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(54) **Light-sensitive silver halide photographic material.**

(57) A light-sensitive silver halide photographic material comprising a support bearing at least one light-sensitive silver halide emulsion layer comprising from 10^{-8} to 10^{-5} mole of metal ion per mole of silver halide present, and silver halide grains containing 80 to 99 mole% of silver chloride and having a silver bromide-rich phase.

EP 0 244 184 A2

LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL

FILED OF THE INVENTION:

The present invention relates to a light-sensitive silver halide photographic material, and, more particularly, to a light-sensitive silver halide photographic material having excellent pressure resistance and suitable for rapid processing.

BACKGROUND OF THE INVENTION

In the method of forming color images by using a light-sensitive silver halide color photographic material, the color images are usually formed, after imagewise exposure, by reacting an oxidized p-phenylenediamine type color developing agent with a dye image-forming coupler. In such a method, usually used is a color reproduction process employing a subtractive color process, according to which dye images of cyan, magenta and yellow corresponding to red, green and blue are each formed in the respective light-sensitive layers. In recent years, in forming dye images like this, it has been generally practiced in order to achieve a shortened developing processing time to carry out a highly active developing processing which uses high pH, high temperature, high density color developing agents and so forth, and to omit processing steps. In particular, in order to achieve the shortened developing processing time in the above highly active developing processing, it is very important to increase the developing speed in color development.

For such a reason, there have been recently taken various countermeasures for carrying out color development rapidly. As one of the measures, it has been known to use development accelerators when light-sensitive silver halide color photographic materials having been exposed are developed by use of aromatic primary amine type color developing agents. Among such development accelerators, compounds having relatively higher activities may often cause fogging disadvantageously. However, even in such compounds, a certain type of white and black developing agent showing a superadditivity can achieve a development-accelerating effect with formation of relatively low fog as compared with other development accelerators. Examples of such a white and black developing agent may include 1-phenyl-3-pyrazolidone disclosed in British Patent No.

811,185; N-methyl-p-aminophenol disclosed in U.S. Patent No. 2,417,514; N,N,N',N'-tetramethyl-p-phenylenediamine disclosed in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 15554/1975; etc. Mechanism of superadditive development in this color development is reported by G.F. Van Veelen in The Journal of Photographic Science, No. 20, p.94 (1972). Methods in which such a white and black developing agent is used as an auxiliary developer to achieve the color development-accelerating effect may include a case in which the agent is contained in a light-sensitive silver halide color photographic material and a case in which it is contained in a color developing solution.

Of the above, in the case where the above white and black developing agent is contained in a light-sensitive silver halide color photographic material for the purpose of accelerating color development, 1-aryl-3-pyrazolidones are particularly preferably used. For example, Japanese Patent O.P.I. Publication No. 89739/1981 discloses that 1-aryl-3-pyrazolidone is added to a light-sensitive silver halide color photographic material having on a support a silver halide emulsion layer wherein the grain size percentage of silver halide grains is different by 50 % or more. However, the light-sensitive silver halide color photographic material disclosed in this publication and containing 1-aryl-3-pyrazolidone is used for intensification processing in the presence of an intensifier such as a cobalt complex salt, and, when processed as a material for usual color developing processing, the development-accelerating effect can be only achieved very insufficiently. In particular, it was found to be almost impossible to achieve the color development-accelerating effect when ordinary color developing processing is carried out with use of a silver halide emulsion comprising silver halide grains having a large average grain size.

Japanese Patent O.P.I. Publication No. 64339/1981 also discloses a method in which a 1-aryl-3-pyrazolidone of particular structure is added to a light-sensitive silver halide color photographic material, and Japanese Patent O.P.I. Publications No. 144547/1982, No. 50532/1983, No. 50533/1983, No. 50534/1983, No. 50535/1983 and No. 50536/1983 each disclose that 1-aryl-3-pyrazolidones are added to a light-sensitive silver halide color photographic material and processing is carried out in a very short developing time.

However, the respective techniques disclosed in these publications may be satisfactory for merely achieving the development-accelerating effect, but can not necessarily be said to be satisfactory when considering comprehensively the photographic performances such as sensitivity, gradation and maximum density.

On the other hand, in respect of light-sensitive silver halide emulsions having silver halide grains used in light-sensitive silver halide photographic materials, the shape, size and composition of a silver halide grain are known to greatly affect the developing speed, and various studies have been made. In particular, chloride-rich silver halide grains are known to exhibit a very high development performance under certain particular conditions, and it is more advantageous with less defects to use chloride-rich silver halide grains than to use the above development accelerator. For this reason, various studies have been made on the chloride-rich silver halide emulsions in order to achieve a shortened developing time.

However, although the chloride-rich silver halide emulsions have remarkably speedy developing performance as compared with silver bromide emulsions or silver iodobromide emulsions, they have low sensitivity and tend to be fogged, disadvantageously, thereby raising a great problem in putting them into practical use.

For the purpose of eliminating the above disadvantages, a great number of methods have been proposed. For example, Japanese Patent O.P.I. Publication

No. 135832/1980 and British Patent No. 1,495,753 disclose a method in which a metal ion is combined with chloride-rich silver halide grains; Japanese Patent O.P.I. Publications No. 95736/1983 and No. 222844/1985, No. 222845/1985 disclose a method in which a laminated chloride-rich silver halide emulsion provided with a layer chiefly comprising silver bromide is used; Japanese Patent O.P.I. Publications No. 95340/1983 and No. 107531/1983 disclose a method in which a chloride-rich silver halide emulsion is combined with a sensitizing dye.

These methods, however, are not necessarily satisfactory because of insufficient effects to be obtained or adverse influence to other photographic performances.

In particular, the chloride-rich silver halide emulsions have a disadvantage of poorer pressure resistance as compared with other silver bromide emulsions or silver iodobromide emulsions.

The pressure characteristics of silver halide grains will be mentioned below:

In general, various type of pressure is applied to light-sensitive materials. Great pressure is applied when light-sensitive materials are produced, for example, the light-sensitive materials are in the step for cutting.

Also, in using light-sensitive materials, particularly those in the form of a sheet, they are manually handled to be often folded, whereby pressure is applied to the folded portion.

On the other hand, in recent years, it has become popular to carry out automatic exposure in a printer or automatic processing using an automatic processor. Accordingly, there are increasing instances that mechanical pressure is applied to the light-sensitive materials in these apparatus. Once various type of pressure is applied to light-sensitive materials in this manner, the pressure is also applied to the silver halide grains in the light-sensitive materials through gelatin which is a binder for the silver halide grains. Once the pressure is applied to silver halide grains, changes are brought about in photographic performances to cause phenomena such as pressure desensitization and pressure marks. These phenomena are conventionally well known as photographic pressure effects, and reported, for example, in The Theory of the Photographic Process, 4th Ed. Macmillan Publishing Co. Inc., New York, 4th paragraph, D. Dautrich, F. Granzer and E. Moisar; The Journal of Photographic Science, 21, 221 (1973); etc.

In the present technical field, it is also well known that the larger grain size and the higher sensitivity the silver halide grains have, the more sensible to the pressure they are to readily cause pressure marks.

Moreover, there are an instance where the pressure is applied to light-sensitive materials in a dry state, and a case where the pressure is applied in a wet state in the course of developing processing. Accordingly, effects can not be said to be sufficient unless the pressure resistance is improved in both of the states.

Therefore, attempts have been hitherto made to provide light-sensitive materials having less influence to the pressure.

As a means for improving the pressure characteristic, known are a method in which a plasticizer such as polymer is contained; a method in which the ratio of silver halide to gelatin is made smaller; etc.

For example, British Patent No. 738,618 discloses a method in which an alkylphthalate is used; British Patent No. 738,639, a method in which an alkyl ester is used; U.S. Patent No. 2,960,404, a method in which a polyhydric alcohol is used; U.S. Patent No. 3,121,060, a method in which a carboxyalkyl cellulose is used; Japanese Patent O.P.I. Publication No. 5017/1974, a method in which paraffin and a carbonate are used; and Japanese Patent Examined Publication No. 28086/1978, a method in which an alkyl acrylate and an organic acid are used.

These techniques, however, have disadvantages that the pressure resistance effect is insufficient for both the dry state and the wet state, and moreover the binder characteristics such as stickiness or drying characteristic of the surface of light-sensitive materials are greatly deteriorated.

As another means for improving the pressure characteristic of silver halide grains, Japanese Patent Examined Publication No. 23248/1982 discloses a method in which a mercapto compound and a water soluble iridium compound are added at the time of forming silver halide grains, and U.S. Patent No. 3,622,318 discloses a method in which a surface-sensitized modified emulsion is used.

These techniques, however, can not afford to achieve satisfactory effects for both the dry state and the wet state.

Moreover, in these techniques, the pressure resistance effect is lowered as the high sensitivity or the grain size of silver halide grains increase.

Accordingly, any of the conventional techniques can achieve only insufficient effects for improving the pressure characteristic in both the dry state and wet state, and further improvement has been sought after.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a light-sensitive silver halide photographic material having excellent pressure resistance in both the dry state and the wet state, and suitable for rapid processing. Other objects of the present invention will be made apparent from the following descriptions.

The above objects of the present invention were able to be achieved, in a light-sensitive silver halide photographic material having at least one light-sensitive silver halide emulsion layer on a support, by providing a light-sensitive silver halide photographic material characterized in that said at least one silver halide emulsion layer contains 10^{-8} to 10^{-5} mole of a metal ion per mole of silver halide, and a silver chloride-rich grain having silver chloride content of 80 to 99 mole % and having a silver bromide-rich phase.

DETAILED DESCRIPTION OF THE INVENTION

In the light-sensitive silver halide photographic material of the present invention, the silver halide grain contained in at least one silver halide emulsion layer is a silver halide grain having silver chloride content of 80 mole % to 99 mole %, and having a silver chloride-rich phase constituting the greater part of a grain and a silver bromide-rich phase locally present in the inside or the surface of said grain.

The "locally present" herein mentioned means that the above silver halide grain, when analyzed by X-ray diffraction, show a diffraction pattern in which a peak assigned to the above silver bromide-rich phase can be clearly distinguished from a peak assigned to the silver chloride-rich phase other than the above silver bromide-rich phase.

The silver bromide-rich phase preferably have the silver bromide composition of 70 mole % or more, and more preferably 90 mole % or more. Also, the proportion of the silver bromide-rich phase held in one silver halide grain is preferably 0.5 to 20 mole %, more preferably 1 to 10 mole %.

The silver halide grain having the above silver bromide-rich phase as a localized phase may be of the laminated structure comprising the above silver bromide-rich phase and the above silver chloride-rich phase, or a grain in which the silver bromide-rich phase has been epitaxially grown on the crystal surface of the grain after the formation of silver halide grain comprising the silver chloride-rich phase and in such a form that the crystal surface is not entirely covered.

It is further preferred that almost all of the bromide-rich phase is contained in the outermost shell portion of a grain.

The above silver bromide-rich phase may comprise two or more localized phases in one silver halide grain. The composition may also be discontinuously varied, or continuously varied, at the boundary between the silver bromide-rich phase and the silver chloride-rich phase.

The silver halide grain of the present invention having the localized silver bromide-rich phase (hereinafter called "silver halide grain of the present invention) may be used alone or as a mix with other silver halide grains.

In the case where the silver halide grain of the present invention is used as a mix with silver halide grains outside the present invention, the ratio of the projected area held by the silver halide grain of the present invention to the projected area held by all the silver halide grains in a silver halide emulsion layer containing the silver halide grain of the present invention is preferably 50 % or more, and more preferably 75 % or more.

Such a silver halide grain can be formed following, for example, the procedures disclosed in Japanese Patent O.P.I. Publications No. 162540/1984, No. 48755/1984, No. 222844/1985, No. 222845/1985, No. 136735/1985, etc.

The silver halide grain of the present invention may have any shape. One of preferable examples thereof is a cube having { 100} face as a crystal surface. There can be also used grains having crystal forms such as an octahedron, a tetradecahedron and a dodecahedron which can be prepared according to the procedures disclosed in the specifications of U.S. Patents No. 4,183,756, No. 4,225,666, Japanese Patent O.P.I. Publication No. 26589/1980 and Japanese Patent Examined Publication No. 42737/1980, and papers such as The Journal of Photographic Science, 21, 39 (1973). Grains having a twin crystal face may be also used.

The silver halide grain of the present invention may be grains comprising a grain of a single shape, or may be grains comprising mixture of grains having various shapes.

There is no particular limitation in the grains size of the silver halide grain of the present invention, but, taking account of other photographic performances such as rapid processability and sensitivity, the grain size is preferably in the range of 0.1 to 1.6 µm, more preferably 0.25 to 1.2 µm. The above grain size can be measured according to a variety of methods generally used in the present technical field. Typical methods are disclosed in Loveland, "Method of Analysis of Grain Size", A.S.T.M. Symposium on Light Microscopy, 1955, pp.94-122, or "The

Theory of the Photographic Process" written by Meath and James, Macmillan Publishing Co. Inc. (1966), Chapter II.

This grain size can be measured by using a projected area of a grain, or a diametrical approximate value thereof. When grains are in substantially the uniform shape, grain size distribution can be expressed as the diameter or projection area in a considerably precise manner.

In the silver halide grains of the present invention, the grain size distribution may be polydisperse or monodisperse. Preferred are monodisperse silver halide grains having a variation coefficient of 0.22 or less, more preferably 0.15 or less, of the grain size distribution of silver halide grains. Here, the variation coefficient is a coefficient showing the width of grain size distribution, and can be defined by the following formula:

$$\text{Variation coefficient } (S/\bar{r}) = \frac{\text{Standard Deviation of grain size distribution}}{\text{Average grain size}}$$

$$\text{Standard deviation of grain size distribution } (S) = \sqrt{\frac{\Sigma(\bar{r}-ri)^2 ni}{\Sigma ni}}$$

$$\text{Average grain size } (\bar{r}) = \frac{\Sigma niri}{\Sigma ni}$$

Here, ri represents the grain size of each grain, and ni represents the number thereof. The grain size herein mentioned refers to its diameter in the case of silver halide grains having a spherical shape, or, in the case of grains having a cubic shape or a shape other than the spherical shape, the diameter determined by calculating the projected area thereof as a round image having the corresponding area.

To the silver halide grain of the present invention, a metal ion is further added in amount of 10^{-8} to 10^{-5} mole per mole of silver halide.

There is no particular limitation in the metal ion used in the present invention, but may be preferably used cadmium, lead, copper, zinc, rhodium, palladium, iridium, platinum, thallium, iron, etc. These metal ions may be preferably used in the form of a metal salt or a metal complex salt.

The amount to be added may range from 10^{-8} to 10^{-5} mole per mole of silver halide as mentioned above, and optimum amount may be suitably selected within this range depending on the size, or crystal habit, of silver halide grains, and also the combination with sensitizing dyes and other additives. Generally speaking, the amount less than 10^{-8} can not be useful for sufficiently exhibiting the effect of the present invention, and the amount more than

10^{-5} may sometimes result in such an adverse influence to other photographic performances as desensitization.

The above metal ions used in the present invention may be used at any stage of the nucleus formation, grain growth and physical ripening of the silver halide grain of the present invention, or may be added in a divided manner. These metal ions are used in the form of a metal salt or a metal complex salt, but these compounds are added by dissolving them in water or other suitable solvents.

Of the metal ions used in the present invention, preferred is iridium, and specific compound thereof may include iridium trichloride, iridium tetrachloride, potassium hexachloroiridate (III), potassium hexachloroiridate (IV), ammonium hexachloroiridate (III), etc.

In the present invention, it was surprising that not only the pressure resistance in the dry state but also the pressure resistance in the wet state as in developing processing can be improved by using the silver halide emulsion containing 10^{-8} to 10^{-5} mole of the metal ion per mole of silver halide, and the silver chloride-rich grain having silver chloride content of 80 to 99 mole % and having the silver bromide-rich phase.

The silver halide grains of the present invention may be obtained by any of an acidic method, a neutral method and an ammoniacal method. The grains may be allowed to grow in one time or to grow after seed grains have been formed. The method for the formation of the seed grains and the method for the growth may be the same or different.

The manner of reacting a soluble silver salt and a soluble halogen salt may be any of an ordinary mixing method, a reversed mixing method, a simultaneous mixing method and a combination of any of these, but preferred are grains obtained by the simultaneous mixing method. As a manner of the simultaneous mixing method, there can be also used the pAg controlled double jet method as disclosed in Japanese Patent O.P.I. Publication No. 48521/1979, etc.

If necessary, there may be further used silver halide solvents such as thioether, or crystal habit-controlling agents such as compounds having the silver ion solubility product of 1 x 10^{-10} or less and sensitizing dyes.

Of the compounds having the silver iron solubility product of 1 x 10^{-10} or less, most preferred are nitrogen-containing heterocyclic compounds having the above characteristic value.

Such compounds are disclosed in detail in E.J. Birr, Stabilization of Photographic Silver Halide Emulsions, 1st Ed. Focul Co., 1974.

The useful sensitizing dyes that can be used in the present invention may include, for example, those disclosed in West German Patent No. 929,080, U.S. Patents No. 2,231,658, No. 2,493,748, No. 2,503,776, No. 2,519,001, No. 2,912,329, No. 3,656,959, No. 3,672,897, No. 3,694,217, 4,025,349, and No. 4,046,572, British Patent No. 1,242,588, Japanese Patent Examined Publication No. 14030/1969 and No. 24844/1977, etc. Typical examples of the useful sensitizing dyes may include cyanine dyes, merocyanine dyes or composite cyanine dyes as disclosed, for example, in U.S. Patents No. 1,939,201, No. 2,072,908, No. 2,739,149 and No. 2,945,763, British Patent No. 505,979, etc. Other typical examples of the useful sensitizing dyes may include cyanine dyes, merocyanine dyes or composite cyanine dyes as disclosed, for example, in U.S. Patents No. 2,269,234, No. 2,270,378, No. 2,442,710, No. 2,454,629 and No.2,776,280, etc. Also, there can be advantageously used cyanine dyes, merocyaninedyes or composite cyanine dyes as disclosed, for example, in U.S. Patents No. 2,213,995, No. 2,493,748 and No. 2,519,001, West German Patent No. 929,080, etc.

The above nitrogen-containing heterocyclic compounds and sensitizing dyes may be dissolved in solvents of the same or different kinds, and these solvents may be mixed before the addition to a silver halide emulsion or may be added separately. When they are added separately, the order, time and interval can be determined arbitrarily depending on the purpose. The time at which the nitrogen-containing heterocyclic compounds and sensitizing dyes used in the present invention are added to the emulsion is particularly preferably such that they are added so as to be contained in the inside of the silver bromide-rich silver halide phase in the above outermost shell portion. Specifically, they can be added at any time before a nucleus of a silver chloride-rich grain having a silver chloride content of 80 to 99 mole % is formed and until the silver bromide-rich silver halide phase is formed. or, alternatively, they may be added in a divided form. They may be preferably added at the time starting from the completion of the formation of the silver chloride-rich silver halide grain and ending with the formation of the silver bromide-rich silver halide phase, in other words, added to the surface of the silver chloride-rich silver halide phase.

