

12

EUROPEAN PATENT APPLICATION

21 Application number: 89116367.7

51 Int. Cl.⁵: **G03C 5/305 , G03C 1/005 ,
G03C 1/09 , G03C 1/10**

22 Date of filing: 05.09.89

30 Priority: 05.09.88 JP 223179/88

43 Date of publication of application:
14.03.90 Bulletin 90/11

64 Designated Contracting States:
DE GB IT NL

71 Applicant: **KONICA CORPORATION**
No. 26-2, Nishishinjuku 1-chome Shinjuku-ku
Tokyo(JP)

72 Inventor: **Fukawa, Junichi**
Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: **Habu, Takeshi**
Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)

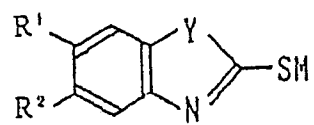
74 Representative: **Henkel, Feiler, Hänzel &**
Partner
Möhlstrasse 37
D-8000 München 80(DE)

54 **Method of developing a silver halide photographic material.**

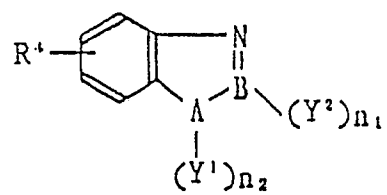
57 A method of developing with a developer containing at least one compound selected from the group consisting of compounds represented by Formulae I , II and III a negative-type silver halide photographic light-sensitive material having a support and provided thereon hydrophilic colloid layers comprising at least one light-sensitive silver halide emulsion layer is disclosed. At least one of said colloid layers on the emulsion layer side comprising at least one compound selected from the group consisting of compounds represented by Formulae I , II and III , the ratio of the silver content represented by g/m^2 of at least one of said colloid layers to the thickness represented by μm of said colloid layers being not less than 0.7 and the ratio of the content of said compound represented by mg/m^2 in at least one of said colloid layers to that of said compound represented by mg/l in said developer being from 0.01 to 1.

EP 0 358 165 A2

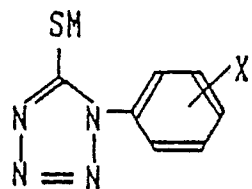
Formula I



Formula II



Formula III



METHOD OF DEVELOPING A SILVER HALIDE PHOTOGRAPHIC MANUAL

FIELD OF THE INVENTION

The present invention relates to a negative-type photographic silver halide photosensitive material. More specifically, the present invention is concerned with a method of developing a photosensitive material, which is extremely effective in ultra high-speed processing.

BACKGROUND OF THE INVENTION

10

Today, there is a growing demand in the printing industry for high-speed processing of a photographic silver halide photosensitive material. This demand stems from a remarkable increase in the amount of information and the need of rapid processing of information. Meanwhile, in the printing industry, for the simplification of procedures and the improvement of the stability of an image, the rapid-access development has come to be employed widely in stead of the conventional lith development. The rapid-access development is excellent in preservability of an image, as compared with the lith development.

In the case of the rapid access development, by adding a contrast developer, such as a tetrazolium compound or a hydrazine compound, to a silver halide emulsion, it is possible to obtain an image which is as contrasty as an image obtained in the lith method, and also to effect development in 20 to 30 seconds. However, in the information-oriented society of today, there is a strong demand for a development method in which development is performed in less than 20 seconds, without causing deterioration of image qualities. Since the process of printing generally includes the step of reduction, it is unpreferable to simply decrease the amount of silver. To perform development rapidly, while avoiding wasteful use of silver, it is of crucial importance to develop a silver halide effectively in a short time. What have long been awaited in the printing industry are a silver halide photosensitive material and a method of developing, which enable a silver halide to be developed effectively.

30

SUMMARY OF THE INVENTION

The object of the present invention is to provide a method of developing a negative-type silver halide photographic light-sensitive material, which enables silver contained in said material to be developed effectively in a short period of time, thereby to obtain an image which is highly contrasty.

The above object can be attained by a process comprising treating in a developer a negative-type silver halide photographic light-sensitive material having at least one photosensitive emulsion layer on a support, wherein one or more hydrophilic colloid layers provided on the same side of said support that said at least one photosensitive emulsion layer is provided contain a specific compound and the ratio of the silver content of said one or more colloid layers to the thickness of said one or more colloid layers is 0.7 or more, provided that the silver content is expressed in terms of mg/m^2 and the thickness is expressed in terms of μm and wherein said developer contains a specific compound and the ratio of the content of said specific compound in said one or more colloid layers to the content of said specific compound in said developer is in the range of 0.01 to 1, provided that the content of said specific compound in said developer is expressed in terms of mg/ml .

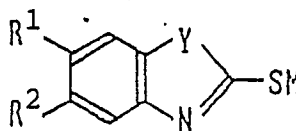
50

DETAILED DESCRIPTION OF THE INVENTION

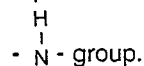
The present invention relates to a method of developing with a developer containing at least one compound selected from the group consisting of compounds represented by Formulae I, II and III negative-type silver halide photographic light-sensitive material having a support and provided thereon hydrophilic colloid layers comprising at least one light-sensitive silver halide emulsion layer, wherein at least one of said colloid layers on the emulsion layer side comprises at least one compound selected from the group

consisting of compounds represented by Formulae I, II and III, the ratio of the silver content represented by g/m² of at least one of said colloid layers to the thickness represented by μ m of said colloid layers is not less than 0.7 and the ratio of the content of said compound represented by mg/m² in at least one of said colloid layers to that of said compound represented by mg/l in said developer is from 0.01 to 1.

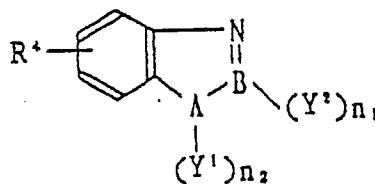
Formula I



wherein R¹ and R² each represent a hydrogen atom, an alkyl group, -COOM, -SO₃M, -OH, -CONHR³ or -NHCOR³, provided that at least one of R¹ and R² is -COOM, SO₃M, -OH, -CONHR³ or -NHCOR³, wherein R³ represents an alkyl group; M represents a hydrogen atom, an alkali metal atom or -NH₄; and Y represents an oxygen atom, a sulfur atom, a selenium atom or a

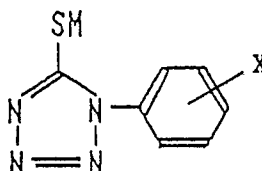


Formula II



wherein Y¹ and Y² each represent a hydrogen atom or a mercapto group; R⁴ represents an alkyl group, an alkenyl group, an alkynyl group, an aryl group, an alkoxy group, each of which may either be substituted or unsubstituted, a hydrogen atom, a halogen atom, a nitro group, an amino group, a cyano group, a hydroxycarbonyl group, an alkoxy carbonyl group, an alkyl carbonyl group, a hydroxy group, a mercapto group or a sulfo group. A represents a nitrogen atom, a carbon atom or an oxygen atom. B represents a nitrogen atom or a carbon atom. When A is a carbon atom, n₂ is 2, and when A is a nitrogen atom, n₂ is 1, and when A is an oxygen atom, n₂ is 0. When B is a carbon atom, n₁ is 1, and when B is a nitrogen atom, n₁ is 0.

Formula III



wherein M represents a hydrogen atom, alkali metal atom or -NH₄. X represents a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, an aryl group, an alkoxy group, a carbamoyl group, a sulfamoyl group, an acylamino group or a sulfoamido group.

According to the present invention, the development time of a negative-type silver halide photosensitive material is normally 19 seconds or less, and "Dry to Dry" is usually 20 to 60 seconds.

