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(54) Silver halide photographic light-sensitive material

Photographisches lichtempfindliches Silberhalogenidmaterial

Matériau photographique à l'halogénure d'argent sensible à la lumière

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- **PATENT ABSTRACTS OF JAPAN vol. 7, no. 42 (P-177)(1187) 19 February 1983 & JP-A- 57 192 942 (KONISHIROKU) 27 November 1982**

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Description

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive material, and more particularly to a silver halide photographic light-sensitive material having an improved gradation's dependence upon illuminance.

BACKGROUND OF THE INVENTION

In the recent dye-image forming method which uses a silver halide color photographic light-sensitive material, in order to shorten the light-sensitive material's processing procedure, a high-temperature processing and simplification of its processing steps are prevailing. Particularly, for shortening the developing time by a high-temperature development, it is very important to raise the developing rate in the color developing process. The developing rate in the color development is affected in two aspects; one, a silver halide color photographic light-sensitive material, and the other, a color developer.

In the former, the form, size and composition of the light-sensitive silver halide emulsion grains used largely affect the developing rate, while in the latter, certain conditions of the color developer used, particularly the type of a development restrainer contained therein, are liable to affect the developing rate. Especially it is known that silver chloride grains show a remarkably high developing rate under such specific conditions.

Accordingly, a silver halide color photographic light-sensitive material having silver halide emulsion layers containing silver halide grains comprised substantially of silver chloride (hereinafter sometimes called a silver chloride color photographic light-sensitive material) can be processed much faster than conventional silver chlorobromide light-sensitive materials, and thus it has high merits to the lately highlighted minilabs requiring a system comprising a compact-type automatic processor for short-time processing with a reduced amount of a replenisher and enabling the reduction in the environmental pollution load. Therefore, various investigations have hitherto been exerted to make the system a practical reality.

However, it has now been found that the silver chloride color photographic light-sensitive material varies larger in the sensitivity and gradation according to exposure illuminance than different silver halide-containing color photographic light-sensitive materials.

It is a conventionally known phenomenon that the sensitivity, even in the same exposure amount, varies with the change in the illuminance. For this reason, a measure is in advance taken to change the exposure amount in consideration of the expected sensitivity change, so that no conspicuous trouble occurs in practice.

However, if the gradation largely changes according to the illuminance in exposure (hereinafter called the gradation's dependence on illuminance), it is the fatal quality defect of a light-sensitive material. Light-sensitive materials have different gradations suited to the purposes for which they are used, and their individual gradations are differently designed. Where these light-sensitive materials are actually exposed, the illuminance at the time of exposure naturally varies according to exposure conditions such as, e.g., the brightness of a subject in the case of a camera film; and difference in the image density due to the over- or under-exposure of an original film in the case of a light-sensitive material for print-making use. In a light-sensitive material having a large gradation's dependence on illuminance, its actual gradation may diverge from the originally designed tolerable range of gradation depending on the degree of the illuminance in exposure. Therefore, depending upon the scene to be photographed, such a light-sensitive material forms an image too contrasty to depict details particularly in both highlight and shadow areas, or contrary, a too soft and unclear image; thus the large gradation's dependence on illuminance badly affects the quality of a light-sensitive material.

In a light-sensitive material for printing use, there are a variety of print sizes, ranging from a small print size called E size to a full size (20x24 in. size). There are many cases where users usually first try to make small-sized prints of some scenes, then choose their favorite scenes from among them, and then enlarge the chosen images into large-sized prints. In this instance, the original film used in making either small-sized prints or large-sized prints is one and the same, and besides, in enlargement for large-sized prints, it is difficult to largely increase the intensity of the light source therefor, so that the exposure illuminance to the printing light-sensitive material is inevitably weakened. For this reason, if a light-sensitive material has a large gradation's dependence on illuminance, it may provide a good quality image on a small-sized print, but would form a degraded image on a large-sized print, thus disappointing the users.

As has been mentioned, against the change in the sensitivity due to the illuminance in exposure, most exposure devices are so improved as to cause little or no problems in practice, while against the change in the gradation it is very difficult to take steps by the improvement of exposure devices alone, so that it is desirable that the gradation's dependence on illuminance be improved in the aspect of light-sensitive materials.

For decreasing such the dependence on illuminance there are already disclosed improving techniques using compounds of metals such as iridium and the like.

For example, JP O.P.I. Nos. 47941/1986, 23146/1986, 97648/1986, 112142/1986, 7042/1987, 316039/1988 and 183467/1989: and U.S. Patent No. 4,269,927 disclose techniques for improving the reciprocity law failure characteristic by having silver halide grains doped with Ir, Cd, Pb, Zn, Fe or Rh, but the technique provides an insufficient effect, causes a sensitivity drop and also bears other photographically undesirable effects, and thus the obtained effect is limited.

JP O.P.I. Nos. 212932/1988, 304253/1988, 121847/1989, 121846/1989 and 167752/1989 also disclose improving techniques with silver halide grains-forming methods or sensitizing methods, but the effect obtained therefrom is not sufficient.

We, the inventors, have continued our investigation concerning the above matter, and as a result, have found that the gradation's dependence on illuminance can be improved by mixing emulsions of the same color sensitivity but containing different doping amounts of an Ir compound.

Gradation adjusting techniques comprising the mixing of silver halide grains of the same color sensitivity but different in the photographic speed are well-known techniques. For example, JP O.P.I. Nos. 148049/1984 and 718383/1988 describe the use of a mixture of silver halide emulsions having sensitivities made different by changing the grain size, crystal havit and composition of silver halide grains, but make no mention of the reciprocity law failure characteristic thereof.

JP O.P.I. No. 192942/1982 discloses the use of a mixture of iridium-containing silver halide grains and iridium-free silver halide grains. It mentions that this combination improves reciprocity law failure.

JP O.P.I. No. 131544/1989 discloses a technique for chemical sensitization by use of a mixture of silver halide emulsions doped with different amounts of a metal compound, but makes no mention of any reciprocity law failure-improving effect.

JP O.P.I. Nos. 71839/1988, 5234/1987 and 172348/1987 describe examples of the use of a mixture of iridium compound-doped emulsions, but make no mention of their reciprocity law failure and sensitivity's dependence on humidity at the time of exposure, so that they are not suggestive of the present invention.

Thus, it is a new reveration to us that the gradation's dependence on illuminance can be improved by use of a mixture of emulsions doped with different amounts of an iridium compound, but at the same time it has been found that the sensitivity of the silver halide light-sensitive material thus obtained largely changes with the change in humidity at the time of exposure.

We tried further improvement, and have found that the light-sensitive material's dependence of its sensitivity on humidity at the time of exposure can be largely improved by growing silver halide grains in the presence of an iridium compound and a compound of a metal selected from the group of metals belonging to Groups Va, VIa, VIIa and VIII of the periodic table.

Examples of the technique to use metallic compounds as dopants in silver halide grains are given below.

JP O.P.I. Nos. 183643/1989, 183647/1989 and 183655/1989 disclose the improvement of the reciprocity law failure characteristic by use of Ir and Rh compounds in combination with a Fe compound. This technique can obtain an intended effect by adding the Ir and Rh compounds to one phase and the Fe compound to another phase of a silver halide grain, but make no mention of the exposure's dependence on humidity at the time of exposure, thus being not suggestive of the effect of the present invention.

U.S. Patent No. 4,828,962 discloses the improvement of the high-intensity reciprocity law failure characteristic by the combined use of a Ru compound and an Ir compound, but makes no mention of the sensitivity's dependence on humidity in exposure and of the mixing use of emulsions, thus being unable to attain the object of the present invention.

Any of the above conventional techniques provides a sufficient sensitivity for the object of the invention, but not sufficient to obtain a silver halide emulsion having little or no dependence of its gradation and sensitivity on illuminance and of its sensitivity's dependence on humidity in exposure. We continued still further improvement, and have found that a silver halide light-sensitive material excellent in the dependence of its gradation and sensitivity on illuminance as well as in the dependence of its sensitivity on humidity in exposure can be obtained by use of a mixture of silver halide emulsions satisfying specific requirements.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a silver halide light-sensitive material having little or no dependence of its gradation and sensitivity on illuminance and of its sensitivity or humidity at the time of exposure.

According to the present invention there is provided a silver halide photographic light-sensitive material comprising a support having thereon a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer, and at least one of said color-sensitive layers comprises iridium-containing silver halide, characterized in that said color-sensitive layer comprises two or more kinds of iridium-containing silver halides having different iridium contents; and at least one of said silver halides is prepared in the presence of an iridium compound and a compound of a metal selected from metals, other than iridium, belonging to Groups Va, VIa, VIIa and VIII of the periodic table.

The above object of the invention can be accomplished by the following silver halide photographic light-sensitive materials (1) to (5):

(1) A silver halide photographic light-sensitive material comprising a support having thereon at least one blue-sensitive layer, at least one green-sensitive layer and at least one red-sensitive layer, in which the silver halide contained in at least one of the above color-sensitive layers satisfies the following requirements 1 and 2:

Requirement 1: The silver halide contained in the layer shall be a mixture of two or more silver halide emulsions different in the Ir content per grain.

Requirement 2: At the time of forming the silver halide grain of at least one of the silver halide emulsions of Requirement 1, an iridium compound and a compound of non-iridium metal selected from the metals belonging to Groups Va, VIa, VIIa and VIII of the periodic table shall be present together.

(2) A silver halide photographic light-sensitive material comprising a support having thereon at least one blue-sensitive layer, at least one green-sensitive layer and at least one red-sensitive layer, in which the silver halide contained in at least one of the above color-sensitive layers satisfies the following Requirements 1, 2 and 3:

Requirement 1: The silver halide contained in the layer shall be a mixture or two or more silver halide emulsions different in the Ir content per grain.

Requirement 2: At the time of forming the silver halide grain of at least one of the silver halide emulsions of Requirement 1, an iridium compound and a compound of non-iridium metal selected from the metals belonging to Groups Va, VIa, VIIa and VIII of the periodic table shall be present together.

Requirement 3: At least one of the silver halide emulsions of Requirement 1 shall be chemically sensitized with a gold compound.

(3) The silver halide photographic light-sensitive material of the above (1) or (2), wherein the iridium compound added at the time of forming the silver halide grains is in an amount of not more than 10^{-21} mol per grain.

(4) The silver halide photographic light-sensitive material of the above (1), (2) or (3), wherein the iridium compound and the compound of a metal selected from the metals belonging to Groups Va, VIa, VIIa and VIII of the periodic table, which should be added at the time of forming the silver halide grain, are added at the time of forming the same phase of the silver halide grain.

(5) The silver halide photographic light-sensitive material of the above (1), (2), (3) or (4), wherein the silver chloride content of the silver halide is not less than 99 mol%.

DETAILED DESCRIPTION OF THE INVENTION

The silver halide photographic light-sensitive material of the invention comprises at least one blue-sensitive layer, at least one green-sensitive layer and at least one red-sensitive layer, in which at least one of the color-sensitive layers contains a silver halide emulsion that satisfies the following Requirements 1 and 2:

Requirement 1: The silver halide contained in the layer shall be a mixture of two or more silver halide emulsions different in the Ir compound content per grain.

Requirement 2: At the time of forming the silver halide grain of at least one of the silver halide emulsions of Requirement 1, an iridium compound and a compound of a metal selected from the metals belonging to Groups Va, VIa, VIIa and VIII of the periodic table shall be present together.

The silver halide grain contained in the emulsion of the invention is formed in the presence of an iridium compound. The silver halide grain of at least one of the silver halide emulsions to be mixed is formed in the presence of a compound of a non-iridium metal selected from the metals belonging to Groups Va, VIa, VIIa and VIII of the periodic table. Herein, the '...formed in the presence of the compound' implies that the compound is added in any one of the stages of the nucleus formation, growth and physical ripening of the silver halide grain. Preferably, the iridium compound and the compound of a non-iridium metal are both added at the same stage during the course of the formation of the silver halide grain.

