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Silver halide color photographic material and method for processing the same.

A novel silver halide color photographic material is provided comprising on a support light-sensitive layers consisting of a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer, at least one of these color-sensitive layers being composed of a plurality of silver halide emulsion layers having substantially the same color sensitivity and different light sensitivities, characterized in that all of said color-sensitive layers contains a compound which reacts with an oxidation product of an aromatic primary amine color developing agent to reaction with an oxidation product of an aromatic primary amine color developing agent a compound which reacts with another molecule of the oxidation product of an aromatic primary amine color developing agent to cleave a development inhibitor (hereinafter referred to as "diffusive development inhibitor-releasing compound").

The above material enables to produce pictures with high quality and to control the gradation when film is being into prints.

The above material is exposed to light and processed by methods comprising developing, bleaching, fixing, prinsing, stabilizing and drying.

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SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL AND METHOD FOR PROCESSING THE SAME

FIELD OF THE INVENTION

The present invention relates to a silver halide color photographic material. More particularly, the present invention relates to a multilayer silver halide color photographic material comprising a diffusive development inhibitor-releasing compound.

BACKGROUND OF THE INVENTION

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In recent years, the photographic properties of color photographic light-sensitive materials have shown a remarkable progress toward higher sensitivity and picture quality. The demand of further improvement in these photographic properties has grown. The industry has made efforts to provide light-sensitive materials having further improved photographic properties. In order to improve the picture quality, efforts have been made to improve the graininess, sharpness and color reproducibility of light-sensitive materials.

In connection with the improvement in the sharpness and color reproducibility of light-sensitive materials, it has heretofore been known to previously incorporate in a silver halide color photographic material a compound which releases a development inhibitor in correspondence to the image density upon development.

As such a compound there has been known a so-called DIR compound as described in British Patent No. 953,454, and U.S. Patents 3,227,554, and 4,095,984 which undergoes coupling reaction with an oxidation product of an aromatic primary amine color developing agent to form a coupling product and release a development inhibitor. There has also been known a so-called DIR hydroquinone which undergoes alternating oxidation reaction with an oxidation product of a developing agent to release a development inhibitor. (These compounds will be hereinafter referred to as "DIR compounds".)

Such a DIR compound releases a development inhibitor which serves to exhibit an edge effect which leads to an improvement in the sharpness, prevent the developed silver from increasing its size, thus improving the graininess, and exhibit an interlayer effect which leads to an improvement in the color reproducibility. However, the DIR compound has an inherent disadvantage that when used in a large amount, it causes a deterioration in the sensitivity of the silver halide emulsion incorporated in the same layer. Therefore, in a color-sensitive layer consisting of a plurality of emulsion layers having different sensitiv ities, the deterioration in the sensitivity of the layer having the highest sensitivity is minimized and a DIR compound is incorporated more in layers having a lower sensitivity. In order to further solve such a disadvantage, a DIR compound as described in JP-A-59-131934 (The term "JP-A" as used herein means an "unexamined published Japanese patent application") has been developed which releases a highly diffusive development inhibitor upon development (hereinafter referred to as "diffusive DIR coupler"). However, this DIR coupler is disadvantageous in that it deteriorates the graininess of the layer in which it is incorporated. In order to eliminate this disadvantage, an approach as described in JP-A-60-93435 has been worked out which comprises the combined use of a diffusive DIR coupler and a nondiffusive DIR coupler wherein the proportion of the diffusive DIR coupler to the nondiffusive DIR coupler is low in the high sensitivity layer but high in the low sensitivity layer so that the reduction in the sensitivity is minimized without deteriorating the graininess. However, even this approach leaves to be desired in that it causes an essential deterioration in the sensitivity. Furthermore, if such a DIR compound is incorporated in the low sensitivity layers, the reduction in the gradation (so-called low contrast) caused by the deterioration in the color density cannot be avoided due to an interlayer effect. Particularly, if an emulsion of finely divided particles is incorporated in low sensitivity layers to improve the graininess thereof, and a DIR coupler is incorporated in some of said low sensitivity layers, the gradation therein is reduced while the interlayer effect between said layer and other layers is lowered. This can be believed because that the increase in the total surface area due to the incorporation of finely divided particles emulsion causes an increase in the amount of a development inhibitor consumed in the layer comprising such an emulsion.

Thus, it has been impossible to provide a high contrast portion with an emulsion of finely divided silver halide particles while improving the sharpness and color reproducibility of a light-sensitive material comprising a diffusive DIR coupler.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a silver halide color photographic material which exhibits an excellent sharpness and color reproducibility.

It is another object of the present invention to provide a color photographic light-sensitive material which exhibits an excellent sharpness and color reproducibility and enables a proper control of the gradation when finished into prints.

These and other objects of the present invention will become more apparent from the following description and examples.

These objects of the present invention are accomplished with a silver halide color photographic material comprising on a support light-sensitive layers consisting of a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer, at least one of these color-sensitive layers being composed of a plurality of silver halide emulsion layers having substantially the same color sensitivity and different light sensitivities, characterized in that all of said color-sensitive layers contains a compound which reacts with an oxidation product of an aromatic primary amine color developing agent to release a diffusive development inhibitor or a precursor thereof and/or a compound which cleaves after the reaction with an oxidation product of an aromatic primary amine color developing agent to cleave a development inhibitor (hereinafter referred to as "diffusive development inhibitor-releasing compound"), that at least one of said color-sensitive layers consists of at least two light-sensitive layers having different sensitivities, and that the content of said diffusive development inhibitor-releasing compound shows the highest value except in the layer having the lowest sensitivity in each of said color-sensitive layers.

In a preferred embodiment, at least one of the silver halide emulsion layers having the lowest sensitivity with regard to the corresponding color-sensitive layer substantially comprises particulate silver halide having a diameter of 0.5 μ m or less as calculated in terms of circle. Preferably the ratio of the gradation (γ 1) of said lowest sensitivity layer to the gradation (γ 2) of the layer having the next lowest sensitivity (γ 1/ γ 2) in the same color-sensitive layer is 1 or more.

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BRIEF DESCRIPTION OF THE DRAWINGS

By way of example and to make the description more clear, reference is made to the accompanying drawings in which:

Fig. 1 is the characteristics curve of a light-sensitive material of the present invention which has been exposed to white light and then color-developed in which the optical density (D) is plotted on the ordinates and the logarithm of the exposure (E) is plotted on the abscissa (shown at 1, 2 and 3 are the curve for yellow density (blue-sensitive layer), magenta density (green-sensitive layer, and cyan density (red-sensitive layer), respectively);

Fig. 2 is the characteristics curve of a specimen which has been exposed to light through a blue separation filter and then color-developed (shown at 4, 5 and 6 are the curve for yellow density, magenta density and cyan density, respectively.).

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DETAILED DESCRIPTION OF THE INVENTION

The present invention will be further described with reference to the diffusive development inhibitorreleasing compounds of the present invention. The diffusive development inhibitor-releasing compounds of the present invention can advantageously be represented by the general formulas [I] to [IV]:

A-TIME-Z₂ [I]

A-Z₁ [II]

55 B-Z₁ [III]

A (or B)-P-Z₂ [IV]

wherein A represents a coupling component which can react with an oxidation product of a color developing agent to release -TIME-Z₂ group or -P-Z₂ group; B represents a redox portion which undergoes reduction-

oxidation reaction with an oxidation product of a color developing agent and then undergoes hydrolysis with alkali to release Z₁; TIME represents a timing group; Z₁ represents a diffusive development inhibitor; -P-represents a group which undergoes reaction with an oxidation product of a developing agent after cleavage from A or B to release a development inhibitor; and Z₂ may be a diffusive development inhibitor or a development inhibitor having a small diffusivity, with the proviso that if -TIME-Z₂ or -P-Z₂ exhibits diffusivity, A-TIME-Z₂ and A (or B)-P-Z₂ are diffusive DIR compounds.

Examples of the development inhibitor represented by Z_1 or Z_2 include those described in Research Disclosure No. 17643 (Dec., 1978). Preferred examples of such a development inhibitor include mercaptotetrazole, selenotetrazole, mercaptobenzothiazole, selenobenzothiazole, mercaptobenzothiazole, selenobenzotriazole, mercaptotriazole, mercaptotriazole, mercaptotriazole, mercaptotriazole, mercaptotriazole, mercaptotriazole, and derivatives thereof.

Preferred diffusive development inhibitors of the present invention are represented by the general formulas:

z-1

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$$z-8$$

$$-s \longrightarrow N$$
H

In the general formulas [Z-1] and [Z-2], R₁₁ and R₁₂ each represents an alkyl group, alkoxy group, acylamino group, halogen atom, alkoxycarbonyl group, thiazolideneamino group, aryloxycarbonyl group, acyloxy group, carbamoyl group, N-alkylcarbamoyl group, N,N-dialkylcarbamoyl group, nitro group, amino group, N-arylcarbamoyloxy group, sulfamoyl group, sulfonamide group, N-alkylcarbamoyloxy group, ureide group, hydroxy group, alkoxycarbonylamino group, aryloxy group, alkylsulfonyl group, or aryloxycarbonylamino group.

The sulffix n represents an integer 1 or 2. When n represents 2, R_{11} and R_2 may be the same or different, and the total number of carbon atoms contained in n number of R_{11} and R_{12} 's is 0 to 20.

In the general formulas [Z-3], [Z-4], [Z-5], and [Z-6], R₁₃, R₁₄, R₁₅, R₁₆, and R₁₇ each represents an alkyl group, aryl group or heterocyclic group.

When R₁₁ to R₁₇ each represents an alkyl group, they may be substituted or unsubstituted, chain or cyclic. If they are substituted, the substituents may be halogen atom, nitro group, cyano group, aryl group, alkoxy group, aryloxy group, alkoxycarbonyl group, aryloxycarbonyl group, sulfamoyl group, carbamoyl group, hydroxyl group, alkanesulfonyl group, arylsulfonyl group, alkylthio group, or arylthio group.

When R₁₁ to R₁₇ each represents an aryl group, they may be substituted. In this case, the substituents may be alkyl group, alkenyl group, alkoxy group, alkoxycarbonyl group, halogen atom, nitro group, amino group, sulfamoyl group, hydroxyl group, carbamoyl group, aryloxycarbonylamino group, alkoxycarbonylamino group, acylamino group, cyano group, or ureide group.

When R₁₁ to R₁₇ each represents a heterocyclic group, they may be five- or six-membered monocyclic or condensed ring groups containing nitrogen atom, oxygen atom or sulfur atom as hetero atom. Examples of such groups include pyridyl group, quinolyl group, furyl group, benzothiazolyl group, oxazolyl group, imidazolyl group, thiazolyl group, triazolyl group, benzotriazolyl group, imide group, and oxazine group. These groups may be further substituted by the substituents described with reference to the above described aryl group.

In the general formulas [Z-1] and [Z-2], the number of carbon atoms contained in R_{11} and R_{12} is 0 to 20, preferably 7 to 20.

In the general formulas [Z-3], [Z-4], [Z-5] and [Z-6], the total number of carbon atoms contained in R_{13} to R_{17} is 0 to 20, preferably 4 to 20.

A preferred development inhibitor of the present invention is a compound which reacts with an oxidation product of a developing agent to release a development inhititor diffuses from the layer in which it has been incorporated to another layer upon development to exhibit a development inhibiting effect.

The coupler component represented by A may be a dye-forming coupler such as acylacetanilides, malondiesters, malondiamides, benzoylmethanes, pyrazolones, pyrazolotriazoles, pyrazolobenzimidazoles, indazolones, phenols, and naphthols, or a coupler component which substantially doesn't form a dye, such as acetophenones, indanones, and oxazolones.

Preferred coupler components can be represented by the general formulas [V] to [VIII]:

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OH
$$CON \stackrel{R_{34}}{\underset{R_{35}}{\longleftarrow}}$$
 [VII]

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In these general formulas, R_{30} represents an aliphatic group, aromatic group, alkoxy group or heterocyclic group; and R_{31} and R_{32} each represents an aromatic group or heterocyclic group.

The aliphatic group represented by R_{30} may be preferably a C_{1-20} substituted or unsubstituted chain or cyclic group. Examples of the substituent for the aliphatic group include alkoxy, aryloxy and acylamino group.

When R_{30} , R_{31} or R_{32} represents an aromatic group, they may be phenyl or naphthyl groups, preferably phenyl groups. These phenyl groups may contain substituents such as alkyl group, alkonyl groups represented by R_{30} , R_{31} and R_{32} may be substituted by alkyl group, alkonyl group, cyano group or halogen atom.

R₃₃ represents a hydrogen atom, alkyl group, halogen atom, carbonamide group or sulfonamide group. The suffix t represents an integer 1 to 5. R₃₄ and R₃₅ each represents a hydrogen atom, alkyl group or aryl group. Preferred examples of such an aryl group include phenyl group. Such an alkyl group or aryl group may contain substituents such as halogen atom, alkoxy group, aryloxy group, and carboxyl group. R₃₄ and R₃₅ may be the same or different.