In the present invention, "Dry to Dry" means the total time taken from the time when a leading edge of

a photosensitive material is introduced in an automatic developing machine having a developing step, a fixing step, a washing step and a drying step until the time when the leading edge comes out of the machine. "Dry to Dry" can be defined by the following equation:

$$\text{Dry to Dry} = \frac{\text{The entire length of the processing line (m)}}{\text{The rate of conveyance (m/sec)}}$$

wherein the processing line includes the conjunction portion of each container. It is a distinctive feature of the present invention that Dry to Dry is merely 60 seconds or less.

In the present invention, the "thickness" means the total thickness of one or more hydrophilic colloid layers which are provided on the same side of a support that a silver halide photosensitive layer is provided, and is not limited to the thickness of a silver halide photosensitive layer. The silver content as referred to herein is defined as the total amount of silver contained in hydrophilic colloid layers, when a plurality of said layers are provided on the same side of a support. In the present invention, in one side of a support, photosensitive silver halide particles of 0.05 to 0.5 μm in average grain size are employed. The "grain size" as referred to herein means a diameter when silver halide particles are spherical. When silver halide particles are in other forms than sphere, "grain size" means one obtained by converting the projected image of the particles to a circular image having the same area as that of the projected image. It is preferred that 60% or more of all silver halide particles have a grain size within the range of $\pm 10\%$ of the average grain size.

In the present invention, there is no restriction as to the kind of silver halide to be employed. Use can be made of silver halides which are employed in an ordinary silver halide emulsion. Examples of such silver halide include silver bromide, silver iodo-bromide, silver chloride, silver bromo chloride and silver iodo-bromo chloride. It is preferable to use silver bromo chloride containing 50 mol% of silver chloride.

A silver halide particle may be obtained by acid process, neutral process or ammonia process.

A silver halide particle may either be one having a uniform composition distribution or one being of a core/shell structure, in which the interior and the surface of the particle are different in composition distribution and also, one in which a latent image may be formed either on the surface of or inside, the particle.

There is no restriction as to the shape of a silver halide particle. One preferable example is a cubical silver halide particle having a (100) face as a crystalized face. It is also possible to employ octahedral, quadrilateral, or dodecahedral silver halide particles obtained by processes described in U.S. Patent Nos. 4,183,756, 4,225,666, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 26589/1980, Japanese Patent Examined Publication 42737/1980, the Journal of Photographic Science, 21, 39 (1973). A silver halide particle having a twin crystal face is also usable.

In the present invention, silver halide particles may either be same or different in shape.

Silver halide particles of any grain size distribution may be employed. Silver halide particles may either be monodispersed or polydispersed. It is also possible to employ a mixture of several kinds of monodispersed silver halide particles. A mixture of monodispersed particles and polydispersed particles is also usable.

In the present invention, it is possible to use a mixture of two or more kinds of silver halide emulsions which are prepared separately.

According to the present invention, a monodispersed silver halide emulsion is preferable. When a monodispersed emulsion is employed, the total weight of silver halide particles with their grain sizes being in the range of $\pm 20\%$ of the average grain size ($\bar{r}$) may account for 60% or more, preferably 70% or more, more preferably 80% or more of the total weight of all silver halide particles.

The "average grain size" as referred to herein is defined as a diameter (r_i) which makes the value of $n_i \times r_i^3$ reach the maximum (wherein n_i represents the frequency of a silver halide particle having a diameter of r_i . Figures of three decimal places are significant figures. The smallest cipher is rounded).

The "grain size" as referred to herein means a diameter of a particle when the particle is spherical. As to particles in other shapes than sphere, the grain size is obtained by converting its projected image into a circular image having the same area.

The grain size can be obtained by measuring the diameter of an electron-microphotographed image of a particle ($\times 10,000$ to $50,000$). Alternatively, the grain size can be obtained by measuring the area of the projected image of a particle. (measurement is done with respect to more than 1,000 particles selected arbitrarily.)

In the present invention, the distribution size of a monodispersed emulsion may preferably be 20% or less, more preferably 15% or less. The distribution size is obtained by the following formula:

$$\frac{\text{Standard deviation of grain diameter}}{\text{Average grain size}} \times 100 = \text{Distribution size (\%)}$$

In the above formula, the average grain size and the standard deviation of grain size can be obtained from the value of r_i , which is defined before.

A monodispersed emulsion can be prepared in accordance with methods described in Japanese O.P.I. Publication Nos. 48521/1979, 49938/1983 and 122935/1985.

Normally, a photosensitive silver halide emulsion is subjected to chemical sensitization. However, it is also possible to use a photosensitive silver halide emulsion in a primitive state, without performing chemical sensitization. Chemical sensitization can be performed according to methods described in books written by Glafkides and Zelikman, or a method described in *Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden*, Akademische Verlagsgesellschaft (edited by H. Frieser, 1968).

As the example of chemical sensitization, there can be mentioned sulfur sensitization (an activated gelatin, or a compound containing sulfur which is reactive with a silver ion is used as a sensitizer), reduction sensitization (a reducing compound is used as a sensitizer) and noble metal sensitization (a noble metal is used as a sensitizer). These sensitization methods can be used either singly or in combination. Examples of the sulfur sensitizer include thiosulfates, thioureas, thiazoles, and rhodanines. The specific examples of these sensitizers are described in U.S. Patent Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668 and 3,656,955. As a reducing compound for reduction sensitization, there can be employed stannous salts, amines, hydrazine derivatives, formamidine sulfinic acid, and silane compounds. The specific examples of these compounds are described in U.S. Patent Nos. 2,487,850, 2,419,974, 2,518,698, 2,983,609, 2,983,610 and 2,694,637. For noble metal sensitization, use can be made of a complex salt of gold, or a complex salt of a metal belonging to the Group VII of the periodic table, such as platinum, iridium, palladium and the like. The specific example of these complex salts are described in U.S. Patent Nos. 2,399,083, 2,448,060, and British Patent No. 618,061. There is no specific restriction as to the conditions (e.g. pH, pAg, temperature) under which chemical sensitization is performed. The pH may preferably be in the range of 4 to 9, more preferably 5 to 8. The pAg may preferably be in the range of 5 to 11, more preferably 8 to 10. The temperature may preferably be in the range of 40 to 90°C, more preferably 45 to 75°C. In the present invention, besides the sulfur sensitization and the combination of the gold sensitization and the sulfur sensitization, which are mentioned above, it is also possible to employ the reduction sensitization (reducing compounds are employed) and the noble metal sensitization (noble metal compounds are employed) in combination with these sensitization methods.

In the present invention, a silver halide photosensitive emulsion may be employed either singly or in mixture.

In the present invention, various stabilizers can be added to a chemically sensitized emulsion. As the example of such additive, there may be mentioned 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 5-mercapto-1-phenyltetrazole, and 2-mercaptobenzothiazole. If need arises, it is possible to employ a solvent for a silver halide such as a thioether, or a crystal habit control agent such as a mercapto group-containing compound and a sensitization dye.

According to the present invention, a metal ion may be added to a silver halide particle during the course of formation and/or growth of the particle, so that the metal ion can be included inside and/or on the surface of the particle. For this purpose, use can be made of a cadmium salt, a zinc salt, a lead salt, a thallium salt, a salt or a complex salt of iridium, a salt or a complex salt of rhodium, a salt or a complex salt of iron.

After the growth of a silver halide particle, unnecessary soluble salts may either be removed or remain unremoved. The removal of these salts can be done in accordance with a method described in Research Disclosure No. 17643.