To be concrete, there are a method of adding the compound to a mother liquid before the nucleus formation, a method for the rush-addition of the compound in the midst of the silver halide formation, a method of in advance adding the compound to either a halide solution or a soluble silver salt solution which are to be provided for the formation and growth of the silver halide, and a method of adding the compound after completion of the growth and immediately before the physical ripening of the silver halide. Further, in an emulsion producing method wherein fine-grained silver halide is supplied to form and grow silver halide grains, the compound may be added in the above manner at the time of preparing the fine-grained silver halide, which is then added to a reaction vessel to form the silver halide.

The iridium compound may be added by instalments in different stages. The iridium compound to be added may be a mixture liquid of two or more different iridium compounds. The two or more different iridium compounds may be added separately in different stages.

Also in the case of the aforementioned non-iridium metallic compound, it may be added on instalments in different stages, a mixture solution of two or more kinds thereof may be added, or solutions of two or more kinds thereof may be added separately in different stages.

As for the iridium compound used in the invention, those industrially suitably usable from the standpoint of stability, safety and economical efficiency include iridium (III) halide compounds, iridium (IV) halide compounds and iridium complex salts having ligands such as halogens, amines, oxalates, etc. The following are the examples of the above compound, but are not limited thereto.

Iridium trichloride, iridium tribromide, potassium hexachloroiridate(III), ammonium iridium(III) sulfate, potassium iridium(III)-disulfate, tripotassium iridium(III) trisulfate, iridium(III) sulfate, ridium(III) trioxalate, potassium hexacyanoiridate(III), iridium tetrachloride, iridium tetrabromide, potassium hexachloroiridate(IV), ammonium hexachloroiridate-(IV), potassium iridate(IV), iridium(IV) trioxalate, and potassium hexacyanoiridate(IV).

In the invention, any discretionary compound may be selected from these compounds and, if necessary, some of them may be used in combination. In many cases, the iridium compound is in the form of a solution of it dissolved in a water-miscible solvent, but to the solution, for its stabilization, may be added a hydrogen halide such as hydrochloric acid or hydrobromic acid; an alkali halide such as potassium chloride, sodium chloride or potassium bromide; or nitric acid.

In the invention, the adding amount of the iridium compound is preferably not less than 10^{-11} mol, and more preferably not less than 10^{-9} mol per mol of silver halide for enhancing the effect of the invention, and preferably not more than $5x10^{-6}$ mol, and more preferably not more than $5x10^{-7}$ mol per mol of silver halide for reducing fog and preventing desensitization.

Further, in the invention, the average adding amount per silver halide grain of the iridium compound to be added at the time of forming the silver halide grain of one emulsion is preferably $1x10^{-23}$ to $1x10^{-21}$ mol, and the adding amount per silver halide grain of the iridium compound to the silver halide grain of the other is preferably 1.2 times the above amount.

However, where emulsions different in the sensitivity are mixed, the adding amount of the iridium compound to the low-speed emulsion is preferably $2x10^{-23}$ to $5x10^{-16}$ mol and more preferably $2x10^{-23}$ to $5x10^{-18}$ mol per grain, while that to the high-speed emulsion is preferably $2x10^{-24}$ to $2x10^{-18}$ mol and more preferably $2x10^{-24}$ to $2x10^{-20}$ mol per grain.

The 'metals' for the 'compounds of the non-iridium metals belonging to Groups Va, VIa, VIIa and VIII of the periodic table' mentioned previously are vanadium, chromium, manganese, iron, cobalt, nickel, niobium, technetium, ruthenium, rhodium, palladium, tantalum, rhenium, osmium and platinum. In the invention, compounds of any of these metals may be used, and complex salts thereof may also be used. Examples of the ligand of these complex salts include chloro, bromo, iodo, ammine, cyano, thiocyano and acetylacetone. Examples of the metallic compound are given below, but are not limited thereto.

Vanadium dichlorooxide, vanadium oxyoxide, vanadium oxysulfate, vanadium oxide-acetylacetic acid, chromic chloride, chromic bromide, chromic nitrate, chromic acetate, potassium-chromic sulfate, manganous acetate, manganous-ammonium sulfate, manganous bromide, manganous carbonate, manganous chloride, ferrous chloride, ferric chloride, ferrous sulfate, ferric sulfate, Mohr's salt, red prussiate of potash, yellow prussiate of potash, ferrous thiocyanate, ferric thiocyanate, ferrous bromide, ferric bromide, ferrous acetate, ferric acetate, ferric pentacyanoammine, cobaltous chloride, cobaltic chloride, cobaltous acetate, cobaltic chlorohexaammine, cobaltous nitrate, nickelous chloride, nickelous oxalate, nickelous benzoate, nickelous cyanide, niobium(V) chloride, ruthenic chloride, ruthenic-acetylacetic acid, rhodium trichloride, rhodium-(III) nitrate, rhodium triacetate, palladium(II) acetate, palladium(II)-acetylacetic acid, ammonium-palladium(II) chloride, palladium(II) chloride, tantalic chloride, platinic chloride, platinum(IV) chloride, potassium tetrachloroplatinate, osmic acid, potassium rhenium(II) hexacyanate, potassium ruthenium(11) hexacyanate, potassium ruthenium(III) hexathiocynate, potassium pentacyanochlororthenate(II), sodium pentachloronitrosylruthenate(III), and potassium pentabromonitrosylosmate-(IV).

In the invention, an appropriate compound may be selected from among these compounds, and, if necessary, some of them may be used in combination.

In the invention, there may be preferably used a mixture of emulsions different in the iridium content, wherein each of the emulsions may additionally contain a compound of non-iridium metal belonging to Group VIII of the periodic table.

In the invention, the adding amount of the non-iridium metal compound is preferably not less than 10^{-10} mol and more preferably not less than 10^{-8} mol per mol of silver halide for enhancing the effect of the invention, and preferably not more than $5x10^{-3}$ mol and more preferably not more than $5x10^{-4}$ mol per mol of silver halide for reducing fog and preventing desensitization.

It is preferable that the iridium compound and non-iridium metal compound be present together at the same time in the silver halide grain formation.

The silver halide grain of the invention may be formed in accordance with one of the methods described in JP O. P.I. Nos. 45437/1984, 162540/1984, 48754/1984, 222844/1985, 222845/1985, 136735/1985 and 113056/1986. Among these methods, preferred for the effect of the invention is the method which uses the controlled double-jet process described in JP O.P.I. No. 45437/-1984, and more preferred is the method described in JP O.P.I. No. 113056/1986, in which the formation and/or growth of silver halide grains is made by pour-in and supply of a soluble silver salt solution and/or soluble halide solution through an under-liquid nozzle of a mixer provided in a photographic emulsion preparation device comprised of a reaction vessel that has therein the mixer sunk under a liquid to spew out its inside liquid through its nozzle to thereby suck in the liquid, and then repeat the spew-out to form a circulation flow for a substantial axial-flow stirring.

The addition of the soluble silver salt solution and soluble halide solution is preferably controlled so that they are added in amounts substantailly proportional to the whole area of the silver halide grains inside the reaction vessel.

The above method is necessary for narrowing the grain size distribution of silver halide grains in order to lessen the influence upon a rapid processing by changes in the developer solution's temperature and time, and at the same time to lessen the gradation's dependence on illuminance. That is, as a result of our investigation, the gradation's dependence on illuminance correlates well with the adding amount of the iridium compound per grain of silver halide rather than the whole amount of the iridium compound to the whole amount of silver halide.

Therefore, as the silver halide's grain size distribution becomes wider, the adding amount of the iridium compound per grain of silver halide widely varies, thus making it difficult to control the gradation's dependence on illuminance.

In the silver halide emulsion of the invention, the formation and/or growth of the silver halide grain is preferably made by the foregoing controlled double-jet process. In this instance, it is preferable that the addition of the soluble halide solution be completed later than the completion of the addition of the soluble silver salt solution. By doing so, the resulting silver halide emulsion can be well fog-resistant, its gradation in the low-density area can be improved, whereby the effect of the invention can be further enhanced.

The grain size of the silver halide grains of the invention is preferably 0.2 to 1.6μm, and more preferably 0.25 to 1.2μm in consideration of the rapid-processability, sensitivity and other photographic characteristics.

The above grain size can be measured in accordance with various methods generally used by those skilled in the art. Typical methods are described in R. P. Loveland, 'Particle-Size Measurement', A.S.T.M Symp. on Light Microscopy, pp.94-122, 1955, and Mees and James, the 'Theory of Photographic Process' 3rd ed., Mcmillan (1966). The grain size can be measured, using the diameter-approximate value of the projection image of the grain. Where the grains are substantially uniformly round, their grain size distribution can be fairly precisely calculated from their grain diameters or projection image area.

The grain size distribution of the silver halide grains of the invention may be polydisperse, but is preferably monodisperse; monodisperse silver halide grains having a variation coefficient of preferably not more than 0.22, and more preferably not more than 0.15, wherein the variation coefficient is a coefficient representing the width of the grain size distribution, which is defined by Standard deviation of grain size distrbution / average grain size.

The configuration of the silver halide grain of the invention may be discretional. A preferred example of the configuration of the grain is a cubic crystal having (100) faces.

The usable grain crystal in the invention may also be an octahedral, tetradecahedral or dodecahedral crystal, which may be produced in accordance with the methods described in U.S. Patent Nos. 4,183,756 and 4,225,666; JP O.P.I. No. 26589/1980; JP E.P. No. 42737/1980: and J. Phot. Sci., 21, 39 (1973). Further, silver halide grains having twin faces or in the irregular form may also be used.

In the silver halide light-sensitive material of the invention, the silver halide grain contained in at least one of its silver halide emulsion layers may be of any composition, but is preferably of silver chlorobromide substantially not containing silver iodide. The 'substantially not containing silver iodide' herein means that the silver iodide content is not more than 1 mol%, preferably not more than 0.5 mol%. The most preferred is that silver chlorobromide contains no silver iodide at all. The effect of the invention appears to the utmost when the silver halide of the invention is silver chlorobromide containing not less than 90 mol% silver chloride, preferably not less than 99 mol% silver chloride, and most preferably is silver chloride alone.

In the invention, the silver chlorobromide containing not less than 99 mol% silver chloride is chemically sensitized with use of at least a sulfur sensitizer and a gold sensitizer.

As the sulfur sensitizer there may be used conventionally known compounds such as a thiosulfate, allylthiocarbamidothiourea, allylisothiocyanate, cystine, p-toluenethiosulfonate and rhodanine. Further, there may also be used those described in U.S. Patent Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313 and 3,656,955; West German Patent No. 1,422,869; JP O.P.I. Nos. 24937/1981 and 45016/1980. The adding amount of the sulfur sensitizer is not restricted, but in the case of sodium thiosulfate, its amount is preferably from $1x10^{-6}$ to $1x10^{-5}$ mol, and more preferably from $2x10^{-6}$ to $8x10^{-6}$ mol per mol of silver halide.

As the gold sensitizer there may be used various gold compounds of which the oxidation number is either +1 or +3. Typical examples of the gold sensitizer include chloroauric acid, potassium chloroaurate, auric trichloride, potassium auricthiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate and pyridyl trichlorogold.

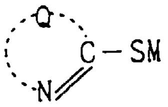
The adding amount of the gold sensitizer depends upon various conditions, but is usually $5x10^{-7}$ to $5x10^{-3}$ mol, preferably $2x10^{-6}$ to $1x10^{-4}$ mol, more preferably $2.6x10^{-6}$ to $4x10^{-5}$ mol, and most preferably $2.6x10^{-6}$ to $9x10^{-6}$ mol per mol of silver halide.

The gold sensitizer may be added in any discretional stage of the silver halide emulsion production process, but is preferably during the period between the completion of the silver halide formation and the completion of the chemical sensitization.

The silver halide emulsion of the light-sensitive material of the invention is subjected to an optimum chemical sensitization, and at the same time may be subjected to the addition of compounds called antifoggants or stabilizers in order to prevent the light-sensitive material from being desensitized or fogged during its storage or processing.