The general formula [III] represents a compound which undergoes reduction-oxidation reaction with an oxidation product of an aromatic primary amine developing agent and then hydrolysis with alkali to release a development inhibitor or its precursor (hereinafter referred to as "DIR redox compound"). In the general formula [III] B represents a redox portion. More particularly, such a DIR redox compound is represented by the general formula [IX]:

In the general formula [IX], G and G each represents a hydrogen atom or a phenolic hydroxyl protective group capable of deblocking a protective group during a photographic processing. Typical examples of such a protective group include hydrogen atom, acyl group, sulfonyl group, alkoxycarbonyl

group, carbamoyl group, and oxazolyl group.

 R_{18} , R_{19} and R_{20} may be the same or different and each represents a hydrogen atom, halogen atom, alkyl group, aryl group, alkoxy group, aryloxy group, alkylthio group, arylthio group, cyano group, alkoxycarbonyl group, carbamoyl group, sulfamoyl group, carboxyl group, sulfo group, sulfonyl group, acyl group, carbonamide group, sulfonamide group or heterocyclic group.

 R_{18} and R_{19} , R_{18} and G, R_{19} and G', and R_{20} and G may be connected to each other to form an aromatic or nonaromatic ring. At least one of R_{18} , R_{19} and R_{20} contains a C_{10-20} nondiffusive group.

Z is a development inhibitor as defined above.

In the present invention, P is preferably a group which becomes a redox group or coupler after the cleavage from A or B.

As described above, a compound which reacts with an oxidation product of a developing agent to release a development inhibitor which diffuses to the layer in which it has been incorporated to another layer upon development to exhibit a development inhibiting effect can be used in the present invention.

The preparation of these compounds of the present invention can be easily accomplished by any suitable method as described in U.S. Patents 3,227,554, 3,617,291, 3,933,500, 3,958,993, 4,149,886, 4,234,678, and 4,248,962, JP-A-51-13239, JP-A-57-56837, JP-A-52-90932, JP-A-56-114946, JP-A-57-154234, JP-A-58-98728, JP-A-58-209736, JP-A-58-209737, JP-A-58-209738, JP-A-58-209740, JP-A-61-255342, JP-A-62-24252, and JP-A-61-156043 British Patent Nos. 2,070,266, and 2,072,363, Research Disclosure No. 21228 (December, 1981), JP-B-58-9942 and JP-B-51-16141 (the term "JP-B" as used herein means an "examined Japanese patent publication") and EP-A-255,085.

Specific examples of suitable diffusive development inhibitors which can be used in the present invention will be shown hereinafter, but the present invention should not be construed as being limited thereto.

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T - 1 0 1

20 T - 1 0 2

T - 1 0 3

T - 1 0 4

 $T - 1 \ 0 \ 5$ $(CH_3)_3 CCOCHCONH - (t) C_5 H_{11} (t)$ $N - C_3 H_7$

N = N

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T - 106

NHCO (CH₂)₃ - O - C₅H₁₁ (t)

(CH₃)₃CCOCHCONH - (t) C₅H₁₁

O C₂

$$CH_2$$
 $N-CO-S$
 NO_2

T - 1 0 7

T - 1 0 8

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(CH₃)₃CCOCHCONH

O₂N

O₂N

CH₂-S

NHSO₂C₁6H₃3

T - 1 0 9

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$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{3}H_{11}$$

$$C_{4}H_{9}$$

$$C_{4}H_{9}$$

$$C_{4}H_{9}$$

$$C_{4}H_{9}$$

$$C_{5}H_{11}$$

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T - 1 1 1

NHCOC 13Hz7

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T - 1 1 2

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N N N N

N N N

N N N

C 6 H 1 3

NHCOCH · O - C 5 H 1 1 (t)

C 2 H 5 (t) C 5 H 1 1

T - 1 1 3

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C₁₃H₂₇CONH

NH

NH

NO

C L

C L

C L

50

0

$$- (CH_2)_3 - NNNN - CH_3$$

$$= NNCOC_9 H_{1.9}$$

T - 114

$$T - 1 1 5$$

5 OH CONH — OC 14 H 2

N N - C 4 H 9

T - 1 1 6

 $\begin{array}{c}
0 \text{ H} \\
(t) \text{ C}_5 \text{ H}_{11} \\
(t) \text{ C}_5 \text{ H}_{11}
\end{array}$ $\begin{array}{c}
0 \text{ CH}_3 \\
N - C - S \\
N \\
N \\
N \\
N
\end{array}$

T - 1 1 7

T - 1 1 8

T - 1 1 9

T - 1 2 0

T - 1 2 1

T - 1 2 2

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T - 1 2 3

OH CONH - OC: 4H

T-124

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T - 1 2 5

5 (CH₃)₃CCOCH NH

N N S - CH₂ COOC_{1 2}H₂₅

15 CAHB

T - 1 2 6

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(CH₃)₃CCOCHCONH — NHSO₂C₁₄H₂₉

0
CH₃
CH₃
CH₄H₉
N — N
CH₂-S — N — N

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C02C12H25

T - 1 2 7

соснсоин 🤄 C = 0

 C_2H_5

1 2 8

1 2 8

(a)
$$C = \frac{1}{2} = \frac{$$

T - 1 2 9

T - 1 3 0

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5**0**

T - 1 3 1

OH CONH - OC14H29

T - 1 3 2

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T - 1 3 4

25 (n) C₁₆ H₃₃ S N N N N OH C₄ H₉

T - 1 3 5

0H
CONHC12H25
N-N
OH
OH
ConhC12H25
N-N
OH
Coll13

T - 1 3 6

T - 1 3 7

T - 1 3 8

55

45

50

T - 1 3 9

$$T - 1 4 0$$

T - 1 4 1

C₂H₅

C₂H₅

NHCOC₃F₇

(t) C₅H₁₁

CH₃O

N

OH

T - 1 4 2

CzHs

T - 1 4 30 H C₂H₅ NHCOC3F7 5 (t)C₅H₁₁ OCHCONH (t)C₅H₁₁ 10 HO HO. CONHC₃H₇ 15 N - C 4 H 9 20 $N \longrightarrow N$

T-144

OH
NHCOC₃F₇

(t)C₅H₁₁

(t)C₅H₁₁

HO
CONHC₃H₇

S
N
CH₃

50

55

S - CHCOOCH 3

T - 1 4 5

$$T - 1 4 6$$

$$T - 1 4 7$$

N = N

$$T - 1 4 8$$

ÓC 4 II 9

T - 1 4 9

CH₃O - COCHCONH CO₂CO₂CO₁ZH₂S

HO CO₂CO₂CO₁ZH₂S

CH₃O - COCHCONH CO₂CH₃

S - C₃H₇

T - 150

25

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35 HO CONHC 1 6 H 3 3

S N S CH 2 CO 2 CH 3

T - 1 5 1

$$T - 1 5 2$$

ĊH 3

CH(CH₅)₂

CH₂-S

CH₂-S

N-C-O

CH₂-S

N-E

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The present light-sensitive material may comprise at least one silver halide emulsion layer made of at least a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer on a support. The number and order of these silver halide emulsion layers and light-insensitive layers are not specifically limited. A typical example of such a layer structure is a silver halide photographic material comprising on a support at least one light-sensitive layer comprising a plurality of silver halide emulsion layers having substantially the same color sensitivity and different light sensitivities. The light-sensitive layer is a unit light-sensitive layer having a sensitivity to any of blue light, green light and red light. In a multilayer silver halide color photographic material, the arrangement of such unit light-sensitive layers is such that a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer are arranged in this order from the support side. However, this order may be reversed depending on the purpose of application. Alternatively, the layer arrangement is such that layers having the same color sensitivity have a layer having a different color sensitivity interposed therebetween.

Various light-insensitive layers such as intermediate layers may be provided interposed between the above described silver halide light-sensitive layers and on the top and under the bottom thereof.

These intermediate layers may comprise couplers and DIR compounds as described in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037, and JP-A-61-20038. These intermediate layers may also comprise a color stain inhibitor as commonly used.

The plurality of silver halide emulsion layers which constitute each unit light-sensitive layer may employ a two-layer structure comprising a high sensitivity emulsion layer and a low sensitivity emulsion layer as described in West German Patent No. 1,121,470 and British Patent No. 923,045. In general, such a layer structure may be employed that the light sensitivity gradually decreases toward the support. Furthermore, a light-insensitive layer may be provided interposed between silver halide emulsion layers. Alternatively, as described in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541, and JP-A-62-206543, such a layer structure may be employed that a low sensitivity emulsion layer is provided remote from the support while a high sensitivity emulsion layer is provided near the support. If the low sensitivity layer comprises an

emulsion of particulate silver halide having a particle size of 0.5 μ m or less, particularly 0.2 μ m or less, as in the present invention, it may preferably be provided remote from the support.

A specific example of suitable layer structures which can be used in the present invention is such that a low sensitivity blue-sensitive layer (BL), a high sensitivity blue-sensitive layer (BH), a high sensitivity green-sensitive layer (GH), a low sensitivity green-sensitive layer (GL), a high sensitivity red-sensitive layer (RH), and a low sensitivity red-sensitive layer (RL) are arranged in this order from the support or that BH, BL, GH, GH, RH, and RL or BH, BL, GH, GL, RL, and RH are arranged in this order remote from the support.

Alternatively, a blue-sensitive layer, GH, RH, GL, and RL may be arranged in this order remote from the support as described in JP-B-55-34932. A blue-sensitive layer, GL, RL, GH, and RH may be arranged in this order remote from the support as described in JP-A-56-25738 and JP-A-62-63936.

Alternatively, such a three-layer structure as described in JP-B-49-15495 may be used in which the upper layer is a silver halide emulsion layer having the highest sensitivity, the middle layer is a silver halide emulsion layer having a sensitivity lower than that of the upper layer, and the lower layer is a silver halide emulsion layer having a sensitivity lower than that of the middle layer. In such a layer structure, the sensitivity decreases toward the support. In such a structure comprising three layers having different sensitivities, a middle sensitivity emulsion layer, a high sensitivity emulsion layer and a low sensitivity emulsion layer may be arranged in this order remote from the support in each color-sensitive layer as described in JP-A-59-202464.

As described above, various layer structures and arrangements may be selected depending on the purpose of application of the light-sensitive material.

The present diffusive DIR compound may be incorporated in at least one layer of the different sensitivity layers in each color-sensitive layer. If the diffusive DIR compound is incorporated in one layer other than the lowest sensitivity layer, it may not be incorporated in the lowest sensitivity layer. For example, when each color-sensitive layer consists of a high sensitivity layer and a low sensitivity layer, such an embodiment may be employed that the high sensitivity layer in each color-sensitive layer contains the present diffusive DIR compound or that at least one color-sensitive layer contains the present diffusive DIR compound in both the high sensitivity layer and the low sensitivity layer.

When a color-sensitivity layer is composed of a single light-sensitive emulsion layer, the diffusive DIR compound is incorporated into the same layer.

Alternatively, when one color-sensitive layer is composed of a high sensitivity layer, a middle sensitivity layer and a low sensitivity layer, at least the high sensitivity layer or the middle sensitivity layer may contain the diffusive DIR compound while the low sensitivity layer may or may not.

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Besides the above diffusive DIR compound, a nondiffusive DIR compound may be used singly or in admixture therewith. The nondiffusive DIR compound is a compound having a relatively higher intralayer development inhibiting effect/interlayer development inhibiting effect ratio than the present diffusive DIR compound.

The amount of the diffusive DIR compound to be incorporated is in the range of 0.01 to 20 mol%, preferably 0.05 to 10 mol%, particularly 0.1 to 5 mol% with regard to the moles of silver halide incorporated in the same layer.

The amount of the nondiffusive DIR compound to be incorporated is as specified above. If the non-diffusive DIR compound and the diffusive DIR compound are used in combination, the proportion of the two components is not specifically limited.

The amount of the diffusive DIR compound to be incorporated is in the range of 1 to 60 mol%, preferably 5 to 50 mol% with regard to the moles of uncolored color coupler which mainly forms color images in the same layer.

The gradation (γ) according to the present invention will be described hereinafter. The gradation (γ) to be used in the present invention can be determined by the slope of the linear portion of D-log E curve made by plotting the exposure (E) on the abscissa and the optical density (D) on the ordinates in the process commonly used in this art.

The term "gradation of the lowest sensitivity layer" as used herein means the slope of the linear portion of D-log E curve in the high exposure range (namely high density portion). The high exposure portion of D-log E curve varies with the exposure. Therefore, in the present method, the high exposure portion of D-log E curve ranges from the exposure point (E_0) at which the optical density on D-log E curve begins to change from the fog density (density of unexposed portion after development) to $\Delta \log E$ (= $\log E$ - $\log E_0$) of -0.5 to +4.5. In this case, the high exposure range is $\Delta \log E$ of about 2.5 to 4.5.