The silver halide grains of the present invention may be grains such that a latent image is chiefly formed on the surface thereof, or grains such that the latent image is chiefly formed in the inside thereof.

However, in order to sufficiently achieve the effect of the present invention, it is preferred that the silver halide grains of the type in which the latent image is chiefly formed in the inside thereof are not used after silver halide grains have been formed, i.e., in the state where no chemical sensitization has been carried out, or after silver halide grains have been finally formed, in the case where the chemical sensitization is carried out in the course of the formation of silver halide grains. To judge whether or not a silver halide grain is of an internal latent image type, evaluations may be carried out following the method disclosed in Japanese Patent Examined Publication No. 34213/1977.

More specifically, the emulsion to be evaluated is applied on a polyethylene-coated support with a silver coating amount of 300 to 400 mg/ft^2. The specimen obtained is divided into two fractions, and each of them is set in a light-intensity scale and exposed for a fixed time of 1 x 10^{-2} to 1 second with use of a tungsten lamp of 500 W. One of the specimens is developed at 18.3°C for 5 minutes in Developing Solution Y (an "internal type" developing solution) shown below, and the other of them is developed at 20°C for 6 minutes in Developing Solution X (a "surface type" developing solution) shown below.

It is preferable in the present invention to use silver halide grains wherein [maximum density after internal development/maximum density after surface development] in that occasion is 5 or less, more preferably 2 or less.

Development Solution X

N-methyl-p-aminophenol sulfate	2.5 g
Ascorbic acid	10.0 g
Potassium methaborate	35.0 g
Potassium bromide	1.0 g

Made up to 1 liter by adding water.

(pH = 9.6)

Development Solution Y

N-methyl-p-aminophenol sulfate	2.0 g
Sodium sulfite (dry)	90.0 g
Hydroquinone	8.0 g
Sodium carbonate.$1H_2O$	52.5 g
Potassium bromide	5.0 g
Potassium iodide	0.5 g

Made up to 1 liter by adding water

(pH = 10.6)

The aforesaid silver halide emulsion containing the silver halide grain of the present invention and 10^{-8} to 10^{-5} mole of the above metal ion per mole of silver halide (hereinafter called silver halide emulsion of the present invention may be either one from which unnecessary soluble salts have been removed after completion of the growth of silver halide grains, or one from which they remain unremoved. When the salts are removed, they can be removed according to the method disclosed in Research Disclosure No. 17643.

The silver halide emulsion of the present invention may be chemically sensitized according to conventional methods. Namely, a sulfur sensitization method using a compound containing sulfur capable of reacting with silver ions, and active gelatin, a selenium sensitization method using a selenium compound, a reduction sensitization method using a reducing substance, and a noble metal sensitization method using noble metal compounds such as gold and so forth can be used alone or in combination.

As the sulfur sensitizer, known compounds can be used. For example, it may include thiosulfate, allythiocarbamide thiourea, allylisothiocyanate, cystine, p-toluenethiosulfonate, rhodanine, etc. Besides these, there can be also used sulfur sensitizers disclosed in U.S. Patents No. 1,574,944, No. 2,410,689, No. 2,278,947, No. 2,728,668, No. 3,501,313 and No. 3,656,955, German Patent No. 14 22 869, Japanese Patent O.P.I. Publications No. 24937/1981 and No. 45016/1980, etc. The sulfur sensitizers may be added in an amount that can effectively increase the sensitivity of an emulsion. This amount may vary in a considerably wide range depending on the various conditions such as the amount of nitrogen-containing heterocyclic compounds, pH, temperature and size of silver halide grains, but, as a standard, may be approximately 0.5 to 2.0 mg, preferably 0.7 to 1.5 mg, per mole of silver halide.

As the gold sensitizer, many kinds of gold compounds can be used, including any of those having the oxidation number of +1 or +3. Typical examples thereof may include chloroaurate, potassium chloroaurate, auric trichloride, potsassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate, pyridyltrichlorogold.

The amount of the gold sensitizer may vary dependingon the various conditions, but, as a standard, may be approximately 0.1 to 10 mg, preferably 1.5×10^{-1} to 4.0×10^{-1} mg, per mole of silver halide.

The silver halide grains according to the present invention may be preferably subjected to chemical sensitization in the presence of a nitrogen-containing heterocyclic compound which forms a complex compound with silver.

In the nitrogen-containing heterocyclic compound used in the present invention, the heterocyclic ring may include a pyrazole ring, a pyrimidine ring, a 1,2,4-

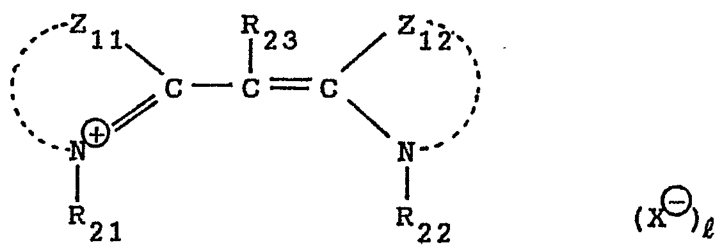
triazole ring, a 1,2,3-triazole ring, a 1,3,4-thiazole ring, 1,2,3-thiadiazole ring, a 1,2,4-thiadiazole ring, a 1,2,5-thiadiazole ring, a 1,2,3,4-tetrazole ring, a pyridazine ring, a 1,2,3-triazine ring, a 1,2,4-triazine ring, a 1,3,5-triazine ring, a ring comprising combination of two or three of these rings, for example, a triazolotriazole ring, a diazaindene ring, a triazaindene ring, a tetrazaindene ring, a pentazaindene ring, etc. There can be also used a heterocyclic ring formed by condensation of a heterocyclic ring comprising a single ring with an aromatic ring, for example, a phthaladine ring, a benzimidazole ring, an indazole ring, a benzothiazole ring, etc.

The silver halide emulsion of the present invention can be optically sensitized to a desired wavelength region by using a dye known as a sensitizing dye in the field of photography. The sensitizing dye may be used alone, or may be used in combination of two or more of the dye.

Together with the sensitizing dye, a dye having itself no action of spectral sensitization, or a supersensitizing agent which is a compound substantially absorbing no visible light and capable of strengthening the sensitizing action of the sensitizing dye, may be contained in the emulsion.

When the silver halide emulsion of the present invention is used as a blue-sensitive emulsion, it is preferable to carry out spectral sensitization with use of any of sensitizing dyes represented by General Formula (A) shown below.

General Formula (A)

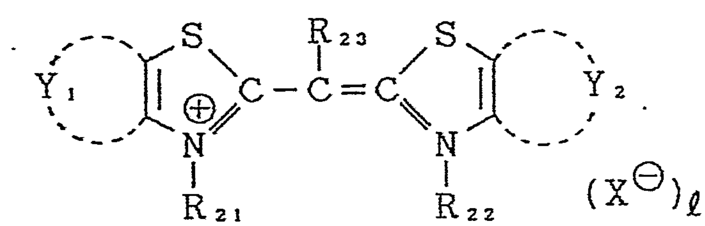


In General Formula (A), Z_{11} and Z_{12} each represent a group of atoms necessary for the formation of a benzoxazole nucleus, a naphthoxazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzimidazole nucleus, a naphthoimidazole nucleus, a pyridine nucleus or a quinoline nucleus, and these heterocyclic rings may include those having a substituent. The substituent of the hetero rings formed by Z_{11} and Z_{12} may include a halogen atom, a hydroxyl group, a cyano group, an aryl group, an alkyl group, an alkoxycarbonyl group, etc., and preferable substituent among these substituents is a halogen atom, a cyano group, an aryl group, or an alkyl group or alkoxy group having 1 to 6 carbon atoms. Particularly preferable substituent includes a halogen atom, a cyano group, a methyl group, an ethyl group, a methoxy group or an ethoxy group.

R_{21} and R_{22} each represent an alkyl group, an alkenyl group or an aryl group; preferably represent an alkyl group; more preferably represent an alkyl group substituted with a carboxyl group or a sulfo group; and most preferably represent a sulfoalkyl group having 1 to 4 carbon atoms. R_{23} is selected from a hydrogen atom, a methyl group and an ethyl group. $X^{\ominus}$ represents an anion; and ℓ represents 0 or 1.

Of the sensitizing dyes represented by General Formula (A), particularly useful dyes are sensitizing dyes represented by General Formula (A') shown below:

General Formula (A')

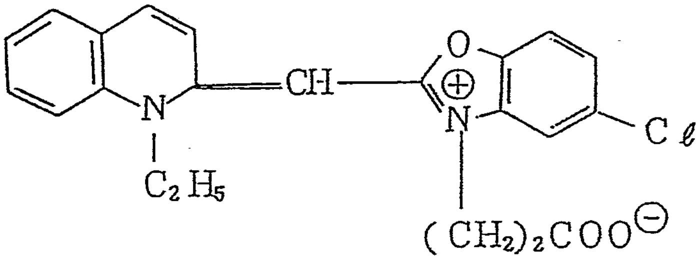


Here, Y_1 and Y_2 each represent a group of atoms necessary for the completion of a benzene ring or naphthalene ring which may have a substituent. The benzene ring and the naphthalene ring formed by Y_1 and Y_2 may include those having a substituent, which substituent may preferably include a halogen atom, a hydroxyl group, a cyano group, an aryl group, an alkyl group, an alkoxy group and an alkoxycarbonyl group. More preferable substituent may include a halogen atom, a cyano group, an aryl group and an alkyl group or alkoxy group having 1 to 6 carbon atoms, and particularly preferable substituent may include a halogen atom, a cyano group, a methyl group, an ethyl group, a methoxy group and an ethoxy group.

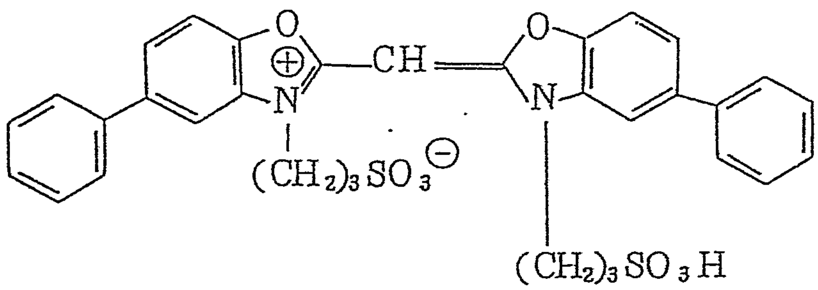
R_{21}, R_{22}, R_{23}, $X^{\ominus}$ and ℓ have the same meaning as those shown in General Formula (A).

Specific examples of the sensitizing dyes represented by General Formula (A) are shown below.