Examples of the above compound include 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 3-methylbenzothiazole, 1-phenyl-5-mercaptotetrazole, and many other heterocyclic compounds and mercapto compounds. Particularly, purine derivatives, and the mercapto compound represented by the following Formula S may be suitably used.

Formula S



wherein Q represents a group of atoms necessary to form a 5-or 6-member heterocyclic ring or a benzene ring-condensed 5-or 6-member heterocyclic ring; and M is a hydrogen atom or a cation.

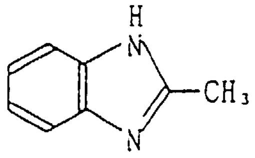
Examples of the heterocyclic ring represented by Q include imidazole, triazole, thiadiazole, oxadiazole, tetrazole, thiazole, oxazole, selenazole, triazine, benzimidazole, naphthoimidazole, benzothiazole, naphthothiazole, benzoselenazole, naphthoselenazole and benzoxazole.

Examples of the cation represented by M include an alkali metal such as sodium or potassium, and an ammonium group.

The following are the typical examples of the heterocyclic compound usable in the invention, which reacts with silver ions to form a less-soluble salt.

Exemplified compounds

S - 1



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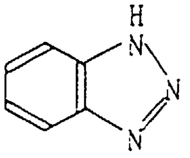

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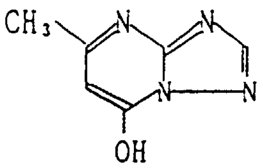

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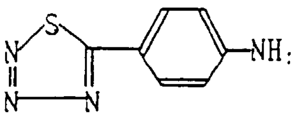

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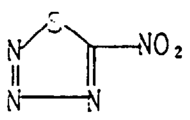
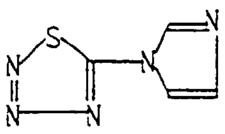
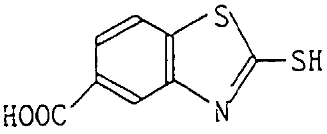


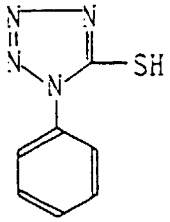
S - 6



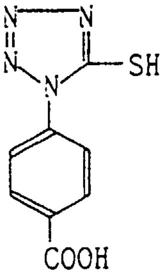
S－7



S－8



S－9



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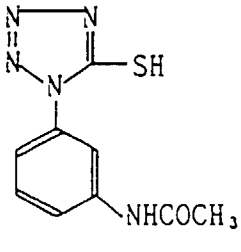

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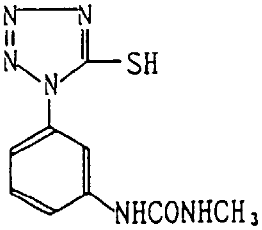

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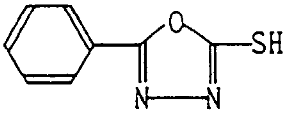

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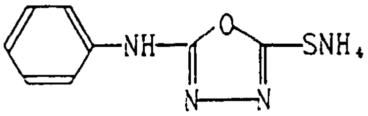

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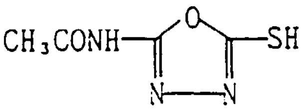

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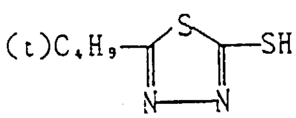

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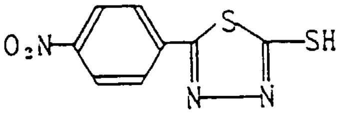
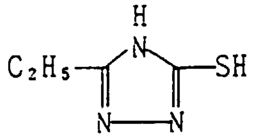
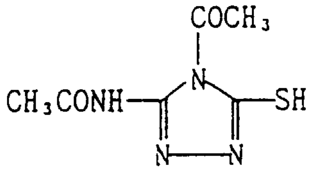


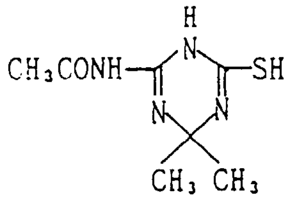
S − 17



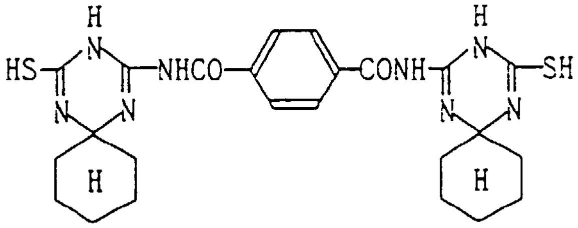
S − 18



S − 19



S − 20



These compounds are described in JP O.P.I. Nos. 36234/1988 and 146044/1988; and Japanese Patent Application No. 20365/1988.

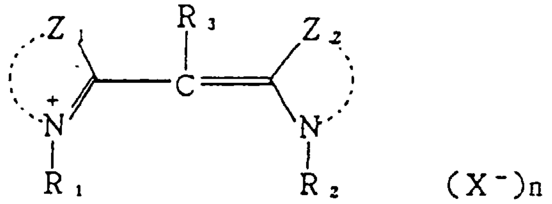
The silver halide emulsion of the invention can be spectrally sensitized to desired wavelength regions with use of sensitizing dyes known to those skilled in the art. Sensitizing dyes may be used alone or in combination. In combination with the sensitizing dye there may be incorporated into the emulsion a supersensitizer that is a dye which in itself has no spectral sensitization effect or a compound which does substantially not absorb visible light, both having a function to increase the spectral sensitization effect of the sensitizing dye.

Various sensitizing dyes may be used alone or in combination.

Sensitizing dyes usable in the blue-sensitive silver halide emulsion include those described in West German Patent No. 929,080; U.S. Patent Nos. 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 3,656,959, 3,672,897, 3,694,217, 4,025,349 and 4,046,572; British Patent No. 1,242,588; JP E.P. Nos. 14030/1969 and 24844/1977.

The blue-sensitive emulsion of the invention is preferably spectrally sensitized by a sensitizing dye represented by the following Formula A:

Formula A



In Formula A, Z_1 and Z_2 each represent a group of atoms necessary to form a benzooxazole nucleus, a naphthooxazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus, a benzothiazole nucleus, naphthothiazole nucleus, a benzimidazole nucleus, a naphthoimidazole nucleus, a pyridine nucleus or a quinoline nucleus. These heterocyclic rings include those having a substituent.

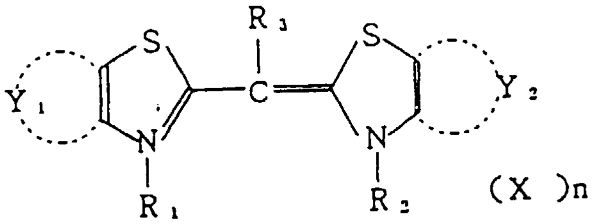
Examples of the substituent of the heterocyclic ring formed with Z_1 or Z_2 include a halogen atom, a hydroxyl group, a cyano group, an aryl group, an alkyl group and an alkoxycarbonyl group. Preferred among these substituents are a halogen atom, a cyano group, an aryl group, and an alkyl or alkoxy group having 1 to 6 carbon atoms, and more preferred are a halogen atom, a cyano group, a methyl group, ethyl group, methoxy group and ethoxy group.

R_1 and R_2 each represent an alkyl group, an alkenyl group or an aryl group; preferably an alkyl group, more preferably an alkyl group substituted by a carboxyl or sulfo group, and most preferably a sulfoalkyl group having 1 to 4 carbon atoms. And R_3 is a hydrogen atom, a methyl group or an ethyl group.

X^- represents an anion; and n is an integer of 0 or 1.

The most useful dyes among these sensitizing dyes represented by Formula A are those having Formula A-1:

Formula A-1



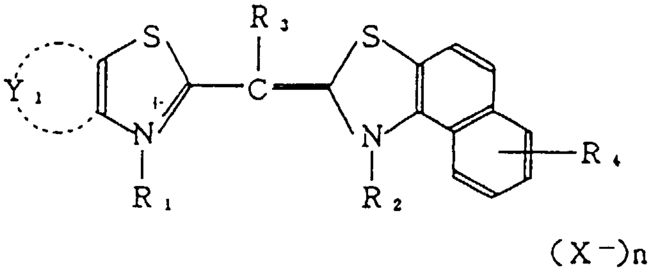
In Formula A-1, Y_1 and Y_2 each represent a group of atoms necessary to complete a benzene or naphthalene ring which may have a substituent.

The substituent to the benzene or naphthalene ring formed by Y_1 or Y_2 is preferably a halogen atom, a hydroxyl group, a cyano group, an aryl group, an alkyl group, an alkoxy group or an alkoxy carbonyl group, more preferably a halogen atom, a cyano group, an aryl group, or an alkyl or alkoxy group having 1 to 6 carbon atoms, and most preferably a halogen atom, a cyano group, a methyl group, an ethyl group, a methoxy group or an ethoxy group.

R_1, R_2, R_3, X^- and n are the same as those defined in Formula A.

The more preferred dyes among these sensitizing dyes having Formula A-1 are those represented by the following Formula A- 2:

Formula A-2



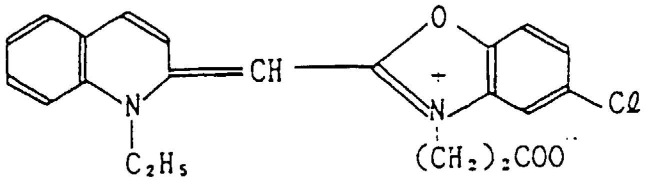
In Formula A-2, R_1, R_2, R_3, Y_1, X^- and n are the same as those defined in Formula A-1; and R_4 is a hydrogen atom or a substituent.

Examples of the substituent represented by R_4 are the same as those of the substituent which may be possessed by the benzene or naphthalene ring formed by Y_1 or Y_2 in Formula A-1.

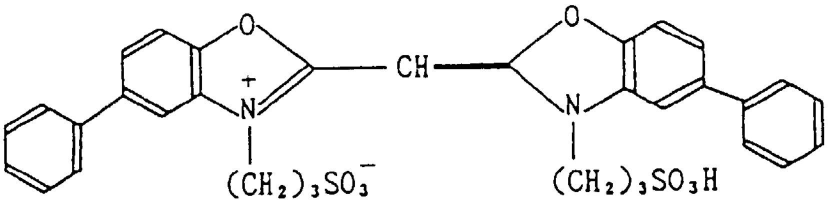
The following are the examples of the sensitizing dye having Formula A used in the invention.

