may distribute decreasing gradually from the center of the outer shell thereof.

From the viewpoint of a production efficiency, the desensitizer preferably distributes locally in the center of the silver halide grains, and if the seed grains with a smaller variation coefficient are used, the processes after growth of the grains can be carried out in the same batch.

In the light-sensitive material of the invention, at least one color-sensitive layer preferably comprises AgX grains containing a desensitizer. Preferably a blue-sensitive layer, more preferably a blue-sensitive layer and a green-sensitive layer, and most preferably the whole color-sensitive layers comprise AgX grains containing a desensitizer.

An oleophilic yellow coupler having a unit molecular weight of 250 to 700 used in the invention is preferably represented by the following Formula Y:

#### Formula Y

$$R_1 - COCIICONII - (R_2)_m$$

wherein R<sub>1</sub> represents an alkyl group or an aryl group; X represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group: R<sub>2</sub> represents a hydrogen atom or a substituent: Z represents a group capable of being split off upon coupling reaction with an oxidation product of a color developing agent: m is an integer of zero to 4, provided, when m is 2 or more, the R<sub>2</sub>s may be the same or different, and R<sub>1</sub>, R<sub>2</sub>, X or Z may be a di- to tetravalent linkage group to form a di- to tetramer of a yellow coupler represented by Formula Y.

Formula Y is further detailed: R<sub>1</sub> is preferably an alkyl group having 1 to 30 carbon atoms, a cycloalkyl group or a phenyl group, each including one having a substituent such as a halogen atom, an alkyl, aryl, alkoxy, aryloxy, alkylthio, arylthio, carbamoyl, sulfamoyl, acylamino, sulfonamido, alkoxycarbonyl, nitro, cyano, hydroxyl, amino, alkylamino, and arylamino group, R<sub>1</sub> is more preferably a tertiary alkyl group or a 4-alkoxyphenyl group. and most preferably a t-butyl or 4-methoxyphenyl group.

X is preferably a hydrogen atom, a halogen atom or an alkoxy group, and particularly preferably a chlorine atom or an alkoxy group having 1 to 24 carbon atoms.

The alkoxy group includes one having a substituent which is similar to those for each group represented by  $R_1$ .

The substituent represented by R<sub>2</sub> includes a halogen atom, an alkyl group having 1 to 20 carbon atoms, an aryl, alkoxy, aryloxy, acylamino, sulfonamido, carbamoyl, sulfamoyl, acyloxy, amino, alkylthio, ureido, sulfamoylamino, cyano, alkoxycarbonyl, alkoxycarbonylamino, imido, alkylsulfonyl, arylsulfonyl, and heterocyclic group.

Each of these groups includes one further having a substituent which is similar to those for each group represented by R<sub>1</sub>.

Preferred one among these groups represented by R<sub>2</sub> is an acylamino group, a sulfonamido group, an alkoxycarbonyl group, a sulfamoyl group or a carbamoyl group.

The group represented by Z and capable of being split off upon coupling reaction with the oxidation product of a color developing agent includes an aryloxy, heterocyclic oxy, alkoxy, acyloxy, alkylsulfonyloxy, arylsulfonyloxy, alkylthio, arylthio, heterocyclic thio, ans -N Q group, wherein Q represents a group of nonmetallic atoms capable of forming a mono or condensed 5- to 7-member heterocyclic ring together with N, such as pyrrole, pyrazole, imidazole, 1,2,4-triazole, tetrazaole, indazole, benzimidazole, benzotriazole, succinic acid imide, phthalic acid imide, saccharin, oxazolidine-2,4-dione, imidazolidine-2,4-dione, thiazolidine-2,4-dione, urazole, 2-pyridone and 5-tetrazolone.

Each of these groups includes one having further a substituent which is similar to those for each group represented by R<sub>1</sub>.

Z is preferably an aryloxy group, an imidazolidine-2,4-dione-3-yl group, an oxazolidine-2,4-dione-3-yl group or a triazolidine-3,5-dione-4-yl group.

m is preferably an integer of zero to 2.

The yellow coupler represented by Formula Y, as has been mentioned, may be a di- to tetramer, but is preferably a monomer or a dimer.

The term 'unit molecular weight' used in the invention represents a value obtained when dividing the molecular weight of a yellow coupler by the number of the coupling sites in one molecule of the coupler.

The yellow coupler of the invention preferably has a unit molecular weight of 400 to 700, more preferably 500 to 650 when R<sub>1</sub> is an alkyl group, and most preferably 500 to 700 when R<sub>1</sub> is an aryl group,

The following are the typical examples of the low molecular weight diequivalent yellow coupler of the invention. The unit molecular weight of each coupler is given in parentheses.

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Y-1

5 CH<sub>3</sub>O COCHCONH COCC<sub>1</sub> 2H<sub>2</sub> 5

5 
$$CH_3O$$
—COCHCONH—COCHCOCH<sub>2</sub>CHC<sub>4</sub>H<sub>5</sub>
 $C_2H_5$ 
 $CR$ 
 $COCH_2CHC_4H_5$ 
 $C_2H_5$ 
 $C_2H_5$ 

$$Y - 3$$
 $CR_3O \longrightarrow COCHCONH \longrightarrow COOCHCOOC_1H_9$ 
 $O \longrightarrow N - CH_2 \longrightarrow CH_3$ 

(664)

$$Y - 5$$

CH<sub>3</sub>O COCHCONH COOC<sub>8</sub>H<sub>17</sub>

$$C_{6}H_{13}O$$
 CH<sub>3</sub> (672)

Y - 7

Y − 8

CH<sub>3</sub>O COCHCONH COOC<sub>8</sub>H<sub>1,7</sub>

$$C_{2}H_{5}O - N - CH_{2}$$
(686)

<sup>35</sup> Y — 9

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CD CD COCHCONH COOC, H; 3

# Y-11

CH<sub>3</sub>O—COCHCONH—CoCHCONH—CoCH<sub>2</sub>CHC<sub>4</sub>H<sub>5</sub> (552)

# y - 12

CD CH<sub>3</sub>O

COCHCONH

NHSO<sub>2</sub>C<sub>1</sub><sub>2</sub>H<sub>2</sub><sub>5</sub>

NO<sub>2</sub>

(688)

45 CN (632)

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$$Y-14$$

$$CQ$$

$$CH_3O \longrightarrow COCHCONH$$

$$CH_3 \longrightarrow O$$

$$CO_2C_4H_3$$

$$CH_3O \longrightarrow COCHCONH$$

$$CO_2C_4H_3$$

$$CO_2C_4H_3$$

<sub>25</sub> Y-15

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CQ (CH<sub>3</sub>)<sub>3</sub>CCOCHCONH COOC<sub>3</sub>H<sub>1,7</sub> 0 N-CH<sub>2</sub>
(598)

Y - 17

CQ  $(CH_3)_3CCOCHCONH$   $COOCH_2CHC_4H_9$   $CH_3 - NH$   $CH_3 - NH$  (583)

Y —18

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30 (CH<sub>3</sub>)<sub>3</sub>CCOCHCONH COOC<sub>12</sub>H<sub>25</sub>
0 N-CH<sub>3</sub> (578)

Y-19  $(CH_3)_3CCOCHCONH$   $COOC_8H_{17}$ 

 $C_6H_{13}O \longrightarrow N \longrightarrow CH_3$  (621)

$$Y - 20$$

$$C_{2}H_{3}O - COC_{4}CONH - COOC_{4}H_{13}$$

$$C_{2}H_{3}O - COC_{4}COOC_{4}H_{13}$$

$$C_{2}H_{3}O - COC_{4}COOC_{4}H_{13}$$

$$C_{1}H_{1} - COC_{4}COOC_{4}H_{13}$$

$$C_{2}H_{3} - COC_{4}COOC_{4}H_{13}$$

$$C_{1}H_{1} - COC_{4}COOC_{4}H_{13}$$

$$C_{2}H_{3} - COC_{4}COOC_{4}H_{13}$$

$$C_{3}H_{13} - COC_{4}COOC_{4}H_{13}$$

$$C_{4}H_{13} - COC_{4}COOC_{4}H_{13}$$

$$C_{5}H_{13} - COC_{5}H_{13}$$

$$C_{7}H_{13} - COC_{7}H_{13}$$

$$C_{7}H_{13} - COC_{7}H_{13$$

Y - 24

QC12H25 5 (CH<sup>3</sup>) <sup>2</sup>CCOCHCONH SO2NHCH3 COOCH 3 10 (621)