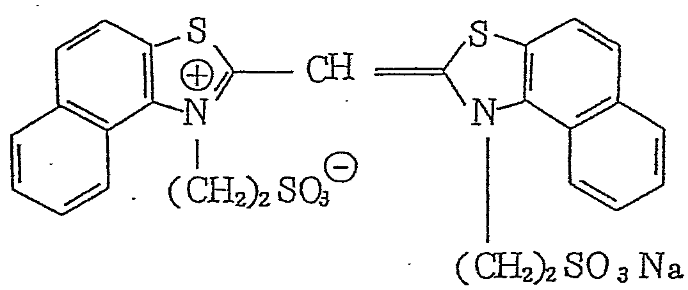
A - 1



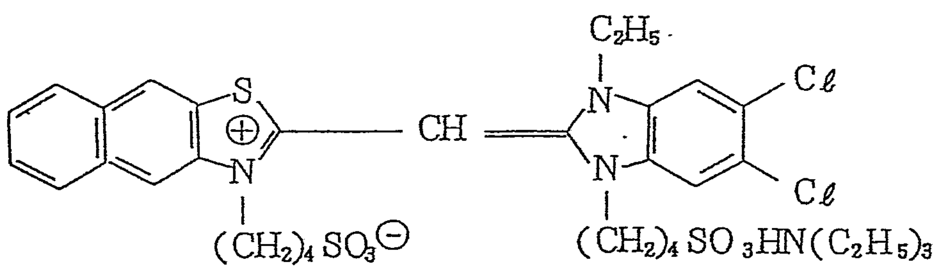
A - 2



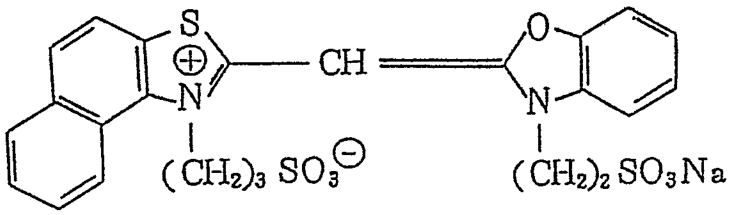
A - 3



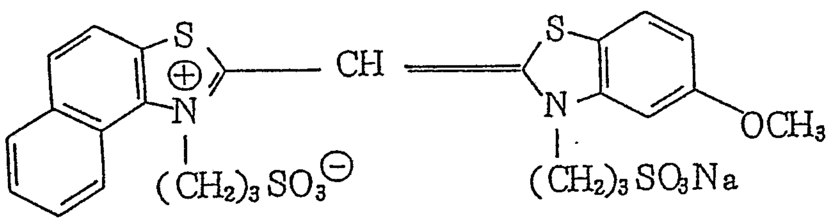
A - 4



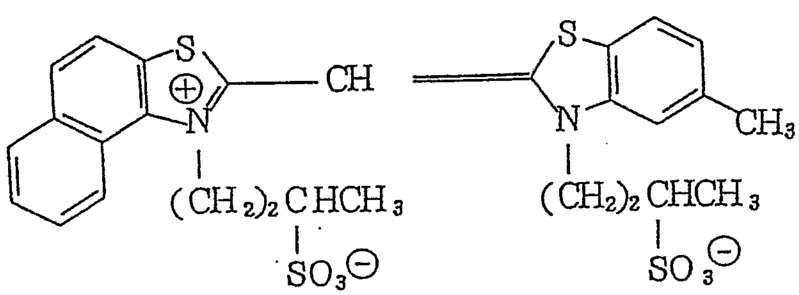
A - 5



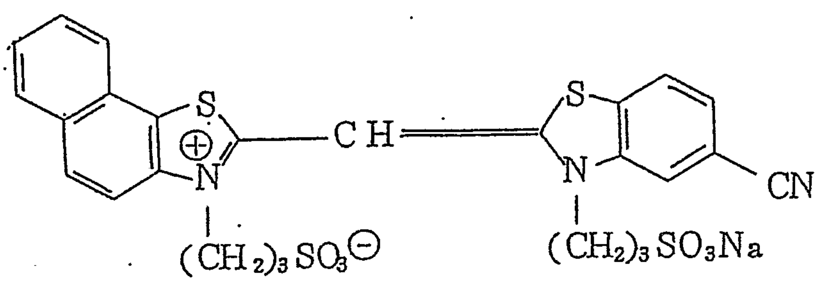
A - 6



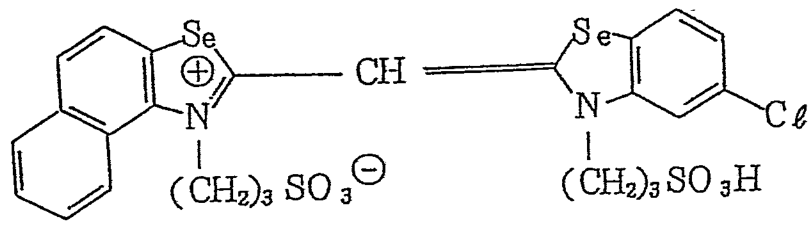
A - 7



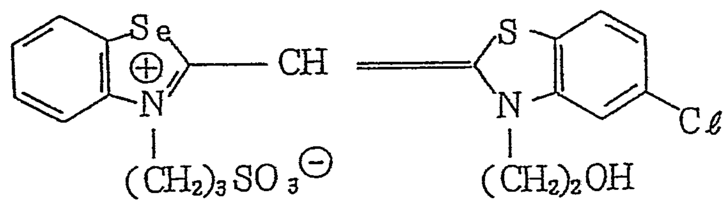
A - 8



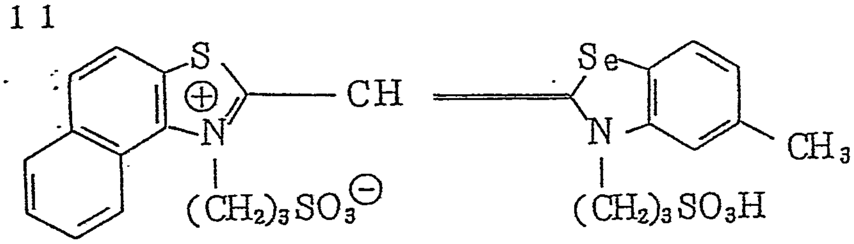
A - 9



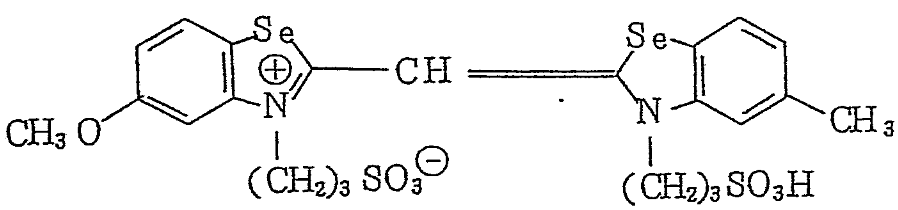
A - 10



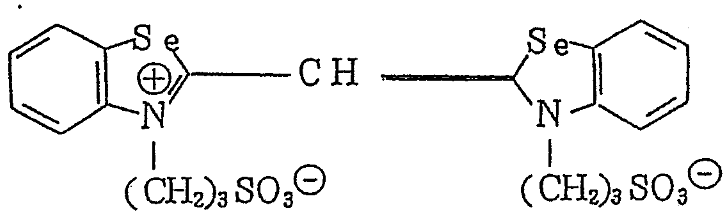
A - 11



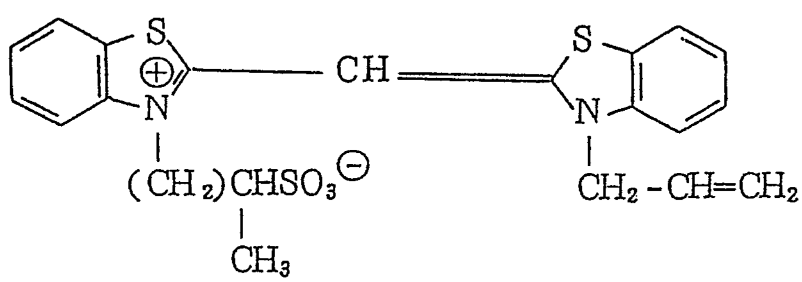
A - 12



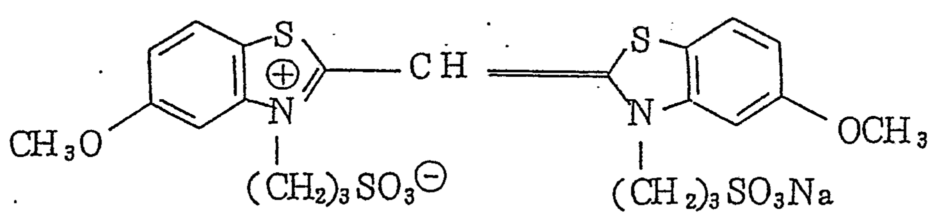
A - 1 3



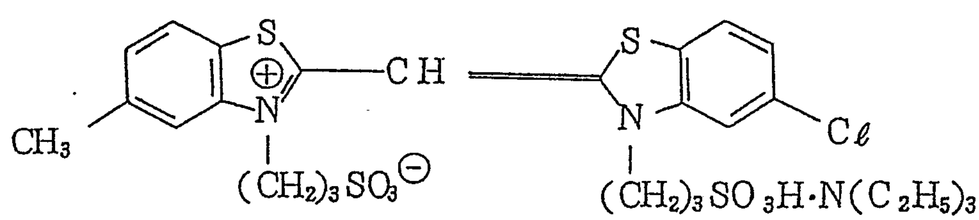
A - 1 4



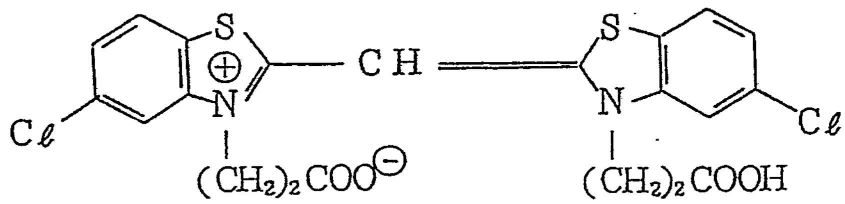
A - 1 5



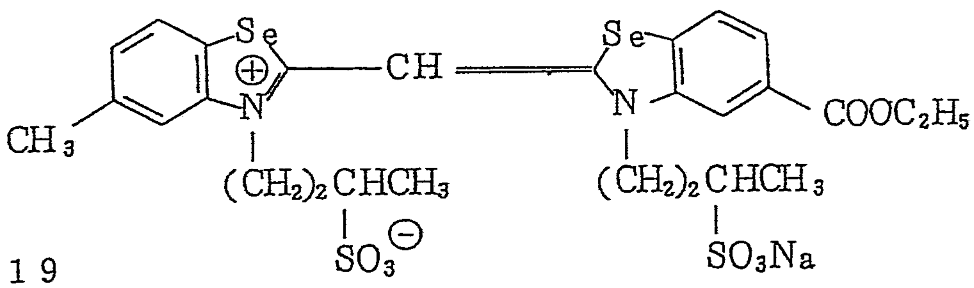
A - 1 6



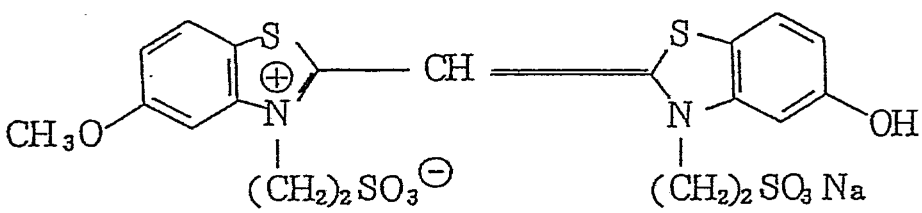
A - 1 7



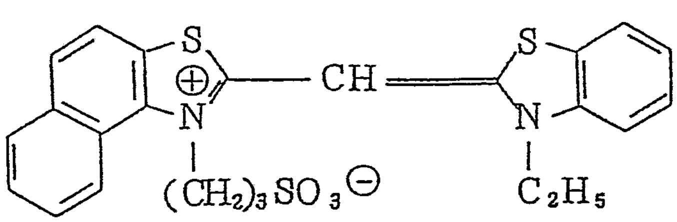
A - 1 8



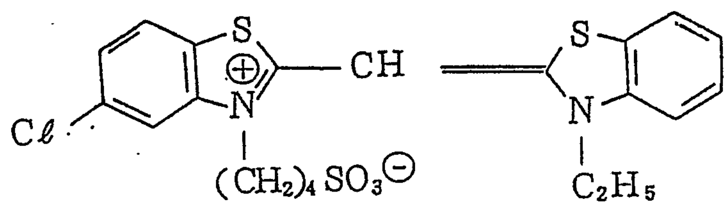
A - 1 9



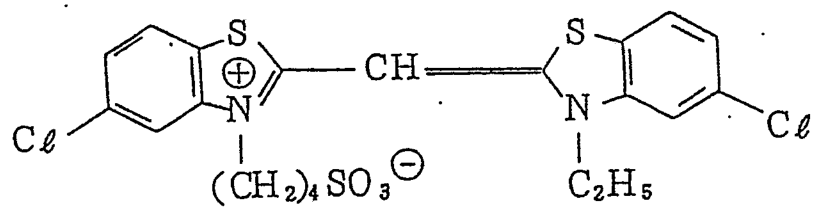
A - 2 0



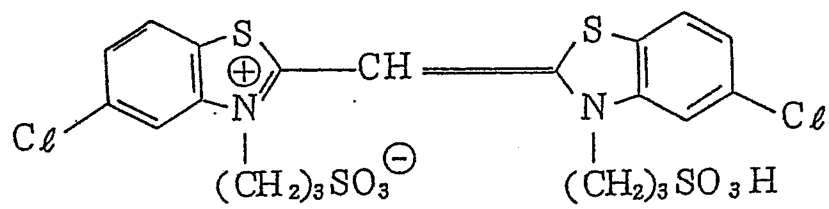
A - 2 1



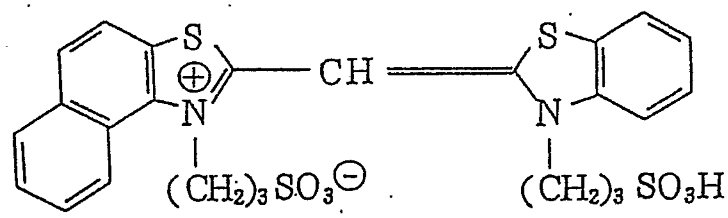
A - 2 2



A - 2 3

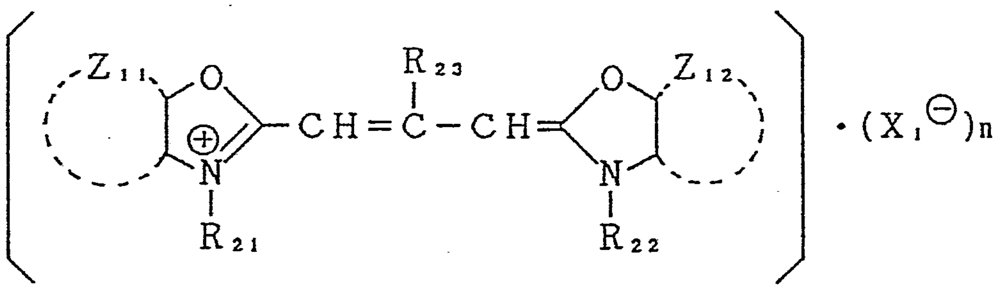


A - 2 4



When the silver halide emulsion of the present invention is used as a green-sensitive emulsion, it is preferable to carry out spectral sensitization with use of any of sensitizing dyes represented by General Formula (B) shown below.

General Formula (B)

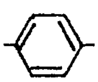


In the formula, Z_{11} and Z_{12} each represent a group of atoms necessary for the formation of a benzene ring or naphthalene ring condensed to oxazoles. The heterocyclic nucleus to be formed may be substituted with a variety of substituents, which substituents may preferably include a halogen atom, an aryl group, an alkyl group and an alkoxy group. More preferable substituents may include a halogen atom, a phenyl group and a methoxy group, and most preferable substituents may include a phenyl group.

According to a preferred embodiment of the present invention, Z_{11} and Z_{12} both represent benzene rings each condensed to an oxazole ring, and at least one of these benzene rings is substituted with a phenyl group at the 5-position thereof, or one of the benzene rings is substituted with a phenyl group at the 5-position thereof and the other benzene ring is substituted with a halogen atom at the 5-position thereof.

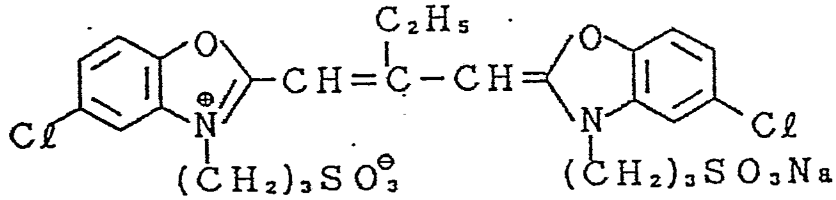
R_{21} and R_{22} each represent an alkyl group, an alkenyl group or an aryl group, and preferably represent an alkyl group. More preferably, R_{21} and R_{22} each represent an alkyl group substituted with a carboxyl group or a sulfo group, most preferably a sulfoalkyl group having 1 to 4 carbon atoms, and further most preferably a sulfoethyl group.

R_{23} represents a hydrogen atom or an alkyl group having 1 to 3 carbon atoms, and preferably represents a hydrogen atom or an ethyl group.

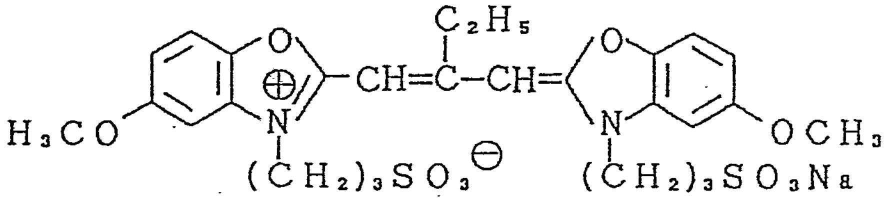
$X_1^{\ominus}$ represents an anion, including, for example, anions such as halide ions of chlorine, bromine or iodine, CH_3--SO_3, CH_3SO_4 and $C_2H_5SO_4$. Symbol n represents 1 or 0, provided, however, that n represents 0 when the compound forms a intramolecular salt.

Specific examples of the sensitizing dyes represented by General Formula (B) preferably used in the present invention are shown below:

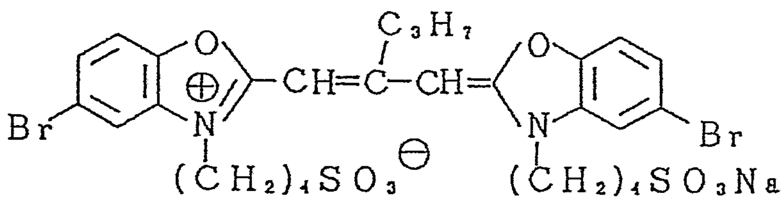
[B –1]



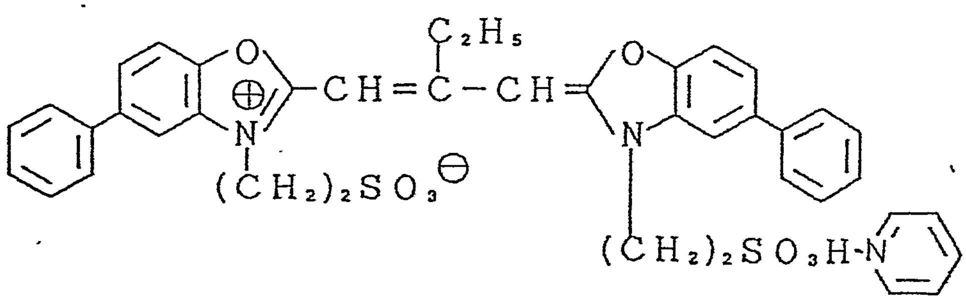
[B –2]



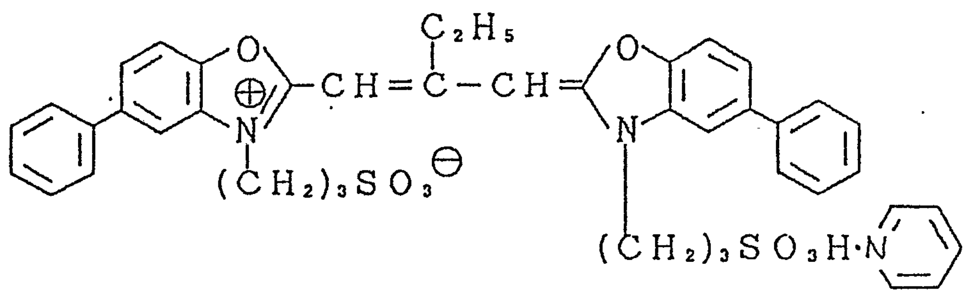
[B –3]



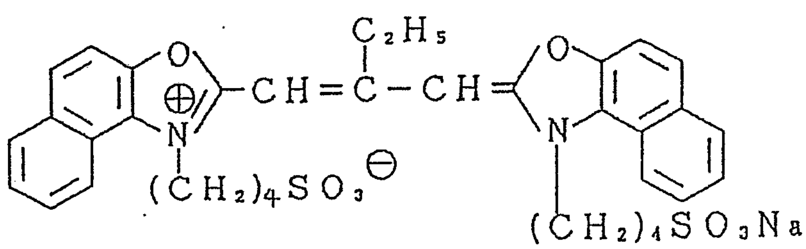
[B –4]



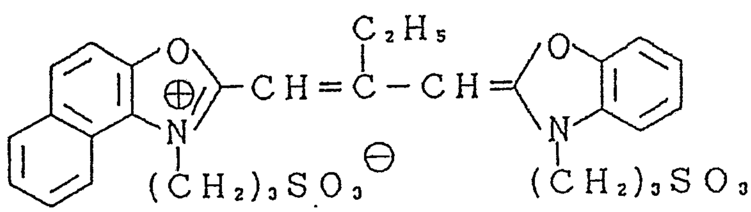
[B -5]



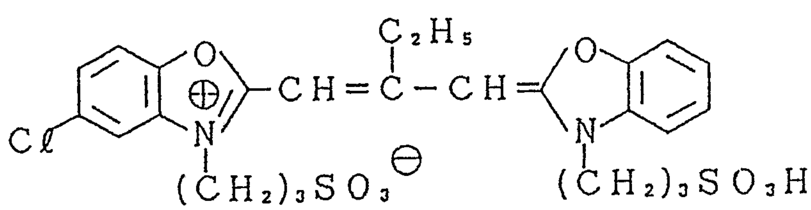
[B -6]



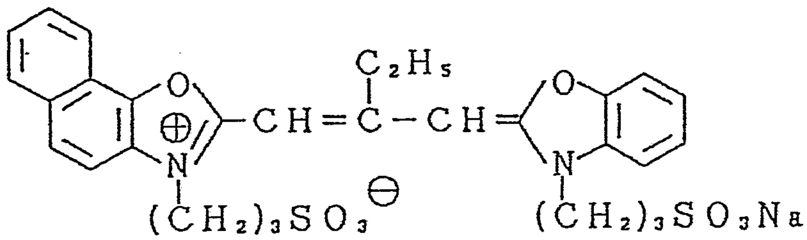
[B -7]



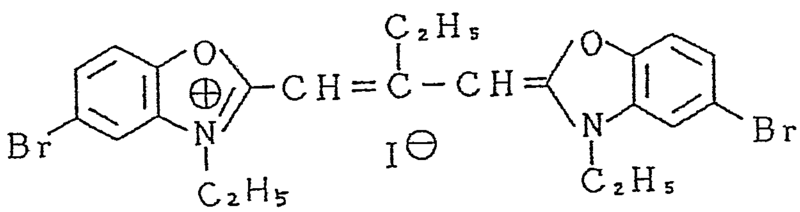
[B -8]



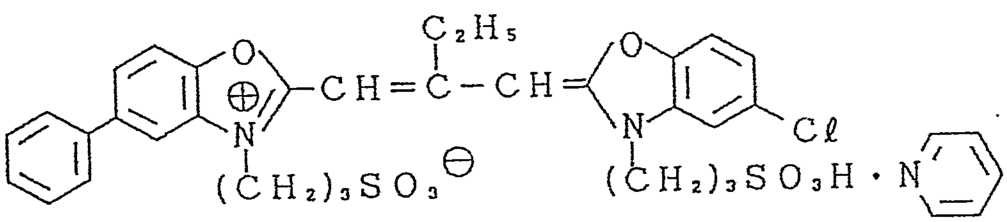
[B -9]



[B.-1 0]

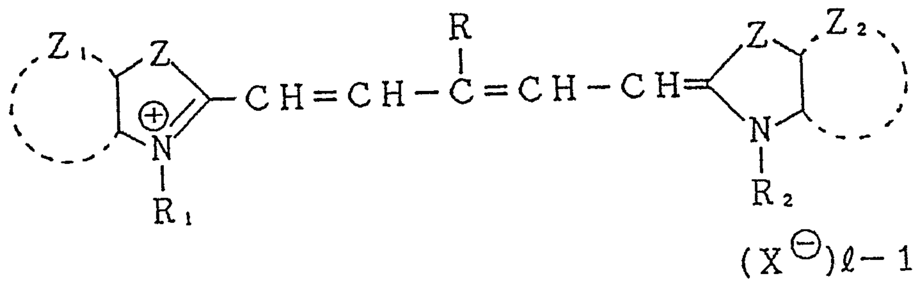


[B.-1 1]

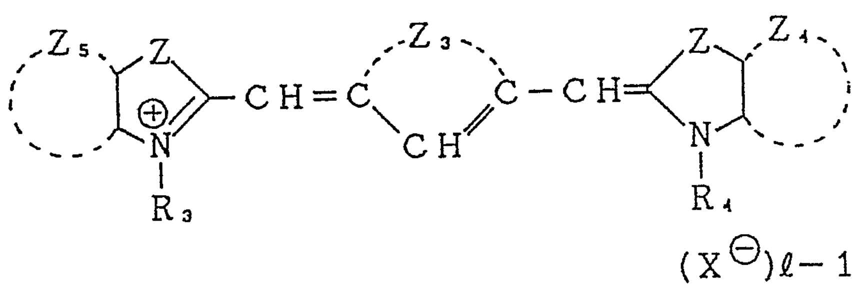


When the silver halide emulsion of the present invention is used as a red-sensitive emulsion, it is preferable to carry out spectral sensitization with use of any of sensitizing dyes represented by General Formula (C) or sensitizing dyes represented by General Formula (D) shown below.

General Formula (C)



General Formula (D)

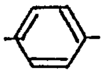


In the formulas, R represents a hydrogen atom or an alkyl group, R_1 to R_4 each represent an alkyl group or an aryl group; Z_1, Z_2, Z_4 and Z_5 each represent a group of atoms necessary for the formation of a benzene ring or naphthalene ring condensed to a thiazole ring or selenazole ring; Z_3 represents a group of hydrocarbon atoms necessary for the formation of a 6-membered ring; ℓ represents 1 or 2; Z represents a sulfur atom or a selenium atom; and $X^{\ominus}$ represents an anion.

