



11) Publication number:

0 507 092 A2

EUROPEAN PATENT APPLICATION

(21) Application number: 92103658.8 (51) Int. Cl.⁵: **G03C 7/30**

2 Date of filing: 04.03.92

Priority: 04.03.91 JP 37614/91

43 Date of publication of application: 07.10.92 Bulletin 92/41

Designated Contracting States:
DE FR GB NL

Applicant: KONICA CORPORATION 26-2, Nishi-shinjuku 1-chome Shinjuku-ku Tokyo(JP)

⁷² Inventor: Shimba, Satoru

Konica Corporation, 1 Sakura-machi

Hino-shi, Tokyo(JP) Inventor: Michiue, Kenji

Konica Corporation, 1 Sakura-machi

Hino-shi, Tokyo(JP)

Inventor: Yabuuchi, Katsuya

Konica Corporation, 1 Sakura-machi

Hino-shi, Tokyo(JP)
Inventor: Tobita, Keisuke

Konica Corporation, 1 Sakura-machi

Hino-shi, Tokyo(JP)

Representative: Türk, Gille, Hrabal, Leifert Brucknerstrasse 20 W-4000 Düsseldorf 13(DE)

- 64 Silver halide color photographic light-sensitive material.
- A silver halide color photographic material light-sensitive is disclosed. The light-sensitive material comprises a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a blue-sensitive silver halide emulsion layer. The light-sensitive material satisfise the following requirements:
 - (1) at least one of the red-sensitive emulsion layer and the green-sensitive emulsion layer comprises two or more emulsion sub-layers,
 - (2) an emulsion sub-layer having the highest speed among the emulsion sub-layers contains silver halide grains having a volume average size of from 0.20 μ m to 0.55 μ m,
 - (3) the light-sensitive material contains a diffusible DIR compound capable of splitting of a development inhibitor or its precursor which has a diffusibility not less than 0.34, and the amount of the DIR compound satisfise the following equation:

 $A/B \ge 5.00 \times 10^{-7} \text{ mole/cm}^2$

wherein A is the sum of molar amount of the diffusible DIR compound contained in one square meter of the light-sensitive material, and B is sum of the surface area of light-sensitive silver halide emulsion grains contained in one square meter of of the light-sensitive material represented by cm². The light-sensitive material is improved in graininess, sharpness and color reproducibility.

FIELD OF THE INVENTION

The present invention relates to a silver halide color photographic light-sensitive material, more specifically to a silver halide color photographic light-sensitive material excellent in graininess and color reproduction.

BACKGROUND OF THE INVENTION

In recent years, the silver halide multilayered color photographic light-sensitive material is making marked progress toward high image quality, and a further improvement is strongly demanded. In general, sharpness, graininess and color reproduction are considered to be the three major factors which control image quality. As a means to improve graininess particularly, it is known to form each of the red-sensitive silver halide emulsion layer and blue-sensitive silver halide emulsion layer into a multilayered structure. British Pat. No. 923,045, for example, discloses a technique to improve sensitivity without lowering graininess by dividing the emulsion layer into a high-sensitivity layer containing nondiffusible couplers and a low-sensitivity layer which are substantially developed in the same hue, and by controlling the maximum color-developed density in the high-sensitivity emulsion layer at a low level. But this technique is not adequate in providing a good graininess. Japanese Pat. Exam. Pub. No. 15495/1974 and Japanese Pat. O.P.I. Pub. No. 91945/1987 disclose techniques to improve graininess by forming at least one emulsion layer into a three-layered structure comprised of a low-sensitivity silver halide emulsion layer, medium-sensitivity silver halide emulsion layer, and by controlling finely the maximum color-developed density in each of these layers. But, these techniques cannot necessarily provide satisfactory results.

As described above, it seems that techniques only to form multilayered silver halide emulsion layers cannot provide a light-sensitive material having a satisfactory quality.

It is also known to minimize the size of silver halide grains as a means to improve graininess. But, as a result of the study made by the present inventors, it is found that a mere minimization of the grain size does not improve graininess.

With respect to the color negative film in which images are formed by the partial reduction of silver halide grains to developed silver, it is also found that when the volume average grain size d of silver halide grains is not more than $0.55~\mu m$, the developability of silver halide grains becomes higher beyond expectation and thereby the improvement in graininess is limited to a very small extent.

For color reproduction, the spectral sensitivity distribution and inter-image effect (hereinafter abbreviated to IIE) of color light-sensitive materials are major influential factors. The improvement in color reproduction based on IIE is disclosed in Japanese Pat. O.P.I. Pub. No. 2537/1975 and others. In those techniques which are applied to a multilayered color photographic light-sensitive material, a developing inhibitor, released from a compound capable of forming a developing inhibitor or its precursor upon coupling with an oxidation product of a color developing agent (the so-called DIR compound), prevents other color forming layers from being developed, and thereby IIE is produced and improves color reproduction. However, the study made by present inventors has proved that IIE cannot be adequately controlled by these conventional techniques, in a system where the size of silver halide grains is so small as described above.

In the color negative film, degradation in color purily due to a useless absorption (secondary absorption) of a dye formed by coupler can be prevented by use of a colored coupler in an amount large enough to compensate the secondary absorption. In addition, an effect similar to IIE can be obtained by use of a colored coupler in an amount larger than that necessary to cancel a secondary absorption.

However, use of a colored coupler in a large amount raises the minimum density of the film; therefore, it makes judgement on color correction and density correction difficult in the printing process and eventually lowers the working efficiency in processing laboratories due to the protraction of printing time. As a result, a poor color quality frequently occurs in prints prepared.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a silver halide color photographic light-sensitive material improved in graininess and color reproduction concurrently.

The object of the invention can be achieved by a silver halide color photographic light-sensitive material comprising a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a blue-sensitive silver halide emulsion layer, wherein the material satisfies the following requirements:

- (1) at least one of the red-sensitive emulsion layer and the green-sensitive emulsion layer comprises two or more emulsion sub-layers,
- (2) an emulsion sub-layer having the highest speed among the emulsion sub-layers in the at least one of the red-sensitive emulsion layer and the green-sernsitive emulsion layer contains silver halide grains having a volume average size of from 0.20 μ m to 0.55 μ m,
- (3) the light-sensitive material contains a diffusible DIR compound capable of splitting of a development inhibitor or its precursor which has a diffusibility not less than 0.34, and the amount of the DIR compound satisfies the following equation:

10 A/B $\ge 5.00 \times 10^{-7} \text{ mole/cm}^2$

5

15

wherein A is the sum of molar amount of the diffusible DIR compound contained in one square meter of the light-sensitive material, and B is the sum of surface area expressed by cm² of light-sensitive silver halide grains contained in one square meter of the light-sensitive material.

DETAILE DESCRIPTION OF THE INVENTION

Silver halide color light-sensitive materials, particularly, color negative films are frequently used to make enlarged prints. In enlargement to a large size such as full size or half size paper sheet, not only graininess is liable to deteriorate, but also saturation of color tends to lower. In this connection, the present inventors have found that when the number of color developing centers is increased by minimizing the size of silver halide grains to solve the problem involved in enlargement, graininess is satisfactorily improved with the decrease in grain size within the area where the volume average grain size of silver haloide grains is not less than 0.55 μ m, but in the area where the volume average grain size is less than 0.55 μ m, the relation between graininess improvement and grain size is weakened and thereby graininess cannot be improved as expected. The reason for the above is presumed that minimizing the size of silver halide grains raises the developability of silver halide to cause excessive development. In addition, it is presumed that this phenomenon also lowers an interlayer inhibiting effect exerted from other layers, namely IIE in itself, and thereby deteriorates color reproduction. In order to solve these problems at the same time, the present inventors have made a study in particulars and found that the following relation should be valid between the amount of a diffusible DIR compound used in the whole light-sensitive material and the sum of the surfaces of all the light-sensitive silver halide emulsions. That is, when the total amount of a diffusible DIR compound contained in all the layers of a light-sensitive material is A mole/m2, and the sum of the surface areas of silver halide light-sensitive emulsions contained in all the layers is B cm²/m²,

 $A/B \ge 5.00 \times 10^{-7}$ mole/cm² is the minimum requirement,

 $A/B \ge 7.00 \times 10^{-7}$ mole/cm² is preferred, and

 $1.50 \times 10^{-7} \text{ mole/cm}^2 \ge \text{A/B} \ge 8.00 \times 10^{-7} \text{ mole/cm}^2$ is particularly preferred.

The surface area of a silver halide emulsion contained in a light-sensitive material can be controlled by changing the coating weight of silver or the shape and size of silver halide grains. In the present invention, the coating weight of silver is not more than 7.5 g/m², preferably not more than 7.0 g/m² and especially 2.0 to 6.5 g/m², in view of a good image sharpness, film-forming properties and stability in processing. The surface area of silver halide grains can be calculated by the equation of $6 \times d^2N$, wherein d is volume average grain size and N is number of grains. The type of silver halide grains used in the invention is preferably a monodispersed one as described below.

The term "monodispersion" means that in an emulsion, the weight of silver halide grains contained within the range of volume average grain size d±20% is not less than 70% of the total weight of the silver halide grains. In the invention, this value is preferably not less than 80% and especially not less than 90%. Specially preferable monodispersed emulsion is ones having a variation coefficient of grain size distribution of 20% or less, most preferable 15% or less. The variation coefficient is defined as follows:

Standard deviation of grain size distribution

Volume average grain size d × 100

= variation coefficient (%)

The volume average grain size d and standard deviation of grain size distribution are calculated by di which

3

50

is defined in the later-mentioned.

These substantially monodispersed silver halide grains according to the invention may be used singly, or in combination, at an arbitrary mixing ratio, with two or more types of silver halide grains different in average grain size.

It is preferable that silver halide grains used in the invention have a core/shell grain structure comprised of two or more layers different in silver iodide content.

The silver iodide content of the uppermost layer, shell, of said two or more layers is preferably lower than that of the inner layers, core.

The effect of the invention can be exhibited much obviously by use of silver halide grains containing silver halide grains having a grain structure in which the silver iodide content of the shell is lower than that of the core.