Exemplified sensitizing dyes

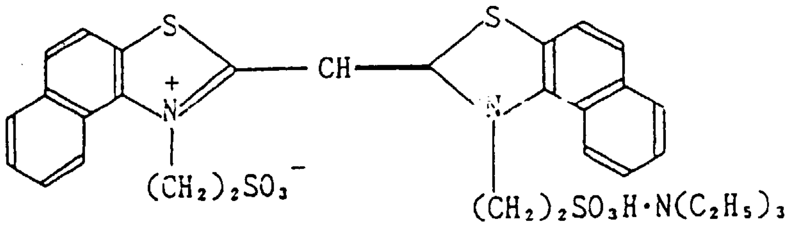
A—1



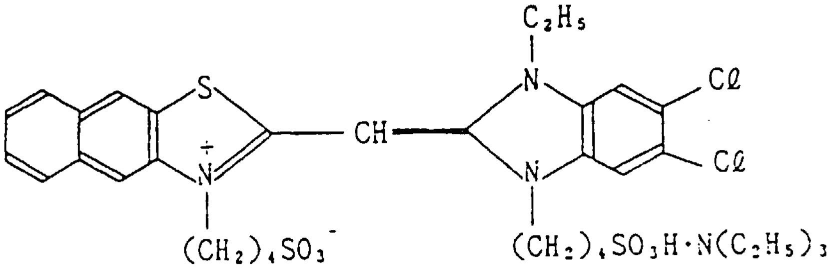
A — 2



A — 3



A — 4



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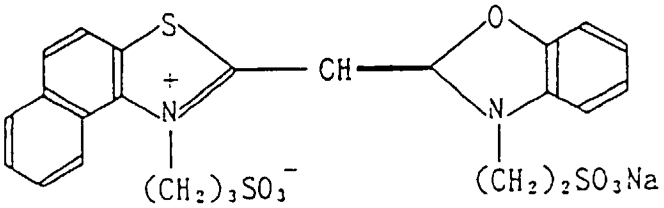

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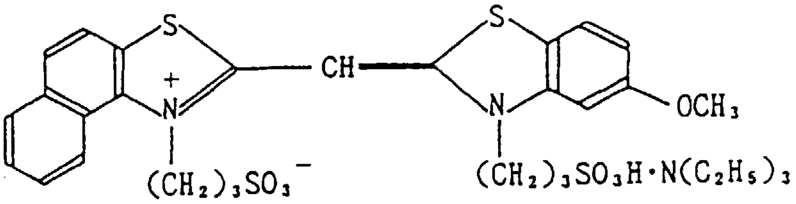
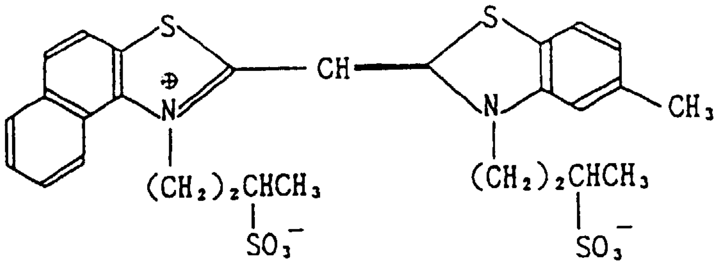


A — 7



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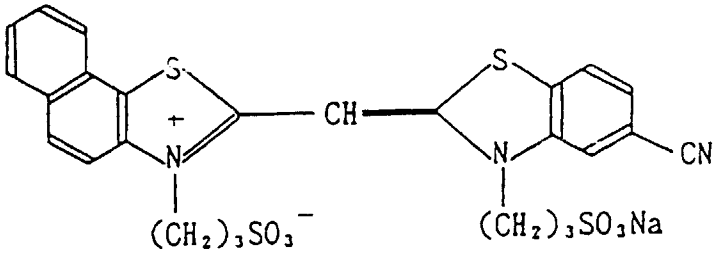

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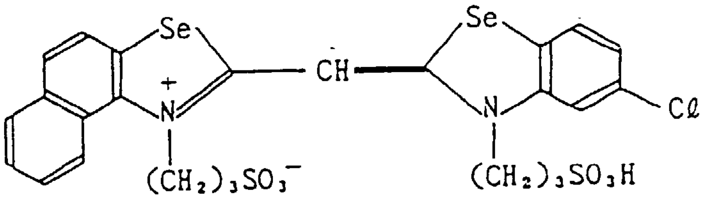

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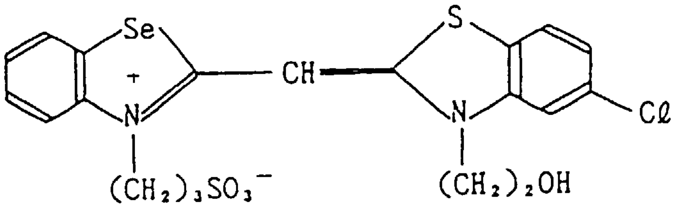

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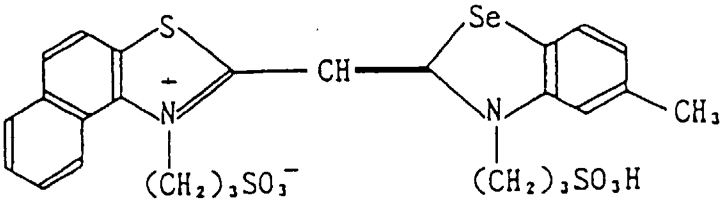

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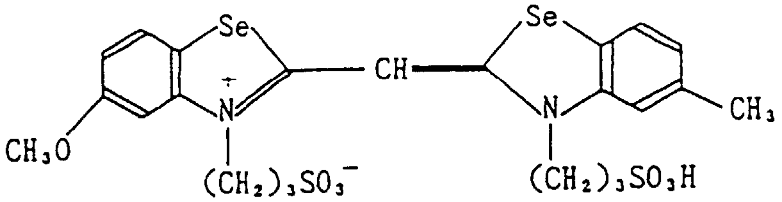

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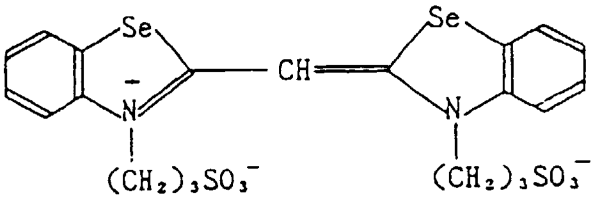

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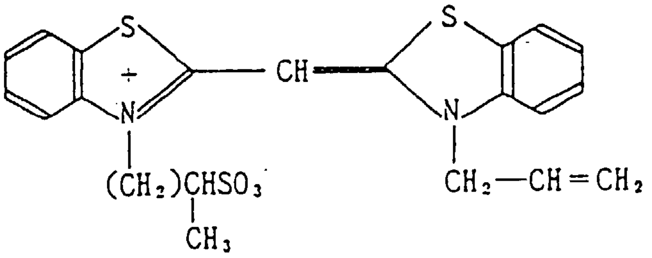

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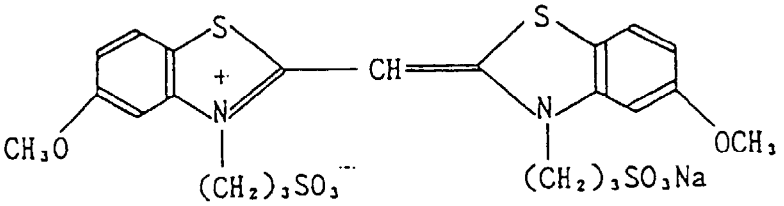

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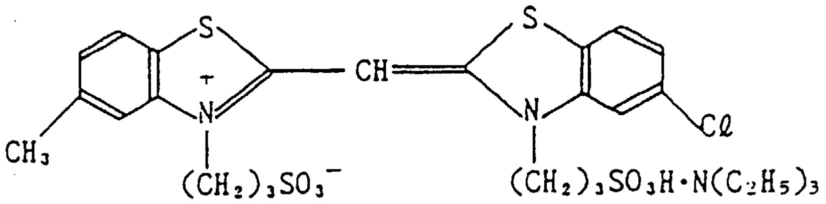

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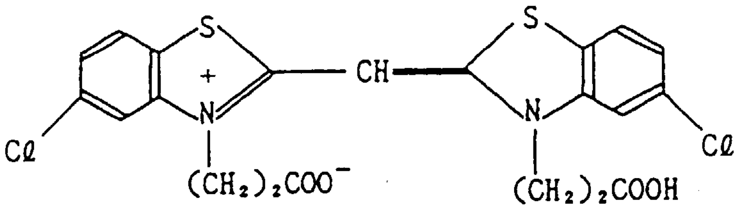

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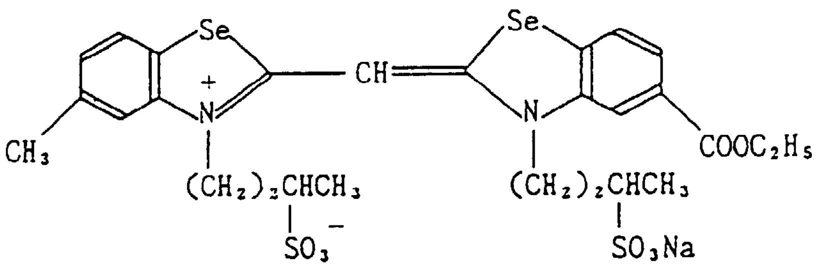

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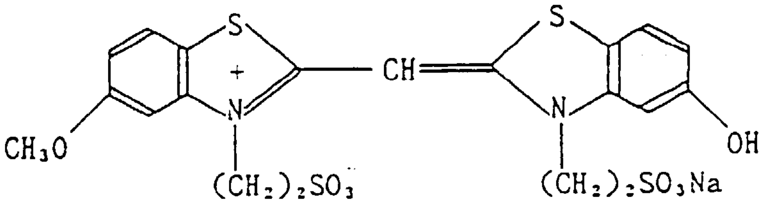

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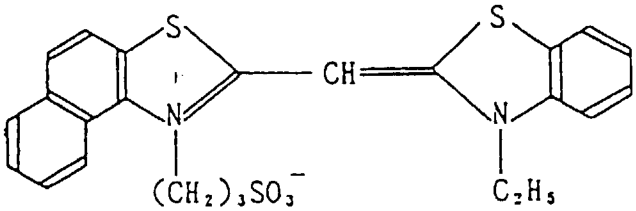

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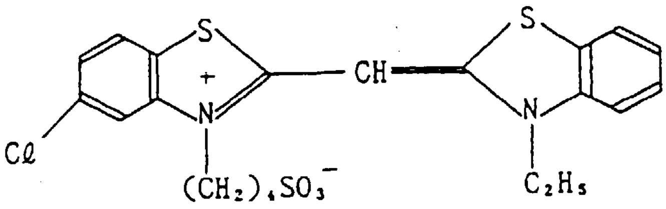

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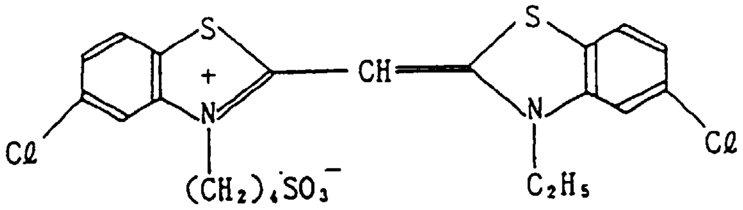

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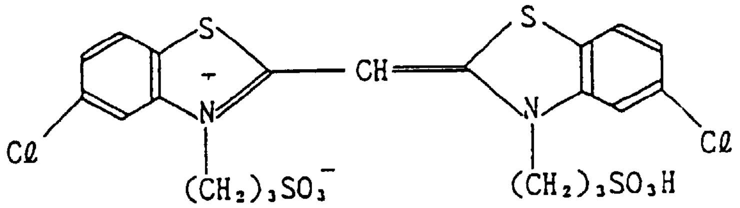

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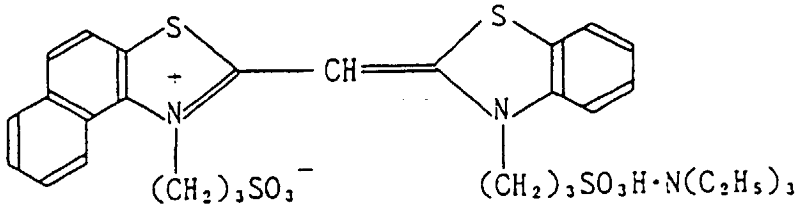

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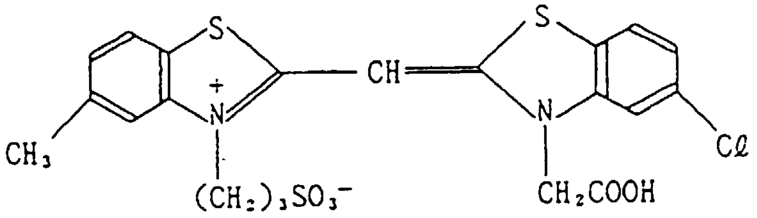