In the above general formulas, the alkyl group represented by R may include a methyl group, an ethyl group and a propyl group, and R is preferably a hydrogen atom, a methyl group or an ethyl group. Particularly preferably, it is a hydrogen atom or an ethyl group.

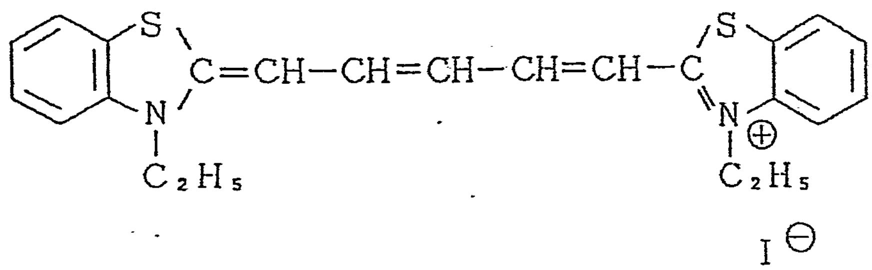
R_1, R_2, R_3 and R_4 each represent a group selected from a straight chain or branched alkyl group, which alkyl group may have a substituent (including, for example, methyl, ethyl, propyl, chloroethyl, hydroxyethyl, methoxyethyl, acetoxyethyl, caboxymethyl, carobxyethyl, ethoxycarbonylmethyl, sulfoethyl, sulfopropyl, sulfobutyl, β-hydroxy-γ-sulfopropyl, sulfate propyl, aryl, benzyl, etc.), and an aryl group, which aryl group may have a substituent (including, for example, phenyl, carboxyphenyl, sulfophenyl, etc.); and the heterocyclic nucleus to be formed by Z_1, Z_2, Z_4 and Z_5 may have a substituent, which substituent may preferably include a halogen atom, an aryl group, an alkyl group and an alkoxy group; more preferably, a halogen atom (for example, a chlorine atom), a phenyl group and a methoxy group.

X represents an anion (for example Cl, Br, I,

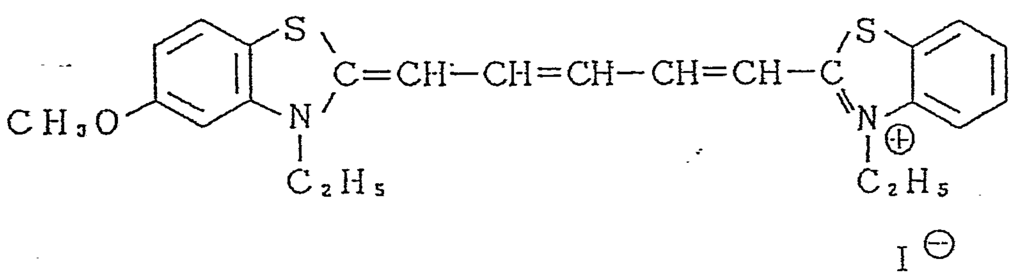
CH_3--SO_3, CH_3SO_4 and $C_2H_5SO_4$); and ℓ represents 1 or 2, provided, however, that ℓ represents 1 when the compound forms an intramolecular salt.

Typical examples of the sensitizing dyes represented by General Formula (C) or (D) preferably used in the present invention are shown below:

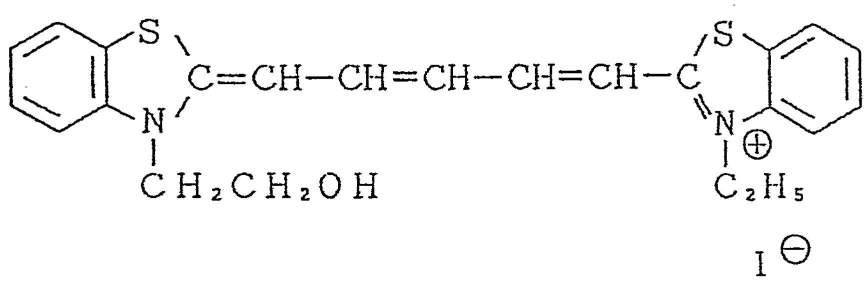
C – 1



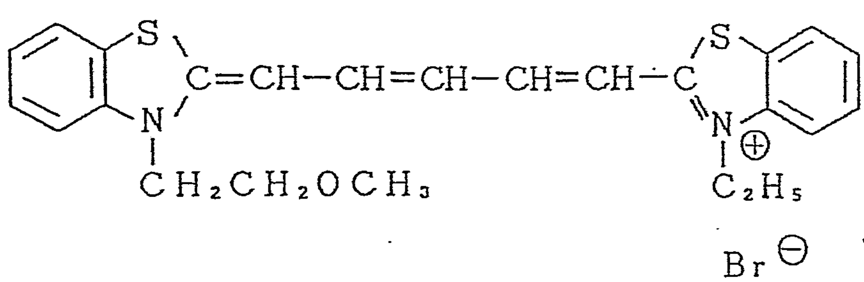
C – 2



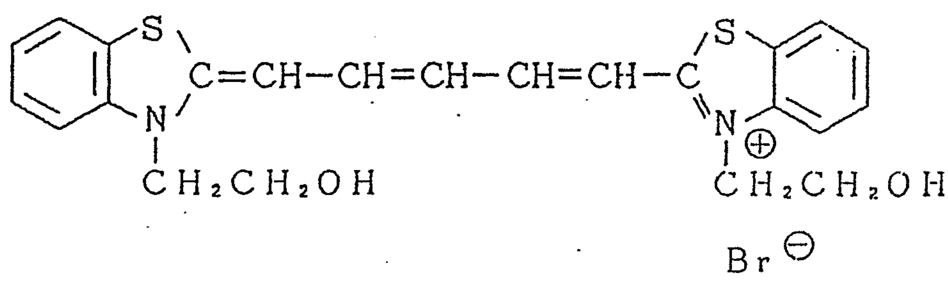
C – 3



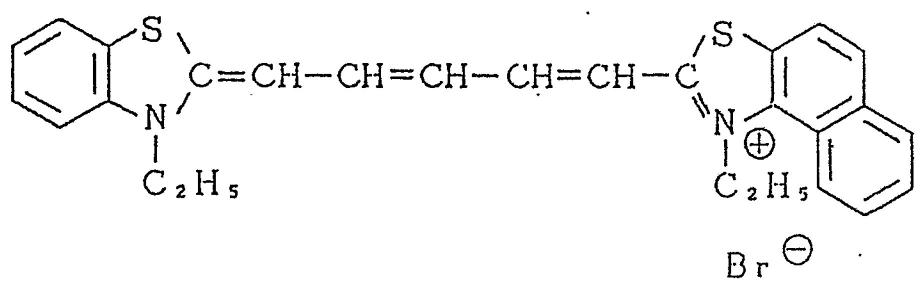
C – 4



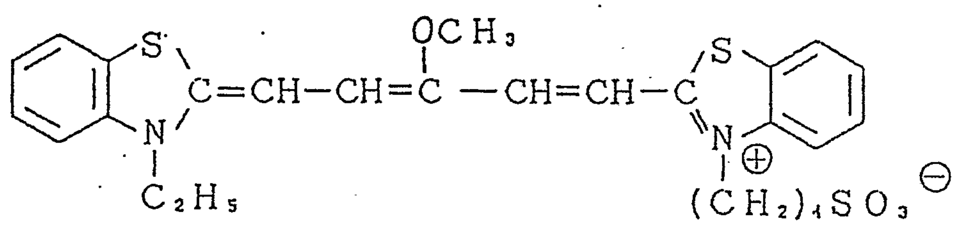
C-5



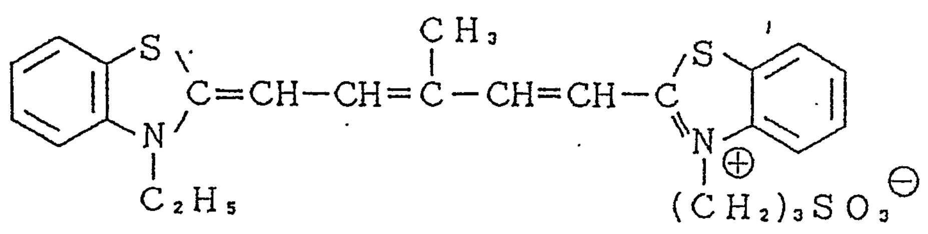
C-6



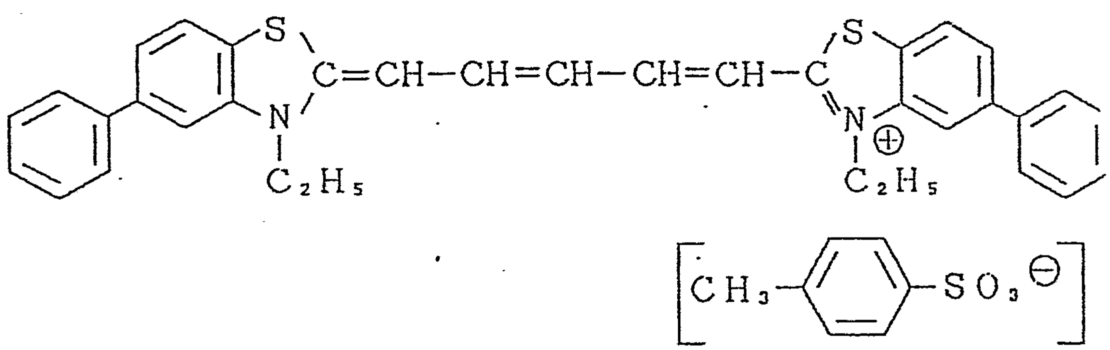
C-7



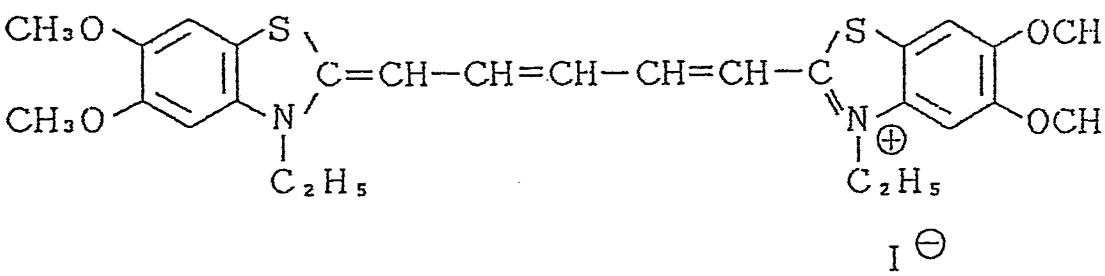
C-8



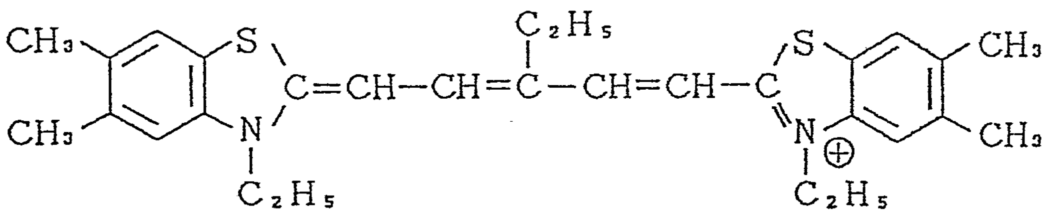
C - 9



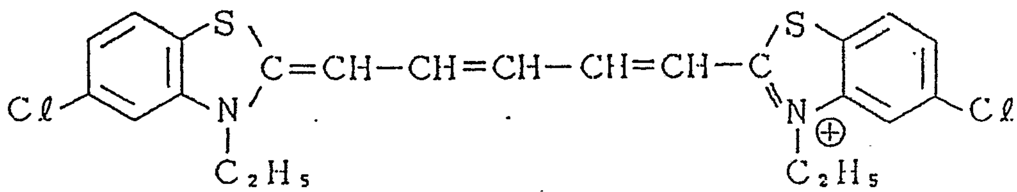
C - 1 0



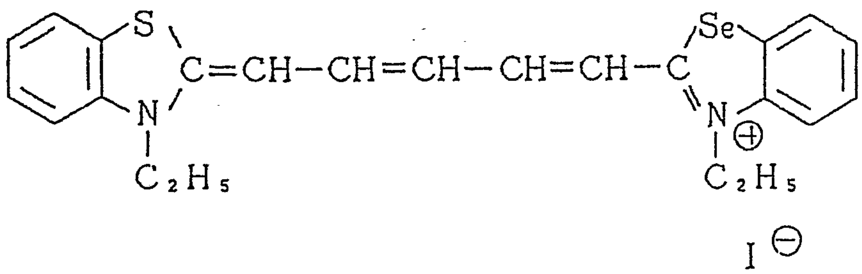
C - 1 1



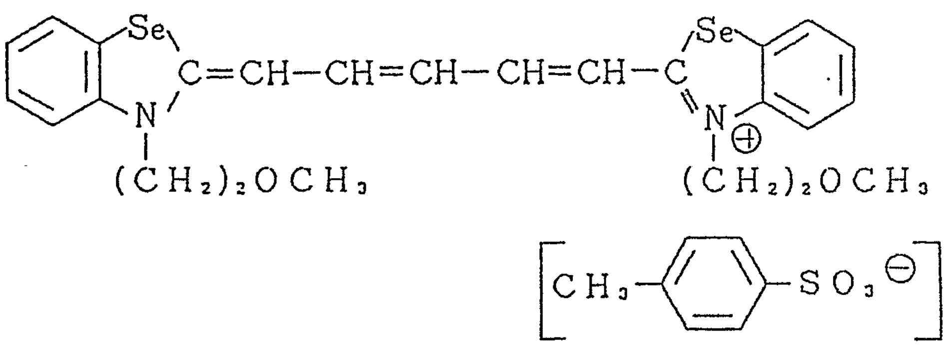
C－１２



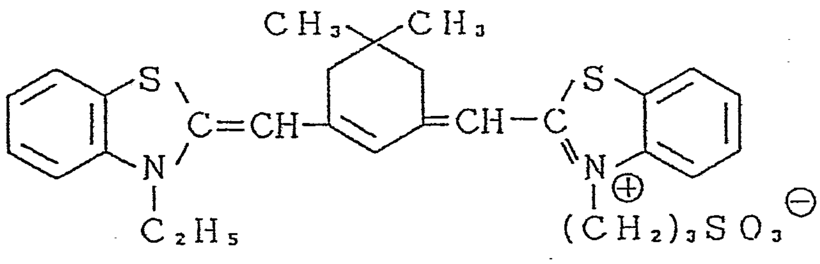
C－１３



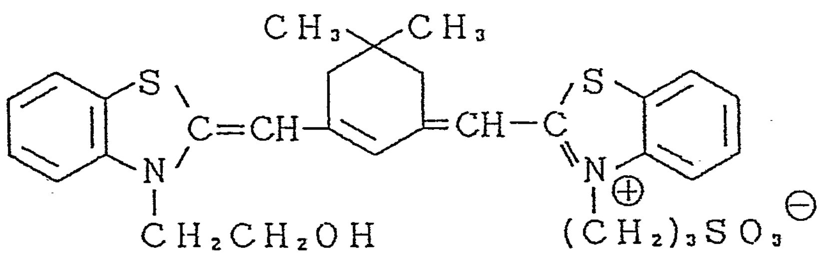
C－１４



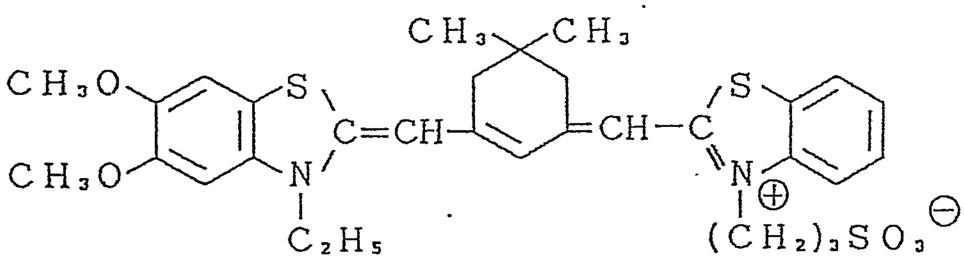
D－1



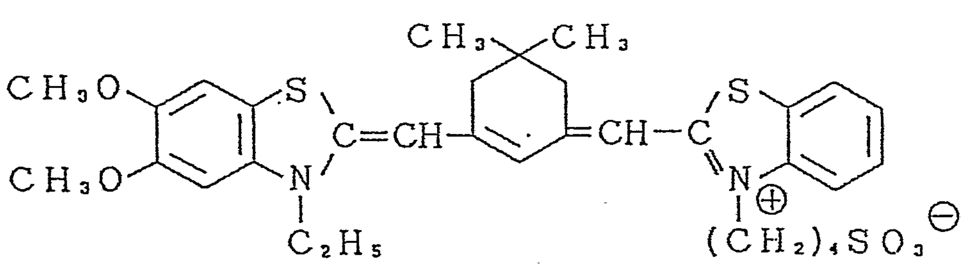
D－2



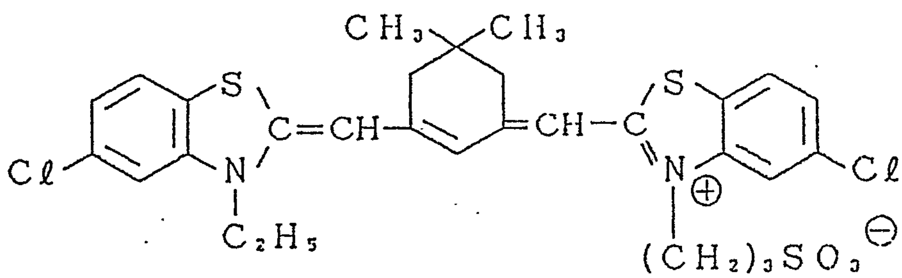
D－3



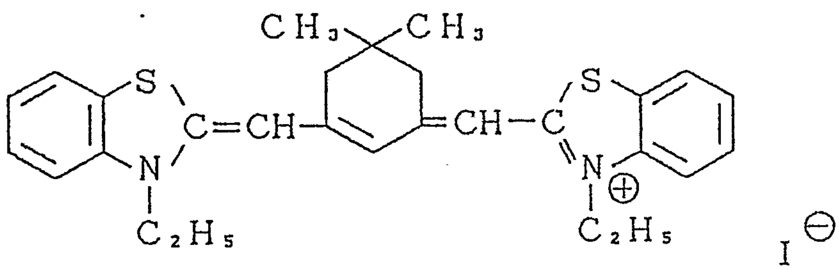
D－4



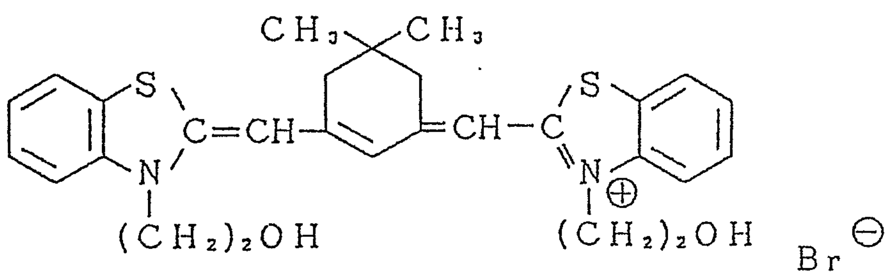
D- 5



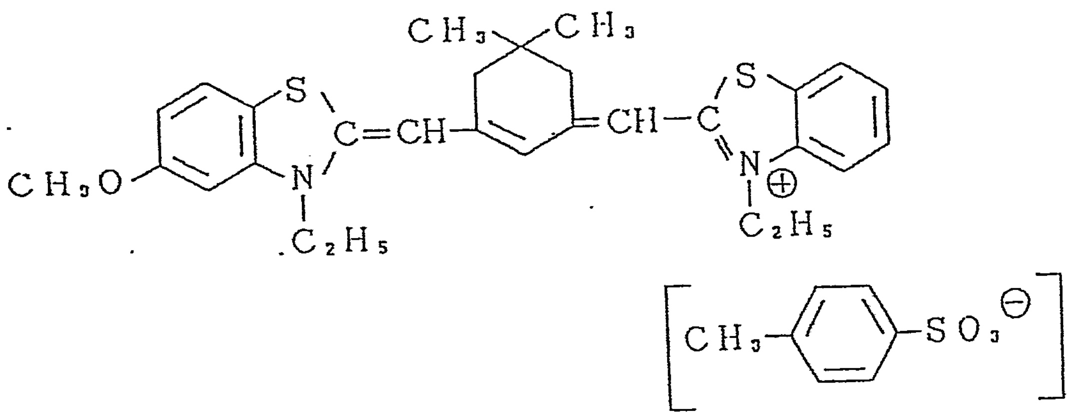
D- 6



D- 7



D – 8



There is no particular limitation in the amount of adding the sensitizing dyes represented by the above General Formula (A), (B), (C) or (D), but they are preferably used in the range of approximately 1×10^{-7} to 1×10^{-3} mole, more preferably 5×10^{-6} to 5×10^{-4} mole, per mole of silver halide.