In the present invention, it is preferable that the silver iodide content of the uppermost layer of silver halide grains be as low as possible, and a content close to 0% is particularly preferred.

In these core/shell type silver halide grains, the inner core may be formed so as to have two or more layers different in silver iodide content.

The difference in silver halide content between a high content layer and a low content layer, which are present between the core and the shell or inside of the core, may form a clear boundary or change continuously without forming a clear boundary.

The silver iodide distribution in these silver halide grains can be detected by various physical measuring methods. It can be determined, for example, by the measurement of luminescence at a low temperature as described in the Summaries of Lectures at 1981 Convention of Photographic Society of Japan.

It is preferable that the core/shell type silver halide grains used in the invention consist of a core comprised of silver halide containing silver iodide and a shell which covers the core and is comprised of silver halide having a silver iodide content lower than that of the core, and that the thickness of the shell be 0.001 to $0.2 \, \mu m$.

One preferable embodiment of silver halide grains according to the invention is silver halide grains having a core comprised of silver halide containing 2 to 24 mole% of silver iodide and a shell comprised of silver halide containing 0 to 4 mole% of silver iodide. The difference in silver iodide content between the core and the shell is preferably not less than 5 mole%.

In silver halide grains used in the invention, the silver halide component other than the above silver iodide is preferably silver bromide. Silver chloride may also be contained as long as it does impair the effect of the invention.

The average silver iodide content of silver halide grains according to the invention is preferably 0.5 to 15 mole%, especially 5 to 12 mole%.

The form of silver halide grains of the invention may be any of hexahedron, octahedron, tetradecahedron, tabular, sphere, and a hybrid of these forms. But octahedral or tetradecahedral grains are preferred.

These silver halide grains according to the invention can be prepared by use of monodispersed silver halide grains as cores and covering them with shells.

Monodispersed core silver halide grains can be prepared in a desired size by the double jet method performed at a constant pAg. Further, the method described in Japanese Pat. O.P.I. Pub. No. 48521/1979 can be applied to the preparation of an emulsion comprised of highly monodispersed silver halide grains. In concrete terms, such silver halide grains can be prepared by adding an aqueous gelatin solution containing potassium bromide, potassium iodide and an ammoniacal silver nitrate solution to an aqueous gelatin solution containing silver halide grains, while changing the addition speed as a function of time. Proper selection of this addition speed-time function, pH, pAg and temperature provides highly monodispesed silver halide grains.

The thickness of a shell which covers a core must be thin enough not to conceal the core's desirable properties, and must be thick enough to conceal the core's undesirable properties. Accordingly, the thickness is selected from a range between such an upper limit and lower limits. Such a shell can be formed by depositing a silver halide on each of cores consisting of monodispersed silver halide grains, through the addition of a water-soluble halide solution and a water-soluble silver salt solution by the double jet method.

Processes for manufacturing such core/shell type silver halide grains can be seen, for example, in West German Pat. No. 1,169,290, British Pat. No. 1,027,146, Japanese Pat. O.P.I. Pub. No. 154232/1982 and Japanese Pat. Exam. Pub. No. 1417/1976.

In the invention, the volume average size of silver halide grains, contained in the highest sensitivity

layer of two or more homochromatic sensitivity sub-emulsion layers constituting the red-sensitive or green-sensitive silver halide emulsion layer, is 0.20 μ m to 0.55 μ m, preferably not more than 0.50 μ m, and especially not more than 0.45 μ m. The term "volume average size d" used here is defined as grain size di at which the product of frequency ni of grains having grain size di and di³ (ni \times di³) takes the largest value (three significant figures, the 4th figure is rounded to the 3rd one). The term "size" means the length of an edge for cubic grains, and the length of an edge of a cube converted in the same volume for non-cubic grains.

In the invention, it is preferable that a blue-sensitive layer contain the following tabular silver halide grains.

That is, a silver halide emulsion used in the blue-sensitive layer is preferably comprised of tabular silver halide grains, in which at least 50% of the total projected area of all the grains is made up of grains which have an aspect ratio of 3.0 to 7.0 and satisfy the following requisites (a) and (b).

(a) Tabular silver halide grains having an even number of twin planes parallel to the principal plane, which has a hexagonal shape whose adjacent side ratio is 2.0 to 1.0, amount to at least 70% of the total projected area of the silver halide grains.

15

(b) The variation coefficient of grain size of the tabular silver halide grains specified in (a) is 21 to 29%, and that of the thickness is not more than 20%.

For the tabular silver halide grains contained in a silver halide emulsion preferably used in the invention (hereinafter occasionally abbreviated to the tabular grain), the aspect ratio means the ratio of grain diameter/grain thickness, the grain diameter means the diameter of a circle having the same area as the projected area of a grain, and the thickness means the distance between two paralellel planes which constitute a tabular silver halide grain.

The hexagonal tabular grain preferably usable in the invention possesses a hexagonal (111) face having a side length ratio of 1.0 to 2.0.

The term "side length ratio" used here means the ratio of the length of the longest side which constitute the hexagon to the length of the shortest side. In the hexagonal tabular grain preferably usable in the invention, the side length ratio may be 1.0 to 2.0, and the hexagonal may be rounded a little at the corner.

The term "variation coefficient of grain size" means the extent of the grain size variation, and is given in percentage by the value obtained by dividing the standard deviation of diameters of circles converted from projected areas of hexagonal tabular grains (each of which has a side length ratio of 1.0 to 2.0 according to the invention) by the average value of grain sizes.

The term "variation coefficient of grain thickness" means the extent of the thickness variation of hexagonal tabular grains of the invention, and is given in percentage by the value obtained by dividing the standard deviation of thicknesses of hexagonal tabular grains, each of which has a side length ratio of 1.0 to 2.0 according to the invention, by the average value of grain thicknesses.

In the tabular emulsion preferably usable in the invention, at least 50% of the total projected area of the tabular silver halide grains is made up of tabular grains having an aspect ratio of 3.0 to 7.0 as described above. It is preferred that at least 70% of the total projected area be made up of grains having an aspect ratio of 3.0 to 7.0. It is also preferred that at least 50% of the total projected area be made up of grains having an aspect ratio of 3.0 to 4.9.

It is particularly preferred that at least 70% of the total projected area be made up of grains having an aspect ratio of 3.0 to 4.9.

In the tabular emulsion, at least 70% of the total projected area of the tabular grains is made up of grains having an even number of twin planes parallel to the principal plane, which is a hexagon whose side length ratio is 2.0 to 1.0. It is preferred that at least 90% of the total projected area be made up of such hexagonal tabular grains.

It is also preferred that at least 70% of the total projected area be made up of hexagonal tabular grains having a side length ratio of 1.0 to 1.5. It is particularly preferred that at least 90% of the total projected area be made up of hexagonal tabular grains having a side length ratio of 1.0 to 1.5.

When the percentage of such hexagonal tabular grains decreases, there comes to mix in, at a higher ratio, other forms of silver halide grains such as regular crystals, triangular twins and various hybrid twins.

Chemical sensitization is considerably influenced by the shape, crystal face index, composition and defect of silver halide grains; therefore, mixing-in of grains in such different forms affects the degree of chemical sensitization, and thereby not only hinders chemical sensitization from providing an optimum sensivity and fog, but also allows insufficiently chemical-ripened grains which are easily desensitized by pressure, and excessively chemical-ripened grains which are easily fogged by pressure, to coexist, deteriorating the grains in overall anti-pressure effect characteristics.

Further, when the grains formed under conditions where formation of hexagonal tabular grains having a

high side length ratio (triangular grains devoid of corners) outnumbers, the side length ratio is liable to fluctuate. In other words, grains formed are greatly different in crystal forms, in such case, an optimum chemical sensitization can be hardly performed, as a result, the anti-pressure characteristics of the emulsion is lowered.

The spectral sensitivity distribution of the blue-sensitive layer of the invention is preferably as follows. That is, the wavelength λ_B^{max} which provides the maximum value in the spectral sensitivity distribution of the blue-sensitive layer is within the range of 415 nm $\leq \lambda_B^{max} \leq 470$ nm, preferably 420 nm $\leq \lambda_B^{max} \leq 460$ nm, and especially within the range of 445 nm + 10 nm. In addition, the spectral sensitivity at 480 nm is required to be not more than 35%, particularly not more than 25%, of the spectral sensitivity of the blue-sensitive layer at λ_B^{max} .

The tabular silver halide emulsion may use pure silver bromide and silver iodobromide. The average silver iodide content in the silver iodobromide is not more than 10 mole%, preferably not more than 8 mole% and especially not more than 6 mole%, in view of color reproducibility. Though use of a silver bromide containing not more than 0.5 mole% of silver iodide is particularly preferred from the viewpoint of color reproducibility, the presence of a little amount of silver iodide exerts a good effect on the stability of the emulsion, and too low a silver iodide content is liable to harden contrast. Accordingly, the optimum range of the silver iodide content is 0.1 to 6 mole%, preferably 0.5 to 4 mole% and especially 1 to 3.5 mole%.

The silver iodide content of each grain can be measured by use of an X-ray microanalyzer. When the ratio of the standard deviation of silver iodide contents of respective grains measured with an X-ray microanalyzer to the average silver iodide content is defined as a relative standard deviation, the relative standard deviation is preferably not more than 20%, especially not more than 15%, in view of pressure characteristics of the emulsion.

The diameter of the hexagonal tabular grain of the invention is not less than 0.4 μ m, preferably 0.5 to 3.0 μ m and especially 0.5 to 1.7 μ m.

The thickness of the hexagonal tabular grain of the invention is 0.05 to 0.3 μ m, preferably 0.05 to 0.25 μ m and especially 0.05 to 0.20 μ m.

In providing the light-sensitive material of the invention with the spectral sensitivity distribution of a blue-sensitive silver halide emulsion layer specified above, there may be employed any method selected from one which spectrally sensitizes a silver halide by use of a sensitizing dye having an absorption spectrum in an objective wavelength region, one which provides a silver halide with an objective spectral sensitivity by properly modifying the halide composition and distribution thereof using no sensitizing dye, and one which adjusts the spectral distribution to an objective distribution by incorporating a suitable optical light-absorbent in a light-sensitive material. Of course, combination of these methods is also useful.