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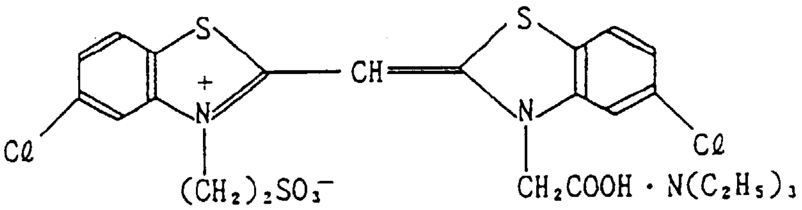

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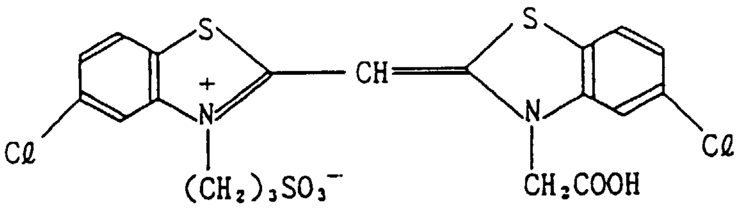

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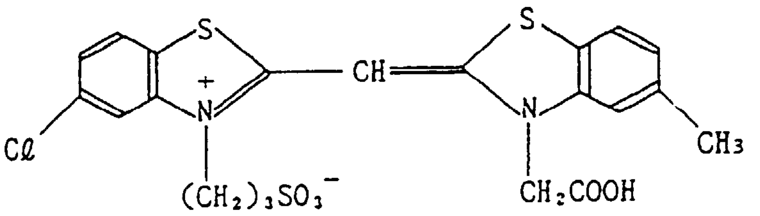

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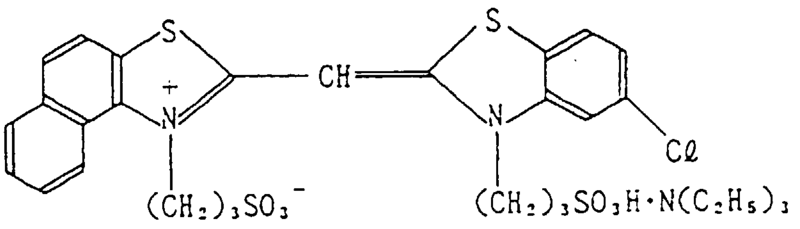

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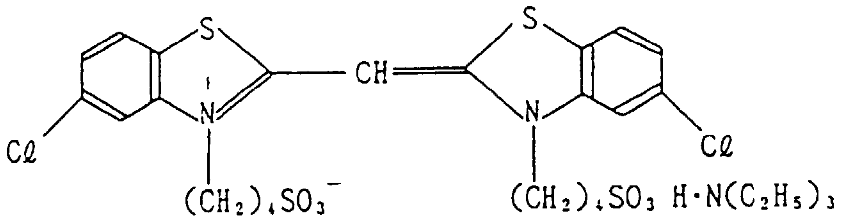
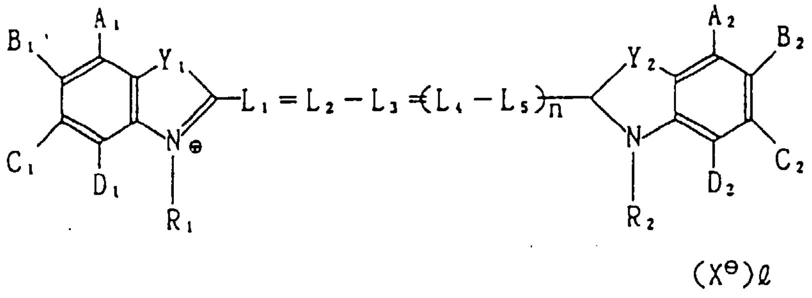


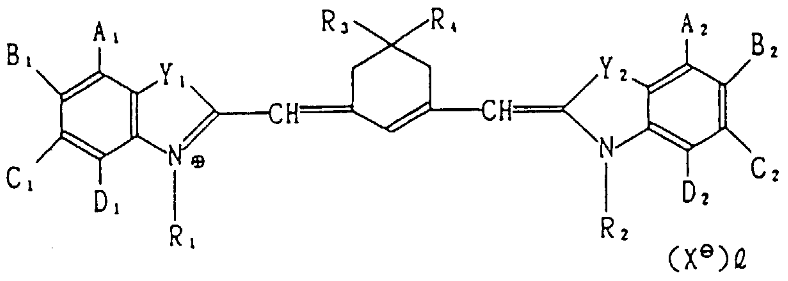
Typical sensitizing dyes for the green-sensitive silver halide emulsion are the cyanine dyes, merocyanine dyes and complex cyanine dyes described in U.S. Patent Nos. 1,939,201, 2,072,908, 2,739,149 and 2,945,763; and British Patent No. 505,979. Typical sensitizing dyes for the red-sensitive silver halide emulsion are the cyanine dyes, merocyanine dyes and complex cyaning dyes described in U.S. Patent Nos. 2,269,234, 2,270,378, 2,442,710, 2,454,629 and 2,776,280. Further, the cyanine dyes, merocyanine dyes and complex cyanine dyes described in U.S. Patent Nos. 2,213,995, 2,493,748 and 2,519,001; and West German Patent No. 929,080 can be advantageously used for the green-sensitive silver halide emulsion or red-sensitive silver halide emulsion.

The silver halide emulsion contained in the red-sensitive silver halide emulsion layer of the silver halide photographic light-sensitive material of the invention is preferably spectrally sensitized with a sensitizing dye represented by the following Formula RS1 or Formula RS2 for highly attaining the object of the invention.

Formula RS1



Formula RS2



In the above formulas, R_1 and R_2 each represent an alkyl group or an aryl group; L_1, L_2, L_3, L_4 and L_5 each represent a methine group; Y_1 and Y_2 each represent an oxygen atom, a sulfur atom or a selenium atom; R_3 and R_4 each represent a lower alkyl group: A_1, A_2, B_1, B_2, C_1, C_2, D_1 and D_2 each represent a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a phenyl group, a cyano group, a nitro group or an alkoxycarbonyl group, provided that at least one of the combinations of A_1 and B_1, B_1 and C_1, C_1 and D_1, A_2 and B_2, B_2 and C_2, and C_2 and D_2 may be condensed to form a benzene ring; $X^{\ominus}$ is an acid anion; and n and 1 each represent an integer of 0 or 1, provided that when the compound forms an intramolecular salt, 1 is 0.

In Formulas RS1 and RS2, the alkyl group represented by R_1 or R_2 may be in the branched form or may have an unsaturated bonding, and is preferably an alkyl having not more than 10 carbon atoms with a substituent such as a sulfo, aryl, carboxy, amine (primary, secondery or tertiary), alkoxy, aryloxy, hydroxy, alkoxycarbonyl or acyloxy group or a halogen atom.

Examples of the alkyl group include methyl, ethyl, sulfobutyl, benzyl, phenethyl, carboxymethyl, dimethylaminopropyl, methoxyethyl, phenoxypropyl, methylsulfonylethyl, cyclohexyl, octyl, decyl, carbamoylethyl, sulfophenethyl, sulfobenzyl, 2-hydroxy-3-sulfopropyl, ethoxycarbonylethyl, 2,3-disulfopropoxypropyl, sulfopropoxyethoxyethyl, trifluoroethyl, carboxybenzyl, cyanopropyl, p-carboxyphenethyl, ethoxycarbanylmethyl, pivaloylpropyl, propionylethyl, anisyl, acetoxyethyl, benzoyloxypropyl, chloroethyl, N-ethylaminocarbonylpropyl, allyl, 2-butynyl and cyanoethyl groups. The aryl group represented by R_1 or R_2 includes phenyl, carboxyphenyl and sulfophenyl groups. R_1 and R_2 are preferably alkyl groups.

The acid anion represented by X in Formulas RS1 and RS2 is, e.g., a chlorine ion, bromine ion, iodine ion, perchloric acid ion, fluoroboric acid ion, p-toluenesulfonic acid ion, ethylsulfonic acid ion or nitric acid ion.

Where the methine group represented by L_1, L_2 or L_3 has a substituent, it is represented by -CR=, wherein the substituent R is a straight-chain or branched-chain alkyl group having 1 to 8 carbon atoms, such as methyl, ethyl, carboxymethyl or benzyl; an alkoxy group such as methoxy or ethoxy; or an aryl group such as phenyl or tolyl.

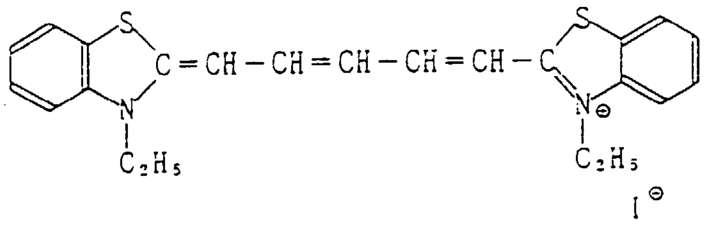
In Formula RS1, n is an integer of preferably 1.

The alkyl group represented by A_1, A_2, B_1, B_2, C_1, C_2, D_1 or D_2 in Formulas RS1 and RS2 is a straight-chain or branched-chain lower alkyl group having 1 to 5 carbon atoms, such as methyl, ethyl, butyl or trifluoromethyl. The alkoxy group represented by the same is a straight-chain or branched-chain alkyloxy group having 1 to 5 carbon atoms, such as methoxy or ethoxy. The halogen atom is fluorine, chlorine, bromine or iodine. The phenyl group is, e.g., phenyl with no substituent, hydroxyphenyl or carboxyphenyl. The alkoxycarbonyl group is, e.g., methoxycarbonyl or ethoxycarbonyl.

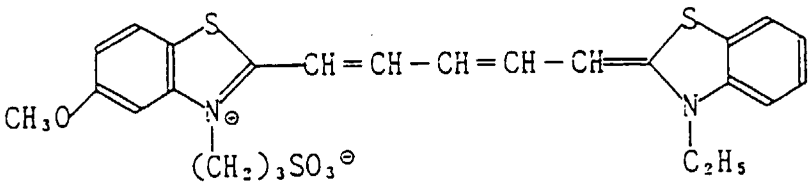
The following are the examples of the sensitizing dye having Formula RS1 or RS2, but are not limited thereto.