Explaining more particularly with reference to density, the gradation of the lowest sensitivity layer in the blue-sensitive layer may be normally represented by the highest value in the gradation of the yellow density range of about 1.5 to 3.0 obtained when color-developed after exposed to while light. The gradation of the

lowest sensitivity layer in the green-sensitive layer may be normally represented by the highest value in the gradation of the magenta density range of about 1.2 to 2.5 obtained when color-developed after exposed to white light, the gradation of the red-sensitive layer may be normally represented by the highest value in the gradation of the cyan density range of about 1.0 to 2.0 obtained when color-developed after exposed to white light.

The gradation of the next lowest sensitivity layer according to the present invention is the gradation of the Δ log E range of 0.5 to 2.5. Explaining more particularly with reference to density, the gradation of the next lowest sensitivity layer in the blue-sensitive layer may be represented by the gradation of the linear portion in the yellow density range of about 0.6 to 1.6 as described above. Similarly, the gradation of the next lowest sensitivity layer in the green-sensitive layer may be represented by the gradation of the linear portion in the magenta density range of about 0.4 to 1.3, and the gradation of the next lowest sensitivity layer in the red-sensitive layer may be represented by the gradation of the linear portion in the cyan density range of about 0.1 to 1.2. In this range, if two or more lines can be drawn above Δ log E of 0.5, the gradation of the next lowest sensitivity layer may be represented by the gradation of the linear portion nearest to the high exposure range.

The gradation (G) according to the present invention (slope of the linear portion of H-D curve (= D - log E curve) wherein D represents optical density and E represents exposure) will be described hereinafter. If the gradation of the lowest sensitivity layer (namely high exposure portion) is represented by γ_1 , and the gradation of the next lowest sensitivity layer is represented by γ_2 , the value of γ_1/γ_2 ratio according to the present invention is in the range of 1.00 to 5.00, preferably 1.25 to 3.50, more preferably 1.50 to 3.00.

The lowest sensitivity layer of the present invention may comprise an emulsion of finely divided particles of silver halide having a diameter of about $0.5~\mu m$ or less, preferably about $0.35~\mu m$ or less, and more preferably about $0.2~\mu m$ or less as calculated in terms of diameter of circle having the same area as the projected area of particle.

The embodiments of the present invention can be applied to general silver halide color photographic materials as well as intermediate photographic materials.

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The current color negative photographic materials are imagewise exposed, color-developed, and then used as original picture through which color print materials are exposed to light. Ideally speaking, these photographic materials preferably have a constant gradation from the low exposure range to the high exposure range. However, this makes it difficult to adjust the gradation during printing. On the other hand, if the exposed portion has a high contrast and a low contrast, it is made possible to adjust the gradation during printing. This technique is widely applied and particularly effective when an intermediate photographic material adapted to be exposed to original picture (transparent positive picture) is used. However, there have never been commercially available an intermediate photographic material comprising the above diffusive DIR couplers and exhibiting a high picture quality and a varying gradation. It has been very difficult to design a high contrast portion with an emulsion of finely divided particles of silver halide while improving the sharpness and color reproducibility by the use of diffusive DIR couplers. The present invention can accomplish this object.

Preferred silver halide incorporated in the photographic emulsion layer in the photographic light-sensitive material to be used in the present invention is silver iodobromide, silver iodochloride or silver iodochlorobromide having a silver iodide content of about 30 mol% or less. Particularly preferred is silver iodobromide having a silver iodide content of about 2 mol% to about 25 mol%.

The silver halide grain to be incorporated in the photographic emulsion may have a regular crystal structure such as cube, octahedron and tetradecahedron, an irregular crystal structure such as sphere and plate, a crystal structure having crystal defect such as twinning plane, or a composite thereof.

The silver halide grain according to the present invention may be either finely divided particles having a particle diameter of about 0.1 μ m or less or large size particle having a particle diameter of up to about 10 μ m as calculated in terms of projected area. The silver halide emulsion according to the present invention may be in the form of a monodisperse emulsion or a polydisperse emulsion. The lowest sensitivity layer of the present invention may preferably comprise finely divided particulate silver halide having a particle diameter of 0.2 μ m or less. The finely divided particulate silver halide may be preferably in the form of monodisperse cubic particle. The blue-sensitive layer and green-sensitive layer may preferably comprise tabular particulate silver halide. More preferably, the blue-sensitive layer may comprise silver chloroiodobromide as described in Japanese Patent Application No. 62-103808.

The preparation of s silver halide photographic emulsion which can be used in the present invention can be accomplished by any suitable method as described in Research Disclosure Nos. 17643 (december, 1978), pp. 22 to 23, "I. Emulsion preparation and types", and 18716 (November, 1979), page 648, P. Glafkides, Chemie et Physique Photographique, Paul Montel, 1967, G. F. Duffin, Photographic Emulsion

Chemistry, Focal Press, 1966, and V. L. Zelikman et al., Making and Coating Photographic Emulsion, Focal Press. 1964.

Monodisperse emulsions as described in U.S. Patents 3,574,628, and 3,655,394, and British Patent No. 1,413,748 may be preferably used in the present invention.

Alternatively, tabular grains having an aspect ratio of about 5 or more may be used in the present invention. The preparation of such tabular grains can be easily accomplished by any suitable method as described in Gutoff, "Photographic Science and Engineering", Vol. 14, pp. 248 to 257, 1970, U.S. Patents 4,434,226, 4,414,310, 4,433,048, and 4,439,520, and British Patent No. 2,112,157.

The crystal structure of the present silver halide grain may be uniform, or such that the halide composition varies between the inner portion and the outer portion thereof, or may be a layer structure. Alternatively, silver halides having different compositions may be connected to each other by an epitaxial junction or by any suitable compound other than silver halide such as silver thiocyanate, and zinc oxide.

Alternatively, a mixture or particles having various crystal structures may be used.

The present silver halide emulsion may be normally subjected to physical ripening, chemical ripening, and spectral sensitization before use. Examples of additives to be used in such processes are described in Research Disclosure Nos. 17643 and 18716. The places where such a description is found are summarized in the table shown below.

Additives	RD 17643	RD 18716
Chemical sensitizer Sensitivity improver	P. 23	Right column on P. 648
3. Spectral sensitizer,	P. 23 to P.	Right column on P. 648 to right column on P. 649
4. Brightening agent	P. 24	Inghit Column on 1 . 040
5. Fog inhibitor,	P. 24 to P.	Right column on P. 649
stabilizer	25	
Light absorber, filter	P. 25 to P.	Right column on P. 649 to
dye, ultraviolet	26	left column on P. 650
absorber		
7. Stain inhibitor	Right column on P. 25	Left column to right column on P. 650
8. Dve image stabilizer	P. 25	
9. Film hardener	P. 26	Left column on P. 651
10. Binder	P. 26	17
11. Plasticizer, lubricant	P. 27	Right column on P. 650
12. Coating aid, surface	P. 26 to P.27	11
active agent		•
13. Antistatic agent	P. 27	19
	1. Chemical sensitizer 2. Sensitivity improver 3. Spectral sensitizer, supersensitizer 4. Brightening agent 5. Fog inhibitor, stabilizer 6. Light absorber, filter dye, ultraviolet absorber 7. Stain inhibitor 8. Dye image stabilizer 9. Film hardener 10. Binder 11. Plasticizer, lubricant 12. Coating aid, surface active agent	1. Chemical sensitizer 2. Sensitivity improver 3. Spectral sensitizer, supersensitizer 4. Brightening agent 5. Fog inhibitor, stabilizer 6. Light absorber, filter dye, ultraviolet absorber 7. Stain inhibitor 8. Dye image stabilizer 9. Film hardener 10. Binder 11. Plasticizer, lubricant 12. Coating aid, surface active agent P. 23 P. 23 P. 24 P. 24 P. 24 to P. 25 P. 25 to P. 26 P. 25 P. 25 P. 25 P. 26 P. 26 P. 26 P. 26 P. 26 P. 26

As suitable color stain inhibitors there may be used compounds as described in U.S. Patents 3,926,436, and 4,447,523, JP-B-61-13748, and Japanese Patent Application No. 60-165511.

The present light-insensitive finely divided particulate silver halide will be described hereinafter.

The term "finely divided particulate silver halide" as used herein means a finely divided particulate silver halide which is not sensitive to light during imagewise exposure and is not substantially developed during development. Such a finely divided particulate silver halide may have previously been fogged, but may preferably have previously not been fogged.

Such a finely divided particulate silver halide may have a silver bromide content of 0 to 100 mol%. The finely divided particulate silver halide may have various compositions so long as it has such a silver bromide content. Particularly, the finely divided particulate silver halide may contain silver chloride and/or silver iodide if desired. Preferably, silver iodobromide containing 0.5 to 10 mol% of silver iodide may be

The present finely divided particulate silver halide may have an average particle diameter of 0.01 to 0.5 μm, preferably 0.02 to 0.2 μm. The average particle diameter of particulate silver halide can be determined by the average value of diameter of particles as calculated in terms of diameter of circle having the same area as the projected area thereof. The measurement of the average particle diameter of particulate silver halide can be accomplished by any suitable method as described in "SHASHINKOGAKU NO KISO-GINENSHASHINHEN", Nihon Shashin Gakkai, January 30, 1979, pp. 227 to 228.

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The present finely divided particulate silver halide can be prepared by the same method as used in the preparation of ordinary light-sensitive silver halide emulsion or in accordance with the method. In this case, the surface of the particulate silver halide doesn't need to be chemically sensitized or spectrally sensitized. However, prior to being added to the coating solution, the finely divided particulate silver halide may preferably have previously contained any known stabilizers such as thiazole compound, azaindene compound, benzothiazolium compound, mercapto compound, and zinc compound incorporated therein.

Such a finely divided particulate light-insensitive silver halide may be incorporated in a protective layer, emulsion layer or intermediate layer in the present light-sensitive layer. Preferably, the finely divided particulate light-insensitive silver halide may be incorporated in the protective layer. The amount of the finely divided particulate light-insensitive silver halide to be incorporated is in the range of 0.05 to 2.0 g/m², preferably 0.1 to 1.0 g/m².

Various color couplers can be used in the present invention. Specific examples of such color couplers are described in patents cited in Research Disclosure No. 17643 (VII-C-G).

Preferred examples of yellow couplers which may be used in the present invention are described in U.S. Patents 3,933,501, 4,022,620, 4,326,024, and 4,401,752, JP-B-58-10739, and British Patent Nos. 1,425,020, and 1,476,760.

As a magenta coupler there may be preferably used a 5-pyrazolone or pyrazoloazole compound. Particularly preferred examples of such a compound are described in U.S. Patents 4,310,619, 4,351,897, 3,061,432, 3,725,067, 4,500,630, and 4,540,654, European Patent No. 73,636, JP-A-60-33552, and JP-A-60-43659, and Research Disclosure Nos. 24220 (June 1984), and 24230 (June 1984).

As a cyan coupler there may be preferably used a phenolic or naphtholic coupler. Preferred examples of such a cyan coupler are described in U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, 4,327,173, 3,446,622, 4,333,999, 4,451,559, and 4,427,767, West German Patent Application (OLS) No. 3,329,729, and European Patent Nos. 121,365A, and 161,626A.

Examples of a colored coupler for correcting unnecessary absorption by color-forming dye are described in Research Disclosure No. 17643 (VII-G), U.S. Patents 4,163,670, 4,004,929, and 4,138,258, and British Patent No. 1,146,368, and JP-B-57-39413.

Examples of a coupler which provides a color-forming dye having a proper diffusivity are described in U.S. Patent 4,366,237, British Patent No. 2,125,570, European Patent No. 96,570, and West German Patent Application (OLS) No. 3,234,533.

Typical examples of polymerized dye-forming couplers are described in U.S. Patent Nos. 3,451,820, 4,080,211, and 4,367,282, and British Patent No. 2,102,173.

Couplers which release a photographically useful residual group upon coupling may be preferably used in the present invention.

Preferred examples of couplers which imagewise release a nucleating agent or a development accelerator upon development are described in British Patent Nos. 2,097,140, and 2,131,188, and JP-A-59-157638, and JP-A-59-170840.

Examples of other couplers which can be used in the present light-sensitive material include competing couplers as described in U.S. Patent 4,130,427, polyvalent couplers as described in U.S. Patents 4,283,472, 4,338,393, and 4,310,618, couplers which release a dye which can be recovered after elimination as described in European Patent No. 173,302A, bleach accelerator releasing couplers as described in RD No. 11449, RD 24241, and JP-A-61-201247, and ligand releasing couplers as described in U.S. Patent 4,553,477.

The incorporation of the present couplers in the light-sensitive material can be accomplished by various known dispersion methods.