The following are typical examples of the sensitizing dye used in a blue-sensitive silver halide emulsion layer of the light-sensitive material of the invention in order to provide the above spectral sensitivity, but usable sensitizing dyes are not limited to them.

35

40

45

50

A-1

A - 2

A - 3

25

S
$$CH_{2})_{3}SO_{3}\Theta$$

$$CH_{2})_{3}SO_{3}\Theta$$

$$CH_{2})_{3}SO_{3}H \cdot N(C_{2}H_{5})_{3}$$

A - 4

55

CH₃

$$A-5$$

CH3 5 C H (CH₂)₃SO₃e (CH₂)₃SO₃H·N(C₂H₆)₃ 10

A - 615

A - 7

25

A -- 8

Se
$$CH_3$$
 CH_3 CCH_3 CCH_3 CCH_3 CCH_3 CCH_3 CCH_3 CCH_3 CCH_3 CCH_3 CCH_3

55

$$A-9$$

$$CH_3$$

A - 10

$$CH_3$$

A - 11

S

CH₃

$$CH_3$$
 CH_2
 CH_2
 CH_2
 CH_3
 CH_2
 CH_3
 CH

25

50

A - 12

O

N

$$CH_2$$
) $_3SO_3HN(C_2H_5)_3$
 CH_2
 CH_2

In the invention, the DIR compound means a compound which can split off, upon reaction with an oxidation product of a color developing agent, a development inhibitor or a compound capable of releasing a development inhibitor.

In the invention, the preferable DIR compounds are those which split off, upon reaction with an oxidation product of a color developing agent, a developing inhibitor or a compound capable of releasing a developing inhibitor, both of which show a diffusibility of not less than 0.34, preferably not less than 0.40, according to the measuring method described below.

The diffusibility is determined by the following method.

There are prepared light-sensitive material samples (I) and (II) each having a layer of the following composition on a support.

Sample (I): a sample having a green-sensitive silver halide emulsion layer

There is coated on a support a gelatin coating solution containing 0.07 mole per mole silver each of silver iodide spectrally sensitized to green-sensitivity (silver iodide content:6 mole%, average grain size:0.48 μ m) and the following coupler so as to give a silver coating weight of 1.1 g/m² and a gelatin coating weight of 3.0 g/m². Then, a protective layer is formed thereon by coating a gelation coating solution containing silver iodide subjected to neither chemical sensitization nor spectral sensitization (silver iodide content:2 mole%, average grain size:0.08 μ m) so as to give a silver coating weight of 0.1 g/m² and a gelatin coating weight of 0.8 g/m².

$$\begin{array}{c|c}
 & C_5H_{11}(t) \\
 & N \\
 & N \\
 & C_5H_{11}(t)
\end{array}$$

$$\begin{array}{c|c}
 & C_5H_{11}(t) \\
 & C_5H_{11}(t)
\end{array}$$

Sample (II): a sample prepared without employing the silver iodide in the protective layer of sample (I)

Besides the above compounds, a gelatin hardener and a surfactant are used in each layer of these samples.

Samples (I) and (II) are exposed to white light through an optical wedge, and then processed in the following procedure. Two types of developers are used: a developer containing a developing inhibitor selected from various ones in an amount necessary to control the sensitivity of sample (II) to 80% (in a logarithmic expression, - Δ log E = 0.22), and a developer containing no developing inhibitor.

Processing (at 38°C)

Color developing	2 min 40 sec
Bleaching	6 min 30 sec
Washing	3 min 15 sec
Fixing	6 min 30 sec
Washing	3 min 15 sec
Stabilizing	1 min 30 sec
Drying	

Composition of the processing solution used in each process is as follows.

Color developer

55

5

25

30

40

45

4-Amino-3-methyl-N-ethyl-N-(β-hydroxylethyl) aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxyl amine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate monohydrate	2.5 g
Potassium hydoxide	1.0 g

Water is added to make 1 liter.

Bleaching solution

15

5

Ammonium ferric ethylenediaminetetracetate	100.0 g
Diammonium ethylenediaminetetracetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml

20

Water is added to make 1 liter, and the pH is adjusted to 6.0 with an aqueous ammonia.

Fixer

25

Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g

30

Water is added to make 1 liter, and the pH is adjusted to 6.0 with acetic acid.

Stabilizer

35

50

55

Formalin (37% aqueous solution)	1.5 ml
Koniducks (product of Konica Corp.)	7.5 ml

40 Water is added to make 1 liter.

When the sensitivity of sample (I) is taken as S_0 and that of sample (II) as S_0 , the sensitivity of sample (I) to which the developing inhibitor is added as S_1 and that of sample (II) as S_{II} , the following relations are valid:

Degree of desensitization of sample (I) $\Delta S = S_0 - S_1$

Degree of desensitization of sample (II) $\Delta S = S_0' - S_{II}$

Accordingly, the diffusibility is expressed as

Diffusibility = $\Delta S/\Delta S_0$.

where, all the sensitivities are expressed in the logarithm (-log E) of a reciprocal of an exposure to give a density of fog density + 0.3.

The diffusibilities of several developing inhibitors determined in this manner are shown in the following table.

Table (1/3)

5	Structure	Addition amount	Degre desens ti	itiza-	Diffusibility
		(mole/l)	∆s ₀	Δs	ΔS/ΔS ₀
10	н з — С Т	1.3 × 10 ⁻⁵	0.22	0.05	0.23
15	"3 N-"N				
20					
25	H H H H=C S	1.3 × 10 ⁻⁵	0.23	0.08	0.34
30	СН.				
35	HS O CH.	2.5 × 10 ⁻⁵	0.22	0.10	0.45

Table (2/3)

5	Structure	Addition amount	Degre desens ti	itiza-	Diffusibility
		(mole/l)	∆s _o	Δs	ΔS/ΔS ₀
10 15	HS — N — N	3.0 × 10 ⁻⁵	0.21	0.10	0.48
20		1.4 × 10 ⁻⁵	0.23	0.11	0.48
25	HO NO_2 $CH_2N-C_3H_7$ $O=C$ $N-N$ $N-N$				
30					·
35 40	HS N-N	2.5 × 10 ⁻⁵	0.22	0.13	0.59

Table (3/3)

5	Structure	Addition amount	Degre desens ti	itiza-	Diffusibility
		(mole/l)	∆s _o	Δs	Δs/Δs ₀
10	H	3.5 × 10 ⁻⁵	0.23	0.15	0.65
15	H C00				
20	H	4.3 × 10 ⁻⁵	0.22	0.16	0.73
25	H N CH,				
30	•	1.7 × 10 ⁻⁵	0.21	0.20	0.95
35	M N				

In the invention, the DIR compound is preferably one which releases a group having the diffusibility specified above, but any of others may be used.

The representative chemical structure of these DIR compounds is shown below. Formula (D-1)

 $A-(Y)_m$

where A represents a coupler residue; m represents 1 or 2; and Y represents a group bonding with coupler residue A at the coupling position, which splits off upon reaction with an oxidation product of a color developing agent to release a development inhibitor or a developing inhibitor precursor.

In Formula (D-1), Y is typically represented by following Formulas (D-2) to (D-19).

55

50

40

Formula (D-2)

$$-N$$
 (Rd_1)

5

10

15

20

25

30

35

45

55

$$-OCH_2-N$$
 N
 $(Rd_1)_n$

Formula (D-4)

$$-s \xrightarrow{N} (Rd_1)_{x}$$

$$-s$$
 N
 $(Rd_1)_n$

$$-S \underset{N}{\overset{X}{\longrightarrow}} Rd_1$$

Formula (D-6)

$$-N$$
 N
 $(Rd_1)_n$

Formula (D-8)

$$-S = \left\langle \begin{array}{c} N - N \\ \parallel \\ N - N \\ \parallel \\ Rd_2 \end{array} \right.$$

$$-S \xrightarrow{\stackrel{N}{\underset{Rd_{3}}{\longrightarrow}}} Rd_{4}$$

In Formulas (D-2) to (D-7), Rd₁ represents a hydrogen or halogen atom, or an alkyl, alkoxy, acylamino, alkoxy, carbonyl, thiazolidinydene amino, aryloxycarbonyl, acyloxycarbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, nitro, amino, N-arylcarbamoyloxy, sulfamoyl, N-alkylcarbamoyloxy, hydroxy, alkoxycarbonylamino, alkylthio, arylthio, aryl, heterocyclic, cyano, alkylsulfonyl or aryloxycarbonylamino group. n represents 0, 1 or 2; when n is 2, two Rd₁s may be the same or different. The total number of carbon atoms contained in Rd₁s is 0 to 10. And the number of carbon atoms contained in Rd₁ in Formula (D-6) is 0 to 15.

X in Formula (D-6) represents an oxygen or sulfur atom.

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

In Formula (D-9), Rd₃ represents a hydrogen atom, or an alkyl, cycloalkyl, aryl or heterocyclic group. Rd₄ represents a hydrogen or halogen atom, or an alkyl, cycloalkyl, aryl, acylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkanesulfonamido, cyano, heterocyclic, alkylthio or amino group.

The alkyl group represented by Rd_1 , Rd_2 , Rd_3 or Rd_4 may have a substituent, and may be either straight-chain or branched.

The aryl group represented by Rd₁, Rd₂, Rd₃ or Rd₄ may have a substituent.

The heterocyclic group represented by Rd₁, Rd₂, Rd₃ or Rd₄ may have a substituent. The heterocyclic group is preferably a 5- or 6-membered monocycle or condensed ring containing a heteroatom selected from nitrogen, oxygen and sulfur; examples thereof include pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl, imidazolyl, tiazolyl, triazolyl, benzotriazolyl, imido and oxazinyl groups.