15 Y - 25

20 (CH<sub>3</sub>)<sub>3</sub>CCOCHCONH NHSO<sub>2</sub>C<sub>12</sub>H<sub>25</sub> 25 (638)

Y - 26

30

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5**0** 

35 (СН3)3ССОСНСОИН NHS02C12H25 40 (637)

СООН

$$Y - 27$$

Y-28

CQ

NHSO<sub>2</sub>C<sub>4</sub>H<sub>9</sub>

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Y **−**29

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CQ (CH<sub>3</sub>)<sub>3</sub>CCOCHCONH—COOC, H<sub>9</sub> ON OCH<sub>2</sub> ON CH<sub>2</sub> (CH<sub>3</sub>)<sub>3</sub>CCOCHCONH—COOC, H<sub>9</sub>

Y - 30

CH 3 O — COCHCONH — COCHCONH

(434)

(580)

COOC, H,

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$$C_{5}H_{11}O \longrightarrow COCHCONII \longrightarrow CQ \qquad (340)$$

$$Y - 36$$

$$CQ \longrightarrow NIISO_{2}C_{5}H_{11}$$

$$CQ \longrightarrow CQ \qquad (437)$$

A yellow coupler of the invention is incorporated into a light-sensitive silver halide emulsion layer or its adjacent layers.

The yellow coupler of the invention may be used in combination of two or more thereof or in combination with other yellow couplers. In the latter instance, it is preferable that the yellow coupler of the invention be used in an amount of not less than 50 mole %.

The yellow coupler of the invention is used preferably in the amount of 0.02 to 3.0g/m², more preferably 0.1 to 1.5g/m² and most preferably 0.2 to 1.0g/m².

The yellow coupler is incorporated into a color light-sensitive material by any of various methods including an oil-in-water-type emulsification dispersion method in which a water-insoluble high-boiling organic solvent is used according to the coupler's physical property (e.g., solubility); an alkali dispersion method in which the yellow coupler is incorporated in the form of an alkaline solution; a latex dispersion method; a solid dispersion method in which the coupler is incorporated in the form of a particulate solid.

It is preferable that a DIR compound be used in the photographic light-sensitive material of the invention.

The DIR compound is one which, upon reaction with an oxidation product of a color developing agent, splits off a development inhibitor or a compound capable of releasing a development inhibitor.

The above compound capable of releasing a development inhibitor may be either one releasing a development inhibitor imagewise or one releasing nonimagewise.

The compound releasing a development inhibitor imagewise includes those releasing it upon reaction with an oxidation product of a developing agent, and the one releasing nonimagewise includes those which utilizes a TIME group described hereinafter.

The DIR compound used in the invention is represented by Formula D-1:

## Formula D-1

 $A_{-}(Y)_{m}$ 

wherein A represents a coupler residue, m is an integer of 1 or 2; and Y, which combines to the coupling position of the coupler residue A and is split off upon reaction with the oxidation product of a color developing agent, represents a development inhibitor group.

In Formula D-1, Y is represented by the following Formulas D-2 through D-10:

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Formula D-2

Formula D-3

$$-OCH_2-N$$
 $(Rd_1)n$ 

Formula D-4

Formula D-5

$$-s \stackrel{H}{\sim} N$$
 (Rd<sub>1</sub>)n

Formula D-6

Formula D-7

$$-s \chi \chi Rd$$

$$N-N$$

$$-N$$
 $(Rd_1)n$ 

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Formula D-8

Formula D-9

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In Formulas D-2 through D-7, Rd<sub>1</sub> each represents a hydrogen atom, a halogen atom, an alkyl, alkoxy, acylamino, alkoxycarbonyl, thiazolidinylideneamino, aryloxycarbonyl, acyloxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, nitro, amino, N-arylcarbamoyloxy, sulfamoyl, N-alkyl carbamoyloxy, hydroxy, alkoxycarbonylamino, alkylthio, arylthio, heterocyclic, cyano, alkylsulfonyl, and aryloxycarbonylamino group.

n is an integer of zero, 1 or 2, provided that when n is 2, Rd<sub>1</sub>s may be either the same or different, and the total carbon atoms contained in all Rd<sub>1</sub>s are zero to 10.

In Formula D-6, the number of carbon atoms contained in Rd1 is zero to 15.

in Formula D-6, X represents an oxygen atom or a sulfur atom.

In Formula D-8, Rd2 represents an alkyl group, an aryl group or a heterocyclic group.

In Formula D-9, Rd<sub>3</sub> represents a hydrogen atom, an alkyl, cycloalkyl, aryl, or heterocyclic group, and Rd<sub>4</sub> represents a hydrogen atom, a halogen atom, an alkyl, cycloalkyl, aryl, acylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkanesulfonamido, cyano, heterocyclic, alkylthio, or amino group.

The heterocyclic group represented by Rd<sub>1</sub>, Rd<sub>2</sub>, Rd<sub>3</sub> or Rd<sub>4</sub> is preferably a 5- or 6-member monocyclic or condensed ring containing at least one selected from the group consisting of a nitrogen atom, an oxygen atom and a sulfur atom, such as pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl, imidazolyl, thiazolyl, triazolyl, benzotriazolyl, imido, and oxazine.

In Formula D-8, the number of carbon atoms contained in Rd2 is zero to 15.

In Formula D-9, the total number of carbon atoms contained in Rd<sub>3</sub> and Rd<sub>4</sub> is zero to 15.

The DIR compound represented by Formula D-1 is further represented by Formula D-10:

## Formula D-10

A-(TIME) \_\_INHIBIT

wherein A represents a coupler residue; TIME which combines to the coupling position of A and can split off upon reaction with the oxidation product of a color developing agent, represents a group which splits off sequentially after splitting off from the coupler residue and finally releases INHIBIT under adequate control; n is an integer of 1 to 3, provided that when n is 2 or 3, TIMEs may be either the same or different.

INHIBIT represents a group which becomes a development inhibitor after being released, exemplified by Formulas D-2 through D-9.

In Formula D-10, -TIME is typified by the groups represented by the following Formulas D-11 through D-19.

Formula D-11

$$(Rd_{5})\ell$$

$$(CII_{2})k-N-CO-$$

$$Rd_{6}$$

Formula D-12

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Formula D-14

$$-0 \xrightarrow{Rd_{\delta}} N$$

$$-0 \xrightarrow{N} Rd_{\delta}$$

$$CH_{2} - Rd_{\delta}$$

Formula D-16

$$(CH_2)k - NCO - Rd_6$$

$$(Rd_5)\ell$$

Formula D-17

$$(Rd_7)m$$

$$-N$$

$$(CH_2)kB-CO-$$

Formula D-18

$$\begin{array}{c}
0 \\
-N \\
0
\end{array}$$
(CH<sub>2</sub>)kB-C0-

Formula D-19

$$\begin{array}{c|c}
 & O \\
 & -N \\
 & O \\
 & O$$

In Formulas D-11 through D-15 and D-18,  $Rd_5$  each represents a hydrogen atom, a halogen atom, an alkyl, cycloalkyl, alkenyl, aralkyl, alkoxy, alkoxycarbonyl, anilino, acylamino, ureido, cyano, nitro, sulfonamido, sulfamoyl, carbamoyl, aryl, carboxy, sulfo, hydroxy, and alkanesulfonyl group. In Formulas D-11 through D-13, D-15 and D-18,  $Rd_5$ s may combine with one another to form a condensed ring. In Formulas D-11, D-14, D-15 and D-19,  $Rd_6$  each represents an alkyl, alkenyl, aralkyl, cycloalkyl, heterocyclic or aryl group. In Formulas D-16 and D-17,  $Rd_7$  each represents a hydrogen atom an alkyl, aikenyl, aralkyl, cycloalkyl, heterocyclic and aryl group. In Formula D-19,  $Rd_8$  and  $Rd_9$  each represent a hydrogen atom or

an alkyl group having preferably 1 to 4 carbon atoms. In Formulas D-11, D-15 through D-18, k is an integer of zero, 1 or 2. In Formulas D-11 through D-13, D-15 and D-18, is an integer of 1 to 4, and in Formula D-16, m is an integer of 1 or 2, provided that when £ and m each is 2 or more, the Rd<sub>5</sub>s and Rd<sub>7</sub>s may independently be either the same or different, respectively. In Formula D-19, n is an integer of 2 to 4, provided that Rd<sub>8</sub>s and Rd<sub>9</sub>s may be either the same or different, respectively. In Formulas D-16 through D-18, B represents an oxygen atom or a

-Ņ-Rđ.