Examples of high boiling solvents which can be used in an oil-in-water dispersion process are described in U.S. Patent 2,322,027.

Specific examples of process and effects of latex dispersion method and latex for use in such dispersion method are described in U.S. Patent 4,199,363, and West German Patent Application (OLS) Nos. 2,541,274, and 2,541,230.

Examples of suitable supports which can be used in the present invention are described on page 28 of Research Disclosure No. 17643 and from the right column on page 647 to the left column on page 648 in Research Disclosure No. 18716.

The invention comprises a process for producing a color image characterized in that the silver halide color photographic material described above is exposed to light and processed by methods comprising developing bleaching, fixing, rinsing, stabilizing and drying.

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The development of a color photographic light-sensitive material according to the present invention can

be accomplished by an ordinary method as described in Research Disclosure No. 17643 (pp. 28 to 29) and Research Disclosure No. 18716 (left column to right column on page 651).

The color developing solution to be used in the development of the present light-sensitive material is preferably an alkaline aqueous solution containing an aromatic primary amine color developing agent as a main component. As such a color developing agent there may be used as aminophenol compound. Preferred examples of such a color developing agent include p-phenylenediamine compounds. Typical examples of such p-phenylenediamine compounds include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxylethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethyl aniline, and sulfate, hydrochloride, phosphate, and p-toluenesulfonate thereof. These compounds may be used in combination depending on the purpose of application.

The color developing solution normally comprises pH buffers such as carbonate, borate, and phosphate of alkaline metal, and development inhibitors or fog inhibitors such as bromide, iodide, benzimidazoles, benzothiazoles, and mercapto compounds. Typical examples of other additives which may be optionally incorporated in the color developing solution include various preservatives such as hydroxylamine, diethyl-hydroxylamine, sulfite, hydrazines, phenyl semicarbazides, triethanolamine, catecholsulfonic acids and triethylenediamine(1,4-diazabicyclo[2,2,2]octane), organic solvents such as ethylene glycol and diethylene glycol, development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts and amines, dye-forming couplers, competing couplers, fogging agents such as sodium boron hydride, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, thickening agents, and chelating agents such as aminopolycarboxylic acid, aminopolyphosphonic acid, alkylphosphonic acid and phosphonocarboxylic acid (e.g., ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediamine tetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N, veteramethylenephosphonic acid, ethylenediamine-N,N,N, veteramethylenephosphonic acid, ethylenediamine-N,N,N, veteramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid), and salts thereof).

In the reversal processing of the light-sensitive material, the color development normally follows the black-and-white development. Examples of black-and-white developing agents which can be incorporated in the black-and-white developing solution include dihydroxybenzenes such as hydroquinone, 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, aminophenols such as N-methyl-p-aminophenol, and combinations there-

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The pH value of these color developing solutions and black-and-white developing solutions is normally in the range of 9 to 12. The replenisher amount of these developing solutions depends on the color photographic light-sensitive material to be processed but is normally in the range of 3 t or less per 1 m² of the light-sensitive material. By using a replenisher solution having a less bromide ion content, the replenisher amount of these developing solutions can be reduced to 500 ml or less. If the replenisher amount of these developing solutions is reduced, the area of contact between the processing tank and air is preferably reduced to prevent evaporation and air oxidation of the solution. Alternatively, a means of inhibiting accumulation of bromide ion in the developing solution may be used to reduce the replenisher amount of the developing solution.

The photographic emulsion layer which has been color-developed is normally bleached. The bleaching may be effected simultaneously with or separately of fixing (blix). In order to expedite the processing, the bleaching may be followed by the blix. Furthermore, the photographic emulsion layer may be processed in two continuous blix baths. The blix may be followed by the fixing. Alternatively, the blix may be followed by the bleaching. These processes may be optionally selected depending on the purpose of application. Examples of bleaching agents which can be used in the present invention include compounds of polyvalent metal such as iron (III), cobalt (III), chromium (VI), and copper (II), peroxide, quinones, and nitro compounds. Typical examples of such bleaching agents include ferricyanides, dichromates, organic complex salts of iron (III) or cobalt (III) with, e.g., aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid and glycoletherdiaminetetraacetic acid, or citric acid, tartaric acid, malic acid, or other organic acid, persulfate, bromate, permanganate, and nitrobenzenes. Among these compounds, aminopolycarboxylic acid-iron (III) complexes such as ethylenediaminetetraacetic acid-iron (III) complex and persulfate may be preferably used in the light of rapidity in processing and prevention of environmental pollution. Furthermore, aminopolycarboxylic acid-iron (III) complexes are particularly useful in the bleaching solution or blix solution. The pH value of a bleaching solution or blix solution comprising such an aminopolycarboxylic acid-iron (III) complex is normally in the range of 5.5 to 8. In order to expedite the processing, the pH value of the solution may be lower than this range.

The present bleaching solution, blix solution, or prebath thereof may optionally contain a bleach accelerator. Specific examples of useful bleach accelerators include compounds containing mercapto group

or disulfide group as described in U.S. Patent 3,893,858, West German Patent Nos. 1,290,812, and Research Disclosure No. 17129 (July 1978), thiazolidine derivatives as described in JP-A-50-140129, thiourea derivatives as described in U.S. Patent 3,706,561, iodides as described in JP-A-58-16235, polyoxyethylene compounds as described in West German Patent No. 2,748,430, polyamine compounds as described in JP-B-45-8836, and bromide ion. Among these compounds, compounds containing mercapto group or disulfide group may be preferably used because of their high accelerating effect. Particularly preferred are compounds as described in U.S. Patent 3,893,858, West German Patent No. 1,290,812, and JP-A-53-95630. Furthermore, compounds as described in U.S. Patent 4,552,834 may be preferably used. These bleach accelerators may be incorporated in the light-sensitive material. These bleach accelerators are useful particularly when a color light-sensitive material for use in photographing is subjected to blix.

Examples of suitable fixing agents include thiosulfates, thiocyanates, thioether compounds, thioureas, and iodides (in a large amount). Among these compounds, thiosulfates are normally used. Particularly, ammonium thiosulfate can be most widely used. As a suitable preservative for the blix solution there may be preferably used sulfite, bisulfite or carbonyl-bisulfite addition product.

The present silver halide color photographic material which has been subjected to desilvering process is normally subjected to rinse and stabilization. The amount of rinsing water to be used at the rinsing step can be widely selected depending on the characteristics of the light-sensitive material (due to materials used, e.g., couplers), the application of the light-sensitive material, the temperature of the rinsing water, the number of rinsing tanks (number of stages), the supply process (countercurrent or forward current), and other various conditions. Among these conditions, the relationship between the number of rinsing tanks and the used amount of water can be determined by the method as described in Journal of the Society of Motion Picture and Television Engineering, Vol. 64, p. 248 to 253, May 1955.

In the multistage countercurrent process as described in the above cited reference, the amount of rinsing water to be used can be drastically reduced. However, this process is disadvantageous in that the increase in the time of retention of water in the tank causes propagation of bacteria which produce suspended matter that can be attached to the light-sensitive material. In the processing of the present color light-sensitive material, such a disadvantage can be extremely effectively eliminated by the method as described in JP-A-62-288838 which comprises reduction in the calcium and magnesium ion content. Alternatively, there may be preferably used isothiazolone compounds and thiabendazoles as described in JP-A-57-8542, chlorinic sterilizers such as sodium chlorinated isocyanurate, or sterilizers as described in Hiroshi Horiguchi, "Anti-bacterial and anti-fungal Chemistry", Eisei Gijutsukai, "Technique for Sterilization and Fungicidal Treatment of Microorganism", and Nihon Bokin Bobai Gakkai, "Dictionary of Sterilizers and Fungicides".

The pH value of the rinsing water to be used in the processing of the present light-sensitive material is in the range of 4 to 9, preferably 5 to 8. The temperature of the rinsing water and the rinsing time can be widely selected depending on the characteristics and application of the light-sensitive material to be processed but is normally in the range of 15 to 45 °C and 20 seconds to 10 minutes, preferably 25 to 40 °C and 30 seconds to 5 minutes, respectively. Furthermore, the present light-sensitive material can be directly processed with a stabilizing solution in stead of the above described rinsing solution. In such a stabilization process, any known method as described in JP-A-57-8543, JP-A-58-14834, and JP-A-60-220345 can be used.

The above described rinse may be optionally followed by another stabilization process such as stabilizing bath for use as the final processing bath for color light-sensitive materials for photographing use which contains formalin and a surface active agent. This stabilizing bath may also comprise various chelating agents or fungicides.

The overflow solution produced by the replenisher of the above described rinsing water and/or stabilizing solution may be recycled at the desilvering step or other steps.

The present silver halide light-sensitive material may comprise a color developing agent for the purpose of simplification and expedition of the processing. Such a color developing agent may be preferably incorporated in the form of various precursors. Examples of such precursors include indoaniline compounds as described in U.S. Patent 3,342,597, Schiff's base type compounds as described in U.S. Patent 3,342,599, and Research Disclosure Nos. 14850 and 15159, aldol compounds as described in Research Disclosure No. 13924, metal complexes as described in U.S. patent 3,719,492, and urethane compounds as described in JP-A-53-135628.

The present silver halide color light-sensitive material may optionally comprise various 1-phenyl-3-pyrazolidones for the purpose of promoting color development. Typical examples of such compounds are described in JP-A-56-64339, JP-A-57-144547, and JP-A-58-115438.

In the present invention, the various processing solutions can be used at a temperature of 10 to 50°C.

These solutions are normally used at a temperature of 33 to 38°C. The temperature range may be raised to promote the processing and thus shorten the processing time. On the contrary, the temperature range may be lowered to improve the picture quality or the stability of the processing solutions. In order to save the silver content in the light-sensitive material, the processing utilizing cobalt intensification or hydrogen peroxide intensification as described in West German patent No. 2,226,770 and U.S. Patent 3,674,499 can be used.

The present invention will be further described in the following examples, but the present invention should not be construed as being limited thereto.

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EXAMPLE 1

In order to evaluate the effectiveness of the present invention, a multilayer color light-sensitive material specimen 101 was prepared by coating various layers of the following compositions on an undercoated cellulose triacetate film support.

Specimen 101

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The coated amount of silver halide and colloidal silver is represented in g/m2 in terms of amount of silver. - The coated amount of coupler, additive and gelatin is represented in g/m2. The coated amount of sensitizing dye is represented by molar number per 1 mol of silver halide incorporated in the same layer.

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1st layer (antihalation layer)	
Black colloidal silver	0.37
Gelatin	2.81
Ultraviolet absorber UV-1	0.03
Ultraviolet absorber UV-2	0.05
Ultraviolet absorber UV-3	0.06
Dispersing high boiling organic solvent Solv-1	0.07

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2nd layer (intermediate layer)	
Gelatin	1.52
Ultraviolet absorber UV-1	0.03
Ultraviolet absorber UV-2	0.05
Ultraviolet absorber UV-3	0.06
Dispersing high boiling organic solvent Solv-1	0.07

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3rd layer (high sensitivity red-sensitive layer)	
Silver iodobromide emulsion (Agl content: 10 mol%; spherical particle having a diameter of 0.7 μ m)	0.90
Silver iodobromide emulsion (Agl content: 12 mol%; spherical particle having a diameter of 0.25 μm)	0.45
Gelatin	2.05
Sensitizing dye D-I	7.0x10 ⁻⁴
Coupler EX-1	0.04
Coupler EX-2	0.19
Coupler EX-3	0.20
Coupler EX-4	0.10
Coupler EX-5	0.11
Dispersing high boiling organic solvent Solv-2	0.10
Dispersing high boiling organic solvent Solv-3	0.20_

4th layer (low sensitivity red-sensitive layer)	
Silver iodobromide emulsion (Agl content: 3.5 mol%; cubic particle having a side length of 0.09 µm)	0.60
Gelatin Sensitizing dye D-I	1.93 9.0x10 ⁻⁴
Coupler EX-1	0.03
Coupler EX-2	0.23
Coupler EX-3	0.24
Coupler EX-4	0.03
Dispersing high boiling organic solvent Solv-2	0.10
Dispersing high boiling organic solvent Solv-3	0.20

5th layer (intermediate layer)	
Gelatin	0.90
Color stain inhibitor Ex-6	0.09
Dispersing high boiling organic solvent Solv-2	0.05
Dye F-1	0.04
Dye F-2	0.04

6th layer (low sensitivity green-sensitive layer)	
Silver iodobromide emulsion (Agl content: 3.5 mol%; cubic particle having a side length of 0.14 μ m)	0.46
Gelatin	0.93
Sensitizing dye D-II	6.0x10 ⁻⁴
Coupler EX-7	0.36
Coupler EX-8	0.07
Dispersing high boiling organic solvent Solv-2	0.32