The number of carbon atoms contained in Rd_2 of Formulas (D-6) and (D-8) is 0 to 15. In Formula (D-9), the total number of carbon atoms contained in Rd_3 and Rd_4 is 0 to 15. Formula (D-10)

5 -TIME-INHIBIT

20

30

35

40

45

50

55

In the formula, the TIME group is a group which bonds with A at its coupling position and can split off upon reaction with an oxidation product of a color developing agent. After splitting off from the coupler, this can release an INHIBIT group at a properly controlled rate. The INHIBIT group is a group which acts, when released, as a development inhibitor represented, for example, by Formulas (D-2) to (D-9). The TIME-INHIBIT group in Formula (D-10) is typically represented by following Formulas (D-11) to (D-19)

Formula (D-11) $-0 \qquad \qquad (Rd_5)_{\varrho}$

$$(CH_2)_k$$
-N-CO-INHIBIT -O

$$-O \longrightarrow CH_2 - INHIBIT$$

$$(Rd_5)_{\varrho}$$

Formula (D-14)

Formula (D-12)

CH2-INHIBIT

Formula (D-15)

$$\begin{array}{c|c}
O & (CH_2)_k - NCO - INHIBIT
\\
-N & Rd_6
\\
(Rd_5)_{\varrho}
\end{array}$$

5

10

15

25

30

35

40

45

50

Formula (D-16)

$$(Rd_7)_m$$
 $(CH_2)_kB-CO-INHIBIT$

Formula (D-17)

$$\begin{array}{c|c}
O & N-Rd_7 \\
-N & (CH_2)_kB-CO-INHIBIT
\end{array}$$

Formula (D-18)

Formula (D-19)

In Formulas (D-11) to (D-15) and (D-18), Rd₅ represents a hydrogen or halogen atom, or an alkyl, cycloalkyl, alkenyl, aralkyl, alkoxy, alkoxycarbonyl, anilino, acylamino, ureido, cyano, nitro, sulfonamide, sulfamoyl, carbamoyl, aryl, carboxy, sulfo, hydroxy or alkanesulfonyl group. In Formulas (D-11) to (D-13), (D-15) and (D-18), 1Rd₅ s may link to each other to form a condensed ring. In Formulas (D-11), (D-14), (D-15) and (D-19), each Rd₅ represents an alkyl, alkenyl, aralkyl, cycloalkyl, heterocyclic or aryl group. In Formulas (D-16) and (D-17), Rd₇ represents a hydrogen atom, or an alkyl, alkenyl, aralkyl, cycloalkyl, heterocyclic or aryl group. In Formula (D-19), Rd₈ and Rd₉ each represent a hydrogen atom or an alkyl

group (preferably, one having 1 to 4 carbon atoms). In Formulas (D-11) and (D-15) to (D-18), k represents an integer of 0, 1 or 2. In Formulas (D-11) to (D-13), (D-15) and (D-18), 1 represents an integer of 1 to 4. In Formula (D-16), m represents an integer of 1 or 2; when n is 2, two Rd₇s may be the same or different. In Formula (D-19), n represents an integer of 2 to 4, and n Rd₈s and n Rd₉s may be the same or different. In Formulas (D-16) to (D-18), B represents an oxygen atom or



 $(Rd_6 \text{ is the same as that defined above})$. In Formula (D-16), —— means that either a single bond or a double bond is applicable; in case of a single bond, m is 2, in case of a double bond, m is 1; and the INHIBIT group is the same as that defined for Formulas (D-2) to (D-9) except the number of carbon atoms.

In the INHIBIT group, the number of carbon atoms contained in each Rd_1 of Formulas (D-2) to (D-7) is 0 to 32 in total, the number of carbon atoms contained in Rd_2 of Formula (D-8) is 1 to 32, and the number of carbon atoms contained in Rd_3 and Rd_4 is 0 to 32 in total.

Among these DIR compounds, preferred ones are those whose Y is represented by Formula (D-2), (D-3) or (D-10); among ones represented by Formula (D-10), the preferred are those whose INHIBIT group is represented by Formula (D-2), (D-6), particularly preferred one is that whose X in Formula (D-6) is an oxygen atom, or (D-8), particularly preferred one is that whose Rd_2 in Formula (D-8) is a hydroxyaryl or alkyl group having 1 to 3 carbon atoms.

Examples of the coupler component represented by A in Formula (D-1) include yellow dye image forming coupler residues, magenta dye image forming coupler residues, cyan dye image forming coupler residues and non-color forming coupler residues.

The following are typical examples of the diffusible DIR compound preferably used in the invention, but usable ones are not limited to them.

80 Exemplified compound

10

35

40

45

50

55

COOCH2CONH-

 $\begin{array}{c} D-1 \\ C_{13}H_{27}CONH \\ \\ N \\ N \\ \\ N \end{array}$

D-36 $OC_{18}H_{37}$ NHCO S ONHCO NHCO NHCO NHCO

D-37 $CO - C_{18}H_{37}$ N-N N-N N-N

25

40

50

45

$$\begin{array}{c} {\tt R_1-COCHCO-R_2} \\ {\tt I} \\ {\tt Y} \end{array}$$

Exemplified compound No.	R ₁	R ₂	Y
D-2	(1)	(1)	(30)
D-3	(2)	(3)	(30)
D-4	(2)	(4)	(30)
D-5	(5)	(6)	(31)
D-6	(2)	(4)	(32)
D-7	(2)	(3)	(32)
D-8	(7)	(8)	(33)
D-33	(2)	(4)	(35)

 R_1 N N O

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

 $\bigcap_{Y}^{OH} R_1$

Exemplified compound No.	R ₁	Y
D-15	(17)	(38)
D-16	(17)	(39)
D-17	(18)	(40)
D-18	(19)	(41)
D-19	(18)	(42)
D-20	(18)	(43)
D-21	(18)	(44)
D-22	(18)	(45)
D-23	(18)	(46)
D-24	(20)	(47)
D-25	(20)	(48)
D-26	(21)	(49)
D-27	(21)	(50)
D-28	(21)	(51)
D-29	(22)	(52)
D-30	(18)	(53)
D-31	(18)	(54)
D-32	(22)	(49)
D-34	(18)	(56)

75

C1 $C_5H_{11}(t)$ NHCOCH₂O $C_5H_{11}(t)$

20

30

50

25 Cl $C_5H_{11}(t)$ NHCO (CH₂) 30 C₅H₁₁(t)

5 6 -NH OC₁₄H₂₉

7 8 C1 -NH

9 -NHCO-NHCOCHO C₅H₁₁(t)
$$C_5H_{11}(t)$$
 C_2H_5

10

C1 C1 11

-NHCOCHO
$$C_2H_5$$
 $C_{15}H_{31}$

20 12

-C₁₇H₃₅

13

$$-\langle N - \rangle$$

25

30

15

15

-CH₃

35 16

-√SO₃H

17

-CONHC₁₈H₃₇

40

-CONH- \bigcirc OC₁₄H₂₉

50

45

 $C_5H_{11}(t)$ -CONH(CH₂)₃O
-C₅H₁₁(t)

-CONHCH₂CH₂COOH

22 —CONHCH₂CH₂COOCH₃

 $C_5H_{11}(t)$ NHCOCHO $C_5H_{11}(t)$

32

$$CH_2NCOS - N-N$$
 $C_2H_5 \quad I$
 C_2H_5

33

$$CH_2S$$
 N
 $COOH$
 C_5H_{11} (t)

 $NHCOCH_2O$
 C_5H_{11} (t)

 $\begin{array}{c|c}
 & 36 \\
 & -N \\
\hline
 & O \\
 & CH_2N-COS \\
 & CH_3 \\
\hline
 & CO_2
\end{array}$

15

45

55

38 39 $-N \longrightarrow CH_3 -S \longrightarrow N \longrightarrow NH_2$

35 40 41 $\begin{array}{c|c} N-N & & & & \\ -S-N & & & & \\ N-N & & & & \\ N-N & & & & \\ \end{array}$

-OCH₂-

NO2 CO₂CH₂CH₂CN

NO2

-NHCOCH₃ `N´ H

$$\begin{array}{c} 49 \\ \\ O_2N - \\ N - \\ N \\ C_{11}H_{23} \end{array}$$

 $CH_2-S \longrightarrow N \longrightarrow N$ $C_{11}H_{23} \longrightarrow C_{14}$

 $\begin{array}{c}
51 \\
O_2N \longrightarrow N \longrightarrow N \\
O_2N \longrightarrow N \longrightarrow N \longrightarrow N
\end{array}$

 $CH_{2} \longrightarrow N \longrightarrow N$ $C_{11}H_{23} \longrightarrow N \longrightarrow N$

54

$$O$$
 CH_2-S
 $N-N$
 $N-N$
 $N-N$
 $N-N$
 $N-N$
 $N-N$

$$N = C$$

$$V = C$$

$$CH_3$$

20

5

10

15

30

50

55

Besides the above compounds, there may also be used DIR compounds described in U.S. Pat. Nos. 4,234,678, 3,227,554, 3,617,291, 3,958,993, 4,149, 886, 3,933,500, 2,072,363, 2,070,266, Japanese Pat. O.P.I. Pub. No. 56837/1982 and Research Disclosure No. 21,228 (December, 1981).

In the present invention, at least one, more preferably at least two of the light-sensitive layers, contains a DIR compound. It is preferable that a light-sensitive layer contains two or more kinds of DIR compounds different from each other in the diffusibility of development inhibitor or its precursor spritted off therefrom. In the invention, it is preferred to combine a DIR compound having an aforesaid diffusibility of 0.34 to less than 0.4 with a DIR compound having an aforesaid diffusibility of not less than 0.4. Further, the molar quantity of the DIR compound capable of releasing a high diffusible inhibitor is not less than 3 times, preferably not less than 5 times, and especially not less than 7 times that of the DIR compound capable of releasing a low diffusible inhibitor contained in the same layer. Preferable examples of the DIR compound having an aforesaid diffusibility of less than 0.4 are those exemplified above bearing the number of D-21, D-23, D-29, D-31, D-33, D-34 or D-37. Preferable examples of the DIR compound having an aforesaid diffusibility of not less than 0.4 are those exemplified above with the number of D-6, D-7, D-17, D-24, D-25, D-26, D-27 or D-32

In the invention, the preferable addition amount of the DIR compound is 1.0×10^{-4} to 1.0×10^{-1} mole, more preferably 4.0×10^{-4} to 5.0×10^{-2} mole, and especially 8.0×10^{-4} to 2.0×10^{-2} mole per mole of silver halide.