The sensitizing dyes may be added by using a method well known in the present industrial field.

For example, these sensitizing dyes can be added in the form of a solution obtained by dissolving them in a water soluble solvent such as pyridine, methyl alcohol, ethyl alcohol, methyl cellosolve and acetone (or a mixture of these solvents), by diluting them with water in some case, or, also in some case, by dissolving them in water. It is also advantageous to use ultrasonic vibration for dissolving them. For the sensitizing dyes used in the present invention, there can be also used a method in which a dye is dissolved in a volatile organic solvent, and the resulting solution is dispersed in a hydrophilic colloid, and then the resulting dispersion is added, as disclosed in U.S. Patent No. 3,469,987; or a method in which a water insoluble dye is dispersed in a water soluble solvent without being dissolved, and the resulting dispersed solution is added, as disclosed in Japanese Patent Examined Publication No. 24185/1971. The sensitizing dyes used in the present invention can be also added in an emulsion in the form of a dispersion obtained by an acid dissolution dispersion method. As other methods for the addition, the methods disclosed in U.S. Patents No. 2,912,345, No. 3,342,605, No. 2,996,287 and No. 3,425,835, etc. can be also used.

The sensitizing dyes to be contained in the silver halide emulsion of the present invention may be dissolved in solvents of the same or different kinds, and then added by mixing these solvents before addition to the silver halide emulsion, or separately. When they are added separately, the order, time and interval of the addition can be arbitrarily determined depending on the purposes. As for the time to add the sensitizing dyes used in the present invention, they may be added at any time in the course of the production of the emulsion, but preferably in the course of chemical ripening or after chemical ripening, and, more preferably, they are added in the course of chemical ripening.

To the silver halide emulsion of the present invention, a compound known as an antifoggant or a stabilizer can be added in the course of chemical ripening and/or at the time of the completion of chemical ripening and/or after completion of chemical ripening, for the purpose of preventing fog from being generated in the course of the production, storage or photographic processing of light-sensitive materials and/or keeping stable the photographic performances.

In the silver halide emulsion of the present invention, mercapto heterocyclic compounds represented by General Formula (I) shown below can be also added in order to efficiently achieve the effect of the present invention.

General Formula (I)

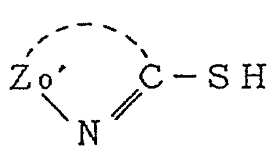
$$Z_0\text{-SH}$$

wherein Z_0 represents a heterocyclic residual group.

The heterocyclic residual group represented by Z_0 in the above General Formula (I) may have a substituent, which substituent may include, for example, an alkyl group, an aryl group, an alkenyl group, a sulfamoyl group, a carbamoyl group, an acyl group, etc.

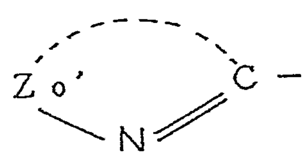
In the mercapto heterocyclic compounds used in the present invention and represented by the above General Formula (I), those preferably used are the mercapto heterocyclic compounds represented by General Formula (I-a) shown below.

General Formula (I-a)



In the formula, Z_0' represents a group of atoms necessary for the formation of a heterocyclic ring such as an imidazoline ring, an imidazole ring, an imidazolone ring, a pyrazoline ring, a pyrazole ring, a pyrazolone ring, an oxazoline ring, an oxazole ring, an oxazolone ring, a thiazoline ring, a thiazole ring, a thiazolone ring, a selenazoline ring, a selenazole ring, a selenazolone ring, an oxadiazole ring, a thiazole ring, a triazole ring, a tetrazole ring, a benzimidazole ring, a benztriazole ring, an indazole ring, a benzoxazole ring, an benzthiazole ring, a benzselenazole ring, a pyrazine ring, a pyrimidine ring, a pyridazine ring, a triazine ring, an oxadine ring, a thiazine ring, a tetrazine ring, a quinazoline ring, a phthalazine ring and a polyazaindene ring (for example, a triazaindene ring, a tetrazaindene ring, pentazaindene ring, etc.).

The heterocyclic residual group represented by:

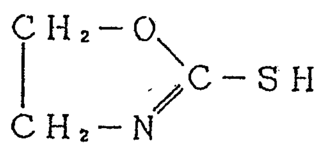


of General Formula (I-a) may have a substituent including the same substituents as those represented by Z_0 in General Formula (I) set out above.

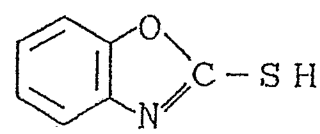
Of the mercapto heterocyclic compounds represented by General Formula (I-a), more preferred are mercapto triazole type compounds comprising a triazole ring.

Specific examples of the compounds represented by the above General Formula (I) are shown below, but by no means limited to these.

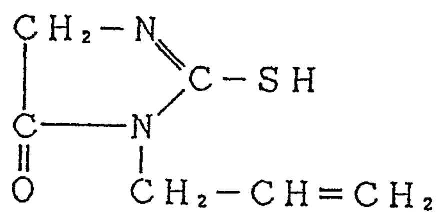
I - 1



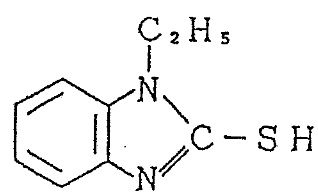
I - 2



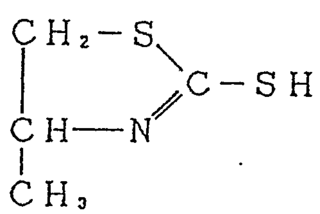
I - 3



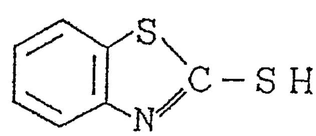
I - 4



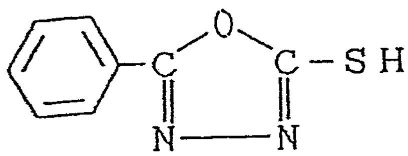
I - 5



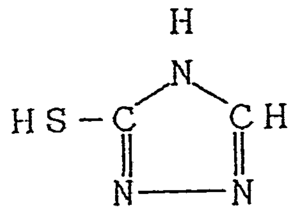
I - 6



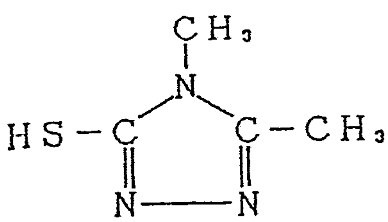
I－7



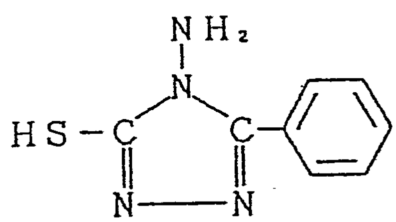
I－8



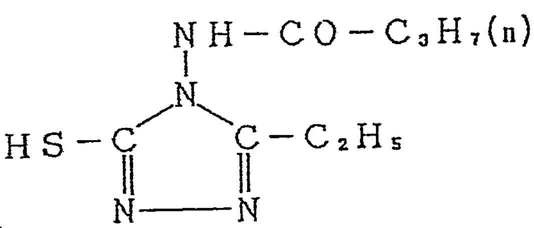
I－9



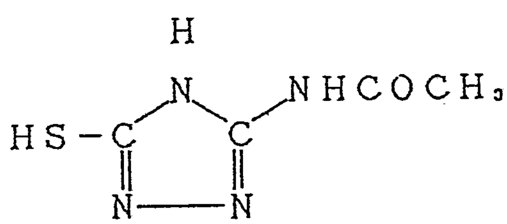
I－10



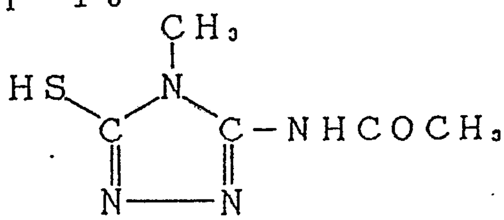
I－11



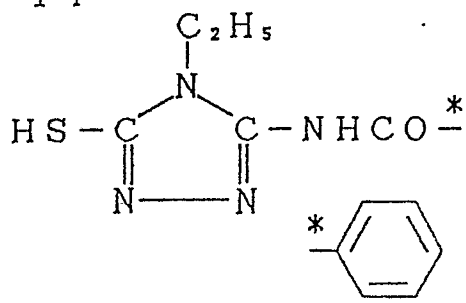
I－12



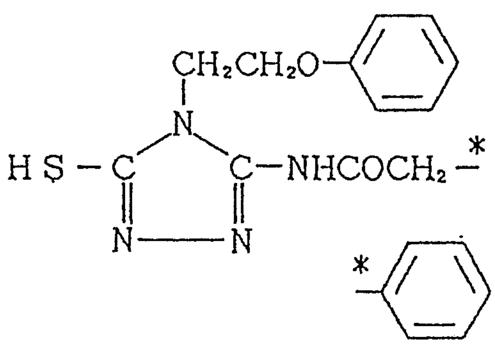
I - 1 3



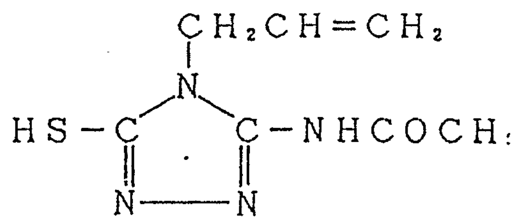
I - 1 4



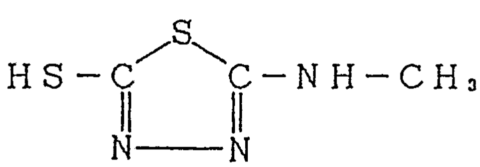
I - 1 5



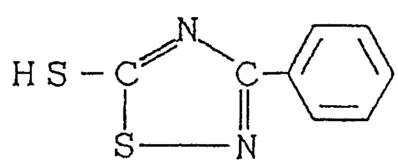
I - 1 6



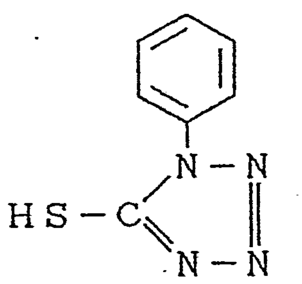
I - 1 7



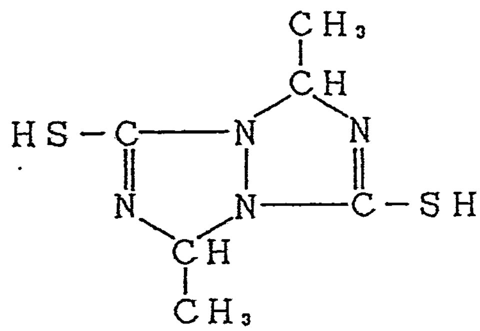
I - 1 8



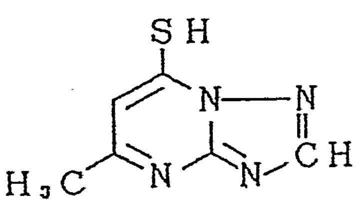
I－19



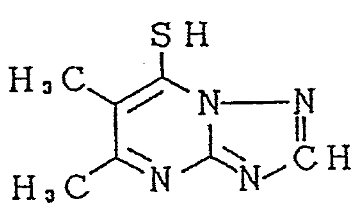
I－20



I－21



I－22



The mercapto heterocyclic compounds represented by General Formula (I) and preferably used in the present invention are disclosed, for example, in Japanese Patent Examined Publications No. 42974/1973 and No. 51666/1982, Japanese Patent O.P.I. Publication No. 102621/1973, French Patents No. 701,053, No. 701,301 and No. 1,563,019, U.S. Patent No. 3,457,078 and The Journal of Photographic Science, 19. pp.83-87.

The mercapto heterocyclic compounds preferably used in the present invention are added in an amount widely ranging depending on the conditions for the silver halide emulsion, for example, silver chloride content, grain size, crystal form, etc., but may be added approximately in an amount of 1×10^{-6} to 1×10^{-2} mole, preferably 1×10^{-5} to 1×10^{-3}, to obtain good results. As for the method for addition, they may be added to the silver halide emulsion according to a method of adding ordinary photographic additives, for example, by dissolving them in water, an acidic or alkaline aqueous solution having a suitable pH value, or an organic solvent such as methanol and ethanol.

The mercapto heterocyclic compounds preferably used in the present invention may be used alone or in combination of two or more kinds, and there may be further additionally added, without any inconvenience, other compounds known as antifoggants or stabilizers in the filed of photographic industry.

The heterocyclic compounds preferably used in the present invention can be effectively added to any of the silver halide photographic emulsion layers of the present invention and/or the other photographic constituent layers, but preferably used in the silver halide emulsion layers.

There is no particular limitation in the time for addition to silver halide emulsion layers, but the compounds may be preferably added in the time after completion of chemical sensitization and right before the coating of a silver halide emulsion, during which they may be added in one time or may be added in a divided form without any inconvenience.

The light-sensitive silver halide photographic material of the present invention may include, for example, color negative films, color positive films, color photographic paper and so forth, but, in particular, the effect of the present invention can be effectively exhibited when used in the color photographic paper used for direct appreciation.

The light-sensitive silver halide photographic material of the present invention, including the color photographic paper, may be for use in monochrome or multicolor. In the case of the light-sensitive silver halide photographic material for multicolor photography, the light-sensitive material has usually such structure that silver halide emulsion layers containing magenta couplers, yellow couplers and cyan couplers, respectively, as couplers for photography are laminated on a support in a suitable number and order of the layers to effect subtractive color reproduction, but the number and order of the layers may be appropriately varied depending on what are important performances and what the materials are used for.

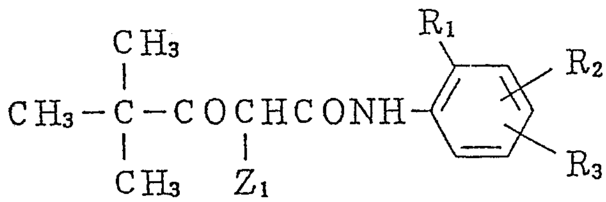
In the case the light-sensitive silver halide photographic material is a multicolor light-sensitive material, the constitution of the silver halide emulsion layers, i.e., the order of layers of a blue-sensitive silver halide emulsion layer, a green-sensitive emulsion layer and a red-sensitive emulsion layer may be arbitrarily selected, and non-light-sensitive layers other than the protective layer of the present invention (for example, an intermediate layer, a filter layer, an irradiation preventive layer, etc.) may be also in arbitrary order. However, preferable specific layer constitution is such that a yellow dye image-forming layer, a first intermediate layer, a magenta dye image-forming layer, a second intermediate layer containing an ultraviolet absorbent, a cyan dye image-forming layer, an intermediate layer containing an ultraviolet absorbent, and a protective layer are provided on a support in this sequence from the support.

Yellow dye-forming couplers used in the present invention may preferably include known acylacetoanilide type couplers. Of these, advantageous are benzoylacetoanilide type and pivaloylacetonitrile type compounds. Specific examples of usable yellow couplers are those disclosed in British Patent No. 1,077,874, Japanese Patent Examined Publication No. 40757/1970, Japanese Patent O.P.I. Publications No.1031/1972, No. 26133/1972, No. 94432/1973, No. 87650/1975, No. 3631/1976, No. 115219/1977, No. 99433/1979, No. 133329/1979 and No. 30127/1981, U.S. Patents No. 2,875,057, No. 3,253,924, No. 3,265,506, No. 3,408,194, No. 3,551,155, No. 3,511,156, No. 3,664,841, No. 3,725,072, No. 3,730,722, No. 3,891,445, No. 3,900,483, No. 3,929,484, No. 3,933,500, No. 3,973,968, No.3,990,896, No. 4,012,259, No. 4,022,620, No. 4,029,508, No. 4,057,432, No. 4,106,942, No. 4,133,958, No. 4,269,936, No. 4,286,053, No. 4,304,845, No. 4,314,023, No. 4,336,327, No. 4,356,258, No. 4,386,155 and No. 4,401,752, etc.

Yellow dye-forming couplers used in the present invention are preferably represented by General Formula

(Y) shown below:

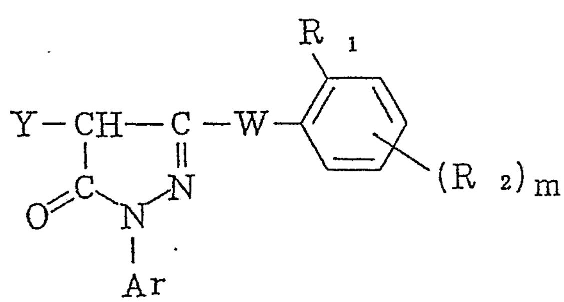
General Formula (Y)



In the formula, R_1 represents a halogen atom or an alkoxy group. R_2 represents a hydrogen atom, a halogen atom, or an alkoxy group which may have a substituent. R_3 represents an acylamino group, alkoxy carbonyl group, alkylsulfamoyl group, arylsulfamoyl group, arylsulfonamide group, alkylureido group, arylureido group, succinimide group, alkoxy group or aryloxy group which may have a substituent. Z_1 represents a group eliminable through the coupling reaction with an oxidized product of a color developing agent.