7th layer (middle sensitivity green-sensitive layer)	
Silver iodobromide emulsion (Agl content: 4 mol%; spherical particle having a diameter of	0.67
0.40 μm) Gelatin	0.86
Sensitizing dye D-II Sensitizing dye D-III	9.0x10 ⁻⁴ 1.0x10 ⁻⁴
Sensitizing dye D-IV Coupler EX-7	5.0x10 ⁻⁵
Coupler EX-8	0.10 0.04
Coupler EX-5 Coupler EX-9	0.09
Dispersing high boiling organic solvent Solv-2	0.20

8th layer (high sensitivity green-sensitive layer)	
Silver iodobromide emulsion (Agl content: 10 mol%; spherical particle having a diameter of 0.7	0.48
μm) Gelatin	0.46
Sensitizing dye D-II	5.0x10 ⁻⁴
Coupler EX-7	0.04
Coupler EX-5	0.01
Dispersing high boiling organic solvent Solv-2	0.04

9th layer (yellow filter layer)	
Gelatin	1.19
Yellow colloidal silver	0.11
Color stain inhibitor Ex-6	0.28
Dispersing high boiling organic solvent Solv-2	0.15

10th layer (low sensitivity blue-sensitive layer)	
Silver chloroiodobromide emulsion (Agl content: 1 mol%; AgCt content: 5 mol%; cubic particle having a side length of 0.17 µm)	0.73
Gelatin	1.31
Sensitizing dye D-V	1.0x10 ⁻²
Coupler EX-10	0.74
Coupler EX-5	0.04
Dispersing high boiling organic solvent Solv-2	0.25

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	11th layer (high sensitivity	
	blue-sensitive layer)	
5	Silver chloroiodobromide emulsion (Agl content: 8 mol%; AgCl	0.10
10	content: 6 mol%; tabular particle (particle diameter: 0.60 µm (as calculated in	
	terms of circle)) having an average aspect ratio of 7) Silver	0.20
20	chloroiodobromide emulsion (Agl content: 4 mol%; AgCl content: 7 mol%; tabular particle (particle	
25	diameter: 0.38 (as calculated in terms of circle)) having an average aspect ratio of 6)	
30	Gelatin Sensitizing dye D-V	1.54 2.0x10 ⁻³
35	Coupler EX-10 Coupler EX-5 Dispersing high boiling organic	0.28 0.08 0.09
	solvent Solv-2	

40	12th layer (1st protective layer)	
	Gelatin	0.60
	Ultraviolet absorber UV-4	0.11
	Ultraviolet absorber UV-5	0.17
	Dispersing high boiling organic solvent Solv-4	0.02
45	Dye F-3	0.05

50	13th layer (2nd protective layer)				
50	Finely divided particulate silver halide emulsion (Agl content: 1 mol%; spherical particulate silver iodobromide having a diameter of 0.07 µm as calculated in terms of circle)	0.74			
	Gelatin	1.87			
55	Particulate polymethyl methacrylate (diameter: 1.5 μm)	0.15			
	Film hardener H-1	0.50			

Besides the above described components, a surface active agent was incorporated in each layer as a

coating aid.

Thus, Specimen 101 was prepared.

In order to improve the preservability and processability of the specimen and stabilize the physical properties of the film, the following compounds were used.

SPC-1

SPC-4

PC-
$$\#$$
 $\xrightarrow{\text{CH-CH}_2 \to n}$ | COOC₂H₅

After being exposed to light, the color photographic light-sensitive material thus prepared was then processed as follows:

Processing A

Step	Processing time	Processing temperature
		(°C)
Color development	3 min. 15 sec.	38
Bleach	6 min. 30 sec.	38
Rinse	2 min. 10 sec.	24
Fixing	4 min. 20 sec.	38
Rinse (1)	1 min. 05 sec.	24
Rinse (2)	1 min. 00 sec.	24
Stabilizing	1 min. 05 sec.	38
Drying	4 min. 20 sec.	55

The composition of the processing solutions used will be described hereinafter.

Color developing solution

	(unit: g)
Diethylenetriaminepentaacetic acid	1.0
1-Hydroxyethylidene-1,1-diphosphonic acid	3.0
Sodium sulfite	4.0
Potassium carbonate	30.0
Potassium bromide	1.4
Potassium iodide	1.5 mg
Hydroxylamine sulfate	2.4
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5
Water to make	1.0 £
Н	10.05

¹⁵ Bleaching solution

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(unit: g) 100.0 20 Sodium ethylenediaminetetraacetato ferrate (trihydrate) 10.0 Disodium ethylenediaminetetraacetate Ammonium bromide 140.0 30.0 Ammonium nitrate 6.5 m t Aqueous ammonia (27%) 1.0 £ 25 Water to make 6.0 pΗ

n Fixing solution

Disodium ethylenediaminetetraacetate
Sodium sulfite
Sodium bisulfite
7.0
Sodium bisulfite
70% aqueous solution of ammonium thiosulfate
Water to make
pH
6.7

Stabilizing solution

1	5	

55

		(unit: g)
	Formalin (37%)	2.0 ml
	Polyoxyethylene-p-monononylphenylether (polymerization degree: 10)	0.3
50	Disodium ethylenediaminetetraacetate	0.05
	Water to make	1.0 £
	рН	5.0 - 8.0

The structural formula of the compounds used in the present example will be shown hereinafter.

UV-1

$$Ce$$
 N
 N
 $(t)C_4H_9$
 $(t)C_4H_9$

UV-2

$$\begin{array}{c|c}
N \\
N \\
N
\end{array}$$
(t)C₄H₉

UV-3

$$(t)C_4H_9$$

$$UV - 4$$

$$CH_3 \qquad CH_3 \qquad CH_3 \qquad CH_2 - C \rightarrow y$$

$$COOCH_2 OCO \qquad COOCH_3$$

$$CH_3 - CH = C \rightarrow C$$

$$x/y=7/3$$

(weight ratio)

$$\begin{array}{c}
C_2H_5\\
N-CH=CH-CH=C\\
C_2H_5
\end{array}$$

E X - /

of OH NHCONH—CN $n - C_4 H_9$ $t) - C_5 H_{11}$ $(t) C_5 H_{11}$

EX-3

30

45

25 $(t)C_5H_{11}$ OH NHCONH—CN

(t)C₅H₁₁

(t)C₅H₁₁

E X - #OH

CONH

O-C 14 H 29(n)

40 N N

50

$$EX-7$$

CH₂CH₃

$$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$$
CONH
N
COOC₄H₉

$$CU$$

$$x/y/z = 2/1/1$$

Cl

(weight ratio)

50

45

E X -
$$\varepsilon$$

C 2H 5

NH

N=N

NHCOC (CH 3) 3

C 15 H 31

C C C

E X — 9

E X - / 0

$$CH_{3}O \longrightarrow COCHCONH \longrightarrow COCC_{12}H_{25}$$

$$O \longrightarrow N \longrightarrow COCHCONH \longrightarrow COCC_{12}H_{25}$$

$$O \longrightarrow N \longrightarrow COCHCONH \longrightarrow COCC_{12}H_{25}$$

D - I

$$\begin{array}{c} C_2H_5\\ S\\ CH=C-CH=\\ N\\ (CH_2)_3SO_3 \\ \hline \end{array}$$

$$(CH_2)_3SO_3 \\ \hline \end{array}$$

$$(CH_2)_3SO_3Na$$

$$D - I$$

$$\begin{array}{c} C_2H_5 \\ O \\ CH=C-CH= \\ O \\ CH_2)_2SO_3 \\ \hline \\ (CH_2)_2SO_3 \\ \hline \end{array} (CH_2)SO_3Na$$

$$D - II$$

C₂H₅

$$CH=C-CH=S$$
 CH_3
 CH_3

$$D - N$$

5

$$C_2H_5$$
 C_2H_5
 C

D - V

F - /

F-2

SOLV-/

COOC₄H₉(n)
$$COOC4H9(n)$$

SOLV-2
$$CH_3$$

$$O \longrightarrow P = O$$

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15

20

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Solv-4

$$(C_6H_{13}O)_{3}P=O$$

H-1

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35

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45

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Specimen 102

Specimen 102 was prepared in the same manner as in Specimen 101 except that the nondiffusive DIR coupler EX-4 to be incorporated in the 3rd layer was replaced by the diffusive DIR coupler T-131 of the present invention in the amount as shown in Table 1 and the nondiffusive DIR coupler EX-4 to be incorporated in the 4th layer was replaced by the diffusive DIR coupler T-131 of the present invention in the amount as shown in Table 1.

Specimen 103 and 104

Specimen 103 was prepared in the same manner as in Specimen 101 except that the nondiffusive DIR coupler EX-5 to be incorporated in the 10th layer was replaced by the diffusive DIR coupler T-104 of the present invention in the amount as shown in Table 1 and the nondiffusive DIR coupler EX-5 to be incorporated in the 11th layer was replaced by the diffusive DIR coupler T-144 of the present invention in the amount as shown in Table 1.

Specimen 104 was prepared in the same manner as in Specimen 102 except that the nondiffusive DIR coupler to be incorporated in the 10th layer and the diffusive DIR coupler to be incorporated in the 11th layer were replaced in the same manner as in Specimen 103.

Specimen 105

Specimen 105 was prepared in the same manner as in Specimen 101 except that the nondiffusive DIR coupler EX-4 to be incorporated in the 3rd layer was replaced by the diffusive DIR coupler T-131 of the present invention in the amount as shown in Table 1, the nondiffusive DIR coupler EX-4 to be incorporated in the 4th layer was replaced by the diffusive DIR coupler T-131 of the present invention in the amount as shown in Table 1, the nondiffusive DIR coupler EX-5 to be incorporated was replaced by the diffusive DIR coupler T-144 of the present invention in the amount as shown in Table 1, and the nondiffusive DIR coupler EX-5 to be incorporated in the 11th layer was replaced by the DIR coupler T-104 of the present invention in the amount as shown in Table 1.

Specimen 106 to 109

Specimens 106 to 109 were prepared in the same manner as in Specimen 105 except that the diffusive DIR coupler T-131 to be incorporated in the 4th layer was replaced by the diffusive DIR couplers T-144, T-104, T-117 and T-118 in the amounts as shown in Table 1, respectively.

Specimen 110

Specimen 110 was prepared in the same manner as in Specimen 106 except that the diffusive DIR coupler T-104 to be incorporated in the 10th layer was replaced by the diffusive DIR coupler T-144 in the amount as shown in Table 1.

Specimens 101 to 110 thus prepared were then subjected to the following tests. The results are shown in Table 1.

These specimens were measured for the MTF value at a frequency of 40 lines per 1 mm in yellow image and cyan image.

The MTF measurement method is described in T. H. James, "The Theory of the Photographic Process", 4th Edition, Macmillan Publishing Co., 1977, pp. 604 to 607.

In order to determine the color reproducibility, particularly saturation, the ratio of the gradation of D-log E curve obtained when exposed to light through a separation filter to the gradation of D-log E curve obtained when exposed to white light was calculated. The D-log E curve was obtained by plotting the logarithm of the exposure (E) on the abscissa and the optical density (D) on the ordinates. The gradation is represented by the slope of D-log E curve. The higher this ratio is, the higher is the saturation.

In order to determine the degree of the capability of adjusting the gradation during printing which is the object of the present invention, the ratio of the gradation of D-log E curve in the lowest sensitivity layer (high exposure range) to that in the next lowest sensitivity layer (low exposure range) was calculated. If this ratio is almost close to 1.0, the gradation is constant from the low exposure range to the high exposure range. In this case, it is difficult to adjust the gradation during printing on a color photographic paper as in ordinary direct photographic negative light-sensitive materials. The more this value exceeds 1.0, the more is the difference in the gradation between the low exposure range and the high exposure range. In this case, it is easy to adjust the gradation during printing. More particularly, a high contrast print can be obtained by forming a negative image on a high contrast portion (high exposure portion) in the present negative light-sensitive material. On the other hand, a low contrast print can be obtained by forming a negative image on a low contrast portion (low exposure portion) in the present negative light-sensitive material. Thus, any print with a desired contrast can be obtained.