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group, wherein Rd<sub>6</sub> is as previously defined. In Formula D-16, — represents a single bond or a double bond, provided that it is the single bond when m is 2, while it is the double bond when m is 1.

Further, the DIR compound represented by Formula D-1 is represented by Formula D-20;

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Formula D-20

 $(T_1)_{\mathcal{Z}} SR(T_2)_{\overline{m}} INHIBIT$ 

wherein A represents a coupler residue;  $T_1$  represents a component capable of splitting off from A and releasing  $SR(T_2)_m$  INHIBIT; SR represents a component which, after  $SR(T_2)_m$  INHIBIT is released, can release  $(T_2)_m$  INHIBIT upon reaction with an oxidation product of a developing agent;  $T_2$  represents a component which, after  $(T_2)_m$  INHIBIT is released, can release INHIBIT; INHIBIT represents a development inhibitor; and t and

The component represented by SR may be anyone as long as it produces the above component upon reaction with the oxidation product of a developing agent, which includes a coupler component subjected to a coupling reaction with the oxidation product of a developing agent and a redox component subjected to a redox reaction with the oxidation product of a developing agent.

Examples of the coupler component include yellow couplers, magenta couplers, cyan couplers and compounds either to form or not to form various dyes, such as acylacetanilides, 5-pyrazolones, pyrazoloazoles, phenols, naphthols, acetophenones, indanones, carbamoylacetanilides, 2(5H)- imidazolones, 5-isooxazolones, uracils, homophthalimides, oxazolones, 2,5-thiazoline-1,1-dioxides, triazolothiadiazines, and indoles.

The  $\{T_1\}_{\mathcal{Z}}$  SR $\{T_2\}_{\overline{m}}$  INHIBIT preferably combines to the active site of the component A of Formula D-1,

When SR is a coupler component, SR combines with  $\{T_1\}_{2^-}$  and  $\{T_2\}_{\overline{m}}$  INHIBIT so as to function as a coupler only after being split off from  $\{T_1\}_{\overline{2}^-}$ . It is preferable that as oxygen atom of a hydroxyl group in the case of a phenol or naphthol compound as the coupler component, an oxygen atom of a hydroxyl group in a 5-position or a nitrogen atom in a 2-position of the tautomer in the case of 5-pyrazolone, and an oxygen atom of a hydroxyl group of the tautomer in the case of an acetophenon or indanone compound combine with  $\{T_2\}_{\overline{m}}$ , and  $\{T_2\}_{\overline{m}}$  INHIBIT combine to the active site of the coupler.

When SR is a redox component, the example thereof include a hydroquinone compound, a catechol compound, a pyrogallol compound, an aminophenol compound, a naphthalenediol compound, and an aminonaphthol compound. Also, when SR is a redox component, SR combining with  $\{T_1\}$  and  $\{T_2\}$  INHIBIT functions as the redox component only after being split off from  $\{T_1\}$ .

The groups represented by T<sub>1</sub> and T<sub>2</sub> include those represented by Formulas D-11 through D-19.

The development inhibitor represented by INHIBIT includes those represented by Formulas D-2 through D-9.

Preferred among the DIR compounds are ones in which Y of Formula D-1 is represented by Formula D-2, D-3, or D-8, and in which INHIBIT of Formulas D-10 and D-20 is represented by Formula D-2, D-3, D-6 (particularly when X of D-6 is an oxygen atom) and D-8.

The coupler component represented by A in Formula D-1 includes a yellow dye image-forming coupler residue, a magenta dye image-forming coupler residue, a cyan dye image-forming coupler residue and a colorless coupler residue.

The following are useful compounds as the DIR compound for the invention.

Exemplified compounds:

-

$$\begin{array}{c} \cdot R_1 - \text{COCIICO} - R_2 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \end{array}$$

Exemplified compound No.	R ,	R 2	Y
D - 2	(1)	(1)	(30)
D - 3	(2)	(3)	(30)
D - 4	(2)	(4)	(30)
D - 5	(5)	(6)	(31)
D - 6	(2)	(4)	(32)
D-7	(2)	(3)	(32)
D - 8	(7)	(8)	(33)
D - 33	(2)	(4)	(55)
D - 40	(2)	(4)	(56)
D - 43	(2)	(25)	(59)

R 1	N.	$T^{Y}$
	\N\	0
	R.	,

Exemplified compound No.	R 1	R 2	Y
D - 9	(9)	(10)	(30)
D - 10	(11)	(10)	(30)
D - 11	(12)	(7)	(34)
D - 12	(12)	(13)	(35)
D - 13	(9)	(14)	(36)
D - 14	(15)	(16)	(37)
D - 35	(56)	(24)	(23)

OH R:

Exemplified compound No.	R i	Y
D - 15	(17)	(38)
D - 16	(17)	(39)
D - 17	(18)	(40)
D - 18	(19)	(41)
D - 19	(18)	(42)
D - 20	(18)	(43)
D - 21	(18)	(44)
D - 22	(18)	(45)
D - 23	(18)	(46)
D - 24	(20)	(47)
D - 25	(20)	(48)
D - 26	(21)	(49)
D - 27	(21)	(50)
D - 28	(21)	(51)
D - 29	(22)	(52)
D - 30	(18)	(53)
D - 31	(18)	(54)
D - 32	(22)	(49)
D - 34	(18)	(56)
D - 38	(19)	. (46)
D - 39	(18)	(57)
D - 41	(18)	(60)
D - 42	(18)	(48)
D - 44	(18)	(58)

In the table,  $R_1$ ,  $R_2$  and Y represent the following groups:

38 39

35 40 . 41

$$-S \stackrel{N-N}{\underset{N-N}{|}}$$

$$C_2H_5$$

5 CH<sub>2</sub> - S - N - N - N - CH<sub>3</sub>

 $CH_2 - S \longrightarrow N \longrightarrow N$   $N \longrightarrow CH_3 \qquad C_2H_5$ 

25 48

O CH<sub>2</sub> - S O CH<sub>3</sub>

O CH<sub>3</sub>

$$\begin{array}{c|c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$$

$$O_2N \longrightarrow N \longrightarrow N \longrightarrow N \longrightarrow N \longrightarrow N$$

The examples of the DIR compounds usable in the invention including these compounds are disclosed in U.S. Patent Nos. 4,234,678, 3,227,554, 3,617,291, 3,958,993, 4,149,886, 3,933,500, 2,072,363, 2,070,266, Japanese Patent O.P.I. Publication Nos. 56837/1982, 13239/1976, and Research Disclosure No. 21228, Dec. 1981.

The DIR compound is used in the amount range of preferably 0.0001 to 0.1 mole, and more preferably 0.001 to 0.05 mole per mole of silver halide.

A place the DIR compound is added to is where the compound can influence the development of the silver halide inside an emulsion layer of a single-layer construction, preferably a silver halide emulsion layer, and more preferably the silver halide emulsion layer of a single-layer construction.