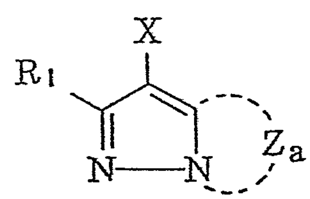
In the present invention, as magenta dye-forming couplers, the couplers represented by General Formulas (M-1) and (M-2) can be preferably used.

General Formula (M-1)



In the formula, Ar represents an aryl group; R_1 represents a hydrogen atom or a substituent; and R_2 represent a substituent. Y represents a group eliminable through the reaction with an oxidized product of a color developing agent; W represents -NH-, -NHCO- (where the nitrogen atom is attached to a carbon atom in the pyrazolone ring) or -NHCONH-; and m is an integer of 1 or 2.

General Formula (M-2)



In the magenta couplers represented by the above General Formula (M-2), Z_a represent a group of non-metallic atoms necessary for the formation of a nitrogen-containing heterocyclic ring, and the ring to be formed by the Z_a may have a substituent.

X represents a hydrogen atom or a substituent eliminable through the reaction with an oxidized product of a color developing agent.

R_1 represents a hydrogen atom or a substituent.

The substituent represented by the above R_1 may include, for example, a halogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, a cycloalkenyl group, an alkynyl group, an aryl group, a heterocyclic group, an acyl group, a sulfonyl group, a sulfinyl group, a phosphonyl group, a carbamoyl group, a sulfamoyl group, a cyano group, a spiro compound residual group, an organic hydrocabon compound residual group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a siloxy group, an acyloxy group, a carbamoyloxy group, an amino group, an acylamino group, a sulfonamide group, an imide group, an ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkoxy carbonyl group, an aryloxycarbonyl group, an alkylthio group, an arylthio group and a heterocyclic thio group.

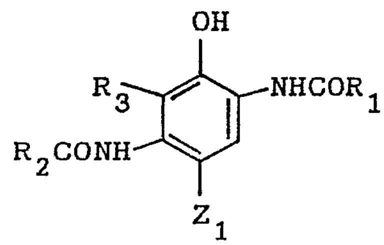
These are disclosed, for example, in U.S. Patents No. 2,600,788, No. 3,061,432, No. 3,062,653, No. 3,127,269, No. 3,311,476, No. 3,152,896, No. 3,419,391, No. 3,519,429, No. 3,555,318, No. 3,684,514, No. 3,888,680, No. 3,907,571, No. 3,928,044, No. 3,930,861, No. 3,930,866 and No. 3,933,500, Japanese Patent O.P.I. Publications No. 29639/1974, No. 111631/1974, No. 129538/1974, No. 13041/1975, No. 58922/1977, No. 62454/1980, No. 118034/1980, No. 38043/1981, No. 35858/1982 and No. 23855/1985, British Patent No. 1,247,493, Belgian Patents No. 769,116 and 792,525, West

German Patent No. 21 56 111, Japanese Patent Examined Publication No. 60479/1971, Japanese Patent O.P.I. Publications No. 125732/1984, No. 228252/1984, No. 162548/1984, No. 171956/1984, No. 33552/1985 and No. 43659/1985, West German Patent No. 10 70 030, U.S. Patent No. 3,725,067, etc.

The cyan dye-forming couplers may typically include four equivalent type or two equivalent type phenol or naphthol cyan dye-forming couplers, and Specific examples are disclosed in U.S. Patents No. 2,306,410, No. 2,356,475, No. 2,362,598, No. 2,367,531, No. 2,369,929, No. 2,423,730, No. 2,474,293, No. 2,476,008, No. 2,498,466 No. 2,545,687, No. 2,728,660, No. 2,772,162, No. 2,895,826, No. 2,976,146, No. 3,002,836, No. 3,419,390, No. 3,446,622, No. 3,476,563, No. 3,737,316, No. 3,758,308, and No. 3,839,044, British Patents No. 478,991, No. 945,542, No.1,084,480, No. 1,377,237, No. 1,388,024 and No. 1,543,040, Japanese Patent O.P.I. Publications No. 37425/1972, No. 10135/1975, No. 25228/1975, No. 112038/1975, No. 117422/1975, No. 130441/1975, No. 6551/1976, No. 37647/1976, No. 52828/1976, No. 108841/1976, No.109630/1978, No. 48237/1979, No. 66129/1979, No. 131931/1979, No. 32071/1980, No. 146050/1984, No. 31953/1984 and No. 117249/1985, etc.

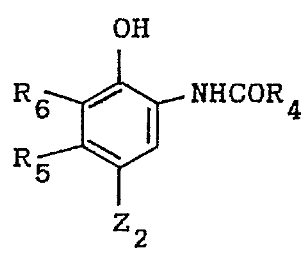
Cyan dye-forming couplers preferably used may include the couplers represented by General Formula (C-1) and (C-2) shown below:

General Formula (C-1)



In the formula, R_1 represents an aryl group, a cycloalkyl group or a heterocyclic group. R_2 represents an alkyl group or a phenyl group. R_3 represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group. Z_1 represents a hydrogen atom, a halogen atom or a group eliminable through the reaction with an oxidized product of an aromatic primary amine type color developing agent.

General Formula (C-2)



In the formula, R_4 represents an alkyl group (for example, a methyl group, an ethyl group, a propyl group, a butyl group, a nonyl group, etc.). R_5 represents an alkyl group, (for example, a methyl group, an ethyl group, etc.). R_6 represents a hydrogen atom, a halogen atom (for example, fluorine, chlorine, bromine, etc.) or an alkyl group (for example, a methyl group, an ethyl group, etc.). Z_2 represents a hydrogen atom, a halogen atom or a group eliminable through the reaction with an oxidized product of an aromatic primary amine type color developing agent.

To add hydrophilic compounds such as dye-forming couplers which are not required to be absorbed on the surface of silver halide crystals, there can be used a variety of methods such as a solid dispersion method, a latex dispersion method and and an oil-in-water emulsification dispersion method. This can be suitably selected depending on the chemical structure of the hydrophobic compounds such as couplers. As the oil-in-water emulsification dispersion method, a conventionally known method for dispersing hydrophobic additives such as couplers can be applied. Usually, the method may be carried out by dissolving the couplers in a high boiling organic solvent having a boiling point of 150°C or more optionally together with a low boiling and/or water soluble organic solvent, and carrying out emulsification dispersion in a hydrophilic binder such as an aqueous gelatin solution by use of a surface active agent and by use of a dispersing means such as a stirrer, a homogenizer, a colloid mill, a flow jet mixer, an ultrasonic device, followed by adding the dispersion to an intended hydrophilic colloid layer. There may be inserted a step of removing the dispersing solution or, at the same time of the dispersion, the low boiling organic solvent.

The high boiling solvent to be used may include organic solvents having a boiling point of 150 ^{o}C or more such as phenol derivatives, phthalates, phosphates, citrates, benzoates, alkyl amides, aliphatic acid esters and trimesic acid esters which do not react with an oxidized product of a developing agent.

The high boiling organic solvents that can be used in the present invention are disclosed in U.S. Patents No. 2,322,027, No. 2,533,514, No. 2,835,579, No. 3,287,134, No. 2,353,262, No. 2,852,383, No. 3,554,755, No. 3,676,137, No. 3,676,142, No. 3,700,454, No. 3,748,141, No. 3,779,765 and No. 3,837,863, British Patents No. 958,441 and No. 1,222,753, OLS 25 38 889, Japanese Patent O.P.I. Publications No. 1031/1972, No. 90523/1974, No. 23823/1975, No. 26037/1976, No. 27921/1976, No. 27922/1976, No. 26035/1976, No. 26036/1976, No. 62632/1975, No. 1520/1978, No. 1521/1978, No. 15127/1978, No. 119921/1979, No. 119922/1979, No. 25057/1980, No. 36869/1980, No. 19049/1981 and No. 81836/1981, Japanese Patent Examined Publication No. 29060/1973, etc.

The low boiling or water soluble organic solvent that can be used together with, or in place of, the high boiling solvent may include those disclosed in U.S. Patent No. 2,801,171 and No. 2,949,360. The low boiling and substantially water insoluble organic solvent may include ethyl acetate, propyl acetate, butyl acetate, butanol, chloroform, carbon tetrachloride, nitromethane, nitroethane, benzene, etc., and the water soluble organic solvent may include, for example, acetone, methyl isobutyl ketone, β-ethoxyethyl acetate, methoxy glycol acetate, methanol, ethanol, acetonitrile, dioxane, dimethylformamide, dimethylsulfoxide, hexamethyl phosphoryl amide, diethylene glycol monophenyl ether, phenoxy ethanol, etc.

The latex dispersion method may preferably include the methods disclosed, for example, in U.S. Patents No. 4,199363, No. 4,214,047, No. 4,203,716 and No. 4,247,627, Japanese Patent O.P.I. Publications No. 74538/1974, No. 59942/1976, No. 59943/1976 and No. 32552/1979, etc.

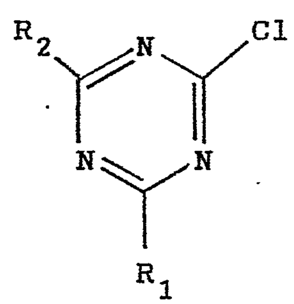
The surface active agent used as a dispersion auxiliary may preferably include, for example, anionic surface active agents such as alkylbenzene sulfonates, alkylnaphthalene sulfonates, alkyl sulfonates, alkyl sulfuric acid esters, alkyl phosphoric acid esters, sulfosuccinic acid esters and sulfoalkyl polyoxyethylene alkyl phenyl ether; nonionic surface active agents such as steroid type saponines, alkylene oxide derivatives and glycidol derivatives; amphoteric surface active agents such as amino acids, aminoalkylsulfonic acids and alkylbetainic acids; and cationic surface active agents such as quaternary ammonium salts. Specific examples of these surface active agents are disclosed in "Handbook of Surface Active Agents", Sangyo Tosho, 1966, and "Data for Studies and Techniques on Emulsifying Agents and Emulsifying Apparatus", Kagaku Hanronsha, 1978.

As a binder (or a protective colloid) for the silver halide emulsion of the present invention, it is advantageous to use gelatin, but it is also possible to use hydrophilic colloids such as gelatin derivatives, a graft polymer of gelatin with other macromolecules, proteins, sugar derivatives, cellulose derivatives and synthetic hydrophilic high molecular substances such as homopolymer or copolymer.

Photographic emulsion layers and other hydrophilic colloid layers of the light-sensitive material in which the silver halide emulsion of the present invention is used can be hardened by using one or more kinds of hardening agents that can crosslink binder (or protective colloid) molecules to enhance the film strength. The hardening agents can be added in such an amount that a light-sensitive material can be hardened to the extent that no hardening agent is required to be added in a processing solution. It, however, is also possible to add the hardening agent in the processing solution.

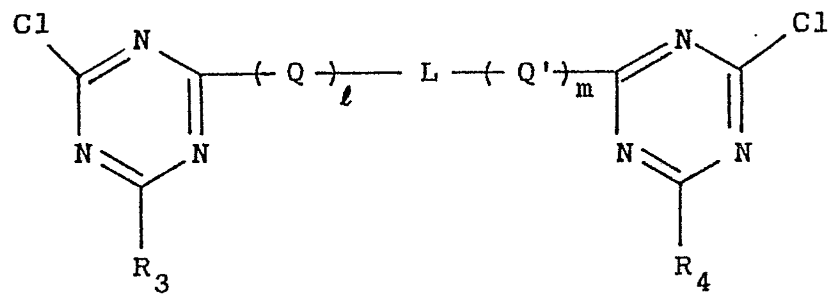
In the light-sensitive silver halide photographic material of the present invention, the compound represented by General Formula (II) shown below or the compound represented by General Formula (III) shown below is preferably used as the hardening agent.

General Formula (II)



In the formula, R_1 represents a chlorine atom, a hydroxyl group, an alkyl group, an alkoxy group, an alkylthio group, a group of -OM (M is a monovalent metallic atom), a group of -NR'R" (R' and R" each represents a hydrogen atom, an alkyl group or an aryl group) or a group of -NHCOR"'(R"' represents a hydrogen atom, an alkyl group or an aryl group); R_2 represents a group having the same meaning as for the above R_1 except that it represents a chlorine atom.

General Formula (III)



In the formula, R_3 and R_4 each represent a chlorine atom, a hydroxyl group, an alkyl group, an alkoxy group or a group of -OM (M represents a monovalent metallic atom). Q and Q' each represent a linking group showing -O-, -S- or -NH-; L represents an alkylene group or an arylene group; and ℓ and m each represent 0 or 1.

The compound represented by General Formula (II) or (III) used in the present invention will be described in greater detail.

The alkyl group component in the groups mentioned as the alkyl group, the alkoxy group and the alkylthio group in General Formulas (II) and (III) may include an alkyl group having 1 to 3 carbon atoms, including, for example, a methyl group, an ethyl group, a methoxy group, an ethoxy group, a methylthio group, an ethylthio group, etc.

The M representing a monovalent metallic atom in the group -OM represented by R_1 may include, for example, sodium, potassium, ammonium, etc. The alkyl group represented by R' and R" in the group -NR'R" may include an alkyl group having 1 to 3 carbon atoms, for example, a methyl group, an ethyl group, etc., and the aryl group may include a phenyl group.

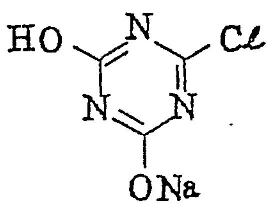
The alkyl group and the aryl group represented by R"' in the group -NHCOR"' represented by R_1 may include the groups having the same meaning as for the alkyl group and the aryl group represented by R' and R" in the above, respectively.

R_2 is a group having the same meaning as that for the above R_1, excluding a chlorine atom as mentioned above.

The groups represented by R_3 and R_4 represent the same groups as the groups represented by the above R_1. The alkylene group represented by L may include an alkylene group having 1 to 3 carbon atoms, for example, a methylene group, an ethylene group, etc. The arylene group may include, for example, a phenylene group.

Typical examples of the compounds of the present invention, represented by the above General Formulas (II) and (III) are shown below.

(Ⅱ-1)



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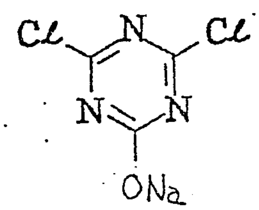
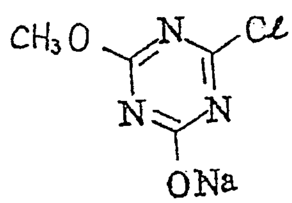
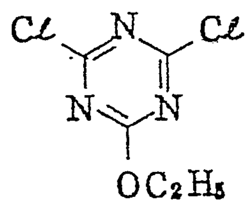


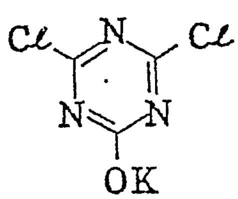
(Ⅱ-3)



(Ⅱ-4)



(Ⅱ-5)



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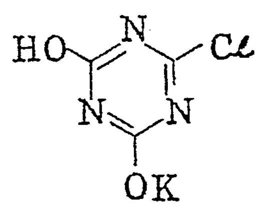

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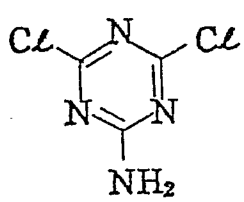

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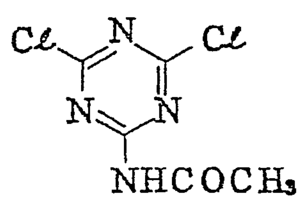

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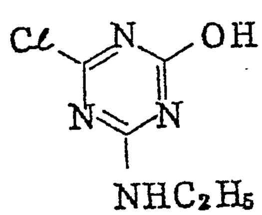
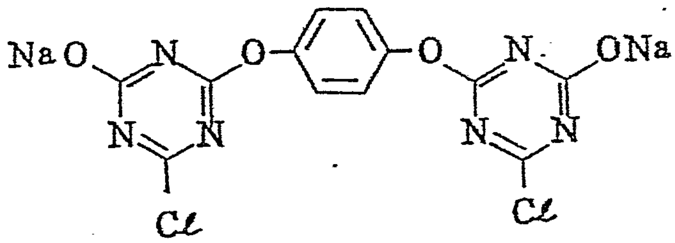


(Ⅲ−1)



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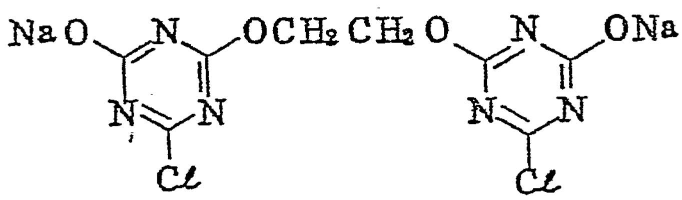
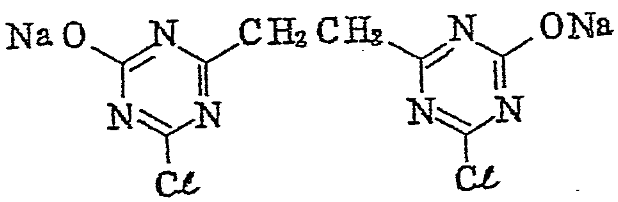
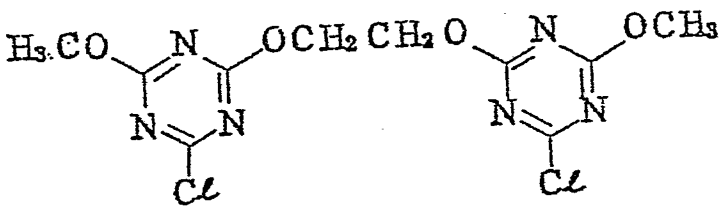


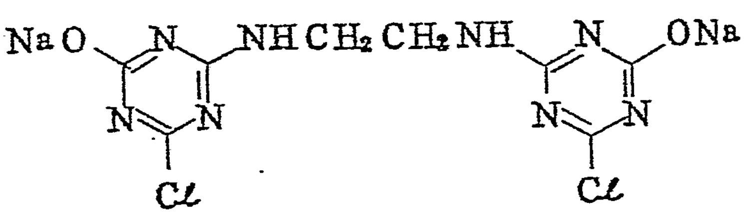
(Ⅲ−3)



(Ⅲ−4)



(Ⅲ−5)



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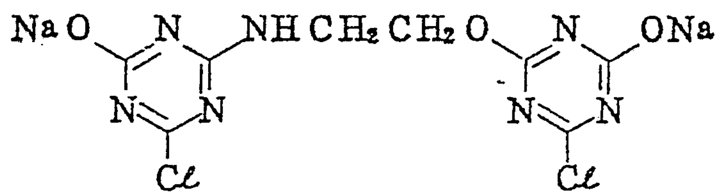

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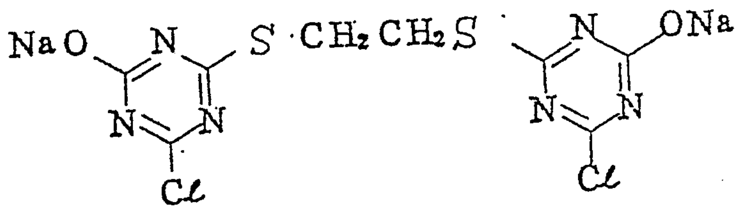

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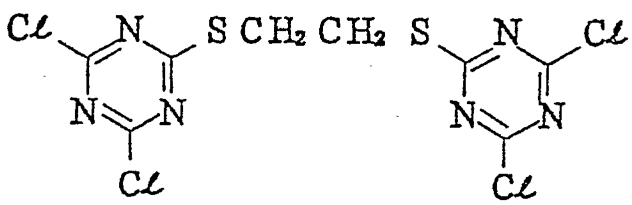
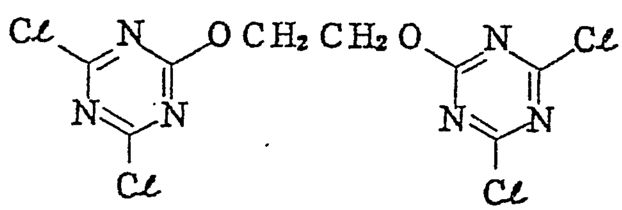


(Ⅲ-9)



The compounds represented by General Formulas (II) and (III) used in the present invention may be used alone or by mixing tow or more of them, and in an amount of 0.5 to 100 mg, preferably 2 to 50 mg per 1 g of coated gelatin.