In the present invention, a photosensitive silver halide emulsion may be spectrally sensitized by a sensitization dye so that it can be sensitive to blue light, green light, red light or infrared ray whose wavelength is relatively long. As the usable sensitization dye, there can be mentioned a cyanine dye, a merocyanine dye, a composite cyanine dye, a composite merocyanine dye, a holopolar-cyanine dye, a hemicyanine dye, a styryl dye, and a hemioxonol dye. Among them, cyanine dyes, merocyanine dyes, and composite merocyanine dyes are especially effective. For these sensitization dyes, any nucleus which is

normally used for cyanine dyes as the basic heterocyclic nucleus can be employed. The specific examples of such nucleus include a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazol nucleus, a thiazole nucleus, a selenazole nucleus, an imidazol nucleus, a tetrazole nucleus, and a pyridine nucleus. Also usable are a nucleus obtained by the fusion of one of the above nuclei with an alicyclic or aromatic hydrocarbon ring. As the example of such nucleus, there can be mentioned an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus, and a quinoline nucleus. These nuclei may be substituted on the carbon ring.

For merocyanine dyes and composite merocyanine dyes, a nucleus having a ketomethylene structure is usable. Examples of such nucleus include a 5- or 6-membered heterocyclic nucleus such as a pyrazoline-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus, and a thiobarbiturate nucleus.

In the present invention, a sensitization dye may be employed in the same concentration as that in the case of ordinary negative type photosensitive emulsions. It is of advantage to employ a sensitization dye in such a concentration as will not have any adverse effect on the inherent sensitivity of a silver halide emulsion. A sensitization dye may preferably be employed in an amount of 1.0×10^{-5} to 5×10^{-4} mole, more preferably 4×10^{-5} to 2×10^{-4} , per mole of a silver halide.

In the present invention, sensitization dyes may either be employed singly or in combination. The specific examples of sensitization dyes which are advantageously employed in the present invention are given below.

As the sensitization dye to be used for a blue-sensitive layer, there can be mentioned those described in German Patent No. 929,080, U.S. Patent Nos. 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 3,656,956, 3,672,897, 3,694,217, 4,025,349, 4,046,572, British Patent No. 1,242,588, Japanese Patent Examined Publication No. 14030/1969, 24844/1977, Japanese Patent O.P.I. Publication Nos. 73137/1973 and 172140/1986. The representative examples of the sensitization dye for a green-sensitive layer include cyanine dyes, merocyanine dyes and composite cyanine dyes disclosed in U.S. Patent Nos. 1,939,201, 2,072,908, 2,739,149, 2,945,763, British Patent No. 505,979, and Japanese Patent Examined Publication No. 42172/1973. As the sensitization dye to be used in a red-sensitive layer and an infrared ray-sensitive layer, it is of advantage to use cyanine dyes, merocyanine dyes, and composite cyanine dyes disclosed in U.S. Patent Nos. 2,269,234, 2,270,378, 2,442,710, 2,454,629, 2,776,280, Japanese Patent Examined Publication No. 17725/1974, Japanese Patent O.P.I. Publication Nos. 62425/1975, 29836/1986 and 80841/1985.

These sensitization dyes may be used either alone or in combination. Two or more sensitization dyes are often employed in combination for the purpose of supersensitization. Examples of the combined use of sensitization dyes are described in U.S. Patent Nos. 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, 4,026,707, British Patent Nos. 1,344,281, 1,507,803, Japanese Patent Examined Publication Nos. 4936/1968, 12375/1978, Japanese Patent O.P.I. Publication Nos. 110618/1979 and 109925/1979.

According to the present invention, a water-soluble dye may be added to a hydrophilic colloid layer(s) as a filter dye, an anti-irradiation dye, an anti-halation dye, or for other various purposes. Examples of such water-soluble dye include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes, and azo dyes. Of them, especially preferable dyes are oxonol dyes, hemioxonol dyes and merocyanine dyes.

In the present invention, when dyes, ultraviolet ray absorbers, or other materials are contained in a hydrophilic colloid layer(s), these materials may be mordanted by a cationic polymer.

Various compounds may be added to the photosensitive silver halide emulsion so that occurrence of fogging and lowering in sensitivity of a photosensitive material, which may occur during the preparation, storage or at the time of processing, of a photosensitive material can be prevented. Many compounds known as a stabilizer are usable for these purposes. Examples of such compounds include azoles such as benzothiazolium salts, nitroindozoles, triazoles, benzotriazoles, benzimidazoles (especially, a nitro-, or halogen-substituted product), heterocyclic mercapto compounds such as mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiazoles, mercaptotetrazoles (especially, 1-phenyl-5-mercaptotetrazole), mercaptopyridines, the above-mentioned heterocyclic mercapto compounds may contain a water-soluble group such as a carboxyl group or a sulfone group, thioketo compounds such as ex-azolinethion, azaindenes such as tetraazindenes (especially, 4-hydroxy-substituted-1,3,3a,7-tetraazindenes, benzenethiosulfonic acids, and benzenesulfonic acids.

Part of the specific examples of usable compounds is described in K. Mees: The Theory of the Photographic Process (3rd ed., 1966), with their original sources.

The more concrete examples of these compounds along with the way of using them are described in U.S. Patent Nos. 3,954,474, 3,982,947, 4,021,248 and Japanese Patent Examined Publication No.

28660/1977.

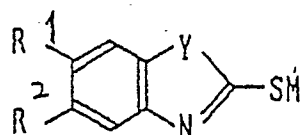
In the present invention, a preferable example of such stabilizer is a compound which is represented by the above-mentioned Formula [I], [II] or [III].

These compounds are added to a hydrophilic colloid layer(s) which is provided on the same side of a support that a silver halide emulsion layer is located, and also to a developer to be used for processing a silver halide photosensitive material. In this case, it is preferred that the ratio of the content of this compound in the colloid layer(s) to that in a developer be in the range of 0.01 to 1, provided that the former content is indicated in terms of mg/m² and the latter content is indicated in terms of mg/l.

The content of the compound represented by Formula I, II or III in the hydrophilic colloid layer(s) is preferably in the range of 1×10^{-6} to 1×10^{-1} mole, more preferably 1×10^{-5} to 1×10^{-2} mole, per mole of silver halide contained in said layer. The content of this compound in a developer is preferably in the range of 1×10^{-6} mole to 1×10^{-1} mole, more preferably 1×10^{-5} mole to 1×10^{-2} mole, per liter of the developer.

The representative examples of the compounds represented by Formula I, II or III are given below:

Example Compound of Formula I

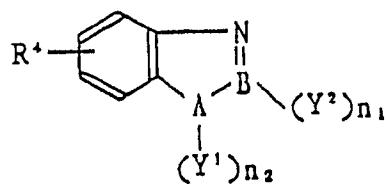


Sub- stituent	R ¹	R ²	Y	M
[I]				
- 1	H	-COOH	$\begin{smallmatrix} \text{H} \\ \\ -\text{N}- \end{smallmatrix}$	H
- 2	H	-COOH	O	K
- 3	H	-COOH	S	H
- 4	H	-COOK	$\begin{smallmatrix} \text{H} \\ \\ -\text{N}- \end{smallmatrix}$	H
- 5	H	-COOH	Se	H
- 6	H	-OH	$\begin{smallmatrix} \text{H} \\ \\ -\text{N}- \end{smallmatrix}$	H
- 7	H	-OH	O	H
- 8	H	-OH	S	Na
- 9	H	-SO ₃ Na	$\begin{smallmatrix} \text{H} \\ \\ -\text{N}- \end{smallmatrix}$	H
-10	-CH ₃	-SO ₃ Na	S	H
-11	H	-SO ₃ Na	O	Na
-12	H	-SO ₃ K	Se	H
-13	-CH ₃	-SO ₃ K	$\begin{smallmatrix} \text{H} \\ \\ -\text{N}- \end{smallmatrix}$	K
-14	-SO ₃ Na	-SO ₃ NH ₄	$\begin{smallmatrix} \text{H} \\ \\ -\text{N}- \end{smallmatrix}$	H