Exemplified sensitizing dyes

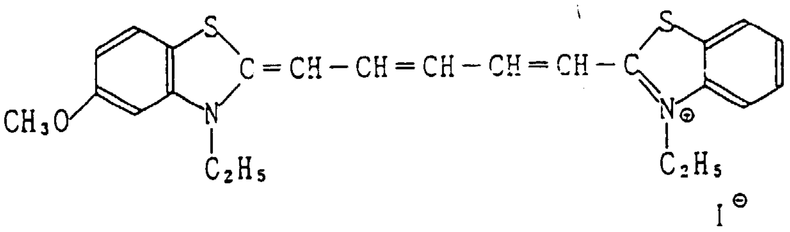
RS-1



RS-2



RS-3



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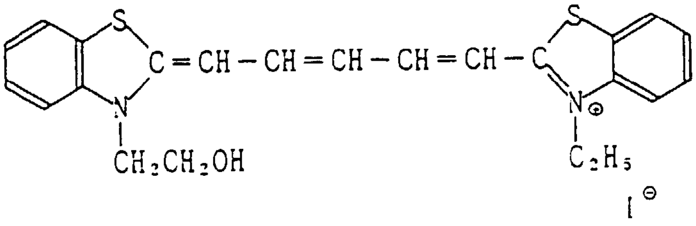

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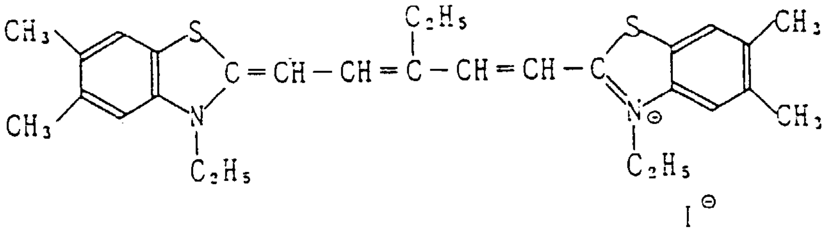

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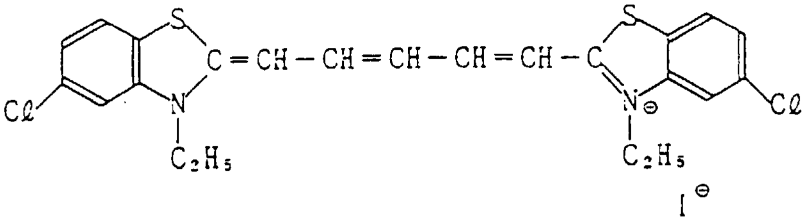

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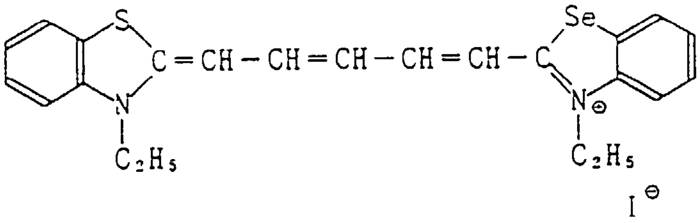

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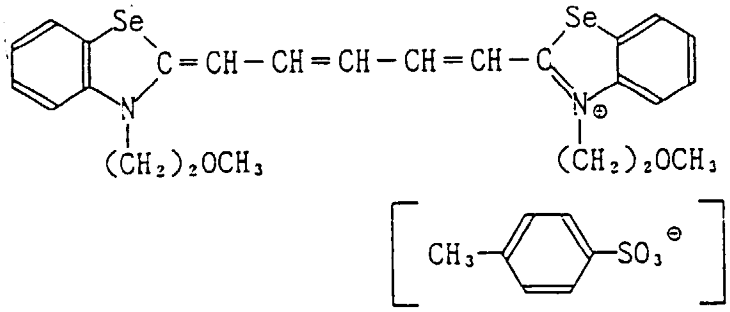

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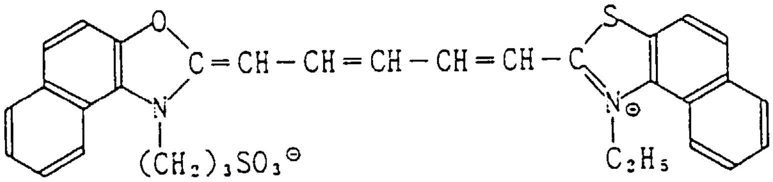

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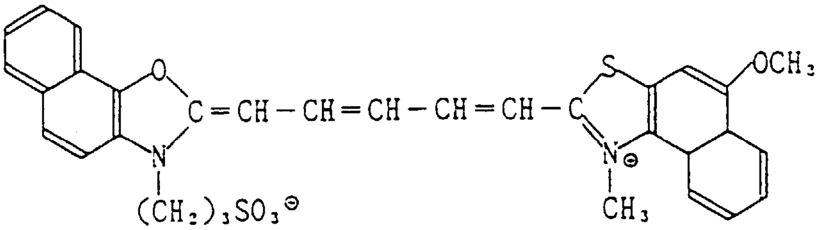

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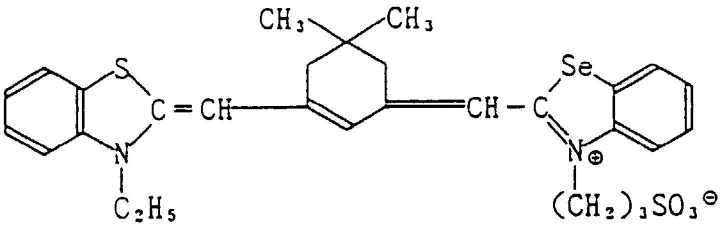

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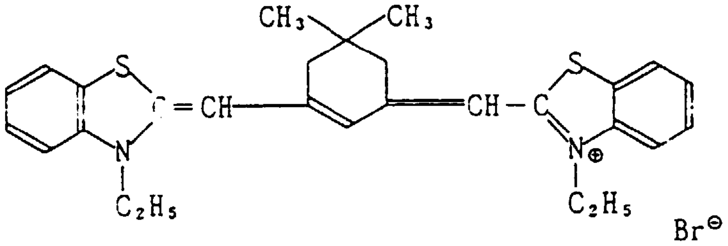

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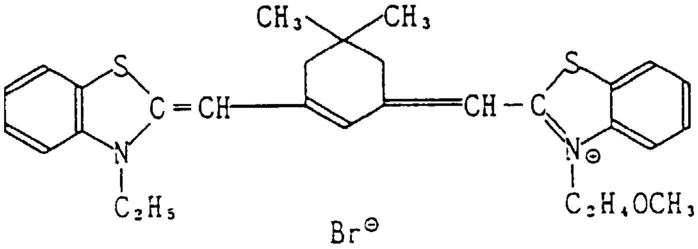

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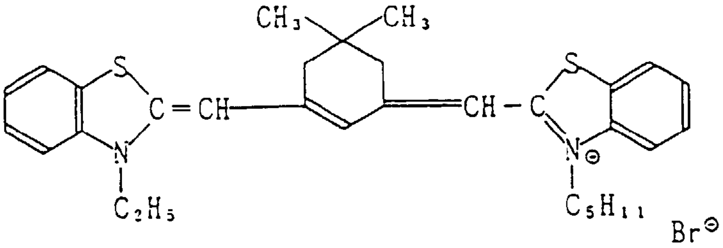

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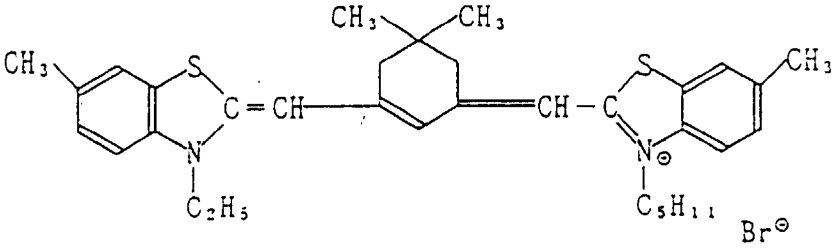

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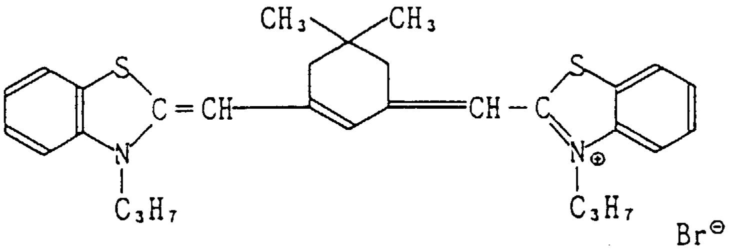

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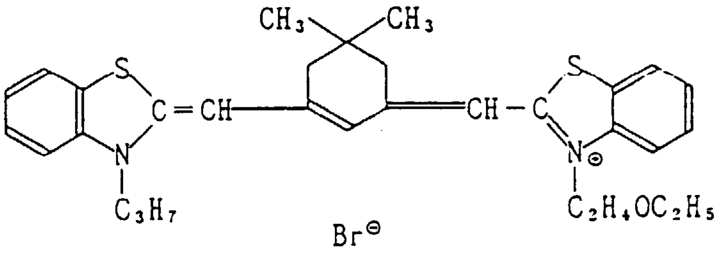

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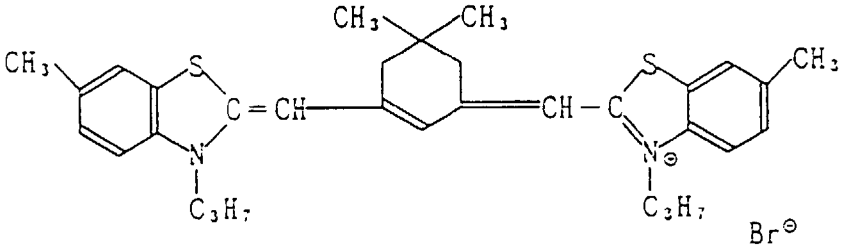

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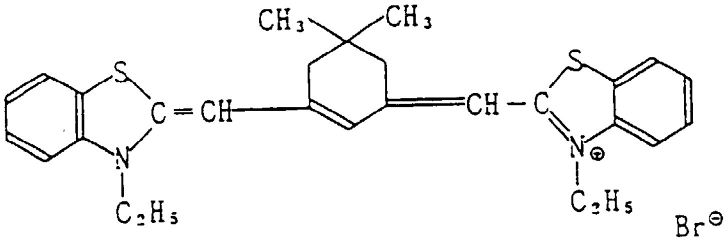

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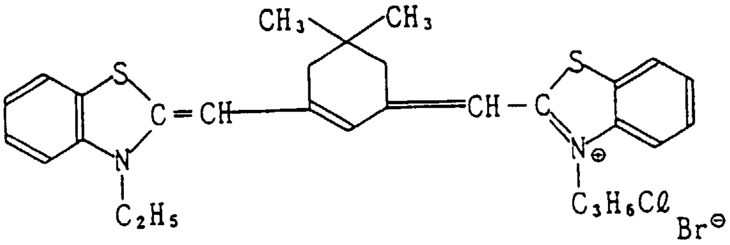
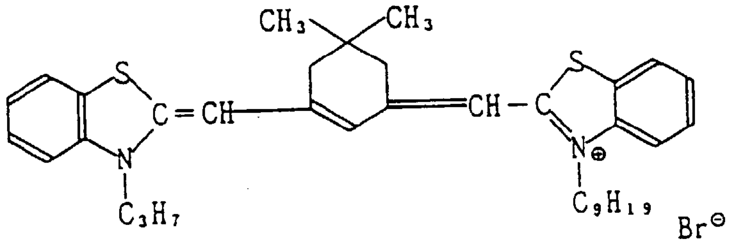
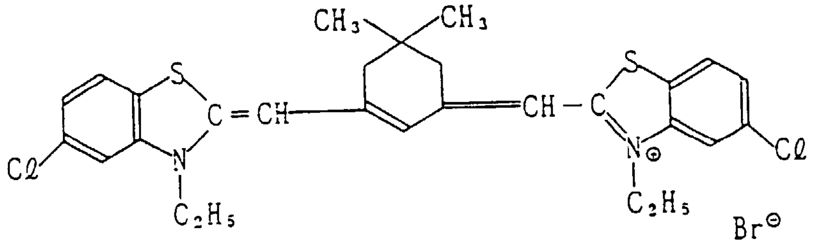