The above compounds may be dissolved in water or alcohols such as methanol and ethanol, and then added.

The addition may be carried out according to any of a batch system or an in-line system.

Examples of the compound represented by the above General Formula (II) is desclosed in U.S. Patent No. 3,645,743, Japanese Patent Examined Publications No. 6151/1972, No. 33380/1972 and No. 9607/1976, Japanese Patent O.P.I. Publications No. 18220/1973, No.78788/1976, No. 60612/1977, No. 128130/1977, No. 130326/1977 and No. 1043/1981, etc., and can be selected from these according to the foregoing standards.

A plasticizer can be added to the silver halide emulsion layers and/or other hydrophilic colloid layers of the light-sensitive material in which the silver halide emulsions of the present invention are used, for the purpose of enhancing flexibility.

For the purpose of improving dimensional stability and so forth, a dispersion (latex) of a water insoluble or hardly soluble synthetic polymer can be contained in the photographic emulsion layers and other hydrophilic colloid layers in which the silver halide emulsions of the present invention are used.

A color fog preventive agent can be used in order to prevent color turbidity from being caused by the migration of an oxidized product or an electron migrator of a developing agent between emulsion layers (between the same color sensitive layers and/or different color sensitive layers) of the light-sensitive material of the present invention, or prevent the deterioration of sharpness or prevent overly conspicuous graininess.

The color fog preventive agent may be contained in the emulsion layers per se, or may be contained in an intermediate layer by providing the intermediate layer between adjacent emulsion layers.

An image stabilizing agent for preventing the deterioration of color images can be used in the color light-sensitive material in which the silver halide emulsions of the present invention are used.

Hydrophilic colloid layer such as protective layers and intermediate layers of the light-sensitive material of the present invention may contain an ultraviolet absorbent in order to prevent the fog due to the discharge caused by static charge by friction or the like of light-sensitive materials and prevent the deterioration due to ultraviolet light.

The light-sensitive silver halide material using the silver halide emulsion of the present invention can be provided with auxiliary layer such as a filter layer, an anti-halation layer and an ant-irradiation layer. These layers and/or the emulsion layers may contain a dye that may be flowed out of the light-sensitive material, or bleached, during the development processing.

To the silver halide emulsion layers and/or other hydrophilic colloid layers of the light-sensitive material using the silver halide emulsion of the present invention, a matte agent can be added for the purposes of decreasing the gloss of the light-sensitive material, improving the writing performance, and preventing mutual sticking of light-sensitive materials..

A lubricant can be added to the light-sensitive material using the silver halide emulsion of the present invention, in order to decrease sliding friction.

An antistatic agent aiming at preventing static charge can be added to the light-sensitive material using the silver halide emulsion of the present invention. The antistatic agent may be used in an antistatic layer provided on the side of a support at which no emulsion layer is laminated, or may be used in an emulsion layer and/or a protective colloid layer other than the emulsion layers provided on the side of a support on which emulsion layers are laminated.

In the photographic emulsion layers and/or other hydrophilic colloid layers of the light-sensitive material using the silver halide emulsion of the present invention, a variety of surface active agents can be used for the purpose of improving coating performance, preventing static charge, improving slidability, emulsification dispersion, preventing adhesion, and improving photographic performances (such as development acceleration, hardening and sensitization).

The light-sensitive material using the silver halide emulsion of the present invention can be applied on flexible reflective supports made of baryta paper, paper laminated with -olefin polymers or synthetic paper; films comprising semisynthetic or synthetic high molecular compounds such as cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate and polyamide; rigid bodies such as glass, metals and ceramics; etc.

The light-sensitive silver halide material of the present invention may be applied, as occasion calls, after having been subjected to corona discharging, ultraviolet irradiation, flame treatment and so forth, directly on the surface of the support or through interposition of one or more subbing layers for improving adhesion, antistatic performance, dimensional stability, abrasion resistance, hardness, anti-halation performance, friction characteristics and/or other characteristics of the surface of the support.

In the coating of the light-sensitive material, using the silver halide emulsion of the present invention, a thickening agent may be used in order to improve the coating performance. Particularly useful coating method may include extrusion coating and curtain coating by which two or more layers can be simultaneously coated.

The light-sensitive material of the present invention can be exposed by use of electromagnetic wave having the spectral region to which the emulsion layers constituting the light-sensitive material of the present invention have the sensitivity. As a light source, there can be used any known light sources including natural light (sunlight), a tungsten lamp, a fluorescent lamp, a mercury lamp, a xenon arc lamp, a carbon arc lamp, a xenon flash lamp, a cathode ray tube flying spot, every kind of laser beams, light from a light-emitting diode, light emitted from a fluorescent substance energized by electron rays, X-rays, gamma-rays, alpha-rays, etc.

As for the exposure time, it is possible to make exposure, not to speak of exposure of 1 millisecond to 1 second usually used in cameras, of not more than 1 microsecond, for example, 100 microseconds to 1 microsecond by use of a cathode ray tube or a xenon arc lamp, and it is also possible to make exposure longer than 1 second. Such exposure may be carried out continuously or may be carried out intermittently.

The light-sensitive silver halide photographic material of the present invention can form images by carrying out color development known in the art.

The color developing agent used for a color developing solution in the present invention includes known ones widely used in the various color photographic processes. These developing agents include aminophenol type and p-phenylenediamine type derivatives. These compounds, which are more stable than in a free state, are used generally in the form of a salt, for example, in the form of a hydrochloride or a sulfate. Also, these compounds are used generally in concentration of about 0.1 to 30 g per 1 liter of a color developing solution, preferably in concentration of about 1 to 15 g per 1 liter of a color developing solution.

The aminophenol type developing agent may include, for example, o-aminophenol, p-aminophenol, 5-amino-2-oxytoluene, 2-amino-3-oxy-toluene, 2-oxy-3-amino-1,4-dimethyl-benzene, etc.

Most useful primary aromatic amine type color developing agent includes N,N'-dialkyl-p-phenylenediamine compound, wherein the alkyl group and the phenyl group may be substituted with any substituent. Of these, examples of particularly useful compounds may include N-N'-dimethyl-p-phenylenediamine hydrochloride, N-methyl-p-phenylenediamine hydrochloride, N,N'-dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-(N-ethyl-N-dodecylamino)-toluene, N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate, N-ethyl-N-β-hydroxyethylaminoaniline, 4-amino-3-methyl-N,N'-diethylaniline, 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluene sulfonate, etc.

In addition to the above primary aromatic amine type color developing agent, known compounds for developing solution components can be added to the color developing solution used in the processing of the light-sensitive silver halide photographic material of the present invention.

For example, there can be contained any of alkali agents such as sodium hydroxide, sodium carbonate and potassium carbonate, alkali metal sulfites, alkali metal bisulfites, alkali metal thiocyanates, alkali metal halides, benzyl alcohol, water softeners, thickening agents, etc.

This color developing solution may have usually the pH of 7 or more, most usually about 10 to 13.

The light-sensitive silver halide photographic material according to the present invention may contain these color developing agents in the hydrophilic colloid layer as the color developing agents per se or a precursor thereof, and can be processed in an alkaline activated bath. The precursor of the color developing agent is a compound capable of forming the color developing agent under an alkaline condition, and may include a Schiff base type precursor with an aromatic aldehyde derivative, a polyvalent metallic ion complex precursor, a phthalimide derivative precursor, phosphoric acid amide derivative precursor, a sugar-amine reaction product precursor and an urethane type precursor. These precursors of the aromatic primary amine color developing agents are disclosed, for example, in U.S. Patents No. 3,342,599, No. 2,507,114, No. 2,695,234, No. 3,719,492 and No. 3,803,783, Japanese Patent O.P.I. Publications No. 185628/1978 and No. 79035/1979, and Research Disclosure No. 15159, No. 12146 and No. 13924.

These aromatic primary amine color developing agents or the precursors thereof are required to be added in an amount only by which a sufficient color can be obtained when an activated processing is carried out. This amount may considerably vary depending on the type of light-sensitive materials, but may approximately range between 0.1 mole and 5 moles, preferably 0.5 mole and 3 moles, per mole of silver halide. These color developing agents or the precursors thereof may be used alone or in combination. To incorporate them into light-sensitive materials, they may be added by dissolving them in a suitable solvent such as water, methanol, ethanol and acetone, or may be added as an emulsified dispersion using a high boiling organic solvent such as dibutyl phthalate, dioctyl phthalate and tricrezyl phosphate. It is also possible to add them by impregnating a latex polymer therewith as disclosed in Research Disclosure No. 14850.

The light-sensitive silver halide photographic material is, after color developing, subjected to bleaching and fixing. The bleaching may be carried out simultaneously with the fixing. As a bleaching agent, a variety of compounds can be used, particularly including polyvalent metallic compounds such as iron (III), cobalt (III) and copper (II); in particular, complex salts of these polyvalent metallic cations with organic acids, for example, aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, nitrilotriacetate and N-hydroxyethyl ethylenediaminebiacetic acid; metal complex salts of malonic acid, tartaric acid, malic acid, diglycolic acid, dithioglycolic acid, and so forth; or ferricyanic acid salts, dicromates, etc., which can be used alone or in suitable combination.

As a fixing agent, there may be used a soluble complexing agent that can solubilize a silver halide as a complex salt. This soluble complexing agent may include, for example, sodium thiosulfate, ammonium thiosulfate, potassium thiocyanate, thiourea, thioether, etc.

After fixing, washing is usually carried out. Also, stabilizing may be carried out as a substitute for the washing, or both of them may be used in combination. A stabilizing solution used in the stabilizing may contain a pH regulator, a chelating agent, an antifungal agent and so forth. Specific conditions for these processings are available by making reference to Japanese Patent O.P.I. Publication No. 134636/1983.

As described in the foregoing, the present invention can provide a light-sensitive silver halide photographic material having goodness in sensitivity and fog, excellent in pressure resistance in both the dry state and the wet state, and feasible for rapid processing.

Specific examples of the present invention will be described below, but the embodiments of the present invention are by no means limited to these.

Example 1

(Emulsion A)

Following the procedures disclosed in Japanese Patent O.P.I. Publication No 48755/1984, an aqueous solution containing potassium chloride and potassium bromide and an aqueous solution of silver nitrate were simultaneously mixed in an aqueous solution of inert gelatin, at 50°C over a period of 60 minutes with vigorous stirring to obtain a silver chloride-rich emulsion containing 2 mole % of silver bromide.

In mixing, pAg was controlled to 7.

Characteristics fo the resulting silver chloride-rich emulsion were measured according to the method described in the foregoing to reveal that it comprised silver chloride-rich grains having an average grain size of 0.8 μm and a variation coefficient of 0.10. The ratio of maximum density (internal development/surface development) was further measured according to the method described above to find that it was 1.2. Subsequently, precipitation washing was carried out, and thereafter sodium thiosulfate was added to this silver chloride-rich grains to carry out chemical sensitization. At the stage of completion of the chemical sensitization, a blue-sensitive sensitizing dye represented by the aforesaid exemplary compound A-23 and a stabilizer were added thereto to prepare a blue-sensitive silver chloride-rich emulsion.

(Emulsion B)

Next, a silver chloride-rich emulsion comprising grains having an average grain size of 0.8 μm, a variation coefficient of 0.1 and a maximum density ratio of 1.3 was prepared in the same manner as that for Emulsion A except that 2 x 10^{-6} mole of K_2IrCl_6 per mole of silver halide was added 30 minutes after start of the addition of the aqueous solution containing potassium chloride and potassium bromide and the aqueous solution of silver nitrate.

(Emulsion C)

An aqueous solution containing potassium bromide and potassium chloride and an aqueous solution of silver nitrate were simultaneously mixed in an aqueous solution of inert gelatin, at 70°C over a period of 120 minutes with vigorous stirring while controlling pAg to 6 to obtain a silver chlorobromide emulsion containing 90 mole % of silver bromide and comprising grains having an average grain size of 0.8 μm, a variation coefficient of 0.11 and a maximum density ratio of 1.0. A blue-sensitive silver bromide emulsion was also prepared in the same manner as that for Emulsion A.

(Emulsion D)

An aqueous solution containing potassium bromide and potassium chloride and an aqueous solution of silver nitrate were simultaneously added to an aqueous solution of inert gelatin, at 50°C with vigorous stirring while controlling pAg to 6. Subsequently, an aqueous solution of potassium bromide and an aqueous solution of silver nitrate were further added simultaneously. Pouring time was 60 minutes. By these procedures, obtained was a silver chloride-rich emulsion comprising grains whose outermost layer is constituted of a silver bromide phase, and containing 2 mole % of silver bromide. The emulsion thus obtained comprised grains having an average grain size of 0.8 μm, a variation coefficient of 0.10 and a maximum density ratio of 1.2. A blue-sensitive silver chloride-rich emulsion was also prepared in the same manner as that for Emulsion A.

(Emulsion E) -Present Invention-

A blue-sensitive silver chloride-rich emulsion comprising grains having an average grain size of 0.8 μm, a variation coefficient of 0.10 and a maximum density ratio of 1.5 was prepared in the same manner as that for Emulsion D except that 2×10^{-6} mole of K_2IrCl_6 per mole of silver halide was added 30 minutes after start of the addition of the aqueous solution containing potassium bromide and potassium chloride and the aqueous solution of silver nitrate.

This Emulsion E was analyzed according to X-ray diffraction to reveal that the peak assigned to the silver bromide-rich phase showed a diffraction pattern clearly distinguishable from the peak assigned to the silver chloride-rich phase other than the silver bromide-rich phase.

On the other hand, 80 g of yellow coupler were dissolved in a mixed solution comprising 30 g of dinonyl terephthalate as a high boiling organic solvent and 100 ml of ethyl acetate as a low boiling organic solvent. To this solution, 300 ml of an aqueous 5 % gelatin solution containing sodium dodecylbenzenesulfonate were added, and thereafter the mixture was dispersed by using an ultrasonic homogenizer to prepare a yellow coupler dispersion.

Subsequently, the following two layers were applied on a support made of polyethylene coated paper in the manner consecutive from the support side to prepare light-sensitive silver halide photographic materials as Samples 1 to 5. The amount of addition shown below refers to the amount per 1 m^2 unless particularly mentioned.

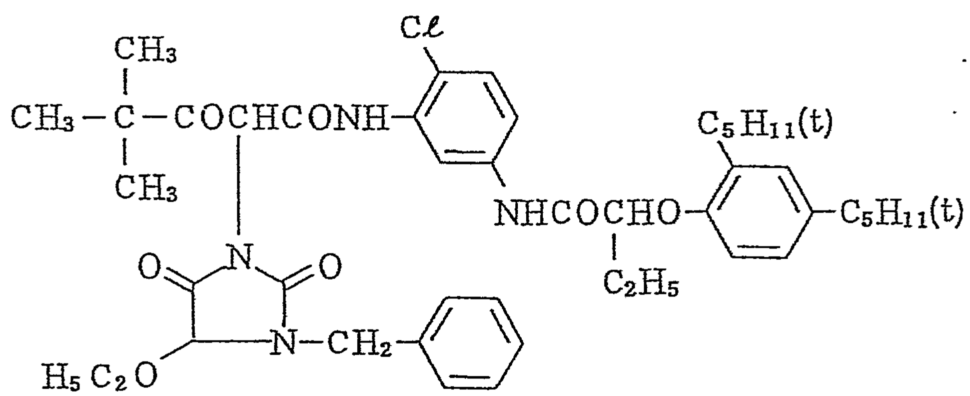
Layer - 1: A layer containing 2.0 g of gelatin, 0.3 g (in terms of silver amount) of a blue-sensitive silver halide emulsion*, 0.8 g of yellow coupler and 0.3 g of dinonylphthalate.

Layer - 2: A layer containing 1.5 g of gelatin and a hardening agent represented by aforesaid exemplary compound II-2.

*: As shown in Table 1.

Yellow coupler:

(Y-1)



Pressure characteristics were evaluated in the following manner:

[Pressure characteristic in dry state]

A ball-point needle of 0.1 mm in ball diameter was vertically stood on end on the surface of a sample and parallelly moved on the surface at a speed of 1 cm/sec while simultaneously applying a load to the ball-point needle.

Thereafter, using a sensitometer (KS-7 Type;

produced by Konishiroku Photo Industry Co., Ltd.), each sample was stepwise exposed to white light, and processed according to the processing steps shown below. In the vicinity of color density of about 0.3, the color densities at the portion where the pressure was applied and at the portion where no pressure was applied were measured by use of Sakura Microdensitometer (PDM-5) to make the following evaluations. The smaller the value ΔD^D is, the better the pressure resistance is.

ΔD^D = (Density at pressure-applied portion) - (Density at no pressure-applied portion)

[Pressure characteristic in wet state]

After each sample was stepwise exposed in the same manner as above, the sample was immersed in pure water of 30°C for 30 minutes, and thereafter a ball-point of 0.3 mm in ball diameter was vertically stood on end on the surface of the sample, and parallelly moved on the surface at a speed of 1 cm/sec while simultaneously applying a continuous load to the ball-point needle. Processing was carried out according to the following processing steps. In the vicinity of color density of about 0.3, the color densities at the portion where the pressure was applied and at the portion where no pressure was applied were measured by use of Sakura Microdensitometer (PDM-5) to make the following evaluations. The smaller the value ΔD^W

is, the better the pressure resistance is.