In addition to the foregoing preferable examples, there may also be used the DIR compounds described, for example, in U.S. Pat. Nos. 4.234,676, 3,227,554, 3,617,291, 3,958,993, 4,149,886, 3,933,500, 2,072,363, 2,070,266, Japanese Pat. O.P.I. Pub. Nos. 56837/1982, 13239/1976 and Research Disclosure No. 21228 (December, 1981).

The using amount of the diffusible DIR compound in the invention is required to meet the relation to the surface area of silver halide grains as described above. And it is preferably not less than 2.0×10^{-4} mole/m², more preferably 5.0×10^{-4} to 2×10^{-3} mole/m² all over a light-sensitive material, when shown as an amount per mole of silver halide. The diffusible DIR compound may be used in an arbitrary manner, but

it is preferred to be used at least in the highest sensitivity layers of red-sensitive layers and green-sensitive layers, respectively.

It is also preferable that the diffusible DIR compound be distributed in layers so as to give an IIE which satisfy the following requirements; that is, maximum gradations obtained by monochromatic exposure with respective wavelengths in the vicinity of spectral sensitivity peaks of red-sensitive, green-sensitive and blue-sensitive silver halide emulsion layers, γ_R^P , γ_G^P and γ_B^P , are

```
0.80 < \gamma_R^P
```

 $0.70 < \gamma_R^F$

 $0.70 < \gamma_{\rm G}^{\rm P}$

 $0.70 < \gamma_B^P$

and gradations obtained by standard white light exposure, γ_R , γ_G and γ_B , are

 $0.65 < \gamma_{R}$

 $0.65 < \gamma_{\rm G}$

 $0.75 < \gamma_{\rm B}$

15

30

In the invention, when an emulsion layer having a spectral sensitivity is comprised of two sub-emulsion layers different in sensitivity, the layer configuration of low speed sub-emulsion layer-high speed sub-emulsion layer is used; when the emulsion layer is comprised of three sub-emulsion layers different in sensitivity, both the layer configurations of low speed sub-emulsion layer-medium speed sub-emulsion layer-high speed sub-emulsion high speed sub-emulsion layer-medium speed sub-emulsion layer-low speed sub-emulsion layer may be applicable. The layer configuration is not necessarily bound to the above ones of the high speed layer, but the effect of the invention can be much exhibited with a configuration where a high speed sub-emulsion layer is provided farthest from a support. In addition, it is preferable that the sensitivity difference between homochromatic sub-emulsion layers be from 0.1 to $1.0 \text{ in } \Delta \log E$.

The conventional photographic additives usable in the invention are described in Research Disclosure Nos. 17643, 18716 and 308119 (hereinafter abbreviated to RD17643, RD18716 and RD308119, respectively).

A variety of couplers can be employed in the invention, typical examples thereof are seen in the above numbers of Research Disclosure.

Additives usable in the invention can be added according to such a dispersion method as is described in RD308119 XIV.

In the invention, supports described in RD17643, p.28, RD18716, pp.647-8 or RD308119, XVII can be used.

The light-sensitive material of the invention may have auxiliary layers such as filter layer and intermediate layer described in RD308119, VII, sec. K.

The invention can be applied to a variety light-sensitive materials represented by negative film for general purposes or for movies, color reversal film for slides or TV, color paper, color positive film and color reversal paper.

The light-sensitive material of the invention can be processed in conventional procedures described in RD 17643, pp.28-29, RD18716, p.647 and RD308119, XVII.

EXAMPLES

The typical examples according to the invention are described hereunder.

In every example described below, the addition amount to a silver halide photographic light-sensitive material is given in grams per 1 m², unless otherwise specified. The amounts of silver halide and colloidal silver are given as an amount of silver present.

Example 1

50

Multilayer color photographic light-sensitive material sample 101 was prepared by forming, on an acetyl cellulose film support, layers respectively having the following compositions in numerical order from the support side.

5 Sample 1

1st layer: antihalation layer (HC)		
Black colloidal silver	0.15 g	
UV absorbent (UV-1)	0.20 g	
Compound (CC-1) 0.02 g		
High boiling solvent (Oil-1)	0.20 g	
High boiling solvent (Oil-2)	0.20 g	
Gelatin	1.6 g	

2nd layer: intermediate layer (IL-1)		
Gelatin	1.3 g	

3rd layer: low speed red-sensitive emulsion layer (R-L)	
Silver iodobromide emulsion (volume average grain size: 0.3 µm)	0.50 g
Silver iodobromide emulsion (volume average grain size: 0.46 µm)	0.50 g
Sensitizing dye (S-1)	3.2×10^{-4} mole/mole Ag
Sensitizing dye (S-2)	3.2 × 10 ⁻⁴ mole/mole Ag
Sensitizing dye (S-3)	0.2 × 10 ⁻⁴ mole/mole Ag
Cyan coupler (C-1)	0.50 g
Cyan coupler (C-2)	0.13 g
Colored cyan coupler (CC-1)	0.07 g
DIR compound (D-1)	0.0007 mole/mole Ag
DIR compound (D-3)	0.0018 mole/mole Ag
High boiling solvent (Oil-1)	0.55 g
Gelatin	1.0 g

4th layer: high speed red-sensitive emulsion layer (R-H)	
Silver iodobromide emulsion (volume average grain size: 0.7 μm)	0.9 g
Sensitizing dye (S-1)	1.7 × 10 ⁻⁴ mole/mole Ag
Sensitizing dye (S-2)	1.6 × 10 ⁻⁴ mole/mole Ag
Sensitizing dye (S-3)	0.1 × 10 ⁻⁴ mole/mole Ag
Cyan coupler (C-2)	0.23 g
Colored cyan coupler (CC-1)	0.03 g
DIR compound (D-2)	0.0024 mole/mole Ag
High boiling solvent (Oil-1)	0.25 g
Gelatin	1.0 g

5th layer: intermediate layer (IL-2)		
Gelatin	0.8 g	

	6th layer: low speed green-sensitive emulsion layer (G-L)	
	Silver iodobromide emulsion (volume average grain size: 0.3 µm)	0.30 g
	Silver iodobromide emulsion (volume average grain size: 0.46 µm)	0.70 g
5	Sensitizing dye (S-4)	6.7×10^{-4} mole/mole Ag
	Sensitizing dye (S-5)	0.8×10^{-4} mole/mole Ag
	Magenta coupler (M-1)	0.17 g
	Magenta coupler (M-2)	0.43 g
	Colored magenta coupler (CM-1)	0.10 g
10	DIR compound (D-3)	0.0032 mole/mole Ag
	High boiling solvent (Oil-2)	0.7 g
	Gelatin	1.0 g

7th layer: high speed green-sensitive emulsion layer (G-H)	
Silver iodobromide emulsion (volume average grain size: 0.7 μm)	0.9 g
Sensitizing dye (S-6)	1.1 × 10 ⁻⁴ mole/mole Ag
Sensitizing dye (S-7)	2.0 × 10 ⁻⁴ mole/mole Ag
Sensitizing dye (S-8)	0.3 × 10 ⁻⁴ mole/mole Ag
Magenta coupler (M-1)	0.30 g
Magenta coupler (M-2)	0.13 g
Colored magenta coupler (CM-1)	0.04 g
DIR compound (D-3)	0.0005 mole/mole Ag
High boiling solvent (Oil-1)	0.35 g
Gelatin	1.0 g

8th layer: yellow filter layer (YC)		
Yellow colloidal silver	0.1 g	
Additive (HS-1)	0.07 g	
Additive (HS-2)	0.07 g	
Additive (SC-1)	0.12 g	
High boiling solvent (Oil-2)	0.15 g	
Gelatin	1.0 g	

	9th layer: low speed blue-sensitive layer (B-L)	
	Silver iodobromide emulsion (volume average grain size: 0.3 µm)	0.30 g
	Silver iodobromide emulsion (volume average grain size: 0.46 µm)	0.30 g
45	Sensitizing dye (S-9)	5.8 × 10 ⁻⁴ mole/mole Ag
45	Yellow coupler (Y-1)	0.6 g
	Yellow coupler (Y-2)	0.32 g
	Colored magenta coupler (CM-1)	0.10
	DIR compound (D-1)	0.0005 mole/mole Ag
50	DIR compound (D-2)	0.0015 mole/mole Ag
50	High boiling solvent (Oil-2)	0.18 g
	Gelatin	1.3 g

Silver iodobromide emulsion (volume average grain size: 0.85 μm)	0.70
Sensitizing dye (S-10)	3.0×10^{-4} mole/mole A
Sensitizing dye (S-11)	1.2×10^{-4} mole/mole A
Yellow coupler (Y-1)	0.18
Yellow coupler (Y-2)	0.10
DIR compound (D-2)	0.00038 mole/mole <i>A</i>
High boiling solvent (Oil-2)	0.05
Gelatin	1.0

11th layer: 1st protective layer (PRO-1)		
Silver iodobromide emulsion (volume average grain size: 0.08 µm) UV absorbent (UV-1) UV absorbent (UV-2) Additive (HS-1) Additive (HS-2) High boiling solvent (Oil-1) High boiling solvent (Oil-3) Gelatin	0.3 g 0.07 g 0.10 g 0.02 g 0.01 g 0.07 g 0.07 g 0.8 g	

12th layer: 2nd protective layer (PRO-2)

Compound A
Compound B
Polymethyl methacrylate (average particle size: 3 μm)
Metyl methacrylate-ethyl methacrylate-methacrylic acid 3:3:4
(weight ratio) copolymer (average particle size: 3 μm)

The silver iodobromide emulsion used in the 10th layer was prepared in the following procedure.

A silver iodobromide emulsion was prepared by the double jet method by use of seed grains comprised of monodispersed silver iodobromide grains having an average grain size of $0.33~\mu m$ and a silver iodide content of 2 mole%.