Sub- stituent	R ¹	R ²	Y	M
-15	-CH ₃	-SO ₃ Na	$\begin{array}{c} \text{H} \\ \\ -\text{N}- \end{array}$	Na
-16	H	-CONHCH ₃	$\begin{array}{c} \text{H} \\ \\ -\text{N}- \end{array}$	H
-17	-CH ₃	-CONHCH ₃	S	H
-18	H	-CONHCH ₃	S	H
-19	H	-NHCOCH ₃	$\begin{array}{c} \text{H} \\ \\ -\text{N}- \end{array}$	H
-20	-SO ₃ Na	H	$\begin{array}{c} \text{H} \\ \\ -\text{N}- \end{array}$	H

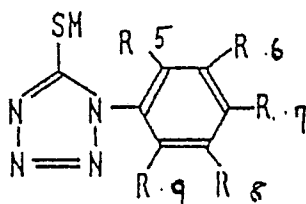
These compounds can be prepared readily by known methods. For example, they can be prepared by a method described in The Chemistry of Heterocyclic Compounds Imidazole and Derivatives, Vol. 1, p. 384.

Example of Formula II

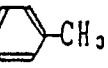


- II-1 Benzotriazole
- II-2 5-methylbenzotriazole
- II-3 5-chlorobenzotriazole
- II-4 5-nitrobenzotriazole
- II-5 5-ethylbenzotriazole
- II-6 Hydroxycarbonylbenzotriazole
- II-7 5-hydroxybenzotriazole
- II-8 5-aminobenzotriazole
- II-9 5-sulfonbenzotriazole
- II-10 5-cyanobenzotriazole
- II-11 5-methoxybenzotriazole
- II-12 5-ethoxybenzotriazole
- II-13 5-mercaptobenzotriazole
- II-14 Benzimidazole
- II-15 5-sulfobenzimidazole
- II-16 5-methoxybenzimidazole
- II-17 5-chlorobenzimidazole
- II-18 5-nitroindazole
- II-19 6-nitroindazole
- II-20 5-sulfoindazole
- II-21 2-mercapto-5-sulfobenzimidazole
- II-22 2-mercapto-5-sulfobenzimidazole
- II-23 2-mercaptobenzoxadole

Example Compound of Formula III



	M	R. 5	R. 6	R. 7	R. 8	R. 9
III-1	H	H	H	Cl	H	H
2	H	H	H	-CONHCH ₃	H	H
3	H	H	H	-CONH- 	H	H
4	H	H	H	H	-CONHC ₂ H ₅	H
5	H	H	H	H	-CONH- 	H
6	H	H	H	H	H	H
7	H	H	H	SO ₂ NHCH ₃	H	H
8	H	H	H	H	SO ₂ NHCH ₃	H
9	H	H	H	H	SO ₂ NHC ₃ H ₇	H
10	H	H	H	H	SO ₂ NH- 	H
11	H	H	H	-NHCOCH ₃	H	H
12	H	H	H	-NHCOC ₃ H ₇	H	H

	M	R ₅	R ₆	R ₇	R ₈	R ₉
13	H	H	H	-NHCOC ₇ H ₁₅	H	H
14	H	H	H	-NHCO- 	H	H
15	H	H	H	H	-NHCOCCH ₃	H
16	H	H	H	H	-NHCOC ₂ H ₅	H
17	H	H	H	H	-NHCO- 	H
18	H	H	H	H	-NHCOC ₁₈ H ₃₇	H
19	Na	H	H	H	-NHCOCCH ₃	H
20	H	H	H	-NHSO ₂ CH ₃	H	H
21	H	H	H	-NHSO ₂ C ₃ H ₇	H	H
22	H	H	H	-NHSO ₂ - 	H	H
23	H	H	H	-NHSO ₂ - 	H	H
24	H	H	H	H	-NHSO ₂ CH ₃	H
25	H	H	H	H	-NHSO ₂ C ₃ H ₇	H
26	H	H	H	H	-NHSO ₂ - 	H

In the present invention, a silver halide photosensitive material may contain in its photographic structural layers an alkylacrylate-type latex described in U.S. Patent Nos. 3,411,911, 3,411,912 and Japanese Patent Examined Publication No. 5331/1970.

Various additives may be added to a silver halide photosensitive material of the present invention. As the thickener and the plasticizer, use can be made of materials described in U.S. Patent No. 2,960,404, Japanese Patent Examined Publication Nos. 4939/1968, 15462/1970, German Patent No. 1,904,604, Japanese Patent O.P.I. Publication No. 63715/1973, Belgian Patent Nos. 762,833, 558,143, U.S. Patent No. 3,767,410. Examples of these materials include a copolymer of styrene and sodium maleate and dextran sulfate. As a hardening agent, use can be made of hardening agents of aldehyde-type, epoxy-type, ethylene imine-type, active halogen-type, vinyl sulfone-type, isocyanate-type, sulfonic acid ester-type, carbodiimido type, mucochloric acid-type, and acyloyl type. As an ultraviolet ray absorbent, compounds described in U.S. Patent No. 3,253,921 and in British Patent No. 1,309,349 are usable. Examples of such compounds include

2-(2'-hydroxy-5-tert-butylphenyl)benzotriazole,
 2-(2'-hydroxy-3',5-di-tert-butylphenyl)benzotriazole,
 2-(2'-hydroxy-3'-tert-butyl-5'-butylphenyl)-5-chlorobenzotriazole,
 2-(2'-hydroxy-3',5-di-tert-butylphenyl)-5-chlorobenzotriazole. Also employable are a coating assisting agent, an emulsifier, an agent for improving the permeability of a photosensitive material in a treatment liquid, a defoaming agent, and a surface-active agent for controlling the physical properties of a photosensitive material. As the surface active agent, there can be employed anion, cation, non-ion, or amphoteric compounds described in British Patent Nos. 548,532 and 1,216,389, U.S. Patent Nos. 2,026,202, 3,514,293, Japanese Patent Examined Publication Nos. 26580/1969, 17922/1968, 17926/1968, 13166/1968, 20785/1973, French Patent No. 202,588, Belgian Patent No. 773,459, and Japanese Patent O.P.I. Publication No. 101118/1973. Of them, an anion surface active agent containing a sulfone group, such as a

sulfonated product of an ester of succinic acid, a sulfonated product of alkylnaphthalene, and a sulfonated product of alkylbenzene, is preferable.

As the antistatic agent, use can be made of compounds described in Japanese Patent Examined Publication Nos. 24159/1971, 39312/1971, 43809/1983, Japanese Patent O.P.I. Publication Nos. 89979/1973, 20785/1973, 43130/1973, 90391/1973, 33627/1972, U.S. Patent Nos. 2,882,157 and 2,972,535.

In the process of the present invention, the pH of a liquid to be coated on a support may preferably be in the range of 5.3 to 7.5. When a plurality of layers are to be formed by coating, the pH of a mixture of individual coating liquids (coating liquids are mixed at the same ratio that the liquids are coated on a support) may preferably be in the range of 5.3 to 7.5. If the pH is smaller than 5.3, prompt hardening of coated layers is impeded. A pH value larger than 7.5 will have adverse effects on the photographic properties.