ΔD^W = (Density at pressure-applied portion) - (Density at no pressure-applied portion)

Results obtained in the above are shown in Table 1.

[Processing steps]

	Temperature	Time
Color Developing	34.7 ± 0.3°C	50 sec.
Bleach-fixing	34.7 ± 0.5°C	50 sec.
Stabilizing	30 to 34°C	90 sec.
Drying	60 to 80°C	60 sec.

[Color developing solution]

Pure water	800 ml
Ethylene glycol	10 ml
N,N-diethylhydroxylamine	10 g
Potassium chloride	2 g
N-ethyl-N-β-methanesulfonamide ethyl-3-methyl-4-aminoaniline sulfate	5 g
Sodium tetrapolyphosphate	2 g
Potassium carbonate	30 g
Brightening agent (a 4,4'-diaminostilbene-disulfonic acid derivative)	1 g

Made up to 1 liter by adding water, and adjusted to pH 10.08.

[Bleach-fixing solution]

Ethylenediaminetetraacetic acid ferric

ammonium dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (70 % solution)	100 ml
Ammonium sulfite (40 % solution)	27.5 ml

Adjusted to pH 7.1 with use of potassium carbonate or glacial acetic acid, and made up to 1 liter by adding water.

[Stabilizing solution]

5-Chloro-2-methyl-4-isothiazolin-3-on	1 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2 g

Made upr to 1 liter by adding water, and adjusted to pH 7.0 with use of sulfuric acid or potassium hydroxide.

Table 1

Sample No.	Emulsion	Pressure characteristic Dry state ΔD^D	Wet state ΔD^W
1	A	0.34	0.41
2	B	0.33	0.39
3	C	0.08	0.09
4	D	0.31	0.38
5*	E	0.05	0.07

*: Present invention

Table 1 tells the following: It is seen from Samples No. 1 and No. 3 that the silver chloride-rich emulsion shows very poor pressure resistance as compared with the silver bromide-rich emulsion. It is also seen from Samples No. 2 and No. 4 that a combination of the silver chloride-rich grains and the metal ion, or the emulsion of the present invention but containing no metal ion, shows little improvement in the pressure resistance. In contrast thereto, however, Sample No. 5 constituted according to the present invention shows improved pressure resistance, achieving the object of the invention.

Using Samples No. 3 and No. 5, exposure and processing were further carried out in the same manner as in the evaluation of the pressure resistance. Here, however, the time of processing by color developing solution was varied to be 30 seconds, 50 seconds, 90 seconds and 210 seconds. On the respective samples thus processed and obtained, sensitivity and maximum density were measured using a optical densitometer (PDA-60; produced by Konishiroku Photo Industry Co., Ltd.). Results obtained are shown in Table 2.

Table 2

Sample No.		Color developing time 30"	50"	90"	210"
5*	Relative sensitivity	95	100	102	103
	Maximum density	2.48	2.51	2.52	2.53
3**	Relative sensitivity	25	35	39	50
	Maximum density	0.42	0.51	0.61	1.15

*: Present invention

**: Comparative sample

It is seen from Table 2 that Sample No. 5 employing a silver chloride-rich emulsion reaches a maximum sensitivity and maximum density in 30 seconds to 50 seconds, while Sample No. 3 employing a silver bromide-rich emulsion is very slow in the proceeding of development and has sensitivity and maximum density of only about 1/2 of silver chloride. Similar tests were carried out also on Samples No. 1, No. 2 and No. 4 to obtain similar results.

Example 2

The following blue-sensitive silver chloride-rich emulsions were prepared in the same manner as that for Emulsion E in Example 1.

Emulsion F: Same as Emulsion E except that this contains 5×10^{-6} mole of cadmium per mole of silver halide.

Emulsion G: Same as Emulsion E except that this contains 5×10^{-6} mole of rhodium per mole of silver halide.

Emulsion H: Same as Emulsion E except that this is a silver chloride-rich emulsion whose outermost layer comprises a silver chlorobromide phase containing 80 mole % of silver bromide, and containing 5 mole % of silver bromide.

Evaluations on the pressure resistance were carried out in the same manner as in Example 1 to reveal that there were shown good pressure resistance in the dry state and in the wet state as in the case of Sample No. 5 in Example 1.

Evaluations on feasibility for rapid processing were further carried out in the same manner as in Example 1 to reveal that there was shown excellent feasibility for rapid processing as in the case of Sample No. 5 in Example 1.

However, sensitivity was slightly lower than the case where K_2IrCl_6 was used in Example 1.

Example 3

The following emulsions were prepared in the same manner as in Example 1.

(Emulsion I)

A green-sensitive silver chloride-rich emulsion similar to Emulsion A, comprising grains having an average grain size of 0.5 µm, a variation coefficient of 0.12 and a maximum density ratio of 1.5, containing 3 mole % of silver bromide, and using the aforesaid exemplary compound B-4.

(Emulsion J) -Present Invention-

A green-sensitive silver chloride-rich emulsion similar to Emulsion E and Emulsion I, comprising grains having an average grain size of 0.5 µm, a variation coefficient of 0.11 and a maximum density ratio of 1.8, and containing 3 mole % of silver bromide.

(Emulsion K)

A red-sensitive silver chloride-rich emulsion similar to Emulsion I except that the aforesaid exemplary compound C-9 was used.

(Emulsion L) -Present Invention-

A red-sensitive silver chloride-rich emulsion similar to Emulsions J and K.

With the constitution shown in Tables 3 and 4, multi-layer samples were produced. These samples were evaluated as to the pressure resistance in the same manner as in Example 1, provided that exposure was carried out according to the separation exposure of blue light, green light and red light, designating the densities of cyan, magenta and yellow as D^R, D^G and D^B, respectively. Results obtained are shown in Table 5.

Further, the color developing time was varied in the same manner as in Example 1 to carry out similar evaluations. Results obtained are shown in Table 6.

Table 3

Layer	Constitution
Seventh layer (Protective layer)	Gelatin (1.0 g/m^2)
Sixth layer (Third intermediate layer)	Gelatin (1.0 g/m^2) Ultraviolet absorbent UV-1 (0.2g/m^2) " UV-2 (0.1g/m^2) Antistain agent AS-1 (0.02 g/m^2) High boiling solvent, dinonylphthalate (0.2 g/m^2)

Fifth layer (Red-sensitive layer)	Gelatin (1.0 g/m^2) Red-sensitive silver halide emulsion (0.25 g/m^2 as silver amount) Cyan coupler* [CC-1/CC-2] (0.4 mole per mole of silver halide) Antistain agent AS-1 (0.01 g/m^2) High boiling solvent, dioctyl-phthalate (0.2 g/m^2)
Fourth layer (Second inter-mediate layer)	Gelatin (1.5 g/m^2) Ultraviolet absorbent UV-1 (0.5g/m^2) " UV-2 (0.2g/m^2) Antistain agent AS-1 (0.03 g/m^2) High boiling solvent, dinonyl-phthalate (0.3 g/m^2)
Third layer (Green-sensitive layer)	Gelatin (1.5 g/m^2) Green-sensitive silver halide emul-sion* (0.2 g/m^2 as silver amount) Magenta coupler* (0.4 g/m^2) Antistain agent AS-1 (0.01 g/m^2) High boiling solvent, dioctyl-phthalate (0.25 g/m^2)

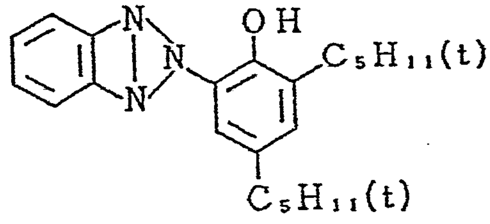
Second layer (First intermediate layer)	Gelatin (1.0 g/m^2) Antistain agent AS-1 (0.07 g/m^2) High boiling solvent, diisodecyl-phthalate (0.04 g/m^2)
First layer (Blue-sensitive layer)	Gelatin (2.0 g/m^2) Blue-sensitive silver halide emulsion* (0.3 g/m^2 as silver amount) Yellow coupler Y-1 (0.8 g/m^2) Antistain agent AS-1 (0.02 g/m^2) High boiling solvent, dinonyl-phthalate (0.3 g/m^2)
Support	Polyethylene-coated paper

Data in parentheses indicate coating amount or addition amount.

*: As shown in Table 6.

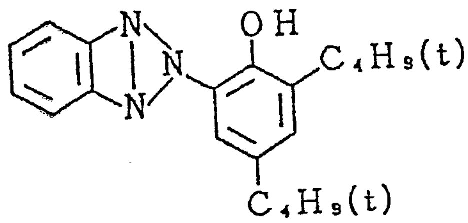
Ultraviolet absorbent

(UV-1)



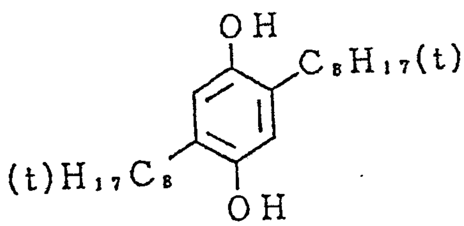
Ultraviolet absorbent

(UV-2)



Antistain agent

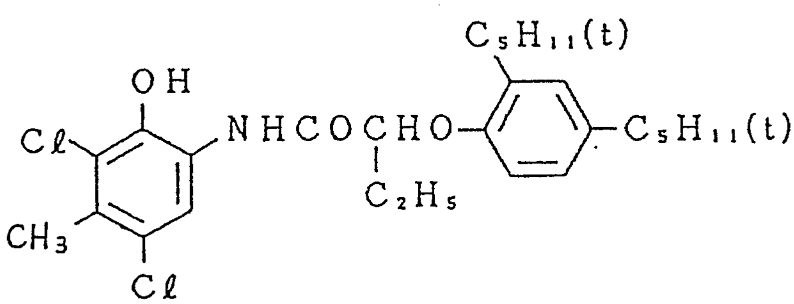
(AS-1)



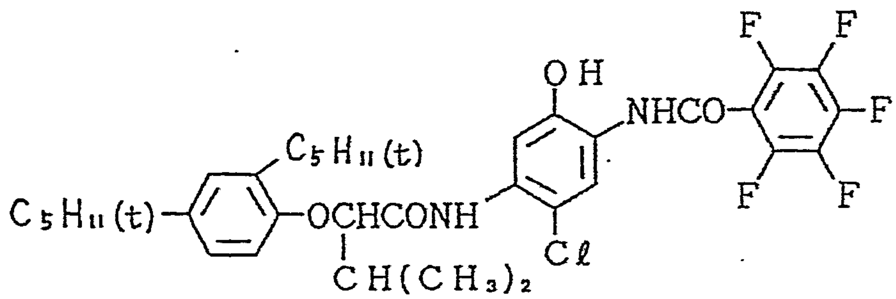
Hardening agent II-2 7 mg/g gelatin

Cyan coupler (CC-1)

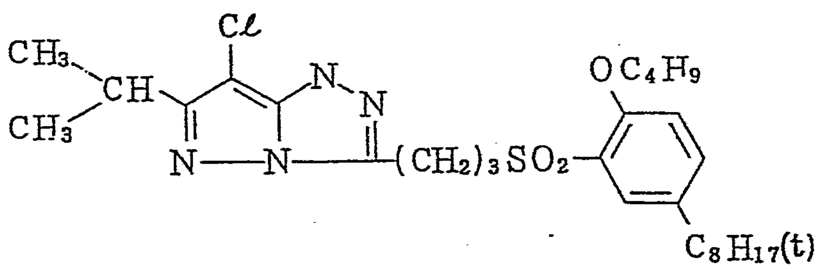
[C-1]



Cyan coupler (CC-2)



Magenta coupler (M-1)



Magenta coupler (M-2)

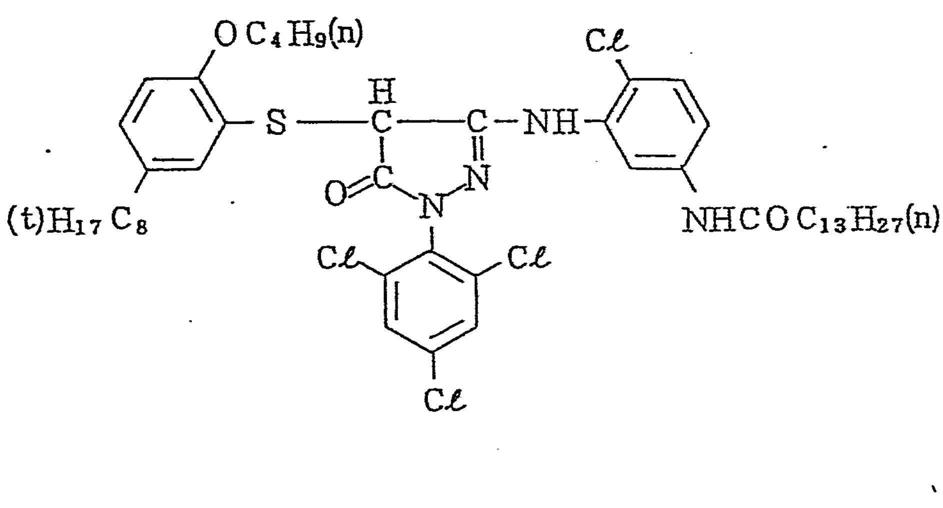


Table 4

Sample No.		Blue sensitive layer	Green sensitive layer	Red sensitive layer
31*	Coupler	Y-1	M-1	CC-1/CC-2
	Emulsion	E	J	L
32*	Coupler	Y-1	M-2	CC-1/CC-2
	Emulsion	E	J	L
33**	Coupler	Y-1	M-2	CC-1/CC-2
	Emulsion	A	I	K

*: Present Invention

**: Comparative Sample

In Sample No. 31, the exemplary compound I-12 represented by the aforesaid General Formula (I) was added to each layer in amount of 50 mg per mole of silver halide.

Table 5

Sample No.	Dry state			Wet state		
	ΔD_B^D	ΔD_G^D	ΔD_R^D	ΔD_B^W	ΔD_G^W	ΔD_R^W
31*	0.02	0.03	0.02	0.03	0.04	0.04
32*	0.05	0.05	0.04	0.06	0.06	0.07
33**	0.33	0.35	0.32	0.41	0.42	0.40

*: Present Invention

**: Comparative Sample

Table 6

Sample No.		Color developing time (sec.) 30	50	90	210
31 (present invention)	Blue-sensitive layer: Relative sensitivity	95	98	100	101
	Maximum density	2.40	2.45	2.48	2.51
	Green-sensitive layer: Relative sensitivity	97	100	101	100
	Maximum density	2.48	2.51	2.50	2.51
	Red-sensitive layer: Relative sensitivity	98	100	101	101
	Maximum density	2.48	2.53	2.54	2.54

As will be seen from Table 5, Samples No. 31 and No. 32 which are in accordance with the constitution of the present invention show excellent pressure resistance similar to Examples 1 and 2 even when multi-layered. It is also seen from Sample 31 that the mercapto compound preferably used in the present invention can improve the pressure resistance when additionally used in the constitution of the present invention, to bring about desirable results.

It is also seen from Table 6 that the chloride-rich silver halide emulsion of the present invention has a very rapid color developing performance even when multi-layered.

Example 4

An aqueous solution of silver nitrate and an aqueous solution containing the compound represented by I-19 and sodium chloride were mixed with vigorous stirring in an aqueous solution of inert gelatin at a temperature of 45^{o}C, controlling pAg to 7.0, over a period of 60 minutes according to a double jet method, provided that an aqueous solution containing 1 x 10^{-5} mole of K_2IrCl_6 per mole of silver halide was added 30 minutes after initiation of the addition, and, right before completion of the addition, a 0.1 % methanol solution of the sensitizing dye represented by A-23 was added.

Subsequently, an aqueous solution of silver nitrate and an aqueous solution of potassium bromide were further added simultaneously. According to these procedures, there was obtained a silver chloride-rich emulsion containing 1 mole % of silver bromide and having an outermost layer comprising a silver bromide phase. The resulting emulsion was comprised of grains having an average grain size of 0.7 μm and a variation coefficient of 0.09, and, as a result of analysis by X-ray diffraction, the peak assigned to the silver bromide-rich phase showed a diffraction pattern clearly distinguishable from the peak assigned to the silver chloride-rich phase other than the silver bromide-rich phase.

Next, precipitation washing was carried out, and, thereafter, the compound represented by I-19, sodium thiosulfate and sodium chloroaurate were added to this silver chloride-rich silver halide emulsion to carry out chemical sensitization. At the time the chemical sensitization was completed, the blue-sensitive sensitizing dye represented by A-23 and the compound represented by I-19 were added to prepare blue-sensitive silver chloride-rich emulsion F.

In the same procedures for the above Emulsion F, a green-sensitive silver chloride-rich emulsion and a red-sensitive silver chloride-rich emulsion (Emulsion G and Emulsion H, respectively) were prepared, provided that the compound B-4 was used in place of A-23 as for Emulsion G, having an average grain size of 0.4 μm, and the compound

C-9 was used in place of A-23 as for Emulsion F, having an average grain size of 0.45 µm.

Using these silver chloride-rich emulsions F, G and H, samples were produced to have the same constitution as in Example 3 and evaluations were made similarly to obtain the same results. Moreover, the samples having the present constitution showed less fog and more preferable results.

As described in the foregoing, the constitution of the present invention has made it possible to provide a light-sensitive silver halide photographic material for use in rapid processing, having excellent pressure resistance in both the dry state and the wet state as aimed in the present invention.

CLAIMS

1. A light-sensitive silver halide photographic material comprising a support bearing at least one light-sensitive silver halide emulsion layer comprising from 10^{-8} to 10^{-5} mole of metal ion per mole of silver halide present, and silver halide grains containing 80 to 99 mole % of silver chloride and having a silver bromide-rich phase.

2. A light-sensitive silver halide photographic material according to claim 1 wherein the metal is iridium, cadmium, lead, copper, zinc, rhodium, palladium, platinum, thallium or iron.

3. A light-sensitive silver halide photographic material according to claim 2 wherein the metal is iridium or rhodium.

4. A light-sensitive silver halide photographic material according to any one of claims 1 to 3 wherein the metal ion is in the form of a metal salt or a metal complex salt.

5. A light-sensitive silver halide photographic material according to claim 4 wherein the metal salt or metal complex salt is iridium trichloride, iridium tetrachloride, potassium hexachloroiridate(III), potassium hexachloroiridate(IV) or ammonium hexachloroiridate(III).

6. A light-sensitive silver halide photographic material according to any one of claims 1 to 5 wherein the silver bromide-rich phase is of such a size that it can be distinguishably detectable by X-ray diffraction analysis.

7. A light-sensitive silver halide photographic material according to any one of claims 1 to 6 wherein the silver halide emulsion layer comprises monodisperse silver halide grains having a variation coefficient, in terms of the ratio of the standard

deviation of grain size distribution to the average grain size, of less than or equal to 0.22.

8. A light-sensitive silver halide photographic material according to claim 7 wherein the variation coefficient is less than or equal to 0.15.