While keeping solution (G-1) at 70 °C, pAg 7.8 and pH 7.0, 0.34 mole of the seed grains were added thereto with stirring.

Formation of inner high iodide content phase - core phase

5

10

15

20

25

30

35

40

50

Then, solutions (H-1) and (S-1) were added over a period of 86 minutes at an accelerated flow rate, the initial flow rate was 3.6 times as large as the final one, while keeping the flow ratio of the solutions 1:1. Formation of outer low iodide content phase - shell phase

Subsequently, while keeping the mother liquor at pAg 10.1 and pH 6.0, solutions (H-2) and (S-2) were added thereto over a period of 65 minutes at a flow ratio of 1:1 and at an accelerated flow rate, the initial flow rate was 5.2 times as large as the final one.

In the process of grain formation, the pAg and pH were controlled by use of an aqueous solution of potassium bromide and 56% acetic acid. The grains formed were subjected to desalting according to a usual flocculation method, and then dispersed again with the addition of gelatin. Then, the pH and pAg were adjusted to 5.8 and 8.06, respectively, at 40 °C.

The emulsion prepared as above was a monodispersed emulsion comprised of octahedral silver iodobromide grains having a volume average grain size of $0.8~\mu m$, a grain size distribution extent of 12.4% and a silver iodide content of 8.5~mole%.

Solution (G-1)	
Ossein gelatin	100.0 g
Compound-1	25.0 ml
28% aqueous ammonia	440.0 ml
56% acetic acid solution	660.0 ml
Water was added to make	5000.0 ml

10

5

15

Solution (H-1)

Ossein gelatin
Potassium bromide
Potassium iodide
Water was added to make

82.4 g
151.6 g
90.6 g
1030.5 ml

20 Solution (S-1)

Silver nitrate

309.2 g

28% aqueous ammonia

equivalent

Water was added to make

1030.5 ml

30

35

40

25

Solution (H-2)	
Ossein gelatin	302.1 g
Potassium bromide	770.0 g
Potassium iodide	33.2 g
Water was added to make	3776.8 ml

Solution (S-2)

Silver nitrate 1133.0 g
28% aqueous ammonia equivalent
Water was added to make 3776.8 ml

45

The other emulsions different in volume average grain size and silver iodide content were prepared in similar manners as the above, by varying the average size of seed grains, temperature, pAg, pH, flow rate, addition time and halide composition.

Each of these emulsions was a monodispersed emulsion comprised of core/shell type grains having a grain size distribution extent of not more than 20%. Each emulsion was subjected to an optimum chemical ripening in the presence of sodium thiosulfate, chloroauric acid ammonium thiocyanate; then, sensitizing dyes, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 1-phenyl-5-mercaptotetrazole were added thereto.

$$C-1$$

$$C_{1}H_{2}$$

$$C_{2}H_{1}$$

$$C_{3}H_{1}(t)$$

$$C_{5}H_{1}(t)$$

$$C_{5}H_{1}(t)$$

$$C_{6}H_{1}(t)$$

C - 2

$$C_{4}H_{3}$$

$$C + C_{2}$$

$$C_{4}H_{3}$$

$$C + C_{5}H_{11}$$

$$C_{5}H_{11}(t)$$

$$C + C_{2}COOCH_{3}$$

$$C + C_{1}H_{2}$$

$$C + C_{2}COOCH_{3}$$

$$M-1$$

$$0$$

$$NHCOCH_2O$$

$$C_5H_{11}(t)$$

$$C_2$$

$$C_2$$

$$C_2$$

Y - 1

Y - 2

CH₃)₃CCOCHCONH C₄H₉
COOCHCOOC₁₂H₂₅

 $\begin{array}{c|c} C \ C \ - \ 1 \\ \hline \\ CONH(CH_2)_{\bullet}O & \\ \hline \\ C_5H_{11}(t) \\ \end{array}$

$$C_5H_{11}(t)$$

OH NHCOCH₃

SO₃Na

NaO₃Ś

CM-1

5
$$CH_3O$$
 $N = N$
 $NHCOCH_2O$
 CQ
 CQ
 CQ
 $C_5H_{11}(t)$

¹⁵ D - 1

³⁵ D - 2

50

D-3

$$UV-2$$

$$CH_3 \qquad O$$

$$CH_3 \qquad O$$

$$CH - CH = CH - CH$$

$$s-1$$

$$C\ell = C - CH - C - CH$$

$$(CH_2)_3 SO_3^{\Theta} C_2 H_5$$

s-2

$$CQ \xrightarrow{\text{C}_2\text{H}_5} CH = C - CH \xrightarrow{\text{C}_2\text{H}_5} CQ$$

$$(CH_2)_3\text{SO}_3^{\ominus} (CH_2)_3\text{SO}_3\text{H}$$

s-3

$$CH = C - CH$$

$$CH_2)_3 SO_3^{\Theta}$$

$$CH_2)_3 SO_3^{\Theta}$$

$$CH_2)_3 SO_3^{\Theta}$$

S - 4

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

$$C_{1}H_{3}C$$

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

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

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

$$C_{2}H_{3}C$$

$$C_{2}H_{3}C$$

$$C_{2}H_{3}C$$

$$C_{2}H_{3}C$$

$$C_{3}H_{3}C$$

$$C_{4}C$$

$$C_{5}H_{5}C$$

$$C_{6}H_{2}C$$

$$C_{7}H_{5}C$$

$$C_{8}H_{1}C$$

$$C_{8}H_{1$$

S-5
$$C_2H_5$$

$$C_2H_5$$

$$C_2H_5$$

$$C_2H_5$$

$$C_2H_5$$

$$C_2H_5$$

$$C_1CH_2$$

$$C_1CH_2$$

$$C_1CH_2$$

$$C_1CH_3$$

$$C_2H_5$$

$$C_2H_5$$

$$C_1CH_3$$

$$C_1CH_4$$

$$C_1CH_2$$

$$C_1CH_3$$

$$C_1CH_4$$

$$S - 6$$

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

$$CH - C - CH - CH_{2}$$

$$CH_{2})_{3}SO_{3}^{\Theta} \qquad (CH_{2})_{3}SO_{3}H \cdot N(C_{2}H_{5})_{3}$$

$$S - 7$$

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

$$CH = C - CH$$

$$(CH_{2})_{3}SO_{3}^{\Theta}$$

$$(CH_{2})_{3}SO_{3}HN(C_{2}H_{5})_{3}$$

S-8
$$C_{2}H_{5}$$

$$CH = C - CH$$

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

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

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

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

$$S-9$$

$$(CH_2)_3SO_3^{\Theta}$$

$$(CH_2)_3SO_3^{\Theta}$$
 $(CH_2)_3SO_3H\cdot N(C_2H_5)_3$

S-I0

CHO₃

CHO₃

CHO₃

CHO₃

CHO₃

CH₂

(CH₂)₃SO₃

(CH₂)₃SO₃H·N(C₂H₅)₃

SD-II

$$(CH_2)_3SO_3\Theta$$

$$(CH_2)_3SO_3Na$$

SC-1:

C18H37(sec) C16H33(sec) (a 2:3 mixture of and ÓΗ ĊН)

0il-1

5

10

30

40

45

-COOC 8 H 1 7 15 COOC 8 H 1 7

0il-220

25 COOC, H, 0 il - 3 COOC, H,

H -- 1 H-235 ONa $(CH_2 = CHSO_2CH_2)_{\overline{2}}O$

50

$$Su-1$$

Su-2

5

HOOC-II

-C00II

SO₃K

10

AI - 115

HOOC
$$CH - CH = CH - CH = CH$$

SO₃K

SO₃K

HO

--CH - CH = CH-

20

25

$$A \quad I \quad - \quad 2$$

30

35

$$ST-1$$

40

SO₃K

50

45

A F - 1

AF-2

IIS—N—N

CII-CII₂

Compound-A:

CH₃ CH₃ CH₃
CH₃ CH₃ CH₃
CH₃ CH₃ CH₃

weight average molecular weight: 30,000

25

5

10

15

20

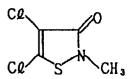
Compound-B:

NaO₃S-CH-COOCH₂(CF₂CF₂)₃H
$$CH_2-COOCH_2(CF_2CF_2)_3H$$

35

30

DI-1: (a mixture of the following three components)



(Component A)

(Component B)

(Component C)

component A:component B:component C=50:46:4 (molar ratio)

50

45

The above light-sensitive material 101 further contained compounds SU-1, SU-2, viscosity conditioner, hardeners H-1, H-2, stabilizer ST-1, antifoggants AF-1, AF-2 (respective weight average molecular weights were 10,000 and 1,100,000), dyes Al-1, Al-2 and compound Dl-1 (9.4 mg/m²).

Besides light-sensitive material 101 obtained as above, light-sensitive material 102 was prepared by changing the components as follows. The layers omitted had the same content as that in 101.