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		MTF value of blue- sensi- tive layer	0.55	.55	09.0
5		YBL/YBL*4)	2.41	2.41	2,43
10		үв '/үво*3)	1.04	1.04	1.06
15 20		Type of DIR in high sensitivity blue-sensitive layer/mol & per 1 mol & per 1 m	EX-5 (non-diffusive)/		T-104 (di- ffusive)/ 0.96
25		Type of DIR in low sensitivity blue-sensitive layer (loth layer)/mol & per 1 mol Ag in the same layer	EX-5 (non-diffusive)/ 0.32		T-144 (di- ffusive)/ 3.01
r	Table 1	MTF value of red-sensitive layer	0.25	0.30	0.25
. 35		үRL/үRH*2)	1.91	1.90	1.91
40		YR'/YR0*1)	1,05	1.07	1.05
45		Type of DIR in high sensitivity red-sensitive layer (3rd layer)/mol & per 1 mol Ag in the same layer	EX-4 (non- diffusive)/ 0.38 EX-5 (non- diffusive)/ 1.65	T-131 (di- ffusive)/ 0.75 EX-5 (non- diffusive)/ 1.78	EX-4 (non-diffusive)/ 0.38 EX-5 (non-diffusive)/ 1.65
50		Type of DIR in low sen- sitivity red- sensitive layer (4th layer)/mol % per 1 mol Ag in the same layer	EX-4 (non- diffusive)/ 0.43	T-131 (di- ffusive)/ 1.01	EX-4 (non-diffusive)/ 0.43
55		Specimen No.	101 (com- parison)	. 102 (")	103 (")

		MTF value of blue- sensi- laver	rayer	0.60	89°0	0.69
5	•	VBC /VBC *4)	lan lan	2.43	2.45	2.45
10		- - - - u-/-u-/-u-/-u-/-u-/-u-/-u-/-u-/-u-/-u-	(= 0a) / a)	1.06	1.10	1.10
75 20		Type of DIR in high sensitivity bluesensitive layer (lith layer)/mol Ag in the		T-104 (di- ffusive)/ 0.96	r-104 (di- ffusive)/ 2.71	z
25	T	· · · · · · · · · · · · · · · · · · ·	same tayer	T-144 (di- ffusive)/ 3.01	T-144 (di- ffusive)/ 0,58	=
30	rable l (cont'd)	9 9	Layer	0.30	0.36	0.35
35	rable	10 knd. / ra.	YRL/YRH" 4)	1.92	1, 94	1.93
40			YR'/YR0-11	1.10	1.16	1.16
45		Type of DIR in high sen- sitivity red- sensitive layer (3rd layer (3rd layer)/mol % per 1 mol	same layer	T-131 (di- ffusive)/ 0.75 EX-5 (non- diffusive) /1.78	ffusive)/ 0.99 EX-5 (non- diffusive)/ /1.92	£
50		Type of DIR in low sensitivity red-sensitive layer (4th layer)/mol 8 per 1 mol Ag in the	same layer	T-131 (di- ffusive)/ 1.01	T-131 (di-) ffusive)/ 0.67	T-144 (di- ffusive)/ 0.65
55		u	No.	104 (com- parison)	105 T-131 (di (Invention) ffusive)/ 0.67	106 (")

		MTF value of blue- sensi- tive	0.68	0.69	0.69	0.69
5		ув с /үвс*4)	2.45	2.45	2.45	2.50
10		тв / уво*3)	1.10	1.10	1.10	1.12
15 20		Type of DIR in high sensitivity bluesensitive layer (lith layer)/mol & per 1 mol Ag in the same layer	T-104 (di- ffusive)/ 2.71		=	T-144 (di- ffusive)/ 1.20
25	d)	Type of DIR in low sen-sitivity blue-sensitive layer (10th layer)/mol & per l mol Ag in the same layer	T-144 (di- ffusive)/ 0.58	:	=	=
30	Table 1 (cont'd)	MTF value of red-sensitive	0.34	0.35	0.36	0.34
35	Table	YRL/YRH*2)	1.96	1.91	1,95	1.94
40		γR¹ /γR0*1)	1,15	1.14	1.14	1.16
45		Type of DIR in high sensitivity red-sensitive layer (3rd layer)/mol 8 per 1 mol Ag in the same layer	T-131 (di- ffusive)/ 0.99 EX-5 (non- diffusive)	=	=	ž
50		Type of DIR in low sen- sitivity red- sensitive layer (4th layer)/mol % per 1 mol Ag in the same layer	T-104 (di- ffusive)/ 0.61	T-117 (di- ffusive)/ 0.64	T-118 (di- ffusive)/ 0.63	T-144 (di- ffusive)/ 0.65
55		Specimen No.	107 (Inven- tion)	108 (")	109 (")) 011

	*1)	γR':	Gradation of red-sensitive layer obtained when
5			exposed to light through red separation filter
		γR ₀ :	Gradation of red-sensitive layer obtained when
10			exposed to white light (See Fig. 2)
	*2)	γRL:	Gradation of high exposure portion in red-
			sensitive layer obtained when exposed to white
15			light
		γRH:	Gradation of low exposure portion in red-
20			sensitive layer obtained when exposed to white
			light (See Fig. 1)
	*3)	γВ':	Gradation of blue-sensitive layer obtained
25			when exposed to light through blue separation
			filter
30		γB ₀ :	Gradation of blue-sensitive layer obtained
			when exposed to white light (See Fig. 2)
	*4)	γBL:	Gradation of high exposure portion in blue-
35			sensitive layer obtained when exposed to white
			light
40		үвн:	Gradation of low exposure portion in blue-
			sensitive layer obtained when exposed to white
			light (See Fig. 1)
45			to title and the second
			hat the present invention provides a color negative light-sensitive material excellent in

EXAMPLE 2

Specimen 201

Oth layer (antihalation layer)			
(Provided opposite side to the light-sensitive emulsion on the support)			
Black colloidal silver Gelatin	0.42 11.80		

1st layer (lowest sensitivity red-sensitive layer)						
(1st layer and the following layers were provided on the same side on the support.)						
Silver iodobromide emulsion (Agl content: 5 mol%, monodisperse particle with a particle diameter of 0.17 µm and a particle diameter fluctuation coefficient of 20%)						
Gelatin	4.02					
Sensitizing dye D-I	6.0x10 ⁻⁴					
Coupler EX-2	0.50					
Coupler EX-13	0.014					
high boiling organic solvent Solv-1	0.03					
high boiling organic solvent Solv-2	0.04					

	2nd layer (intermediate layer)	
	Gelatin	0.94
	Coupler EX-14	0.10
	Coupler EX-15	0.09
	Color stain inhibitor EX-16	0.08
ĺ	Dispersing high boiling organic solvent Solv-2	0.04
	Dye F-1	0.04

Silver iodobromide emulsion (Agl content: 3 mol%, monodisperse particle with a particle diameter of 0.20 μ m and a particle diameter fluctuation coefficient of	0.80
16%)	
Sensitizing dye D-VI	4.0x10 ⁻⁴
Sensitizing dye D-VII	1.0x10 ⁻⁴
Sensitizing dye D-VIII	1.0x10 ⁻⁴
Coupler EX-17	0.53
Dispersing high boiling organic solvent Solv-2	0.35

4th layer (intermediate layer)	
Gelatin	0.67
Color stain inhibitor EX-16	0.08
Dispersing high boiling organic solvent Solv-2	0.04

5th layer (highest sensitivity red-sensitive layer)	
Silver iodobromide emulsion (Agl content: 5 mol%; spherical particle with a particle diameter of 1.5 µm)	2.20
Gelatin	4.00
Sensitizing dye D-I	6.0×10 ⁴
Coupler EX-12	0.30
Coupler EX-23	0.15
Coupler EX-18	0.05
Coupler EX-13	0.07
Dispersing high boiling organic solvent Solv-2	0.10
Dispersing high boiling organic solvent Solv-3	0.20

6th layer (intermediate layer)	
Gelatin Color stain inhibitor EX-16	0.95 0.10
Dispersing high boiling organic solvent Solv-2	0.10

7th layer (highest sensitivity green-sensitive layer)	
Silver iodobromide emulsion (Agl content: 5 mol%; tabular particle with a particle diameter of 1.5 μ m and an aspect ratio of 5:1)	2.00
Gelatin	4.42
Sensitizing dye D-VI	3.8x10 ⁻⁴
Sensitizing dye D-VII	1.1x10 ⁻⁴
Sensitizing dye D-VIII	1.0x10 ⁻⁴
Coupler EX-17	0.39
Coupler EX-19	0.11
Coupler EX-20	0.02
Dispersing high boiling organic solvent Solv-2	0.30

8th layer (intermediate layer)	
Gelatin	1.34
Color stain inhibitor EX-16	0.10
Dispersing high boiling organic solvent Solv-2	0.05

9th layer (yellow filter layer)	
Gelatin	1.0
Yellow colloidal silver	0.26

10th layer (highest sensitivity blue-sensitive layer)	
Silver iodobromide (Agl content: 6 mol%; tabular particle with a particle size of 2.0 μ m and an aspect ratio of 8:1)	0.90
Gelatin	3.62
Sensitizing dye D-IX	6.0x10 ⁻⁴
Coupler EX-21	1.07
Coupler EX-22	0.07
Dispersing high boiling organic solvent Solv-2	0.30

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11th layer (lowest sensitivity blue-sensitive layer)	
Silver iodobromide (Agl content: 4 mol%; monodisperse particle with a particle size of 0.16 μ m and a particle size fluctuation coefficient of	0.90
18%) Gelatin	2.70
Sensitizing dye D-IX	5.0x10 ⁻⁴
Coupler EX-21	0.57
Dispersing high boiling organic solvent Solv-2	0.16

25

12th layer (1st protective layer)	
Gelatin	1.07
Ultraviolet absorber UV-6	0.10
Ultraviolet absorber UV-7	0.12
Dispersing high boiling organic solvent Solv-4	0.02
Dye F-4	0.05

30

	13th layer (2nd protective layer)	
35	Gelatin Particulate polymethyl methacrylate (diameter: 1.5 μm)	1.00 0.15

Besides the above components, a surface active agent as coating aid and a film hardener H-1 were incorporated in each layer.

Thus, Specimen 201 was prepared.

Specimen 202

45

Specimen 202 was prepared in the same manner as in Specimen 201 except that the nondiffusive DIR coupler EX-20 was incorporated in the 3rd layer in the amount as shown in Table 2.

50 Specimen 203 to 205

Specimens 203 to 205 were prepared in the same manner as in Specimen 201 except that the nondiffusive DIR coupler EX-20 to be incorporated in the 7th layer was replaced by the diffusive DIR couplers T-117, T-104 and T-118 of the present invention in the amounts as shown in Table 2, respectively.

55

Specimen 206

Specimen 206 was prepared in the same manner as in Specimen 203 except that the silver halide emulsion with an average particle size of 0.20 μm to be incorporated in the 3rd layer was replaced by a silver halide emulsion with an average particle size of 0.55 μm .

S	ı
1	2
2	2
Ë	3

Specimen No.	Type of DIR in low sensitivity green-sensitive layer	Type of DIR in low sensitivity green-sensitive layer Type of DIR in high sensitivity green-sensitive layer $\gamma G'/\gamma G_0$ $\gamma GL/\gamma GH$	r γG′γG₀	уGL/γGH	MTF value of
	(3rd layer)/mol% per 1 mol Ag in the same layer	(7th layer)/mol% per 1 mol Ag in the same layer			green-sensitive
					layer
201 (Comparison)		EX-20 (nondiffusive)/0.15	1.08	1.89	0.47
202 (")	EX-20 (non-diffusive)/0.10	=	1.07	1.87	0.52
203 (Invention)		T-117 (diffusive)/0.20	1.15	1.92	0.61
204(")	•	T-104 (diffusive)/0.21	1.16	1.91	0.62
205(")	•	T-118 (diffusive)/0.23	1.14	1.93	0.61
206 (Comparison)		T-117 (diffusive)/0.21	1.16	1.30	0.62

"5) $\gamma G^{'}$: Gradation of green-sensitive layer obtained when exposed to light through green separation filter

 γG_0 : Gradation of green-sensitive layer obtained when exposed to white light (See Fig. 2) *6) *GL : Gradation of high exposure portion in green-sensitive layer obtained when exposed to white light

γGH: Gradation of low exposure portion in green-sensitive layer obtained when exposed to white light (See Fig. 1)

Specimens 201 to 206 thus prepared were then subjected to the same tests as conducted in Example 1. The results are shown in Table 2. Table 2 shows that the present invention provides a color negative light-sensitive material excellent in the color reproducibility and sharpness which enables the gradation adjustment during printing.

The structural formula of the compounds used in the preparation of the specimens in Example 2, in addition to the compounds used in Example 1, will be shown hereinafter.

UV-7
$$C_{6}H_{13} > N-CH=CH-CH=C < \frac{CN}{CN}$$

EX-12
$$\begin{array}{c}
 & \text{OH} \\
 & \text{NHCONH} \\
 & \text{CN} \\
 & \text{O-CHCONH} \\
 & \text{OCH}_{3}
\end{array}$$

- ·

E X - / 8 EX-16 E X - 1 3 EX-/* E X - / 3

EX-20

EX-18

D - M

CH₂CH₂CHCH₃ (CH₂)₃SO₃Na

SO₃
$$\Theta$$

 $\mathbf{N} - \mathbf{Q}$

$$\begin{array}{c} C_2H_5 \\ CH=C-CH= \\ O \\ CH_2)_4SO_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_3 \\ SO_3Na \\ CH_2 \\ CH_2 \\ CH_3 \\ CH_3$$

D - M

$$\begin{array}{c} C_2H_5 \\ C \\ CH_2CH_2CHCH_3 \\ SO_3 \\ \end{array}$$

15 D - X

5

10

25

35

45

U V - 6

$$CH_3O \longrightarrow CH = C < CN COOC_3H_7$$

Ŭ V − 7

F-4

NaOCO
$$N=N$$
—SO₃Na

SO₃Na

EXAMPLE 3

Specimens 101 to 110 and Specimens 201 to 206 were developed in accordance with the processing methods B to I and then subjected to the same tests as conducted in the preceding examples. Almost the same results as in Examples 1 and 2 were obtained. Thus, it can be seen that the present light-sensitive materials can accomplish the objects of the present invention even when developed in accordance with the processing methods B to I.