In the photographic material of this invention containing the DIR compound, the sharpness is remarkably improved than in that containing a conventional yellow coupler and the DIR compound.

Gelatin is preferably used as the binder of a silver halide emulsion.

An emulsion layer and other hydrophilic colloid layers may be hardened, and may contain a plasticizer and a water-insoluble or less-soluble synthetic polymer latex.

Further, there may be used color correction effect-having colored couplers, competing couplers and compounds capable of releasing photographically useful fragments such as a developing agent, a silver halide solvent, a toning agent, a hardener, an antifoggant, a chemical sensitizer, a spectral sensitizer and a desensitizer upon coupling reaction with an oxidation product of a developing agent.

The light-sensitive material may comprise auxiliary layers including a filter layer, an antihalation layer, and an antiirradiation layer. These layers and/or emulsion layers may contain a dye which is eluted out of the light-sensitive material or bleached in the course of development.

The light-sensitive material may also contain a formalin scavenger, a brightening agent, a matting agent, a lubricant, an image stabilizer, a surfactant, an anti-color-stain agent, a development accelerator, a development retarder and a bleaching accelerator.

Materials usable as a support include polyethylene-laminated paper, polyethylene terephthalate film, baryta paper and cellulose triacetate film.

The light-sensitive material of the invention is particularly useful as a negative light-sensitive material.

#### **EXAMPLES**

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The present invention is illustrated in detail by the following examples.

Preparation example 1:

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## Preparation of a seed emulsion

To 500 ml of a 2.0% gelatin aqueous solution heated up to 40° C was added 5x10<sup>-5</sup> mole of K<sub>3</sub>RhCl<sub>6</sub>, and then added in 35 minutes, 250 ml of a 4M AgNO<sub>3</sub> aqueous solution and 250 ml of a 4M KBr aqueous solution, controlling pAg and pH at 9.0 and 2.0, respectively, by a double-jet method, in accordance with the method described in Japanese Patent O.P.I. Publication No. 45437/1975. To the emulsion, after being adjusted to pH 5.5 with a potassium carbonate solution, were added 364 ml of a 5% aqueous solution of Demol N (product of Kawo Atlas) and 244 ml of a 20% magnesium sulfate aqueous solution as a precipitant for coagulation and precipitation, and the supernatant was removed by decantation. To the product were added 1,400 ml of distilled water for redispersion, and then 36.4 ml of a 20% aqueous solution of magnesium sulfate for coagulation and precipitation to remove the supernatant by decantation. Aqueous solution containing 28g of Osein gelatin was added to make the whole quantity 425 ml, which was then dispersed in 40 minutes at 40° C to thereby prepare an AgX seed emulsion NE-1.

As a result of electron-microscopic observation, the seed emulsion NE-1 was a monodispersed emulsion comprising cubic grains having an average grain size of 0.093 μm.

A seed emulsion NE-2 was prepared in the same manner as the above except that  $K_3RhCl_6$  was removed. NE-2 was a monodispersed emulsion comprising cubic grains having an average grain size of 0.093 $\mu$ m as a result of electron-microscopic observation.

The results are shown in Table 1.

Table 1

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EM No.	Additive	Added amount (mol/mol Ag)	Grain size (µm)
NE-1	K <sub>3</sub> RhCl <sub>6</sub>	5x10-5	0.093
NE-2		n w)	0.093

## Preparation example 2:

The seed emulsions prepared in preparation example 1 and the following seven solutions were used to prepare core/shell-type monodispersed silver iodobromide emulsions Em-1 and Em-2 each comprising 15 mole%, 5 mole% and 3 mole% Agl contents in this order from the inside core of the grain, having an average grain size of 0.4 µm and an average Agl content of 8 mole%.

The emulsions and their details are shown in Table 2.

## Solution A

Osein gelatin

28.6 g

$$HO-(CH_2CH_2O) + (CHCH_2O) + (CH_2CH_2O) +$$

16.5 ml

CH, Ethanol solution of Pronon, average molecular weight 1700 (Nippon Oil and Fats Co.)

TAI\*

247.5 mg

56% acetic acid solution

72.6 ml

28% aqueous ammonia solution

97.2 ml

Seed emulsion prepared in preparation example 1

an amount equivalent to 0.134 mole

Distilled water to make 6600 ml.

ml.

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Solution B		
Osein gelatin	13 g	
KBr	460.2 g	
KI	113.3 g	
TAI	665 mg	
Distilled water to make 1300		

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Distilled water to make 1700 ml.

Solution D		
Osein gelatin KBr KI TAI	8 g 323.2 g 13.94g 409 mg	
Distilled water to make 800 ml.		

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Solution E		
AgNO₃ 28% aqueous ammonia solution	1777.2 g 1470 ml	
Distilled water to make 2989 ml.		

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## Solution F

25 20% KBr solution an amount necessary for pAg adjustment

#### Solution G

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56% acetic acid solution

an amount necessary for pH adjustment

\*TAI: 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene

To solution A were added solution E and solution B at 40 °C by means of a mixer-stirrer in accordance with a simultaneous mixing method. Upon completion of the addition of solution B, solution C was added, and upon completion of the addition of solution D was added.

The control of pAg and pH during the simultaneous mixing and the adding speed of solutions E, B, C and D were performed as follows:

pAg and pH were controlled by changing the flow of solutions F and G, respectively, with a flow-variable roller tube pump.

After completion of the addition of solutions D and E, pH was adjusted to 6.0 with solution G.

The emulsion was desalted and washed in usual manner, and then dispersed in an aqueous solution containing 197.4g of Osein gelatin.

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# Grain growth conditions

Solution E

Solution B

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	Time (min.)	Adding speed (ml/min.)	Time (min.)	Adding speed (ml/min.)	
	0.0	8.4	0.0	8.0	
10	2.8	12.7	2.8	12.2	
	4.8	17.0	4.8	16.3	
15	19.0	57.2	8.7	26.7	
	21.5	58.6	16.2	48.8	
	30.7	38.7	19.5	55.3	
20	36.6	32.1	21.0	56.6	
	41.5	29.2	22.0	55.0	
25	45.6	29.3	27.8	42.5	
	47.5	31.0	29.9	38.3	
	49.4	35.3	31.5	37.2	
30	58.7	48.3	33.1	35.3	
	64.2	60.8	34.8	33.8	
35	70.1	83.4	36.6	32.7	
	71.2	83.4	38.5	32.2	

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Solution C

# Solution D

	Time	Adding speed	Time	Adding speed
	(min.)	(ml/min.)	(min.)	(ml/min.)
5	38.5	32.2	54.8	40.9
	39.5	32.2	56.8	43.9
	40.5	32.5	58.7	47.1
	41.5	33.0	60.5	<b>50.5</b>
	42.5	33.8	61.6	<b>52.9</b>
10	43.5	35.1	62.7	55.4
	44.5	36.9	63.7	57.9
	45.6	39.4	64.7	60.6
	46.6	42.8	65.7	63.4
	47.5	47.7	66.6	66.3
15	48.5	54.7	67.4	69.3
	49.4	34.4	68.2	72.5
	51.8	37.1	69.0	75.8
	53.3	39.0	70.1	81.1
	54.8	40.9	71.2	81.1
20				

Time	рН
(min.)	-
0.0	9.00
4.8	8.92
9.7	8.77
11.5	8.70
13.0	8.62
14.4	8.55
15.6	8.47
17.9	8.32
20.0	8.17
23.1	7.95
25.3	7.80
27.8	7.65
<b>29.2</b>	7.57
30.7	7.50
71.2	7.50

Time	pн
(min.)	
0.0	8.55
30.7	8.55
32.3	8.71
33.9	8.88
35.7	9.04
37.5	9.21
39.5	9.37
41.5	9.54
43.5	9.70
45.6	9.87
46.6	9.95
47.5	10.03
48.5	10.11
49.4	10,20
71.2	10.20

Table 2

Em No.	Seed emulsion		Average grain size (μm)	Coefficient of variation
	No.	Metallic ion contained		
Em-1 Em-2	NE-1 NE-2	Rh None	0.4 0.4	0.19 0.19

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EXAMPLE 1

# Preparation of sample No.101 (comparative)

On a subbed cellulose acetate support were coated the compositions layers having the following to prepare a multilayer color light-sensitive material No.101.