Silver iodobromide emulsion (volume average grain size: 0.27 µm)	1.0
Sensitizing dye (S-1)	4.5×10^{-4} mole/mole A
Sensitizing dye (S-2)	4.5×10^{-4} mole/mole A
Sensitizing dye (S-3)	0.28×10^{-4} mole/mole A
Cyan coupler (C-1)	0.50
Cyan coupler (C-2)	0.13
Colored cyan coupler (CC-1)	0.07
DIR compound (D-1)	0.0010 mole/mole A
DIR compound (D-3)	0.0024 mole/mole A
High boiling solvent (Oil-1)	0.55
Gelatin	1.0

Cityon in delayamide annulaina (valuma avana avaig aire. O.E.F. u.m.)	0.00 =
Silver iodobromide emulsion (volume average grain size: 0.55 µm)	0.90 g
Sensitizing dye (S-1)	2.2 × 10 ⁻⁴ mole/mole Ag
Sensitizing dye (S-2)	2.0 × 10 ⁻⁴ mole/mole Ag
Sensitizing dye (S-3)	0.13 × 10 ⁻⁴ mole/mole Ag
Cyan coupler (C-1)	0.23 g
Colored cyan coupler (CC-1)	0.03 g
DIR compound (D-1)	0.0003 mole/mole Ag
DIR compound (D-2)	0.0031 mole/mole Ag
High boiling solvent (Oil-1)	0.25 g
Gelatin	1.0 g

6th layer: G-L	
Silver iodobromide emulsion (volume average grain size: 0.27 µm)	1.0 g
Sensitizing dye (S-4)	9.5×10^{-4} mole/mole Ag
Sensitizing dye (S-5)	1.1×10^{-4} mole/mole Ag
Magenta coupler (M-1)	0.17 g
Magenta coupler (M-2)	0.43 g
Colored magenta coupler (CM-1)	0.10 g
DIR compound (D-1)	0.0005 mole/mole Ag
DIR compound (D-3)	0.0038 mole/mole Ag
High boiling solvent (Oil-1)	0.7 g
Gelatin	1.0 g
	1

	7th layer: G-H	
	Silver iodobromide emulsion (volume average grain size: 0.52 μm)	0.9 g
	Sensitizing dye (S-4)	6.6 × 10 ⁻⁴ mole/mole Ag
50	Sensitizing dye (S-5)	0.8 × 10 ⁻⁴ mole/mole Ag
	Magenta coupler (M-1)	0.30 g
	Magenta coupler (M-2)	0.13 g
	Colored magenta coupler (CM-1)	0.04 g
	DIR compound (D-1)	0.0005 mole/mole Ag
55	DIR compound (D-3)	0.0072 mole/mole Ag
	High boiling solvent (Oil-2)	0.35 g
	Gelatin	1.0 g

	9th layer: B-L	
	Silver iodobromide emulsion (volume average grain size: 0.30 µm)	0.60 g
	Sensitizing dye (S-9)	7.3 × 10 ⁻⁴ mole/mole Ag
5	Yellow coupler (Y-1)	0.60 g
	Yellow coupler (Y-2)	0.32 g
	DIR compound (D-1)	0.0002 mole/mole Ag
	DIR compound (D-2)	0.0025 mole/mole Ag
	High boiling solvent (Oil-2)	0.18 g
10	Gelatin	1.30 g

	10th layer: B-H		
15	Silver iodobromide emulsion (volume average grain size: 0.50 μm)	0.70 g	
	Sensitizing dye (S-9)	4.4 × 10 ⁻⁴ mole/mole Ag	
	Yellow coupler (Y-1)	0.18 g	
	Yellow coupler (Y-2)	0.10 g	
20	DIR compound (D-1)	0.00005 mole/mole Ag	
	High boiling solvent (Oil-2)	0.05 g	
	Gelatin	1.0 g	

Light-sensitive materials 103 to 109 each having the composition shown in Table 1 were prepared in similar manners as above. In preparing them, the amounts of DIR compound (D-1) and couplers were varied a little with layers in order to make their gradations close to one another as much as possible.

Light-sensitive materials 101 to 109 prepared as above were evaluated for the following properties.

(Graininess)

30

40

50

55

Light-sensitive materials 101 to 109 were subjected to white light exposure through an optical step wedge for sensitometry and then processed under the conditions described later.

The RMS value of each processed sample was measured at a color developed portion having a density of Dmin (minimum density) + 0.4. To be concrete, the RMS value was determined by scanning the density of a measured portion of a sample with a microdensitometer with an scanning aperture of 1800 μ m² (slit width: 10 μ m, slit length: 180 μ m) and multiplying the standard deviation of variation in densities (of more than 1000 samplings) by 1000.

In Table 2, a reciprocal of the RMS value of each sample was standardized against the value of sample 101 which was set at 100. In the table, the larger the value is, the better the graininess is.

(Gradation)

A standard white light exposure and a B, G, R color separated light exposure with Wratten filters (W-98, W-99, W-26) were performed, followed by processing in a similar manner as the above. Then, the gradation, γ -value, in the exposed portion from Dmin + 0.1 to Δ log E = 1.0 was determined for each sample. The results are shown in Table 2.

(Color reproduction)

A color rendition chart made by Macbeth Co. (a color chart consisting of 18 colored patterns and 6 achromatic patterns) was photographed with light-sensitive materials 101 to 109, followed by the processing described above.

Then, the photographed patterns were printed on color paper (PC paper Type SR made by Konica Corp.) from the processed film, so as to print the gray of optical density 0.7 in the same density.

The reproduced color of each sample and the original color were measured in the L*a*b* system with a Color Analyzer Model CMS-1200 made by Murakami Shikisai Co., and a coordinate in the CIE 1976 L*a*b* color coordinate system was determined. Then, the brightness of color was determined by the following equation.

$$C^* = \sqrt{a^{*2}} + \overline{b^{*2}}$$

10

15

25

30

35

40

45

50

The coordinate of the original color was measured likewise to determine C_0^* . And the value of $(C^*/C_0^* \times 100)$ was shown in Table 2 as an index of color brightness; the color brightness becomes better as the value becomes larger.

The processing was made as follows.

Processing	Processing time	Processing temprature	Replenishing amount*
Color developing	3 min 15 sec	38±0.3°C	780 ml
Bleaching	45 sec	38±2.0 ° C	150 ml
Fixing	1 min 30 sec	38±2.0 ° C	830 ml
Stabilizing	60 sec	38±5.0 ° C	830 ml
Drying	1 min	55±5.0°C	

^{*} The amount is per m² of light-sensitive material.

The compositions of the color developer, bleaching solution, fixer, stabilizer and their replenishers are as follows.

Color developer	
Water	800 ml
Potassium carbonate	30 g
Sodium hydrogencarbonate	2.5 g
Potassium sulfite	3.0 g
Sodium bromide	1.3 g
Potassium iodide	1.2 mg
Hydroxylamine sulfate	2.5 g
Sodium chloride	0.6 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate	4.5 g
Diethylenetriaminepentacetic acid	3.0 g
Potassium hydroxide	1.2 g

Water is added to make 1 liter, and the pH is adjusted to 10.06 with potassium hydroxide or 20% sulfuric acid.

Color developing replenisher	
Water	800 ml
Potassium carbonate	35 g
Sodium hydrogencarbonate	3 g
Potassium sulfite	5 g
Sodium bromide	0.4 g
Hydroxylamine sulfate	3.1 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate	6.3 g
Potassium hydroxide	2.0 g
Diethylenetriaminepentacetic acid	3.0 g

Water is added to make 1 liter, and the pH is adjusted to 10.18 with potassium hydroxide or 20% sulfuric acid.

Bleaching solution	
Water	700 ml
Ammonium ferric 1,3-diaminopropanetetracetate	125 g
Ethylenediaminetetraacetic acid	2 g
Sodium nitrate	40 g
Ammonium bromide	150 g
Glacial acetic acid	40 g

Water is added to make 1 liter, and the pH is adjusted to 4.4 with aqueous ammonia or glacial acetic acid.

Bleaching replenisher	
Water	700 ml
Ammonium ferric 1,3-diaminopropanetetracetate	175 g
Ethylenediaminetetraacetic acid	2 g
Sodium nitrate	50 g
Ammonium bromide	200 g
Glacial acetic acid	56 g
Ammonium nitrate	50 g

The pH is adjusted to 4.0 with an aqueous ammonia or glacial acetic acid, and then water is added to make 1 liter.

Fixer	
Water	800 ml
Ammonium thiocyanate	120 g
Ammonium thiosulfate	150 g
Sodium sulfite	15 g
Ethylenediaminetetraacetic acid	2 g

The pH is adjusted to 6.2 with an aqueous ammonia or glacial acetic acid, and then water is added to make 1 liter.

Fixing replenisher	
Water	800 ml
Ammonium thiocyanate	150 g
Ammonium thiosulfate	180 g
Sodium sulfite	20 g
Ethylenediaminetetraacetic acid	2 g

The pH is adjusted to 6.5 with an aqueous ammonia or glacial acetic acid, and then water is added to make 1 liter.

Stabilizer and its replenisher					
Water	900 ml				
Octyl-phenyl polyethylene oxyether (average polymerization degree: 10)	2.0 g				
Dimethylol urea	0.5 g				
Hexamethylenetetramine	0.2 g				
1,2-Benzisothiazoline-3-one	0.1 g				
Siloxane (L-77 made by UCC)	0.1 g				
Aqueous ammonia	0.5 ml				

Water is added to make 1 liter, and the pH is adjusted to 8.5 with an aqueous ammonia or 50% sulfuric acid.

The results obtained are shown in Table 2.

Table 1 (a)

	Red-sensitive layer						Green-sensitive layer							
	RL			RH			GL			GH				
	A	gx	Amount of	A	gx	Amount of	1 1		Agx Amou		Amount of	А	gx	Amount of
Sample No.	Grain size	Amount of silver coated	diffu- sive DIR used	Grain size	Amount of silver coated	diffu- sive DIR used	Grain size	Amount of silver coated	diffu- sive DIR used	Grain size	Amount of silver coated	diffu- sive DIR used		
	(μm)	(g/m ²)	(x10 ⁻⁵ mole/ m ²)	(µm)	(g/m ²)	(x10 ⁻⁵ mole/ m ²)	(µm)	(g/m ²)	(x10 ⁻⁵ mole/ m ²)	(µm)	(g/m ²)	(x10 ⁻⁵ mole/		
101	0.46	0.50	4.80	0.70	0.90	5.70	0.46 0.30	0.70 0.30	8.40	0.70	0.90	1.20		
102	0.27	1.00	6.25	0.55	0.90	7.40	0.27	1.00	10.0	0.52	0.90	1.70		
103	0.27	1.00	8.70	0.42	0.90	10.3	0.27	1.0	15.10	0.42	0.90	7.00		
104	0.27	1.50	30.0	0.42	1.50	14.0	0.27	1.30	17.0	0.42	1.30	15.0		
105	0.46	0.50 0.50	10.6	0.70	0.90	12.5	0.46	1.00	16.0	0.70	0.90	5.00		
106	0.27	1.00	31.0	0.55	0.90	13.0	0.27	1.00	23.0	0.52	0.90	12.0		
107	0.27	1.00	21.2	0.42	0.90	9.80	0.27	1.00	13.0	0.42	0.90	13.0		
108	0.27	1.00	29.0	0.42	0.90	13.0	0.27	1.00	17.0	0.42	0.90	17.0		
109	0.30	0.83	25.0	0.42	1.00	13.0	0.27	0.83	17.0	0.38	0.90	18.0		