The color photographic light-sensitive material specimens thus prepared were exposed to light, and then processed by means of an automatic developing machine in accordance with the following method until the accumulated supply amount of the processing solution reached 3 times the volume of the tank.

Processing method B

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	Step	Processing time	Processing temperature	Replenisher amount	Tank volume
20			(°C)	(ml)	(L)
	Color development	3 min. 15 sec.	38	33	20
	Bleach	6 min. 30 sec.	38	25	40
	Rinse	2 min. 10 sec.	24	1,200	20
	Fixing	4 min. 20 sec.	38	25	30
25	Rinse (1)	1 min. 05 sec.	24	Countercurrent process (from tank 2 to tank 1)	10
	Rinse (2)	1 min. 00 sec.	24	1,200	10
	Stabilizing	1 min. 05 sec.	38	25	10
	Drying	4 min. 20 sec.	55		
30	(The replenisher am	ount is represen	ted by the am	ount supplied per 35 mm width and 1 m length.)	

The composition of the processing solutions used will be described hereinafter.

35 Color developing solution

40		Tank solution	Replenisher
		(- g)	(- g)
	Diethylenetriaminepentaacetic acid	1.0	1.1
45	1-Hydroxyethylidene-1,1-diphosphonic acid	3.0	3.2
	Sodium sulfite	4.0	4.4
	Potassium carbonate	30.0	37.0
	Potassium bromide	1.4	0.7
	Potassium iodide	1.5 mg	_
50	Hydroxylamine sulfate	2.4	2.8
	4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5	5.5
	Water to make	1.0 £	1.0 l
	pH	10.05	10.10

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Bleaching solution

Tank Replenisher solution (g) (g) 100.0 120.0 Sodium ethylenediaminetetraacetato ferrate (trihydrate) 10.0 11.0 Disodium ethylenediaminetetraacetate 160.0 140.0 Ammonium bromide 35.0 Ammonium nitrate 30.0 Aqueous ammonia (27%) 6.5 ml 4.0 ml 1.0 2 1.0 £ Water to make 5.7 6.0 рΗ

15 Fixing solution

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Tank Replenisher solution 20 (g) (g) 0.5 0.7 Disodium ethylenediaminetetraacetate Sodium sulfite 7.0 8.0 5.0 5.5 Sodium bisulfite 25 170.0 ml 200.0 ml 70% aqueous solution of ammonium thiosulfate 1.0 L 1.0 £ Water to make 6.7 6.6 рΗ

Stabilizing solution

35		Tank solution	Replenisher
		(g)	(g)
40	Formalin (37%) Polyoxyethylene-p-monononylphenylether (average polymerization degree: 10) Disodium ethylenediaminetetraacetate Water to make pH	2.0 ml 0.3 0.05 1.0 t 5.0-8.0	3.0 ml 0.45 0.08 1.0 £ 5.0-8.0

Processing method C

55

Step	Processing time	Processing temperature
	:	(°C)
Color development	2 min. 30 sec.	40
Blix	3 min. 00 sec.	40
Rinse (1)	20 sec.	35
Rinse (2)	20 sec.	35
Stabilizing	20 sec.	35
Drying	50 sec.	65

The composition of the processing solutions used will be described hereinafter.

Color developing solution

20		(unit: g)
20	Diethylenetriaminepentaacetic acid	2.0
	1-Hydroxyethylidene-1,1-diphosphonic acid	3.0
	Sodium sulfite	4.0
	Potassium carbonate	30.0
25	Potassium bromide	1.4
	Potassium iodide	1.5 mg
	Hydroxylamine sulfate	2.4
	4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5
	Water to make	1.0 L
30	pH	10.05

Blix solution

		(unit: g)
5	Ammonium ethylenediaminetetra- acetato ferrate (dihydrate)	90.0
	Disodium ethylenediaminetetraacetate	5.0
	Sodium sulfite	12.0
10	70% aqueous solution of ammonium thiosulfate	260.0 ml
	Acetic acid (98%)	5.0 ml
15	Bleach accelerator	0.01 ml
20	N NH SH	
	Water to make	1.0 <i>e</i>
25	рН	6.0

30 Rinsing solution

Tap water was passed through a mixed bed column filled with a strongly acidic H-type cation exchange resin (Amberlite IR-120B of Rohm & Haas Co.) and an OH type anion exchange resin (Amberlite IR-400) so that the concentration of calcium and magnesium each reached 3 mg/£ or less. Sodium dichlorinated isocyanurate and sodium sulfate were added to the solution in amounts of 20 mg/£ and 1.5 g/£, respectively.

The pH value of the solution thus prepared was in the range of 6.5 to 7.5.

40 Stabilizing solution

		(unit: g)
45	Formalin (37%)	2.0 ml
	Polyoxyethylene-p-monononylphenylether (average polymerization degree: 10)	0.3
	Disodium ethylenediaminetetraacetate Water to make	1.0 1
	pH	5.0-8.0
50		L

Processing method D

	Step	Processing time	Processing temperature	Replenisher amount	Tank volume
			(°C)	(m t)	(L)
5	Color Development	2 min. 30 sec.	40	10	8
	Blix	3 min. 00 sec.	40	20	8
	Rinse (1)	20 sec.	35	Countercurrent process (from tank 2 to tank 1)	2
	Rinse (2)	20 sec.	35	10	2
10	Stabilizing	20 sec.	35	10	2
	Drying	50 sec.	65		
	(The replenisher amount is represented by the amount supplied per 35 mm width and 1 m length.)				

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Color developing solution

		T	
20		Tank solution	Replenisher
		(g)	(g)
	Diethylenetriaminepentaacetic acid	2.0	2.2
25	1-Hydroxyethylidene-1,1-diphosphonic acid	3.0	3.2
	Sodium sulfite	4.0	5.5
	Potassium carbonate	30.0	45.0
	Potassium bromide	1.4	-
	Potassium iodide	1.5 mg	-
30	Hydroxylamine sulfate	2.4	3.0
00	4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5	7.5
	Water to make	1.0 £	1.0 L
	nH	10.05	10.20

3**5**

Blix solution

(The tank solution was used also as the replenisher.)

40		(unit:	g)
	Ammonium ethylenediaminetetraacetato ferrate (dihydrate)	90.0	
45	Disodium ethylenediaminetetraacetate	5.0	
	Sodium sulfite	12.0	
50	70% aqueous solution of ammonium thiosulfate	260.0	ml
	Acetic acid (98%)	5.0	ml

Bleach accelerator

0.01 mol

Water to make 10

1.0 €

рН

6.0

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Rinsing solution

(The tank solution was used also as the replenisher)

Tap water was passed through a mixed bed column filled with a strongly acidic H-type cation exchange resin (Amberlite IR-120B of Rohm & Haas Co.) and an OH-type anion exchange resin (Amberlite IR-400) so that the concentration of calcium and magnesium each reached 3 mg/t or less. Sodium dichlorinated isocyanurate and sodium sulfate were added to the solution in amounts of 20 mg/t and 0.15 g/t, respectively.

The pH value of the solution thus prepared was in the range of 6.5 to 7.5.

Stabilizing solution

(The tank solution was used also as the replenisher)

	(unit: g)
Formalin (37%)	2.0 ml
Polyoxyethylene-p-monononylphenylether (average polymerization degree: 10)	0.3
Disodium ethylenediaminetetraacetate	0.05
Water to make	1.0 £
pH ·	5.0-8.0

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Processing method E

	Step	Processing time	Processing temperature	Replenisher amount	Tank volume
		[(°C)	(mt)	(L)
50	Color Development	3 min. 15 sec.	37.8	50	10
	Bleach	6 min. 30 sec.	37.8	10	20
	Fixing	3 min. 15 sec.	37.8	30	10
	Rinse (1)	1 min. 00 sec.	35.0	Countercurrent process (from tank 2 to tank 1)	4
55	Rinse (2)	1 min. 40 sec.	35.0	30	4
	Stabilizing Drying	1 min. 20 sec. 1 min. 30 sec.	37.8 52.0	30	4

The composition of the processing solutions used will be described hereinafter.

Color developing solution

Tank Replenisher solution (g) (g) 6.0 5.0 Diethylenetriaminepentaacetic acid 4.0 4.4 Sodium sulfite 37.0 30.0 Potassium carbonate 1.3 0.9 Potassium bromide 1.2 mg Potassium iodide 2.0 2.8 Hydroxylamine sulfate 4.7 5.3 4-(N-Ethyl-N-\(\beta\)-hydroxyethylamino)2-methylaniline sulfate 1.0 1 1.0 £ Water to make 10.00 10.05 рΗ

Bleaching solution

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	Tank solution	Replenisher
	(g)	(g)
Ammonium ethylenediamine tetraacetato ferrate (dihydrate) Disodium ethylenediaminetetraacetate Ammonium bromide Ammonium nitrate Aqueous ammonium (27%) Water to make pH	100.0 10.0 160.0 30.0 7.0 ml 1.0 £	120.0 12.0 180.0 50.0 5.0 ml 1.0 <i>l</i>

Fixing solution

45

	Tank solution	Replenisher
	(g)	(g)
Disodium ethylenediaminetetraacetate	0.5	0.7
Sodium sulfite	7.0	8.0
Sodium bisulfite	5.0	5.5
70% aqueous solution of ammonium thiosulfate	170.0 ml	200.0 ml
Water to make	1.0 L	1.0 L
pH	6.7	6.6

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Rinsing solution

(The tank solution was used also as the replenishe.)

5-Chloro-2-methyl-4-isothiazoline-3-one	6.0 mg
2-Methyl-4-isothiazoline-3-one	3.0 mg
Ethylene glycol	1.5 g
Water to make	1.0 £
ρΉ	5.0 - 7.0

10 Stabilizing solution

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(The tank solution was used also as the replenisher.)

Processing method F

40	Step	Processing time	Processing temperature	Replenisher amount	Tank volume
		0 45	(°C)	(m£)	(L)
	Color	3 min. 15 sec.	37.8	40	10
	Development				_
45	Bleach	3 min. 00 sec.	37.8	5	10
	Fixing	4 min. 00 sec.	37.8	30	10
	Stabilizing (1)	45 sec.	35.0	Countercurrent process (from tank 3 to tank 1)	5
	Stabilizing (2)	45 sec.	35.0		5
	Stabilizing (3)	45 sec.	35.0	40	5
50	Drying	1 min. 20 sec.	55.0		
	(The replenisher amount is represented by the amount supplied per 35 mm width and 1 m length)				

The composition of the processing solutions used will be described hereinafter.

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Color developing solution

	Tank solution	Replenisher
	(g)	(g)
Diethylenetriaminepentaacetic acid	5.0	6.0
Sodium sulfite	4.0	4.4
Potassium carbonate	30.0	37.0
Potassium bromide	1.3	0.9
Potassium iodide	1.2 mg	-
Hydroxylamine sulfate	2.0	2.8
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.7	5.3
Water to make	1.0 1	1.0 £
рН	10.00	10.05

Bleaching solution

	Tank solution	Replenisher
	(g)	(g)
Ammonium ethylenediaminetetraacetato ferrate (dihydrate)	70.0	120.0
1,3-Diaminopropane tetraacetato ferrate	35.0	55.0
Ethylenediamine tetraacetate	4.0	5.0
Ammonium bromide	100.0	160.0
Ammonium nitrate	30.0	50.0
Aqueous ammonia (27%)	20.0 ml	23.0 ml
Acetic acid (98%)	9.0 ml	15.0 ml
Water to make	1.0 L	1.0 L
. Ha	5.5	4.5

Fixing solution

	Tank solution	Replenisher
	(g)	(g)
Disodium ethylenediaminetetraacetate	0.5	0.7
Sodium sulfite	7.0	8.0
Sodium bisulfite	5.0	5.5
70% aqueous solution of ammonium thiosulfate	170.0 ml	200.0 ml
Water to make	1.0 £	1.0 £
pH	6.7	6.6

Stabilizing solution

(The tank solution was used also as the replenisher.)