In the present invention, a matting agent may be contained in photographic structural layers. As the matting agent, there can be employed inorganic particles, such as silica described in Swiss Patent No. 330,158, glass powder described in French Patent No. 1,296,995; carbonates of alkali earth metals, cadmium and zinc described in British Patent No. 1,173,181; and organic particles, such as starch described in U.S. Patent No. 2,322,037, starch derivatives described in Belgian Patent No. 625,451 and British Patent No. 981,198, polyvinyl alcohol described in Japanese Patent Examined Publication No. 3643/1969, polystyrene and polymethyl methacrylate described in Swiss Patent No. 330,158, polyacrylonitrile described in U.S. Patent No. 3,079,257, and polycarbonate described in U.S. Patent No. 3,022,169.

The photographic structural layers of a photosensitive silver halide material may contain a lubricant. As the lubricant, there can be employed an ester of higher fatty alcohol described in U.S. Patent Nos. 2,558,756 and 3,121,060, casein described in U.S. Patent No. 3,295,979, a calcium salt of higher fatty acid described in British Patent No. 1,263,722, and a silicon compound described in British Patent No. 1,313,384, U.S. Patent Nos. 3,042,522 and 3,489,567. A dispersed product of fluid paraffin is also usable for this purpose. As the dyes which are employable for various purposes (e.g. filter dyes, anti-irradiation dyes), there can be mentioned oxonol dyes, hemioxonol dyes, merocyanine dyes, cyanine dyes, styryl dyes, and azo dyes. Among them, oxonol dyes, hemioxonol dyes and merocyanine dyes are effective. The specific examples of the employable dyes include those described in German Patent No. 616,007, British Patent Nos. 584,609 and 1,117,429, Japanese Patent Examined Publication No. 7777/1951, 22069/1964, 38129/1979, Japanese Patent O.P.I. Publication Nos. 85130/1973, 99620/1974, 114420/1974, 129537/1974, 28827/1975, 108115/1979, 185038/1982, U.S. Patent Nos. 1,878,961, 1,884,035, 1,912,797, 2,098,891, 2,150,695, 2,274,782, 2,298,731, 2,409,612, 2,461,484, 2,527,583, 2,533,472, 2,865,752, 2,956,879, 3,094,418, 3,125,448, 3,148,187, 3,177,078, 3,247,127, 3,269,601, 3,282,699, 3,409,433, 3,540,887, 3,575,704, 3,653,905, 3,718,472, 3,865,817, 4,070,352, 4,071,312, PB report No. 74175, and Photographic Abstract, 1, 28 (1921). As the optical bleaching agent, it is preferable to employ an optical bleaching agent of stilbene type, triazine type, pyrazoline, coumarin type, and acetylene type.

These compounds may either be soluble or insoluble in water.

As the anion surface active agent, there can be employed one containing an acid group such as a carboxy group, a sulfo group, a phospho group, a sulfuric ester group, and a phosphoric ester group. The specific examples of these agents include a salt of alkylcarboxylic acid, a salt of alkylsulfonic acid, a salt of alkylbenzene sulfonic acid, a salt of alkylnaphthalene sulfonic acid, an ester of alkylsulfuric acid, an ester of alkylphosphoric acid, an N-acyl-alkyltaurine, an ester of sulfosuccinic acid, an ether of sulfoalkylpolyoxyethylenealkylphenyl, and an ester of polyoxyethylenealkylphosphoric acid.

As the amphoteric surface active agent, there may preferably be employed amino acids, aminoalkylsulfonic acids, an ester of aminoalkylsulfuric acid or aminoalkylphosphoric acid, alkylbetaines, and amineoxides.

As the cation surface active agent, there may preferably be employed a salt of alkylamine, an aliphatic or aromatic quaternary ammonium salt, a heterocyclic quaternary ammonium salt such as pyridium and imidazolium, a salt of aliphatic or heterocyclic phosphonium or sulfonium.

As the anion surface active agent, there may preferably be employed saponin (steroid type), an alkyleneoxide derivative (e.g. polyethylene glycol, a condensation product of polyethylene glycol and polypropylene glycol, an alkylether of polyethylene glycol, an alkylarylether of polyethylene glycol, an ester of polyethylene glycol, an ester of polyethylene glycol sorbitan, an alkylamine or an alkylamide of polyalkyleneglycol, an addition product of a silicone and a polyethylene oxide), a glycide derivative (e.g. an alkenylsuccinic acid polyglyceride, an alkylphenol polyglyceride), an aliphatic acid ester of polyhydric alcohol, and an alkylester of sugar.

As the examples of matting agent, there can be mentioned organic matting agents described in British Patent No. 1,055,713, U.S. Patent Nos. 1,939,213, 2,221,873, 2,268,662, 2,332,037, 2,376,005, 2,391,181,

2,701,245, 2,992,101, 3,079,257, 3,262,782, 3,516,832, 3,539,344, 3,591,379, 3,754,924, 3,767,448, and inorganic matting agents described in German Patent No. 2,592,321, British Patent Nos. 760,775, 1,260,772, U.S. Patent Nos. 1,201,905, 2,192,241, 3,053,662, 3,062,649, 3,257,206, 3,322,555, 3,353,958, 3,370,951, 3,411,907, 3,437,484, 3,523,022, 3,615,554, 3,635,714, 3,769,020, 4,021,245, and 4,029,504.

5 As the antistatic agent, there may preferably be employed compounds described in British Patent No. 1,466,600, Research Disclosure Nos. 15840, 16258, 16630, U.S. Patent Nos. 2,327,828, 2,861,056, 3,206,312, 3,245,833, 3,428,451, 3,775,126, 3,963,498, 4,025,342, 4,025,463, 4,025,691, and 4,025,704.

In an especially preferred embodiment of the present invention, a tetrazolium compound, a polyethylene oxide derivative, a quaternary microcosmic salt, and a hydrazine compound described in Japanese Patent
10 O.P.I. Publication Nos. 210458/1987 and 139546/1987 are used as a contrast-controlling agent which helps an image to be more contrasty.

It is possible to add a polymer latex to a silver halide photosensitive emulsion layer and a backing layer in order to improve size-stability. This technique is disclosed, for example, in Japanese Patent Examined Publication Nos. 4272/1964, 17702/1964, 13482/1968, U.S. Patent Nos. 2,376,005, 2,763,625, 2,772,166,
15 2,852,386, 2,853,457, and 3,397,988.

As the binder to be used in a silver halide photosensitive material of the present invention, gelatin is normally employed as a binder. It is also possible to use, in combination with gelatin, a hydrophilic colloid of a gelatin derivative, a cellulose derivative, a graft polymer of gelatin and other polymer than gelatin, other protein than gelatin, a derivative of sugar, or a synthesized high molecular compound such as homo- or
20 copolymer.

As the gelatin, besides lime-treated gelatin, use can be made of acid-treated gelatin and oxygen-treated gelatin such as those described in Bulletin of Society of Japan, No. 16, p. 30 (1966). Also usable are a hydrolyzed product or an enzyme-decomposed product of gelatin. As the gelatin derivative, there may be employed those obtained by allowing gelatin to react with various products including an acid halide, an acid
25 anhydride, an isocyanate, a bromoacetic acid, an alkanesulton, a vinylsulfoneamido, a maleic imido compound, a polyalkylene oxide, an epoxy compound. The specific examples of these gelatin derivatives are described in U.S. Patent Nos. 2,614,928, 3,132,945, 3,186,846, 3,312,553, British Patent Nos. 861,414, 1,033,189, 1,005,784, and Japanese Patent Examined Publication No. 26845/1967.