The coated amounts of silver halide and colloidal silver are given in g/m<sup>2</sup> converted to silver, those of additives and gelatin are given in g/m<sup>2</sup>, and those of sensitizing dyes, couplers and DIR compounds are given in moles per mole of silver halide.

The emulsion contained in each color-sensitive emulsion layer was optimally sensitized by sodium thiosulfate and chloroauric acid.

Black colloidal silver  Gelatin  Ultraviolet absorbing agent UV-1  ,, UV-2	0.20 1.5 0.1
Ultraviolet absorbing agent UV-1	0.1
UV-2	
•	0.2
Diaghed mbtholato /DOD)	V . Z
Dioctyl phthalate (DOP)	0.03
Gelatin	2.0
Antistain agent (AS-1)	0.1
DOP	0.1
Em-2	1.2
Gelatin	1.1
Sensitizing Dye I	$6 \times 10^{-5}$
°° II	1x10 <sup>-5</sup>
Coupler C-1	0.06
Coupler CC-1	0.003
DIR compound D-23	0.001
DIR compound D-39	0.002
DOP	0.6
Em-A*	1.0
Gelatin	1.1
Sensitizing dye I	3x10 <sup>-5</sup>
"" II	1x10 <sup>-5</sup>
Coupler C-1	0.03
DIR compound D-39	0.001
DOP	0.2
	Antistain agent (AS-1)  DOP  Em-2  Gelatin  Sensitizing Dye I  ,, II  Coupler C-1  Coupler CC-1  DIR compound D-23  DIR compound D-39  DOP  Em-A*  Gelatin  Sensitizing dye I  ,, II  Coupler C-1  DIR compound D-39

	Gelatin	0.8
(intermediate layer)	AS-1	0.03
	DOP	0.1
Layer 6(G-1)	Em-2	1.1
(first green- sensitive	Gelatin	1.2
emulsion layer)	Sensitizing dye III	2.5x10
	· · · IV	1.2x10
	Coupler M-2	0.045
	Coupler CM-1	0.009
	DIR compound D-23	0.001
	DIR compound D-26	0.003
	Tricresyl phosphate (TCP)	0.5
Layer 7(G-2)	Em-A*	1.3
(second green- sensitive	Gelatin	0.8
emulsion layer)	Sensitizing dye III	1.5x10
•	· · IV	1.0x10
·	Coupler M-1	0.03
	DIR compound D-26	0.001
	TCP	0.3
Layer 8(YC)	Gelatin	0.6
(yellow filter layer)	Yellow colloidal silver	0.08
	AS-1	0.1
	DOP	0.3
***************************************	(continued)	

	Layer 9(B-1)	Em-2	0.5
5	(first blue- sensitive	Gelatin	1.1
	emulsion layer)	Sensitizing dye V	1.3x10 <sup>-5</sup>
		Coupler Y-5	0.29
10		TCP	0.2
	Layer 10(B-2)	Em-A*	0.7
4-	(second blue- sensitive	Gelatin	1.2
15	emulsion layer)	Sensitizing dye V	1x10 <sup>-5</sup>
		Coupler Y-5	0.08
20		DIR compound D-39	0.0015
		TCP	0.1
	Layer 11(Pro-1) (first protec-	Gelatin	0.55
25	tive layer)	Ultraviolet absorbing agent UV-1	0.1
		'' UV-2	0.2
30		DOP	0.03
		Silver iodobromide, AgI: 1 mol%, average grain size: 0.07μm	0.5
35	Layer 12(Pro-2) (second protec-	Gelatin	0.5
30	tive layer)	Polymethyl methacrylate particles particle diameter 1.5 µm	0.2
		Formalin scavenger HS-1	3.0
40	-	Hardener H-1	0.4

<sup>\*</sup>Em-A: Silver halide iodobromide emulsion having an average AgI content of 8.5 mol and an average grain size of 0.7 mm, prepared in making reference to the foregoing preparation method, in which the AgI content is higher in the inside than in the surface of the grain.

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Besides the above components, a surface active agent was added as a coating aid to the respective layers.

UV-1

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UV-2

$$\begin{array}{c|c} CH_3 & CH & CH & CH \\ \hline CH_3 & CH & CH & CONHC_{12}H_{28} \\ \hline C_2H_5 & CH & CH & CN \\ \hline \end{array}$$

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C-1

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CC-1

OH 
$$CONH(CH_2), O \longrightarrow C_5H_{11}(t)$$

SO<sub>3</sub>Na

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NaO<sub>3</sub>S

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M-1

$$C_{\mathfrak{g}}H_{11}(\mathfrak{t})$$

$$C_{\mathfrak{g}}H_{11}(\mathfrak{t})$$

$$C_{\mathfrak{g}}H_{11}(\mathfrak{t})$$

$$C_{\mathfrak{g}}H_{11}(\mathfrak{t})$$

M-2

CM-1

# Sensitizing dye I

$$CQ$$

$$CQ$$

$$CH = C - CH = S$$

$$CQ$$

$$CH_2)_3SO_3 = (CH_2)_3SO_3H \cdot N(C_2H_5)_3$$

# Sensitizing dye II

$$\begin{array}{c} S \\ \Rightarrow \\ CH = C - CH = \\ \\ CH_2)_3SO_3 \\ \end{array}$$

$$\begin{array}{c} C_2H_5 \\ \\ CH_2)_3SO_3H \cdot N(C_2H_5)_3 \\ \end{array}$$

# Sensitizing dye III

$$\begin{array}{c} C_2H_6 \\ C_1 \\ C_2H_6 \\ C_3 \\ C_2H_6 \\ C_3 \\ C_2H_6 \\ C_3 \\ C_3 \\ C_3 \\ C_4 \\ C_5 \\ C_7 \\ C_8 \\ C_9 \\$$

# Sensitizing dye IV

$$\begin{array}{c} C_2 H_5 \\ \Theta \\ N \\ CH = C - CH \\ O \\ O \\ CH_2)_3 SO_3 \Theta \\ (CH_2)_3 SO_3 H \cdot N(C_2 H_5)_3 \end{array}$$

# Sensitizing dye V

CH<sub>3</sub>O

$$CH_3$$
 $CH_3$ 
 $CH_3$ 

# Preparation of samples No. 102 to 105 (comparative)

Samples No.102 to 105 were prepared in the same manner as in sample No.101 except that the coupler Y-5 of Layer 9 and Layer 10 of sample No. 101 was replaced by the couplers of equimoles as shown in Table 3.

## Preparation of sample No.106 (invention)

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This sample was prepared as follows. The emulsions of the sample were as optimally sensitized as those of sample No.101.

Layer 1: HC the same as the layer 1 of sample No.101.

Layer 2: IL-1 the same as the layer 2 of sample No.101.

Layer 3: R-1 the same as the layer 3 of sample No.101.

Layer 4: R-2 the same as the layer 4 of sample No.101.

Layer 5: IL-2 the same as the layer 5 of sample No.101.

Layer 6: G-1 the same as the layer 6 of sample No.101.

Layer 7: G-2 the same as the layer 7 of sample No.101.

Layer 8: YC the same as the layer 8 of sample No.101.

Layer 9: B-1 the same as the layer 9 of sample No.101,

provided, the emulsion Em-2 replaced with an emulsion prepared by mixing equimolar amounts of optimally sensitized Em-2 and Em-A was used in a coating amount of 0.63 g/m<sup>2</sup> with 1.4 g/m<sup>2</sup> of gelatin and 0.25 g/m<sup>2</sup> of TCP.

Layer 10: Pro-1 the same as the layer 11 of sample No.101.