Formalin (37%) 5-Chloro-2-methyl-4-isothiazoline-3-one 2-Methyl-4-isothiazoline-3-one Surface active agent	1.2 ml 6.0 mg 3.0 mg 0.4 g	
(C ₁₀ H ₂₁ -O (CH ₂ CH ₂ O) 10 H)	
Ethylene glycol Water to make pH	1.0 g 1.0 £ 5.0-7.0	

Tank

volume

(L)

20

40

20

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Processing method G

Replenisher amount Processing Step Processing time temperature (°C) (mt) 20 Color 15 Development 3 min. 15 sec. 38 10 Bleach 6 min. 30 sec. 38 Rinse 2 min. 10 sec.. 35 10 25 4 min. 20 sec. 38 20 Fixing Countercurrent process (from tank 2 to tank 1) 35 1 min. 05 sec. Rinse (1) Rinse (2) 1 min. 00 sec. 35 Stabilizing 1 min. 05 sec. 38 10

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The composition of the processing solutions used will be described hereinafter.

(The replenisher amount is represented by the amount supplied per 35 mm width and 1 m length.)

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Drying

Color developing solution

4 min. 20 sec.

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40		Tank solution	Replenisher
		(g)	(g)
	Diethylenetriaminepentaacetic acid	1.0	1.1
45	1-Hydroxyethylidene-1,1-diphosphonic acid	3.0	3.2
	Sodium sulfite	4.0	4.9
	Potassium carbonate	30.0	30.0
	Potassium bromide	1.4	-
	Potassium iodide	1.5 mg	-
50	Hydroxylamine sulfate	2.4	3.6
	4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5	7.2
	Water to make	1.0 L	1.0 Ł
	Hq	10.05	10.10
	' · · · ·		

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Bleaching solution

Replenisher Tank solution (g) (g) 140.0 100.0 Sodium ethylenediamine tetraacetato ferrate (trihydrate) 10.0 11.0 Disodium ethylenediaminetetraacetate Ammonium bromide 180.0 140.0 30.0 40.0 Ammonium nitrate 6.5 ml 2.5 ml Aqueous ammonia (27%) 1.0 1 1.0 1 Water to make 6.0 5.5 рΗ

Fixing solution

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Replenisher Tank solution 20 (g) (g) 0.5 1.0 Disodium ethylenediaminetetraacetate 12.0 7.0 Sodium sulfite 5.0 9.5 Sodium bisulfite 70% aqueous solution of ammonium thiosulfate 170.0 mi 240.0 ml 25 1.0 £ 1.0 L Water to make 6.7 6.6 Ηа

30 Rinsing solution

(The tank solution was used also as the replenisher)

Tap water was passed through a mixed bed column filled with a strongly acidic H-type cation exchange resin (Amberlite IR-120B of Rohm & Haas Co.) and an OH-type anion exchange resin (Amberlite IR-400) so that the concentration of calcium and magnesium each reached 3 mg/t or less. Sodium dichlorinated isocyanurate and sodium sulfate were added to the solution is amounts of mg/t and 1.5 g/t, respectively.

The pH value of the solution thus prepared was in the range of 6.5 to 7.5.

Stabilizing solution

45		Tank solution	Replenisher
		(g)	(g)
50	Formalin (37%) Polyoxyethylene-p-monononylphenylether (Average polymerization degree: 10) Disodium ethylenediamine tetraacetate Water to make pH	2.0 ml 0.3 0.05 1.0 l 5.0-8.0	3.0 ml 0.45 0.08 1.0 <i>l</i> 5.0-8.0

Processing method H

Processing Step Processing time temperature (°C) Color Development 3 min. 15 sec. 38 Bleach 1 min. 00 sec. 38 3 min. 15 sec. 38 Blix 35 Rinse (1) 40 sec. Rinse (2) 1 min. 00 sec. 35 Stabilizing 40 sec. 38 1 min. 50 sec. 55 Drying

The composition of the processing solutions used will be described hereinafter.

Color developing solution

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20 (unit: g) 1.0 Diethylenetriaminepentaacetic acid 1-Hydroxyethylidene-1,1-diphosphonic acid 3.0 4.0 Sodium sulfite 30.0 Potassium carbonate 25 1.4 Potassium bromide Potassium iodide 1.5 mg 2.4 Hydroxylamine sulfate 4.5 4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate Water to make 1.0 t 30 10.05 рΗ

35 Bleaching solution

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		(unit: g	l).
·	Ammonium ethylenediaminetetra- acetato ferrate (dihydrate)	120.0	
5	Disodium ethylenediaminetetraacetate	10.0	
	Ammonium bromide	100.0	
10	Ammonium nitrate	10.0	
	Bleach accelerator	0.005	mol
15	$\left(\begin{pmatrix} H_3C \\ H_3C \end{pmatrix} N - CH_2 - CH_2 - S - \frac{1}{2} \\ \end{pmatrix} \cdot 2HC\ell$		
20	Aqueous ammonium (27%)	15.0 ml	
	Water to make	1.0 e	
	рН .	6.3	

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Blix solution

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	(unit: g)
Ammonium ethylenediaminetetraacetato ferrate (dihydrate)	50.0
Disodium ethylenediaminetetraacetate Sodium sulfite	5.0 12.0
70% aqueous solution of ammonium thiosulfate	240.0 ml
Aqueous ammonia (27%) Water to make	6.0 ml
pH	7.2

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Rinsing solution

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Tap water was passed through a mixed bed column filled with a strongly acidic H-type cation exchange resin (Amberlite IR-120B of Rohm & Haas Co.) and an OH-type anion exchange resin (Amberlite IR-400) so that the concentration of calcium and magnesium each reached 3 mg/t or less. Sodium dichlorinated isocyanurate and sodium sulfate were then added to the solution is amounts of 20 mg/t and 1.5 g/t, respectively.

The pH value of the solution thus prepared was in the range of 6.5 to 7.0.

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Stabilizing solution

		(unit: g)
5	Formalin (37%) Polyoxyethylene-p-monononylphenylether (average polymerization degree: 10) Disodium ethylenediaminetetraacetate Water to make pH	2.0 ml 0.3 0.05 1.0 £ 5.0-8.0

¹⁰ Processing method I

15	Step	Processing time	Processing temperature	Replenisher amount	Tank volume
			(°C)	· (mt)	(L)
20	Color Development Bleach Blix Rinse (1) Rinse (2)	3 min. 15 sec. 1 min. 00 sec. 3 min. 15 sec. 40 sec. 1 min. 00 sec.	38 38 38 35 35	45 20 30 Countercurrent process (from tank 2 to tank 1) 30	10 4 8 4 4
25	Stabilizing Drying	40 sec. 1 min. 15 sec.	38 55	20	4
	(The replenishe	er amount is repres	sented by the a	mount supplied per 35 mm width and 1 m length.)

(The composition of the processing solutions used will be described hereinafter.

Color developing solution

35		Tank solution	Replenisher
		(g)	(g)
	Diethylenetriaminepentaacetic acid	1.0	1.1
40	1-Hydroxyethylidene-1,1-diphosphonic acid	3.0	3.2
	Sodium sulfite	4.0	4.4
	Potassium carbonate	30.0	37.0
	Potassium bromide	1.4	0.7
	Potassium iodide	1.5 mg	-
45	Hydroxylamine sulfate	2.4	2.8
	4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5	5.5
	Water to make	1.0 £	1.0 £
	На	10.05	10.10

Bleaching solution

(The tank solution was used also as the replenisher.)

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(unit: g) 120.0 Ammonium ethylenediaminetetraacetato ferrate (dihydrate) 5 10.0 Disodium ethylenediaminetetraacetate Ammonium bromide 100.0 10 10.0 Ammonium nitrate 0.005 mol Bleach accelerator $\begin{pmatrix} H_3C \\ H_3C \end{pmatrix} N-CH_2-CH_2-S-$ 15 20 15.0 ml Aqueous ammonia (27%) 1.0 € Water to make

Blix solution

pH

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(The tank solution was used also as the replenisher.)

	(unit: g)
Ammonium ethylenediaminetetraacetato ferrate (dihydrate)	50.0
Disodium ethylenediaminetetraacetate	5.0
Sodium sulfite	12.0
70% aqueous solution of ammonium thiosulfate	240.0 m
Aqueous ammonia (27%)	6.0 m
Water to make	1.0 £
На	7.2

6.3

Rinsing solution

(The tank solution was used also as the replenisher)

Tap water was passed through a mixed bed column filled with a strongly acidic H-type cation exchange resin (Amberlite IR-120B of Rohm & Hass Co.) and an OH-type anion exchange resin (Amberlite IR-400) so that the concentration of calcium and magnesium each reached 3 ml/t or less. Sodium dichlorinated isocyanurate and sodium sulfate were added to the solution is amounts of mg/t and 1.5 g/t, respectively.

The pH value of the solution thus prepared was in the range of 6.5 to 7.5.

Stabilizing solution

(The tank solution was used also as the replenisher.)

	(unit: g)
Formalin (37%) Polyoxyethylene-p-monononylphenylether (average polymerization degree: 10) Disodium ethylenediaminetetraacetate Water to make pH	2.0 ml 0.3 0.05 1.0 t 5.0-8.0

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

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1. A silver halide color photographic material comprising on a support light-sensitive layers consisting of a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer, at least one of these color-sensitive layers being composed of a plurality of silver halide emulsion layers having substantially the same color sensitivity and different light sensitivities, characterized in that all of said color-sensitive layers comprises a compound which reacts with an oxidation product of an aromatic primary amine color developing agent to release a diffusive development inhibitor or a precursor thereof and/or a compound which cleaves after the reaction with an oxidation product of an aromatic primary amine color developing agent a compound which reacts with another molecule of the oxidation product of an aromatic primary amine color developing agent to cleave a development inhibitor (hereinafter referred to as "diffusive development inhibitor-releasing compound"), that at least one of said color-sensitive layers consists of at least two light-sensitive layers having different sensitivities, and that the content of said diffusive development inhibitor-releasing compound shows the highest value except in the layer having the lowest sensitivity in each of said color-sensitive layers.

2. A silver halide color photographic material as claimed in Claim 1, wherein said diffusive development inhibitor-releasing compound is represented by the general formulas [I] to [IV]:

A-TIME-Z₂ [I]

 $A-Z_1$ [II]

B-Z₁ [III]

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A(orB)-P-Z₂ [IV]

wherein A represents a coupling component which can react with an oxidation product of a color developing agent to release -TIME- Z_2 group or -P- Z_2 group; B represents a redox portion which undergoes reduction-oxidation reaction with an oxidation product of a color developing agent and then undergoes hydrolysis with alkali to release Z; TIME represents a timing group; Z_1 rep[resents a diffusive development inhibitor; -P-represents a group which undergoes reaction with an oxidation product of a developing agent after cleavage from A or B to release a development inhibitor; and Z_2 may be a diffusive development inhibitor or a development inhibitor having a small diffusivity.

3. A silver halide color photographic material as claimed in Claim 2, wherein said Z_1 and Z_2 are represented by the general formulas (Z-1) to (Z-9):

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z-1

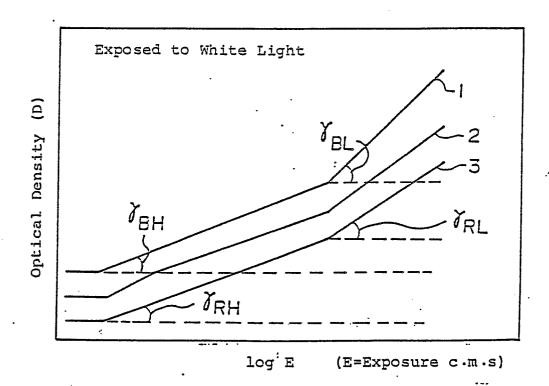
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wherein R₁₁ and R₁₂ each represents an alkyl group, alkoxy group, acylamino group, halogen atom, alkoxycarbonyl group, thiazolideneamino group, aryloxycarbonyl group, acyloxy group, carbamoyl group, N-alkylcarbamoyl group, nitro group, amino gorup, an-arylcarbamoyloxy group, sulfamoyl group, sulfonamide group, N-alkylcarbamoyloxy group, ureide group, hydroxy group, alkoxytcarbonylamino gorup, aryloxy group, alkylthio group, arylthio group, anilino group, aryl group, imide group, hetero group, cyano group, alkylsulfonyl group, or aryloxycarbonylamino group; n represents an integer 1 or 2; and R₁₃, R₁₄, R₁₅, R₁₆, and R₁₇ each represents an alkyl group, aryl group or heterocyclic group.

4. A silver halide color photographic material as claimed in Claim 1, wherein at least one of said silver halide emulsion layers having the lowest sensitivity substantially comprises silver halide grains having a diameter of $0.5~\mu m$ as calculated in terms of circle.

5. A silver halide color photographic material as claimed in Claim 2, wherein the ratio of the gradation (γ_1) of said lowest sensitivity layer to the gradation (γ_2) of the layer having the next lowest sensitivity (γ_1/γ_2) is 1 or more.

FIG. 1



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FIG. 2