As the protein, use can be made of albumin, casein, or the like. As the cellulose derivative, use can be
30 made of a hydroxyethylcellulose, a carboxymethylcellulose, a sufuric ester of cellulose, or the like. As the derivative of sugar, there can be employed soda alginate and starch derivatives. These compounds can be used in combination with gelatin.

As the graft polymer of gelatin and other polymer, there may be employed one obtained by graft polymerization of gelatin with an acrylic acid, a methacrylic acid, a derivative thereof including an ester and
35 an amido, a homo- or copolymer of a vinyl monomer such as acrylonitrile and styrene. Especially preferred is a graft polymer of gelatin with a polymer which shows mutual solubility with gelatin to some extent, such as a polymer of acrylic acid, acrylamido, methacrylamide, hydroxyalkylmethacrylate, and the like. Examples of these polymers are described in U.S. Patent Nos. 2,763,625, 2,831,767, and 2,956,884.

In the present invention, if need arises, it is possible to use other additives than those mentioned above.
40 These additives are described in detail in Research Disclosure Vol. 176, Item 17643 (1978, December) and 187, Item 18716 (1979, November). The kind of additive and the pertinent portions of RD are given in the following table:

45

50

55

Type of Additive	RD17643	RD18716
1. Chemical sensitizer	p23	p648, right column
2. Sensitivity-increasing agent		ditto
3. Spectral sensitizer Supersensitizer	p23 - 24	p648, right column to p649, right column
4. Bleaching agent	p24	
5. Anti-fogging agent and stabilizer	p24 - 25	p649, right column
6. Light-absorbing agent, filter dye, ultraviolet ray absorbent	p25 - 26	p649, right column to p650, left column

Type of Additive	RD17643	RD18716
7. Anti-stain agent	p25 right column	p649, right to left column
8. Color image stabilizer	p25	
9. Hardening agent	p26	p651, left column
10. Binder	p26	ditto
11. Plasticizer, lubricant	p27	p650, right column
12. Coating assisting agent surface active agent	p26 - 27	ditto
13. Anti-static agent	p27	ditto

As the support to be employed in a silver halide photosensitive material of the present invention, use can be made of a paper obtained by laminating α -olefin polymers (e.g. polyethylene, polypropylene, a ethylene/butene copolymer); a flexible reflective support such as a synthetic paper; a film of a semi-synthesized or synthesized polymer such as cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, a polycarbonate, and a polyamide; a flexible support obtained by providing a reflective layer on one of above films; and a metallic film.

Of them, a support of polyethylene terephthalate is especially preferred.

As the undercoating layer imployable in the present invention, there may be mentioned an undercoating layer obtained by using an organic solvent such as polyhydroxybenzenes, examples of which being described in Japanese Patent O.P.I. Publication No. 3972/1974 and an undercoating layer obtained by using a water-type latex, examples of which being described in Japanese Patent O.P.I. Publication Nos. 11118/1974, 104913/1977, 19941/1984, 19940/1984, 18945/1984, 112326/1976, 117617/1976, 58469/1976, 114120/1976, 121323/1976, 123139/1976, 114121/1976, 139320/1977, 65422/1977, 109923/1977,

119919/1977, 65949/1980, 128332/1982, and 19941/1984.

Normally, the surface of an undercoating layer may be subjected to chemical or physical treatment. Examples of such treatment include chemical treatment, mechanical treatment, corona discharge treatment, flame treatment, ultraviolet ray treatment, high frequency treatment, glow discharge treatment, active
5 plasma treatment, laser treatment, mixed acid treatment, and ozone oxidation treatment.

An undercoating layer should be distinguished from coating layers which fall in the scope of the present invention. There is, therefore, no restriction as to the time and conditions of providing this layer.

In the present invention, dyes may be employed for various purposes. (e.g. a filter dye, an anti-halation dye). Examples of employable dyes include triallyl dyes, oxanol dyes, hemioxanol dyes, merocyanine dyes,
10 cyanine dyes, styryl dyes, and azo dyes. Of them, oxanol dyes, hemioxanol dyes and merocyanine dyes are effective. The specific examples of these dyes are described in German Patent No. 616,007, British Patent Nos. 584,609 and 1,177,429, Japanese Patent Examined Publication Nos. 7777/1951, 22069/1964, 38129/1979, Japanese Patent O.P.I. Publication Nos. 85130/1973, 99620/1974, 114420/1974, 129537/1974, 28827/1975, 108115/1977, 185038/1982, 24845/1984, U.S. Patent Nos. 1,878,961, 1,884,035, 1,912,797,
15 2,098,891, 1,150,695, 2,274,782, 2,298,731, 2,409,612, 2,461,484, 2,527,583, 2,533,472, 2,865,752, 2,956,879, 3,094,418, 3,125,448, 3,148,187, 3,177,078, 3,247,127, 3,260,601, 3,282,699, 3,409,433, 3,540,887, 3,575,704, 3,653,905, 3,718,472, 3,865,817, 4,070,352, 4,071,312, PB Report No. 74175, and Photographic Abstract, 1, 28 (1921).

These dyes are advantageously employed especially in a photosensitive material for contact printing to
20 be treated in a lighted room. In this case, it is preferred that a dye be employed in such an amount that the sensitivity of a photosensitive material to light of 400 nm becomes 30 times as large as that to light of 360 nm.

In the present invention, it is also possible to use an organic desensitizer described, for example, in Japanese Patent O.P.I. Publication No. 26041/1986. In this desensitizer, the sum of an anode potential and
25 a cathode potential is positive in its polarogram.

In the present invention, imagewise exposure may be performed by using an electromagnetic wave of a spectral region to which a photosensitive emulsion layer of a silver halide photosensitive material exhibits sensitivity. As the light source, any of conventional light sources may be employed. Examples of employable light sources include sunlight, tungsten lamps, fluorescent lamps, iodine quartz lamps, mercury
30 lamps, microwave-emitting ultraviolet lamps, xenon arc lamps, carbon arc lamps, xenon flash lamps, cathode ray tubes, flying spots, various laser beams, light-emitting diodes, light emitted from a fluorescent substance excited by electron beam, X ray, γ ray or α ray. It is also preferable to use a light source described in Japanese Patent O.P.I. Publication No. 210458/1987 which is obtained by attaching to an ultraviolet ray light source an absorption filter capable of absorbing light of not more than 370 nm in
35 wavelength. Also possible is to use an ultraviolet ray light source emitting light of 370 to 420 nm in main wave length.

Exposure time may be 1 millisecond to 1 second, as is employed in normal photographing by a camera. It is also possible that light exposure be effected for such a short time as less than 1 microsecond. For example, by using a cathode ray tube or a xenon flash tube, exposure can be effected for 100
40 nanosecond to 1 microsecond. On the other hand, it is also possible to perform exposure for 1 second or longer. Imagewise exposure may be performed either continuously or intermittently.

The present invention can be applied to a variety of photosensitive materials. For example, the present invention can be applied to films for printing, films for X-ray photography, a negative film for ordinary photographing, a reversal film for ordinary photographing, and a positive film for direct photographing.