Layer 11: Pro-2 the same as the layer 12 of sample No.101.

## Preparation of samples No.107 to 110 (invention)

Samples No.107 to 110 were prepared in the same manner as in sample No.106 except that the coupler Y-5 of the layer 9 of sample No.106 was replaced by the couplers of equimoles as shown in Table 3.

## Preparation of sample No.111 (invention)

The sample was prepared as follows:

- Layer 1: HC the same as the layer 1 of sample No.101.
- Layer 2: IL-1 the same as the layer 2 of sample No.101.
- Layer 3: R-1 the same as the layer 3 of sample No.101,
- provided that the emulsion Em-2 replaced with an emulsion prepared by mixing equimolar amounts of optimally sensitized Em-2 and Em-A was used in a coating amount of 1.5 g/m<sup>2</sup> with 1.4 g/m<sup>2</sup> of gelatin and 0.75 g/m<sup>2</sup> of DOP.
  - Layer 4: IL-2 the same as the layer 5 of sample No.101.
  - Layer 5: G-1 the same as the layer 6 of sample No.101,
- 10. provided that the emulsion Em-2 replaced with an emulsion prepared by mixing equimolar amounts of optimally sensitized Em-2 and Em-A was used in a coating amount of 1.4 g/m² with 1.5 g/m² of gelatin and 0.6 g/m² of TCP.
  - Layer 6: YC the same as the layer 8 of sample No.101.
  - Layer 7: B-1 the same as the layer 9 of sample No.101,
- provided that the emulsion Em-2 replaced with an emulsion prepared by mixing equimolar amounts of optimally sensitized Em-2 and Em-A was used in a coating amount of 0.63 g/m² with 1.4 g/m² of gelatin and 0.25 g/m² of TCP.
  - Layer 8: Pro-1 the same as the layer 11 of sample No.101.
  - Layer 9: Pro-2 the same as the layer 12 of sample No.101.

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# Preparation of sample No.112 (invention)

Sample No.112 was prepared in the same manner as in sample No.111 except that the coupler Y-5 of the layer 7 was replaced by coupler Y-8 of equimoles.

## Preparation of sample No.113 (invention)

Sample No.113 was prepared in the same manner as in sample No.111 except that the Em-2/Em-A mixture emulsion contained in the layers 3, 5 and 7 was replaced by an emulsion prepared by mixing equimolar amounts of optimally sensitized Em-1 and Em-2.

# 35 Preparation of sample No.114 (invention)

Sample No.114 was prepared in the same manner as in sample No.113 except that the coupler Y-5 of the layer 7 of sample No.113 was replaced by coupler Y-8 of equimoles.

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#### Preparation of sample No.115 (invention)

Sample No.115 was prepared in the same manner as in sample No.111 except that the emulsion in the layers 3, 5 and 7 of sample No.111 was replaced by emulsion Em-2, which was optimally sensitized.

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#### Preparation of sample No.116 (comparative)

Sample No. 116 was prepared in the same manner as in sample No. 101 except that the coupler Y-5 of Layer 9 and Layer 10 of sample No.101 was replaced by the coupler YY-1 of equimoles as in Table 3.

# Preparation of sample No.117 (comparative)

Sample No. 117 was prepared in the same manner as in sample No.106 except that the coupler Y-5 of Layer 9 of sample No. 106 was replaced by the coupler YY-1 of equimoles as in Table 3.

These samples No.101 through 117 were exposed through an optical wedge and then processed in the following steps:

Processing steps: (38°C)				
Color developing Bleaching Washing Fixing Washing Stabilizing	3 minutes and 15 seconds 6 minutes and 30 seconds 3 minutes and 15 seconds 6 minutes and 30 seconds 3 minutes and 15 seconds 1 minute and 30 seconds			
Drying				

The compositions of the processing solutions used in the above steps are as follows:

15	Color developer				
	4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate	4.75g			
	Anhydrous sodium sulfite	4.25g			
	Hydroxylamine 1/2 sulfate	2.0 g			
20	Anhydrous potassium carbonate	37.5 g			
	Potassium bromide	1.3 g			
	Trisodium nitrilotriacetate	2.5 g			
	Potassium hydroxide	1.0 g			
25	Water to make 1 liter (pH = 10.02).	•			

Bleaching bath	
Ferric-ammonium ethylenediaminetetraacetate Diammonium ethylenediaminetetraacetate Ammonium bromide Glacial acetic acid	100.0 g 10.0 g 150.0 g 10.0 g
Water to make 1 liter. Adjust pH to 6.0 with aqueous ammonia.	

Fixer			
Ammonium thiosulfate Anhydrous ammonium sulfite Sodium metabisulfite	175.0 g 8.6 g 2.3 g		
Water to make 1 liter. Adjust pH to 6.0 with acetic acid.			

Stabilizer	
Formalin (37% solution) Konidax (product of KONICA Corporation	1.5 ml ) 7.5 ml
Water to make 1 liter.	

The sharpness (MTF), preservability and processing stability of each processed sample were evaluated. The results of the blue-sensitive layer are shown in Table 3.

The sharpness is expressed by MTF (Modulation Transfer Function) at a spatial frequency of 10 lines/mm, and is shown by the value relative to that of sample No.101, which is set at 100.

Table 3

Samp	ole No.	Coupler	(unit lar wt)	Sharpness	Preserv- ability*1	Processing stability*2
101	(comp.)	Y-5	(672)	100	100	100
102	(comp.)	Y-10	(526)	105	101	95
103	(comp.)	Y-8	(686)	98	100	98
104	(comp.)	Y-6	(680)	101	102	101
105	(comp.)	Y-30	(434)	99	105	103
106	(inv.)	Y-5	(672)	121	42	60
107	(inv.)	Y-10	(526)	127	41	58
108	(inv.)	Y-8	(686)	120	42	60
109	(inv.)	Y-6	(680)	121	40	57
110	(inv.)	Y-30	(434)	118	41	63
111	(inv.)	Y-5	(672)	144	39	5 5
112	(inv.)	Y-8	(686)	143	38	54
113	(inv.)	Y-5	(672)	150	37	30
114	(inv.)	Y-8	(686)	151	37	32
115	(inv.)	Y-5	(672)	150	37	31
116	(comp.)	<b>YY-1</b>	(748)	85	105	105
117	(comp.)	YY-1	(748)	95	45	70

<sup>\* 1</sup> Preservability:

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Shown by a variation in the sensitivities of the sample in developing just after preparation thereof and after preserving at 40°C and RH 80% for seven days; it is shown by the value relative to that of sample No. 101, which is set at 100. The smaller the value, the better the preservation.

<sup>\*\*</sup>Processing stability:
Shown by a variation in the sensitivities of the sample in developing at pH of 10.02 and 9.8; it is shown by the

value relative to that of sample No. 101, which is set at 100. The smaller the value, the better the stability to processing fluctuation.

As is apparent from Table 3, in the samples containing coupler YY-1, sample No. 117 has a little improved sharpness, but samples No.106 to 115 for the invention have more improved sharpness, preservability and processing stability than comparative samples No.101 to 105.

Comparison of the samples for the invention themselves exhibits that samples No.111 in which all light-sensitive layers are of a single layer are more improved in the sharpness than samples No.106 to 110, and that especially, samples No.113 to 115 containing silver halide grains with a narrow grainsize distribution are further more improved in the processing stability and sharpness, as well as in the sensitivity.

Furthermore, the sample No.118 was prepared in the same manner as in sample No. 111 except that the amounts of DIR compounds were reduced by 50% compared with that of sample No.111. The sample No.111 showed similar inter-image effect to sample No.101 and the speed of sample No.118 was higher than that of sample No.111.

#### **EXAMPLE 2**

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Samples No.201 to 215 were prepared in the same manner as in samples No.101 to 115 except that the coupler contained in the blue-sensitive layers of samples No.101 to 115 was replaced as shown in Table 4, and processed in the same manner as in Example 1 to evaluate for the blue-sensitive layers thereof.