Table 1 (b)

	ō		

	Red-sensitive layer							
	RL				RH		Total	
	A	gx	Amount of	A	Agx Amo			
Sample No.	Grain size	Amount of silver coated	sive DIR	Grain size	Amount of silver coated	sive DIR	Amount of silver coated	Remarks
	(ħw)	(g/m ²)	(x10 ⁻⁵ mole/ m ²)	(µm)	(g/m ²)	(x10 ⁻⁵ mole/ m ²)	(g/m ²)	
101	0.46	0.30 0.30	2.40	0.85	0.70	0.70	5.65	Comparioson
102	0.30	0.60	4.00	0.50	0.70	_	5.65	Comparioson
103	0.30	0.60	7.50	0.50	0.70	_	5.65	Comparioson
104	0.30	0.80	15.0	0.50	1.00	5.20	7.95	Comparioson
105	0.46	0.60	8.00	0.85	0.70	-	5.65	Comparioson
106	0.30	0.60	14.0	0.50	0.70	-	5.65	Invention
107	0.30	0.60	11.0	0.50	0.70	-	5.65	Invention
108	0.30	0.60	14.0	0.50	0.70	-	5.65	Invention
109	0.30	0.40	15.0	0.55	0.20	-	5.21	Invention

5		

Remarks	Comparison	Comparison	Comparison	Comparison	Comparison	Invention	Invention	Invention	Invention		
		၁	7.5	65	89	73	7.0	85	83	06	87
ction	00	Σ	19	7.0	7.5	74	11	06	85	63	95
Color reproduction	C*/C* ₀ × 100	>1	7.5	67	69	7.0	73	85	82	06	87
r rek	*/C*	æ	7.5	7.0	7.5	67	72	85	81	97	95
Colo	O	b	11	75	77	70	73	90	87	95	92
		В	75	70	73	67	65	88	85	93	95
		γ^{ρ}_{R}	0.66	0.67	0.68	0.67	0.63	0.56	09.0	0.57	0.54
ion, rd light		γP _G	0.68	0.70	0.69	0.67	0.66	0.58	0.62	09.0	0.56
Gradation, standard white light exposure		₽ ^P B	0.78	08.0	0.80	67.0	0.75	0.70	0.72	0.71	0.70
ic		γ. R	0.83	0.83	0.85	0.85	0.82	0.80	0.82	0.80	0.85
Gradation, homochromatic	ion, ire		0.78	08.0	0.81	08.0	0.79	0.83	0.85	0.82	08.0
Gradatio		yo _B	0.86	0.88	06.0	0.92	0.87	06.0	0.87	06.0	0.88
89 80		æ	100	109	111	120	120	175	165	160	170
Graininess		U	100	107	109	125	125	160	155	160	170
Gre		æ	100	105	110	120	122	150	145	150	145
A/B (10-7/ mole/ cm ²)			2.82	2.65	4.13	3.35	6.33	8.41	5.78	7.65	8.47
c of sive	(10 ⁻⁵ mole/m ²)		23.2	29.35	48.6	96.2	52.1	93.0	68.0	0.06	88.0
Sum of the surface area of all light- sensitive AgX emulsions in the light-	sensitive material	(10 ² cm ² /m ²)	8.23	11.06	11.77	23.68	8.23	11.06	11.77	11.77	10.39
Sample No.			101	102	103	104	105	106	101	108	109

As apparent from Table 2, the graininess and color reproduction cannot be improved concurrently by changing the size of silver halide grains or by a merely increase in addition amount of diffusible DIR compounds; the improvement can be made only when a specific relation is valid between the sum of the surfaces of light-sensitive silver halide grains and the amount of diffusible DIR compounds used.

Example 2

Light-sensitive material 110 was prepared by changing the silver halide emulsions, sensitizing dyes and DIR compounds used in the 9th and 10th layers of light-sensitive material 109 in Example 1 as shown below. In addition to the evaluation in Example 1, a bluish green cloth was photographed, and prints were made from the processed film as in Example 1. Comparison of the image of the cloth on the print with the original bluish green cloth showed that the reproduced color was much closer to the original color, as compared with the result obtained by sample 109. That is to say, in addition to the improvement in graininess and color saturation of pure dyes, color reproduction of the bluish green can also be improved by incorporating tabular silver halide grains in the bule-sensitive layer and controlling the spectral sensitivity distribution of the blue-sensitive layer in accordance with the invention.

Preparation of sample 110

20

9th layer: B-L	
Tabular silver iodobromide grain emulsion (volume average grain size: 0.30 μm, aspect ratio: 4.00)	0.60 g
Sensitizing dye (A-7)	7.3 × 10 ⁻⁴ mole/mole Ag
Yellow coupler (Y-1)	0.60 g
Yellow coupler (Y-2)	0.32 g
DIR compound (D-2)	0.0030 mole/mole Ag
High boiling solvent (Oil-2)	0.18 g
Gelatin	1.30 g

30

25

35

40

50

55

10th layer: B-H	
Tabular silver iodobromide grain emulsion (volume average grain size: 0.42 µm, aspect ratio: 4.40)	0.50 g
Cubic silver iodobromide grain emulsion (volume average grain size: 0.65 µm)	0.20 g
Sensitizing dye (A-7)	8.3 × 10 ⁻⁴ mole/mole Ag
Yellow coupler (Y-1)	0.18 g
Yellow coupler (Y-2)	0.10 g
DIR compound (D-1)	0.00003 mole/mole Ag
High boiling solvent (Oil-1)	0.05 g
Gelatin	1.0 g

Claims

- 1. A silver halide color photographic light-sensitive material comprising a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a blue-sensitive silver halide emulsion layer, wherein said light-sensitive material satisfies the following requirements:
 - (1) at least one of said red-sensitive emulsion layer and said green-sensitive emulsion layer comprises two or more emulsion sub-layers,
 - (2) an emulsion sub-layer having the highest speed among said emulsion sub-layers in said at least one of said red-sensitive emulsion layer and said green-sensitive emulsion layer contains silver halide grains having a volume average size of from $0.20~\mu m$ to $0.55~\mu m$,
 - (3) said light-sensitive material contains a diffusible DIR compound capable of splitting off a development inhibitor or its precursor which has a diffusibility not less than 0.34, and the amount of said DIR compound satisfies the following equation:

 $A/B \ge 5.00 \times 10^{-7} \text{ mole/cm}^2$

wherein A is the sum of molar amout of said diffusible DIR compound contained in one square meter of said light-sensitive material, and B is the sum of surface area, expressed by cm², of light-sensitive silver halide grains contained in one square meter of said light-sensitive material.

5 2. The light-sensitive material of claim 1, wherein said ratio of A/B satisfies the following equation:

 $1.50 \times 10^{-7} \text{ mole/cm}^2 \ge A/B \ge 8.00 \times 10^{-7} \text{ mole/cm}^2$.

10

15

25

30

- 3. The light-sensitive material of claim 1 or 2, wherein said volume average size of silver halide grais contained in the highest speed sub-emulsion layer is $0.20 \mu m$ to $0.45 \mu m$.
- **4.** The light-sensitive material of claim 1, 2 or 3, wherein the total amount of light-sensitive silver halide contained in said light-sensitive material is not more than 7.5 g/m² in terms of silver.
 - **5.** The light-sensitive material of claim 4, wherein the total amount of light-sensitive silver halide contained in said light-sensitive material is within the range of from 2.0 g/m² to 6.5 g/m² in terms of silver.
- 20 **6.** The light-sensitive material of claims 1 or 2 to 5, wherein said DIR compound is a compound capable of splitting off a development inhibitor or its precursor which has a diffusibility of not less than 0.4.
 - 7. The light-sensitive material of claim 1 or 2 to 5, wherein said light-sensitive material contains a DIR compound capable of splitting off a development inhibitor having a diffusibility of less than 0.4, and a DIR compound capable of splitting off a development inhibitor or its precursor having a diffusibility of not less than 0.4.
 - **8.** The light-senensitive material of claim 1 or 2 to 7, wherein said DIR compound is contained in said light-sensitive material in an amount of from 1.0 x 10⁻⁴ mole to 1.0 x 10⁻¹ mole per mole of silver halide contained in said light-sensitive material.
 - 9. The light-senensitive material of claim 8, wherein said DIR compound is contained in said light-sensitive material in an amount of from 8.0×10^{-4} mole to 2.0×10^{-2} mole per mole of silver halide contained in said light-sensitive material.

35

- **10.** The light-sensitive material of claim 1 or 2 to 9, wherein said blue-sensitive emulsion layer comprises tabular silver hlaide grains.
- **11.** A silver halide color photographic light-sensitive material comprising a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a blue-sensitive silver halide emulsion layer, wherein said material satisfies the following requirements:
 - (1) at least one of said red-sensitive emulsion layer and said green-sensitive emulsion layer comprises two or more emulsion sub-layers ,
 - (2) an emulsion sub-layer having the highest speed among said emulsion sub-layers in said at least one of said red-sensitive emulsion layer and said green-sensitive emulsion layer contains silver halide grains having a volume average size of from $0.20~\mu m$ to $0.45~\mu m$,
 - (3) said light-sensitive material contains a diffusible DIR compound capable of splitting of a development inhibitor or its precursor which has a diffusibility not less than 0.40, and the amount of said DIR compound satisfies the following equation:

50

45

 $1.5 \times 10^{-7} \text{ mole/cm}^2 \ge A/B \ge 8.00 \times 10^{-7} \text{ mole/cm}^2$

- wherein A is the sum of molar amount of said diffusible DIR compound contained in one square meter of said light-sensitive material, and B is the sum of surface area of light-sensitive silver halide grains, expressed by cm², contained in one square mater of said light-sensitive material.
- (4) the total amount of light-sensitive silver halide contained in said light-sensitive material is not more than 7.5 g/m² in terms of silver,
- 5) said blue-sensitive emulsion layer comprises tabular silver halide grains.