In the present invention, the fixing liquid may contain various substances such as thiosulfates, sulfites,
45 various acids, salts, fixing accelerators, wetting agents, surface active agents, chelating agents, hardening agents, and the like. Examples of thiosulfates and sulfites include potassium salts, sodium salts, and ammonium salts thereof. Examples of the acids include sulfuric acid, hydrochloric acid, nitric acid, boric acid, formic acid, acetic acid, propionic acid, oxalic acid, tartaric acid, citric acid, malic acid, and phthalic acid. Examples of the salts include potassium salts, sodium salts, and ammonium salts of these acids. As
50 the fixing accelerator, there may be mentioned thiourea derivatives and an alcohol containing a triple bond in its molecule disclosed in Japanese Patent Examined Publication No. 35754/1970, Japanese Patent O.P.I. Publication Nos. 122535/1983 and 122536/1983, a thioether disclosed in U.S. Patent No. 4,126,459, an ether of cyclodextran which releases an anion, a crown ether, diazabicyclo undecene, and di(hydroxyethyl)-
55 butamine. As the wetting agent, use can be made of an alkanol amine and an alkylene glycol. As the chelating agent, use can be made of a nitrilotriacetic acid and an aminoacetic acid such as a disodium salt of ethylenediamine tetraacetic acid. Examples of the hardening agent include chrome alum, potassium alum, and Al compounds.

In the present invention, it is preferred that the fixing liquid contain Al compounds so that a hardened layer of a photosensitive emulsion can be kept in a stable condition. In this case, the content of an Al compound in a fixing liquid may preferably be 0.1 to 3 g per liter of a fixing liquid (calculated in terms of Al in the fixing liquid).

The concentration of sulfite in a fixing liquid may preferably be 0.03 to 0.4 mole, more preferably 0.04 to 0.3 mole per liter of a fixing liquid.

The preferred pH value of a fixing liquid is 3.9 to 6.5. This pH value contributes to the improvement of photographic properties of an image. Moreover, when use is made of a fixing liquid having this pH value, a silver halide photosensitive material can produce remarkable effects. It is especially preferred that the pH of a fixing liquid be 4.2 to 5.3.

EXAMPLES

The present invention will be described in detail with reference to the following examples which are meant to be illustrative but not limitive.

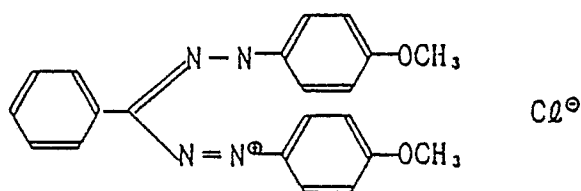
Example 1

Various silver halide photosensitive materials are prepared by the following process.

An aqueous silver nitrate, an aqueous sodium chloride and sodium bromide are mixed simultaneously in an aqueous gelatin solution, thereby forming silver halide granules. Desalting is performed by an ordinary method to obtain a photosensitive emulsion. The so-formed emulsion is chemically sensitized by known technique. Subsequently, 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene is added to the emulsion as a stabilizer. To this emulsion, further added are a compound represented by Formula I, II, or III, nonylphenyloxy polyethylene glycol, and a latex of a copolymer of an acrylic acid and butyl methacrylate as described in Table 1. Then, a tetrazolium compound (A) is added in an amount of 1.3 g per mole of silver. Further added are saponin, dodecylbenzene sodium sulfonate, a latex of a copolymer of acrylic acid and butyl methacrylate and a 280 mg of a copolymer of styrene and maleic acid as a thickner. The resulting emulsion is then coated on a support of a polyethylene terephthalate film having a thickness of 100 μ m, which is undercoated with a polymer latex. A protective layer is provided on the emulsion layer.

The amount of silver and the thickness of a hydrophilic colloid layer(s) are varied as shown in Table 1.

Compound (A)



The so-formed photosensitive materials are subjected to imagewise exposure through a glass wedge, by using lighted room printer P627FM (manufactured by Dainippon Screen Co., Ltd.). Then, the photosensitive materials are subjected to development and fixing. The compositions of a developer and a fixing liquid, and the conditions under which development is performed are given below. The amount of silver is measured by using a fluorescent X-ray analyzer. In a photosensitive material after development, the amount of silver means the amount of silver in a portion which gives a maximum density. The thickness of a hydrophilic colloid layer(s) is measured by a swelling degree measuring machine (manufactured by Shinko Denshi Co., Ltd.).

Composition of Developer-1

(Ingredients A)	
Pure water (ion exchange water)	150 ml
Disodium salt of ethylenediamine tetraacetic acid	2 g
Diethylene glycol	50 g
Potassium sulfite (an aqueous 55 W/V% solution)	100 ml
Potassium carbonate	50 g
Hydroquinone	15 g
1-phenyl-5-mercaptotetrazole (Example compound III-6)	30 mg
Potassium hydroxide (in such an amount that the pH of the liquid becomes 10.4)	
Potassium bromide	4.5 g

(Ingredients B)	
Pure water (ion exchange water)	3 ml
Diethylene glycol	50 g
Disodium salt of ethylenediamine tetraacetic acid	25 mg
Acetic acid (an aqueous 90% solution)	0.3 mg
1-phenyl-3-pyrazolidone	500 mg
2-mercapto-benzimidazol-5-sodium sulfonate (Example compound I-9)	50 mg

The above ingredients (A) and (B) are dissolved in this sequence in 500 ml of water so that the amount of the developer becomes 1 l.

Composition of Developer-2

(Ingredients A)	
Pure water (ion exchange water)	150 ml
Disodium salt of ethylenediamine tetraacetic acid	2 g
Diethylene glycol	50 g
Potassium sulfite (an aqueous 55 W/V% solution)	100 ml
Potassium carbonate	50 g
Hydroquinone	15 g
Potassium hydroxide (in such an amount that the pH of the liquid becomes 10.4)	
Potassium bromide	4.5 g

(Ingredients B)	
Pure water (ion exchange water)	3 ml
Diethylene glycol	50 g
Disodium salt of ethylenediamine tetraacetic acid	25 mg
Acetic acid (an aqueous 90% solution)	0.3 mg
1-phenyl-3-mercaptotetrazole	500 mg

The above ingredients (A) and (B) are dissolved in this sequence in 500 ml of water so that the amount of the developer becomes 1 l.

Composition of Fixing Liquid

(Ingredients A)	
Ammonium thiosulfate (an aqueous 72.5 W/V% solution)	230 ml
Sodium sulfite	9.5 g
Sodium acetate trihydrate	15.9 g
Boric acid	6.7 g
Sodium citrate dihydrate	2 g
Acetic acid (an aqueous 90 W/W% solution)	8.1 ml

(Ingredients B)	
Pure water (ion exchange water)	17 ml
Sulfuric acid (an aqueous 50 W/W% solution)	5.8 g
Aluminum sulfate (an aqueous 8.1 W/W% solution calculated in terms of Al_2O_3)	25.6g

The above ingredients (A) and (B) are dissolved in this sequence in 500 ml of water so that the amount of the developer becomes 1 l. The pH of the fixing liquid is about 4.3.

(Conditions for high-speed development)			
Treatment	Temperature	Time	Capacity of tank
	(° C)	(second)	(l)
Development	35	15	20 (40)
Fixing	34	15	20
Washing	18	10	10 (20)
Drying	40	10	20

The results are shown in Table 1.

As is apparent from Table 1, when the ratio of the silver content to the thickness of a hydrophilic colloid layer(s) is 0.7 or more, more than 90% of silver is effectively developed, and then, a highly contrasty image with a γ value of 6 or more can be obtained.

Example 2

Photosensitive silver halide materials are prepared in substantially the same manner as in Example 1, except that chemical sensitization is performed by using the following sensitization dye (B). Imagewise exposure is carried out through a glass wedge by using a tungsten lamp as a light source. The results obtained are same as those obtained in Example 1.