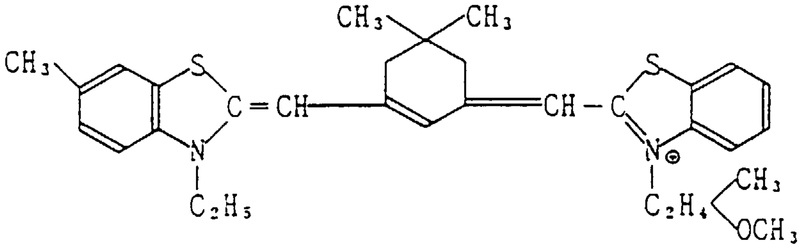
R S - 21



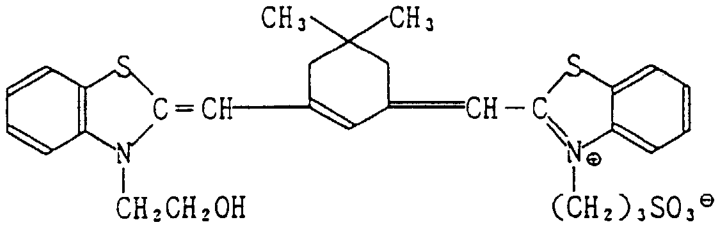
R S - 22



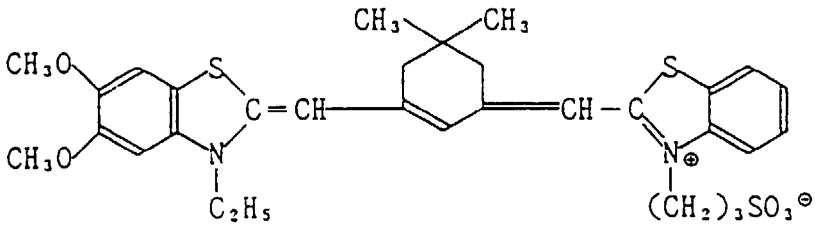
R S - 23



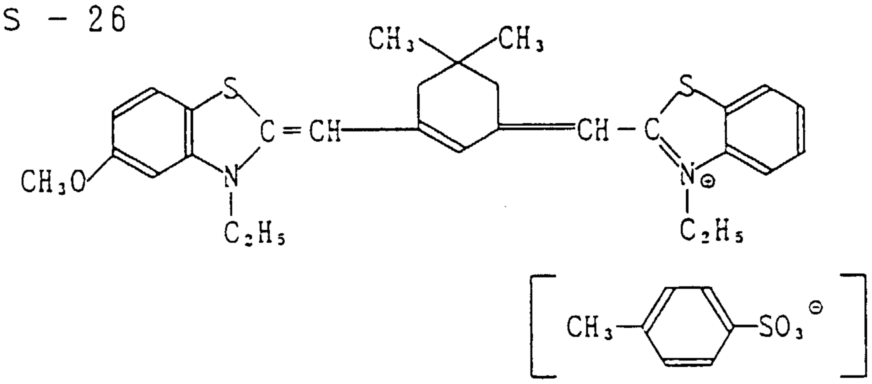
R S - 24



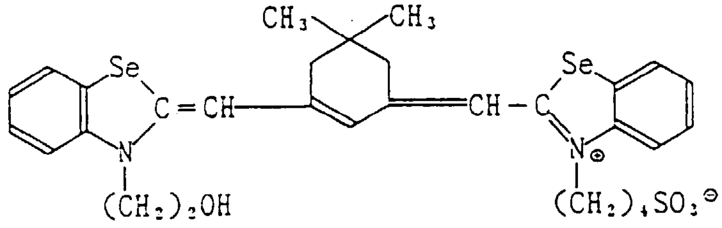
RS - 25



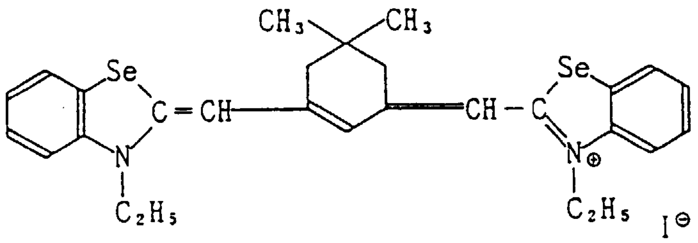
RS - 26



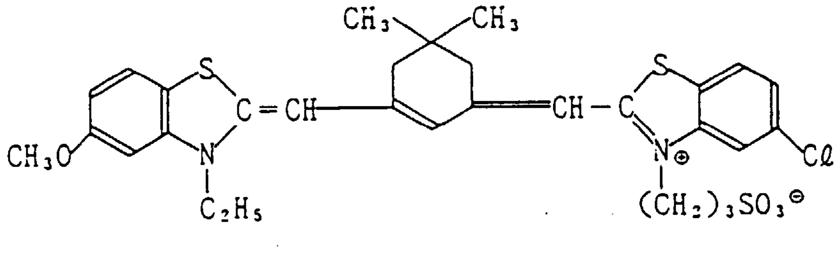
RS - 27



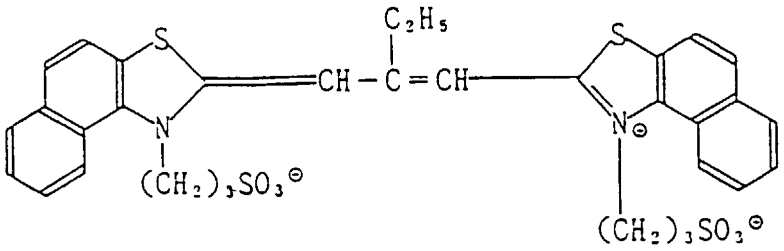
RS - 28



RS - 29



RS - 30



These sensitizing dyes may be used alone or in combination. The combination of sensitizing dyes is often used for the purpose of supersensitization, examples of which are described in U.S. Patent Nos. 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377 and 4,026,707; British Patent Nos. 1,344,281 and 1,507,803; JP E.P. Nos. 4936/1968 and 12375/1978; and JP O.P.I. Nos. 110618/1977 and 109925/1977.

The adding amount of any of the above sensitizing dyes is not restricted, but is preferably $1x10^{-7}$ to $1x10^{-3}$ mol, and more preferably $5x10^{-6}$ to $5x10^{-4}$ mol per mol of silver halide.

The addition of the sensitizing dye may be performed in the manner well-known to those skilled in the art.

When different kinds of the sensitizing dye should be added in combination to the silver halide emulsion, they may be dissolved in one and the same solvent or different solvents to make their separate solutions, which may be added in a mixture to or separately to the silver halide emulsion. In the case of the separate addition, the order, time, and interval of adding the solutions may be discretionally determined according to purposes. The addition of the sensitizing dye to the emulsion may be made in any of the stages of the emulsion manufacturing process, but preferably in the midst of or after the chemical ripening of the emulsion, and more preferably in the course of the chemical ripening.

The silver halide photographic light-sensitive material of the invention preferably contains at least two dyes having different intralayer absorption maximums within the intralayer speral absorption range of 565 to 700nm, wherein the dyes may be contained in any of the hydrophilic colloid layers on the same side of the red-sensitive silver halide emulsion layer on the support, and more preferably contained in the red-sensitive silver halide emulsion layer.

If the dyes are diffusible into other layers, they may be added to any layers such as protective layer, intermediate layer or emulsion layers other than the red-sensitive emulsion layer because they eventually diffuse into the red-sensitive layer to give the same effect as if they were added directly thereto.

The dye content of the emulsion depends on the intended effect and not restricted, but is generally coated so as to have a coating weight of preferably 1.0 to $200mg/m^2$, and more preferably 3.0 to $100mg/m^2$.

In the invention, the two or more dyes used in combination may be added simultaneously or separately at different points of time. They may be added in the form of separate solutions or dispersions. Alternatively, they may be in advance mixed (e.g., in the form of a mixture of the solutions) and then added. Further, where the dyes should be added making the most of their diffusibility to photographic component layers other than the red-sensitive silver halide emulsion layer, they may be added to either one and the same layer or to different layers.

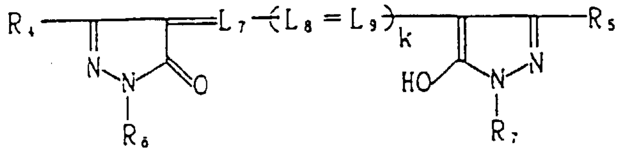
The ratio of the using amounts of the dyes depends on the intended effect and the kinds thereof and is not restricted, but the molar ratio of one dye used in the smallest amount to the whole amount of the dyes is preferably not less than 1 mol%, and more preferably not less than 5 mol%.

In the invention, at least one dye of the two or more different dyes used in combination has preferably an intralayer absorption maximum wavelength region of 565 to 640nm, and at least another dye has preferably an intralayer absorption maximum wavelength region of 650 to 710nm.

The incorporation of the dyes into the silver halide light-sensitive emulsion layer or other hydrophilic colloid layer may be carried out generally by a method in which the dyes or organic or inorganic alkali salts thereof are dissolved in water or an organic solvent such as alcohol, glycol, cellosolve, dimethylformaldehyde, dibutyl phthalate or tricresyl phosphate, and, if necessary, emulsifiedly dispersed, and the solution or dispersion is added to the coating liquid for coating, whereby the dyes can be incorporated into the silver halide photographic light-sensitive material.

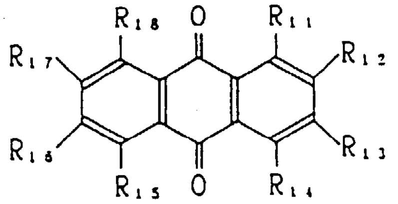
The dyes of the invention are preferably selected from among those represented by the following Formulas AI, AII and AIII:

Formula AI



wherein R_4 and R_5 each represent -CN, $-COR_8$, $-COOR_8$ or $-CONR_9R_{10}$; R_6 and R_7 each represent a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group; L_7, L_8 and L_9 each represent a methine group; k is an integer of o, 1 or 2, provided that when k is 2, each $-L_8=L_9-$may be the same or different; R_8 is an alkyl group or an aryl group; and R_9 and R_{10} each represent a hydrogen atom, an alkyl group, an alkenyl group, an aryl group or a heterocyclic group; wherein R_8 and R_9 and the adjacent N atom may form together a 5- or 6-member ring, provided that R_9 and R_{10} are not hydrogen atoms at the same time, and at least one out of the R_4, R_5, R_6 and R_7 is a water-soluble group or a group containing a water-soluble group.

Formula AII

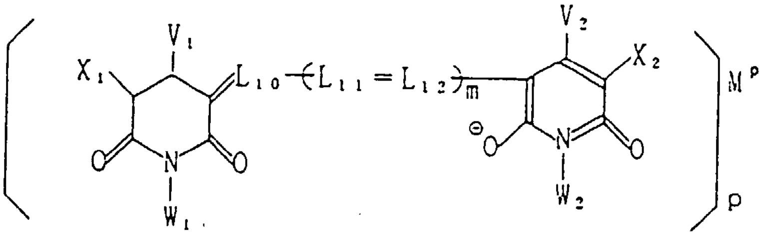


wherein R_{11}, R_{14}, R_{15} and R_{18} each represent a hydrogen atom, a hydroxyl group, a $-OR_{19}$ group or a

$$-N\genfrac{}{}{0pt}{}{R'}{R''},$$

group, wherein R_{19} is an alkyl group or an aryl group, and R' and R″ each represent a hydrogen atom or an alkyl or aryl group having at least one sulfo or carboxyl group; and R_{12}, R_{13}, R_{16} and R_{17} each represent a hydrogen atom, a carboxyl group, a sulfo group or an alkyl or aryl group having at least One carboxyl or sulfo group.

Formula AIII



wherein V_1 and V_2 each represent a hydrogen atom, a cyano group, a hydroxyl group, a carboxyl group, $-COOR^1$,

COR^1, -CONR^{1}R^2, -OR^1, -NR^{1}R^2, -NR^{1}COR^2, -NR^{1}SO$_2$R^2, an alkyl group, an aralkyl group, a cycloalkyl group, an aryl group, a heterocyclic group or an amino group; W$_1$ and W$_2$ each represent a hydrogen atom, -NR^{1}R^4, -NR^{2}COR^4, -NR^{3}SO$_2$R^4, an alkyl group, an aralkyl group, a cycloalkyl group, an aryl group, a heterocyclic group or an amino group; X$_1$ and X$_2$ each represent a hydrogen atom, a cyano group, a carboxyl group, a sulfo group, -COOR^5, -COR^5, -CONR^{5}R^6, -NR^{5}R^6, -NR^{5}COR^6, -NR^{5}SO$_2$R^6, -SO$_2$R^5, an alkyl group, an aralkyl group, a cycloalkyl group, an aryl group or a heterocyclic group; L$_{10}$, L$_{11}$ and L$_{12}$ each represent a methine group; m is an integer of 1 or 2; p is an integer of 1, 2 or 3; and M^{P+} is a p-value cation; wherein R^1, R^2, R^3, R^4, R^5 and R^6 each represent a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group, provided that each of the pairs of R^1 and R^2, R^3 and R^4, and R^5 and R^6 may combine with each other to form a 5- or 6-member ring, and at least one out of the V$_1$, V$_2$, W$_1$, W$_2$, X$_1$ and X$_2$ is a group containing a carboxyl or sulfo group.