The results are shown in Table 4.

Table 4

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Sample No.	Coupler (unit molecular wt)	Sharpness	Preservability*1	Processing stability*2
201 (comp.)	Y-18 (578)	100	100	100
202 (comp.)	Y-19 (621)	99	101	97
203 (comp.)	Y-17 (536)	101	102	102
204 (comp.)	Y-16 (598)	102	100	98
205 (comp.)	Y-36 (437)	104	104	104
206 (inv.)	Y-18 (578)	122	40	89
207 (inv.)	Y-19 (621)	121	41	82
208 (inv.)	Y-17 (536)	123	42	83
209 (inv.)	Y-16 (598)	119	42	86
210 (inv.)	Y-36 (437)	114	43	81
211 (inv.)	Y-18 (578)	137	39	70
212 (inv.)	Y-19 (621)	133	39	72
213 (inv.)	Y-18 (578)	150	37	39
214 (inv.)	Y-19 (621)	149	37	40
215 (inv.)	Y-18 (578)	149	37	40

<sup>\*1</sup>Preservability and

Similarly to Table 3, each is shown in a value relative to that of sample No.101, which is set at 100.

As is apparent from Table 4, samples No.206 to 215 for the invention have more improved sharpness, preservability and processing stability than comparative samples No.201 to 205.

Comparison of the samples for the invention themselves exhibit that samples No.211 to 215 in which the whole light-sensitive layers are of single-layer constructions have more improved sharpness, and that

<sup>\*2</sup>processing stability

especially, samples No.213 to 215 containing silver halide grains with a narrow grainsize distribution, have a significantly improved processing stability.

#### 5 Claims

- 1. A silver halide color photographic light-sensitive material comprising a support and provided thereon, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and a redsensitive silver halide emulsion layer, wherein said blue-sensitive silver halide emulsion layer is of a single layer construction and contains a yellow coupler having a molecular weight of 250 to 700 per coupling site of said yellow coupler.
- 2. The light-sensitive material of claim 1, wherein said green-sensitive silver halide emulsion layer further is of a single layer construction.
- 3. The light-sensitive material of claim 2, wherein said red-sensitive silver halide emulsion layer further is of a single layer construction.
  - 4. The light-sensitive material of claim 1, wherein said blue-senitive silver halide emulsion layer contains at least two kinds of silver halide emulsions containing silver halide grains having different average grain sizes.
- 5. The light-sensitive material of claim 4, wherein the silver halide grains contained in one of said silver halide emulsions have the largest average grain size of 0.2 to 2.0 µm.
  - 6. The light-sensitive material of claim 4, wherein the silver halide grains contained in one of said silver halide emulsions have the smallest grain size of 0.05 to 1.0  $\mu m$ .
  - 7. The light-sensitive material of claims 5 or 6, wherein the ratio of said maximum-average grain size to said minimum-average grain size is 1.5 to 40.
    - 8. The light-sensitive material of claim 1, wherein said yellow coupler is represented by Formula Y:

## Formula Y

 $R_1 - \text{COCHCONH} - \left(R_2\right) \text{m}$ 

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wherein  $R_1$  represents an alkyl group or an aryl group; X represents a hydrogen atom, a halogen atom, an alkyl group, or an alkoxy group;  $R_2$  represents a hydrogen atom or a substituent; Z represents a group capable of splitting off upon coupling with an oxidation product of a developing agent; m represents an integer of 0 to 4; provided that  $R_2$ 's may be the same or different when m is two or more, and that  $R_1$ ,  $R_2$ , X or Z may be a di- to tetravalent linkage group to form a di- to tetramer of said yellow coupler.

- 9. The light-sensitive material of claim 8, wherein R<sub>1</sub> is an alkyl group having 1 to 30 carbon atoms, a cycloalkyl group, or a phenyl group.
  - 10. The light-sensitive material of claim 9, wherein R<sub>1</sub> is a tert-alkyl group or a 4-alkoxy phenyl group.
- 11. The light-sensitive material of claim 10, wherein  $R_1$  is a tert-butyl group or a 4-methoxy phenyl group.
- 12. The light-sensitive material of claim 8, wherein X is a chlorine atom or an alkoxy group having 1 to 24 carbon atoms.
- 13. The light-sensitive material of claim 8, wherein said substituent represented by  $R_2$  is a halogen atom, an alkyl group having 1 to 20 carbon atoms, an aryl group, an alkoxy group, an aryloxy group, an acylamino group, a sulfonamide group, a carbamoyl group, a sulfamoyl group, an acyloxy group, an amino group, an alkylthio group, a ureido group, a sulfamoylamino group, a cyano group, an alkoxycarbonyl group, an alkoxycarbonylamino group, an alkylsulfonyl group, an arylsulfonyl group, or a heterocyclic group.
- 14. The light-sensitive material of claim 13, wherein said substituent is an acylamino group, a sulfonamide group, an alkoxycarbonyl group, a sulfamoyl group, or a carbamoyl group.
- 15. The light-sensitive material of claim 8, wherein Z is an aryloxy group, a heterocyclicoxy group, an alkoxy group, an acyloxy group, an alkylsulfonyloxy group, an arylsulfonyloxy group, an alkylthio group, an arylthio group, heterocyclicthio group, or



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wherein Q represents the group of non-metallic atoms necessary to form a monocyclic or condensed 5-to 7-membered heterocyclic ring together with N.

- 16. The light-sensitive material of claim 15, wherein said ring formed by Q and N is pyrrole, pyrazole, imidazole, 1,2,4-triazole, tetrazole, indazole, benzimidazole, benzotriazole, succinateimide, phthalateimide, saccharin, oxazolidine-2,4-dione, imidazolidine-2,4-dione, thiazolidine-2,4-dione, urazole, 2-pyridone, triazolidine-3,5-dione, or 5-tetrazolone.
- 17. The light-sensitive material of claim 15, wherein Z is an aryloxy group, an imidazolidine-2,4-dione-3-yl group, an oxazoidine-2,4-dione-3-yl group, or a triazolidine-3,5-dione-4-yl group.
  - 18. The light-sensitive material of claim 8, wherein m is 0 to 2.
  - 19. The light-sensitive material of claim 8, wherein said yellow coupler is a monomer or dimer.
  - 20. The light-sensitive material of claim 8, wherein said molecular weight is 400 to 700.
- 21. The light-sensitive material of claim 8, wherein said molecular weight is 500 to 650 when  $R_1$  is an alkyl group.
- 23. The light-sensitive material of claim 8, wherein said molecular weight is 500 to 700 when R<sub>1</sub> is an aryl group.
  - 24. The light-sensitive material of claim 1, further containing a DIR compound.
  - 25. The light-sensitive material of claim 24, wherein said DIR compound is selected from the compounds represented by Formula D-1:

Formula D-1

A - (Y)m

wherein A represents a coupler residue; Y, which combines to a coupling site of A and splits off upon a reaction with an oxi dation product of a developing agent, represents a development inhibitor group; and m is 1 or 2.