Compound (B)

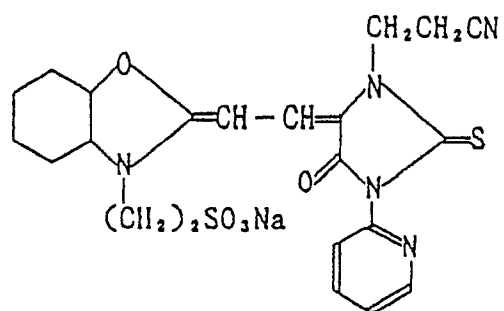


Table 1

Run No.	Sample	Amount of silver coated (A) g/m ²	Thickness of hydrophilic layers (B) μ m	(A)/(B)	Compound represented by Formula I, II or III		Content ratio of Compound I, II or III Hydrophilic colloid layer/developer	Developer composition	Amount of silver after development g/m ²	Gamma value
					Kind of compound	Amount added mg/m ²				
1	Comparative	2.0	6.0	0.33	-	-	0	Developer composition-1	1.7	3.8
2	"	"	4.0	0.50	-	-	0	"	1.7	4.2
3	"	"	2.5	0.80	-	-	0	"	1.9	5.0
4	Invention	"	2.5	0.80	{II}-2 {III}-6	2.0 3.0	0.0625	"	1.9	7.2
5	"	"	2.0	1.00	"	"	"	"	2.0	7.3
6	Comparative	3.0	8.0	0.38	"	"	"	"	2.1	5.6
7	"	"	6.0	0.50	"	"	"	"	2.7	5.8
8	Invention	"	4.0	0.75	"	"	"	"	2.8	9.1
9	"	"	3.0	1.00	"	"	"	"	2.9	9.2
10	Comparative	4.0	10.0	0.40	"	"	"	"	3.2	6.2
11	"	"	8.0	0.50	"	"	"	"	3.3	6.4
12	Invention	"	5.0	0.80	"	"	"	"	3.7	10.1
13	"	"	4.0	1.00	"	"	"	"	3.8	9.5
14	"	"	3.0	1.33	"	"	"	"	3.8	10.2
15	"	"	2.0	2.00	"	"	"	"	3.9	10.3
16	Comparative	"	"	2.00	-	-	0	"	3.9	6.1
17	"	5.0	10.0	0.50	{I}-9 {II}-11	2.0 2.0	0.05	"	4.2	7.3
18	"	"	8.0	0.63	"	"	"	"	4.3	7.4
19	Invention	"	6.0	0.83	"	"	"	"	4.6	10.3
20	"	"	5.0	1.00	"	"	"	"	4.7	9.9
21	"	"	4.0	1.25	"	"	"	"	4.8	10.3
22	"	"	3.0	1.67	"	"	"	"	4.8	10.0
23	Comparative	4.0	4.0	1.00	{II}-2 {III}-6	0.3 0.3	0.0075	"	3.5	4.1
24	"	"	"	"	"	40 50	1.125	"	2.9	3.9
25	"	"	"	"	"	2.0 3.0	-	Developer composition-2	3.6	4.2
26	"	5.0	6.0	0.83	{I}-9 {II}-11	2.0 2.0	-	"	4.5	5.6

In the Table 1, the γ value is obtained with respect to an image having a density of 0.3 to 3.0.

50 An image having a γ value of not more than 6 is poor in resolution, and therefore, can hardly be put to practical use.

As to Samples 4 to 15, the content of a compound represented by Formula I, II or III in a hydrophilic colloid layer(s) (mg/m² to that a developer (mg/l) is 0.0625. This ratio is 0.5 in Samples 17 to 22.

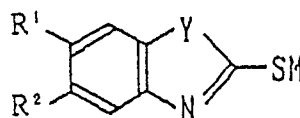
55

Claims

1. A method of developing with a developer containing at least one compound selected from the group

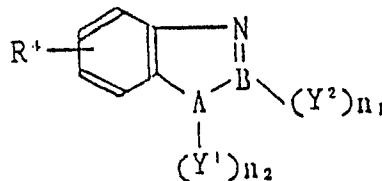
consisting of compounds represented by Formulae I, II and III a negative-type silver halide photographic light-sensitive material having a support and provided thereon hydrophilic colloid layers comprising at least one light-sensitive silver halide emulsion layer, wherein at least one of said colloid layers on the emulsion layer side comprises at least one compound selected from the group consisting of compounds represented by Formulae I, II and III, the ratio of the silver content represented by g/m^2 of at least one of said colloid layers to the thickness represented by μm of said colloid layers is not less than 0.7 and the ratio of the content of said compound represented by mg/m^2 in at least one of said colloid layers to that of said compound represented by mg/l in said developer is from 0.01 to 1.

Formula I



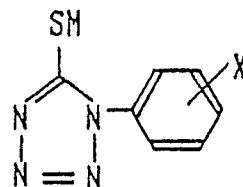
wherein R^1 and R^2 each represent a hydrogen atom, an alkyl group, $-COOM$, $-SO_3M$, $-OH$, $-CONHR^3$ or $-NHCOR^3$, provided that at least one of R^1 and R^2 is $-COOM$, $-SO_3M$, $-OH$, $CONHR^3$ or $-NHCOR^3$ wherein R^3 represents an alkyl group; M represents a hydrogen atom, an alkali metal atom or $-NH_4$; Y represents an oxygen atom, a sulfur atom, a selenium atom or a $-NH-$ group.

Formula II



wherein Y^1 and Y^2 each represent a hydrogen atom or a mercapto group; R^4 represents an alkyl group, an alkenyl group, an alkynyl group, an aryl group, an alkoxy group, each of which may either be substituted or unsubstituted, a hydrogen atom, a halogen atom, a nitro group, an amino group, a cyano group, a hydroxycarbonyl group, an alkoxycarbonyl group, an alkylcarbonyl group, a hydroxy group, a mercapto group or a sulfo group; A represents a nitrogen atom or a carbon atom, a carbon atom or an oxygen atom; B represents a nitrogen atom or a carbon atom; when A is a carbon atom, n_2 is 2, when A is a nitrogen atom, n_2 is 1 and when A is an oxygen atom, n_2 is 0; when B is a carbon atom, n_1 is 1 and when B is a nitrogen atom, n_1 is 0.

Formula III



wherein M represents a hydrogen atom, an alkali metal atom or $-NH_4$; X represents a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, an aryl group, an alkoxy group, a carbamoyl group, a sulfamoyl group, an acylamino group or a sulfonamide group.

2. The method of claim 1, wherein said photographic light-sensitive material is developed with said developer in not more than 19 seconds.

3. The method of claim 1, wherein the total time taken from the time when a leading edge of said

photographic light-sensitive material is introduced in an automatic developing machine having a developing step, a fixing step, a washing step and a drying step until the time when the leading edge comes out of the machine is from 20 to 60 seconds.

4. The method of claim 1, wherein said silver halide emulsion layer comprises silver chlorobromide
5 containing not less than 50 mol % of silver chloride

5. The method of claim 1, wherein not less than 60 % of total number of silver halide particles contained in said silver halide emulsion have a grain size within the range of ± 10 % of an average particle diameter of the silver halide particles.

6. The method of claim 1, wherein the content of at least one compound selected from the group
10 consisting of compounds represented by Formula I, II and III in at least one of said colloid layers on the emulsion layer side is from 1×10^{-6} to 1×10^{-1} mole per mole of silver halide in at least one of the colloid layers.

7. The method of claim 1, wherein the content of at least one compound selected from the group consisting of compounds represented by Formula I, II and III in said developer is from 1×10^{-6} to 1×10^{-1}
15 mol per l of the developer.

20

25

30

35

40

45

50

55