26. The light-sensitive material of claim 25, wherein Y is represented by Formulas D-2 to D-9:

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Formula D-2

Formula D-3

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$$-OCH_2-N$$
 $(Rd_1)n$ 

Formula D-4

Formula D-5

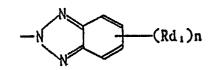
$$-s \stackrel{\mathsf{N}}{=} \overset{\mathsf{(Rd_1)n}}{=}$$

$$-s \stackrel{H}{\swarrow}_{N}$$
 (Rd<sub>1</sub>)n

Fromula D-6

Formula D-7

$$-s \underset{N--N}{\bigvee}^{X} \underset{Rd}{\bigvee}^{Rd}$$



Formula D-8

Formula D-9

$$-s \stackrel{N-N}{\underset{N-N}{=}}$$

wherein Rd<sub>1</sub> in Formulas D-2 through D-7 each represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an acylamino group, an alkoxycarbonyl group, a thiazolidinyl ideneamino group, an aryloxycarbonyl group, an acyloxy group, a carbamoyl group, an N-alkylcarbamoyl group, an N-alkylcarbamoyl group, an an N-alkylcarbamoyloxy group, a nitro group, an amino group, an N-arylcarbamoyloxy group, a sulfamoyl group, an N-alkylcarbamoyloxy group, a hydroxy group, an alkoxycabonylamino group, an alkylthio group, an arylthio group, an aryl group, a heterocyclic group, a cyano group, an alkylsulfonyl group, and an aryloxycarbonylamino group; n is 0 to 2, provided that Rd<sub>1</sub>'s may be the same of different when n is 2; the total carbon atoms contained in all Rd<sub>1</sub>'s are 0 to 10, provided that in Formula D-6, cabon atoms contained in Rd<sub>1</sub> are 0 to 15; in Formula D-6, X represents an oxygen or sulfur atom; in Formula D-8, Rd<sub>2</sub> represents an alkyl group, an aryl group or a heterocyclic group, provided that the carbon atoms contained in Rd<sub>2</sub> are 1 to 15; in Formula D-9, Rd<sub>3</sub> represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group, an acylamino group, an alkoxycarbonylamino group, an alkyl group, an acylamino group, an alkoxycarbonylamino group, an alkylthio group, or an amino group, provided that the total of carbon atoms contained in Rd<sub>3</sub> and Rd<sub>4</sub> is 0 to 15;

- 27. The light-sensitive material of claim 26, wherein said heterocyclic ring represented by Rd<sub>1</sub> to Rd<sub>4</sub> is a 5- or 6-membered monocyclic or condensed ring containing at least one atom selected from a nitrogen atom, an oxygen atom and a sulfur atom.
- 28. The light-sensitive material of claim 27, wherein said heterocyclic ring is pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl, imidazolyl, thiazolyl, benzotriazolyl, imido, or oxazine.
  - 29. The light-sensitive material of claim 26, wherein Y is represented by Formulas D-2, D-3 and D-8.
  - 30. The light-sensitive material of claim 24, wherein said DIR compound is represented by Formula D-

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Formula D-10

#### A-(TIME)n-INHIBIT

wherein A represents a coupler residue; TIME, which combines to a coupling site of A and can split off upon a reaction with an oxidation product of a developing agent, repersents a group which splits off sequently after splitting off from the coupler residue, and finally releases INHIBIT; n is 1 to 3, provided that TIME's may be the same or different when n is 2 or 3; INHIBIT represents a group which becomes a development in hibitor after splitting off from said TIME.

31. The light-sensitive material of claim 30, wherein said TIME is represented by Formulas D-11 to D-

# Formula D-11

$$(Rd_{\bullet}) \mathcal{L}$$

$$-0 \longrightarrow (Rd_{\bullet}) \mathcal{L}$$

$$(CH_{2})k - N - CO - I$$

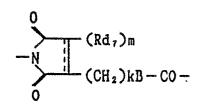
$$Rd_{\bullet}$$

## Formula D-12

# -0 (Rd.)

# Formula D-14

## Fromula D-16



# Fromula D-18

$$-N \longrightarrow (Rd_6) Q$$

$$(CH_2)kB-CO-$$

# Formula D-13

# Formula D-15

$$(CH_2)k - NCO - Rd_6$$

$$(Rd_6)\ell$$

## Formula D-17

$$\begin{array}{c}
0 \\
-N \\
0
\end{array}$$

$$\begin{array}{c}
N - Rd_7 \\
(CH_2)kB - CO - Rd_7
\end{array}$$

## Formula D-19

$$\begin{array}{c|c}
Rd_{\bullet} \\
\hline
-0-(C)_{\overline{n}} & N-C0-\\
\hline
Rd_{\bullet} & Rd_{\bullet}
\end{array}$$

wherein Rd<sub>5</sub> in Formulas D-11 to D-15 and D-18 each represents a hydrogen atom, a halogen atom, an

alkyl group, a cycloalkyl group, an alkenyl group, an aralkyl group, an alkoxy group, an alkoxycarbonyl group, an anilino group, an acylamino group, a ureido group, a cyano group, a nitro group, a sulfonamide group, a sulfamoyl group, a carbamoyl group, an aryl group, a carboxy group, a sulfo group, a hydroxy group, and an alkanesulfonyl group, provided that Rds's in Formula D-11 to D-13, D-15 and D-18 may combine with each other to form a condensed ring; Rds in Formulas D-11, D-14, D-15 and D-19 each represents an alkyl group, an alkenyl group, an aralky group, a cycloalkyl group, a heterocyclic group, and an aryl group; Rdr in Formulas D-16 and D-17 each represents a hydrogen atom, an alkyl group, an alkenyl group, an aralky group, a cycloalkyl group, a heterocyclic group, and an aryl group; Rds and Rds in Formula D-19 represents independently a hydrogen atom and an alkyl group; k in Formulas D-11 and D-15 to D-18 each represents an integer of 0 to 2; £ in Formulas D-11 to D-13, D-15 and D-18 each represents an integer of 1 to 4, and m in Formula D-16 is 1 or 2, provided that Rds's and Rdr's may be the same or different, respectively, when £ and m are two or more; n in Formula D-19 represents an integer of 2 to 4, provided that Rds's and Rdg's may be the same or different, respectively; B in Formulas D-16 to D-18 each represents an oxygen atom and

- N -, | | R d.

wherein Rd<sub>6</sub> represents the same group as defined in Formula D-11; ---- in Formula D-16 represents a single bond or a double bond, provided that it is the single bond when m is 2 and that it is the double bond when m is 1.

32. The light-sensitive material of claim 30, wherein said INHIBIT is selected from the groups represented by D-2, D-3, D-6 and D-8.

33. The light-sensitive material of claim 24, wherein said DIR compound is represented by formula D-

Formula D-20

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 $A - (T_1)_{\xi} - SR - (T_2)m - INHIBIT$ 

wherein A represents a coupler residue;  $T_1$  represents a component capable of splitting off from A and releasing SR- $(T_2)_m$ -INHIBIT; SR represents a component capable of releasing - $(T_2)_m$ -INHIBIT upon reaction with an oxidation product of a developing agent after -SR- $(T_2)_m$ -INHIBIT is split off;  $T_2$  represents a component capable of releasing INHIBIT after - $(T_2)_m$ -INHIBIT is split off; INHIBIT represents a development inhibitor; and £ and m each is 0 or 1.

34. The light-sensitive material of claim 33, wherein SR is a coupler component or a redox component.

- 35. The light-sensitive material of claim 34, wherein said coupler component is acylacetanilide, 5-pyrazolone, pyrazoloazole, phenol, naphthol, acetophenone, indanone, carbamoylacetanilide, 2(5)H-imidazolone, 5-isoxazolone, uracil, homophthalimide, oxazolone, 2,5-thiazoline-1,1-dioxide, triazolothiadiazine, or indole.
- 36. The light-sensitive material of claim 34, wherein said redox component is hydroquinone, catecol, pyrogallol, aminophenol, or aminonaphthol.
  - 37. The light-sensitive material of claim 33, wherein  $T_1$  and  $T_2$  are independently selected from the groups represented by Formulas D-11 to D-19.
  - 38. The light-sensitive material of claim 33, wherein INHIBIT is selected from the groups represented by Formulas D-2 to D-9.
  - 39. The light-sensitive material of claim 38, wherein said INHIBIT is selected from the groups represented by Formulas D-2, D-3, D-6 and D-8.
  - 40. The light-sensitive material of claim 25, wherein an addition amount of said DIR compound is 0.0001 to 0.1 mol per mol of silver halide.
  - 41. The light-sensitive material of claim 40, wherein said addition amount is 0.001 to 0.05 mol per mol of silver halide.
  - 42. The light-sensitive material of claim 1, wherein said blue-sensitive silver halide emulsion layer contains silver halide grains containing a desensitizer.
    - 43. The light-sensitive material of claim 42, wherein said desensitizer is a rhodium ion.