In Formula AI, the alkyl group represented by R$_6$, R$_7$, R$_8$, R$_9$ or R$_{10}$ is a methyl, ethyl, propyl, isopropyl, butyl or t-butyl group. These alkyl groups each may be substituted further by a hydroxyl group, a sulfo group, a carboxyl group, a halogen atom such as fluorine, chlorine or bromine; an alkoxy group such as methoxy or methoxy; an aryloxy group such as phenoxy, 4-sulfophenoxy or 2,4-disulfophenoxy; an aryl group such as phenyl, 4-sulfophenyl or 2,5-disulfophenyl; a cyano group; an alkoxycarbonyl group such as methoxycarbonyl or ethoxycarbonyl; or an aryloxycarbonyl group such as phenoxycarbonyl.

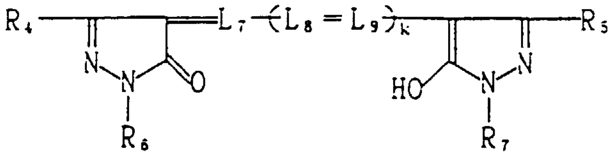
The aryl group represented by R$_6$, R$_7$, R$_8$, R$_9$ or R$_{10}$ is a phenyl or naphthyl group such as phenyl, 2-methoxyphenyl, 4-nitrophenyl, 3-chlorophenyl, 4-cyanophenyl, 4-hydroxyphenyl, 4-methanesulfonyl, 4-sulfophenyl, 3-sulfophenyl, 2-methyl-4-sulfophenyl, 2-chloro-4-sulfophenyl, 4-chloro-3-sulfophenyl, 2-chloro-5-sulfophenyl, 2-methoxy-5-sulfophenyl, 2-hydroxy-4-sulfophenyl, 2,5-dichloro-4-sulfophenyl, 2,6-diethyl-4-sulfophenyl, 2,5-disulfophenyl, 3,5-disulfophenyl, 2,4-disulfophenyl, 4-phenoxy-3-sulfophenyl, 2-chloro-6-methyl-4-sulfophenyl, 3-carboxy-2-hydroxy-5-sulfophenyl, 4-carboxyphenyl, 2,5-dicarboxyphenyl, 3,5-dicarboxyphenyl, 2,4-dicarboxyphenyl, 3,6-di-sulfo-α-naphthyl, 8-hydroxy-3,6-disulfo-a-naphthyl, 5-hydroxy-7-sulfoβ-naphthyl or 6,8-disulfo-β-naphthyl.

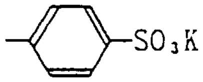
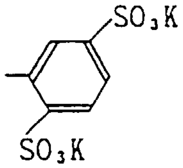
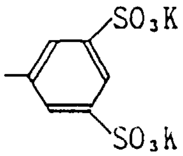
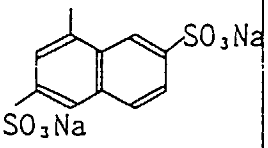
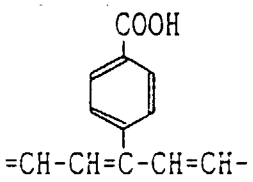
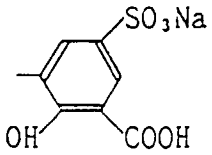
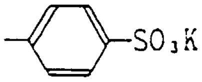
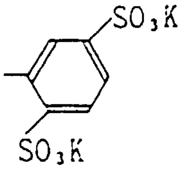
The alkenyl group represented by R$_9$ or R$_{10}$ is a vinyl or aryl group. The heterocyclic group represented by R$_6$, R$_7$, R$_9$ or R$_{10}$ is a pyridyl group such as 2-pyridyl, 3-pyridyl, 4-pyridyl, 5-sulfopyridyl, 5-carboxy-2-pyridyl, 3,5-dichloro-2-pyridyl, 4,6-dimethyl-2-pyridyl, 6-hydroxy-2-pyridyl, 2,3,5,6-tetrafluoro-4-pyridyl or 3-nitro-2-pyridyl; an oxazolyl group such as 5-sulfo-2-benzooxazolyl, 2-benzooxazolyl or 2-oxazolyl; a thiazolyl group such as 5-sulfo-2-benzothiazolyl, 2-benzothiazoly or 2-thiazolyl; an imidazolyl group such as 1-methyl-2-imidazolyl or 1-methyl-5-sulfo-2-benzoimidazolyl; a furyl group such as 3-furyl; a pyrrolyl group such as 3-pyrrolyl; a thienyl group such as 2-thienyl; a pyradinyl group such as 2-pyradinyl; a pyrimidinyl group such as 2-pyrimidinyl or 4-chloro-2-pyrimidinyl; a pyridazinyl group such as 2-pyridazinyl; a purinyl group such as 8-purinyl; an isooxazolinyl group such as 3-isooxazolinyl; a selenazolyl group such as 5-sulfo-2-selenazolyl; a sulforanyl group such as 3-sulforanyl; a piperidinyl group such as 1-methyl-3-piperidinyl; a pyrazolyl group such as 3-pyrazolyl; or a tetrazolyl group such as 1-tetrazolyl.

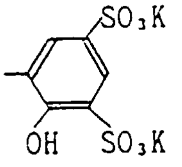
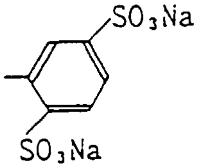
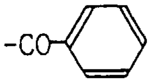
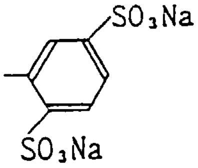
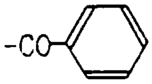
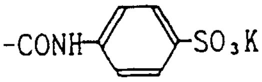
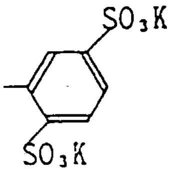
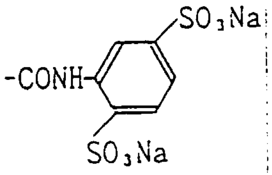
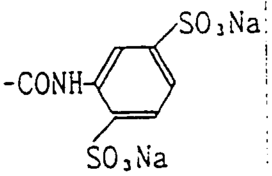
The cycloalkyl group represented by R$_6$ or R$_7$ is a cyclopentyl group or cyclohexyl group.

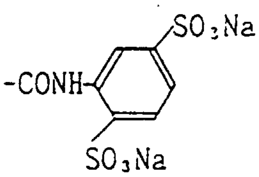
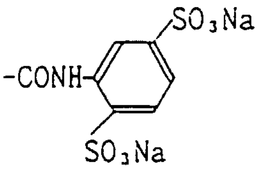
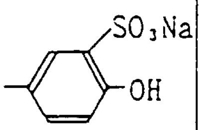
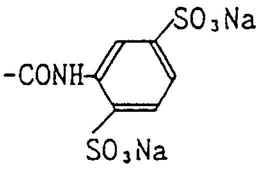
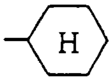
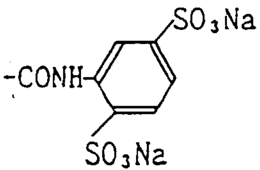
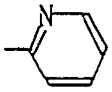
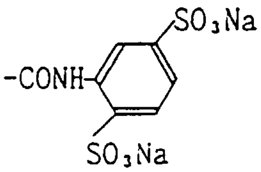
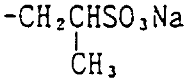
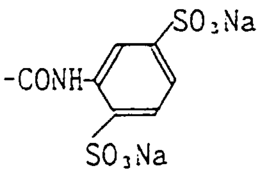
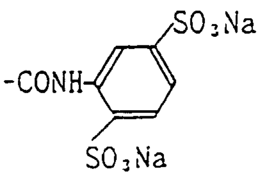
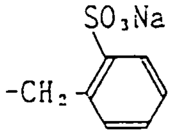
The following are the typical examples of the dyes having Formula AI, but are not limited thereto.

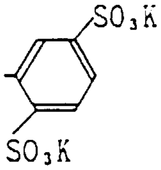
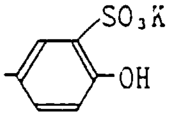
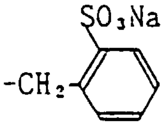
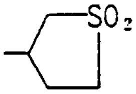
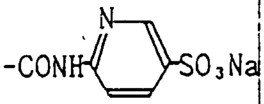
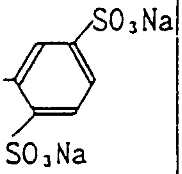
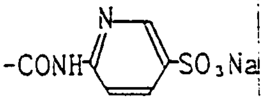
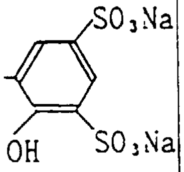
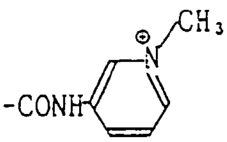
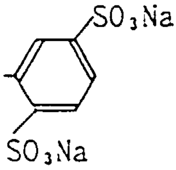
Exemplified compounds

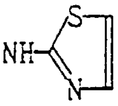
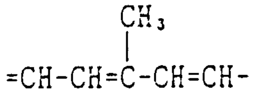
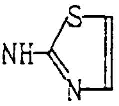
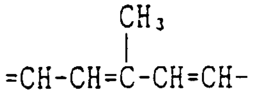
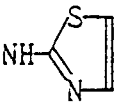
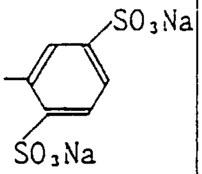
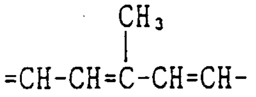
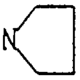
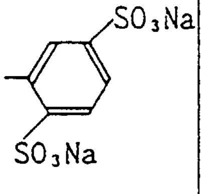
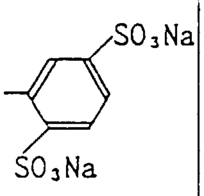
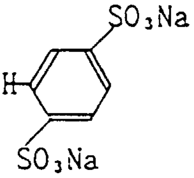
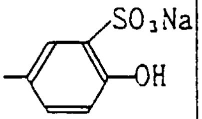


No.	=L₇-(L₈=L₉)ₖ	R₄, R₅	R₆, R₇
AI-1	=CH-CH=CH-CH=CH-	-CN	
AI-2	=CH-CH=CH-CH=CH-	-CN	
AI-3	=CH-CH=CH-CH=CH-	-CN	
AI-4	=CH-CH=CH-CH=CH-	-CN	
AI-5	 =CH-CH=C-CH=CH-	-CN	
AI-6	=CH-CH=CH-CH=CH-	$-COCH_3$	
AI-7	=CH-CH=CH-CH=CH-	$-COCH_3$	

No.	$=L_7-(L_8=L_9)_k$	R_4, R_5	R_6, R_7
AI-8	=CH-CH=CH-CH=CH-	$-COCH_3$	
AI-9	=CH-CH=CH-CH=CH-	$-COC_2H_5$	
AI-10	=CH-CH=CH-CH=CH-	$-COCH_3$	$-CH_2CH_2SO_3K$
AI-11	=CH-CH=CH-CH=CH-		
AI-12	=CH-CH=CH-CH=CH-		$-(CH_2)_3SO_3Na$
AI-13	=CH-CH=CH-CH=CH-		
AI-14	=CH-CH=CH-CH=CH-		$-CH_3$
AI-15	=CH-CH=CH-CH=CH-		$-CH_2CH_2OH$

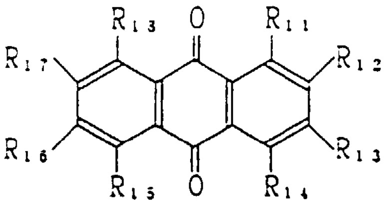
No.	$=L_7{-}(L_8=L_9)_k$	R_4, R_5	R_6, R_7
AI-16	=CH-CH=CH-CH=CH-		$-(CH_2)_3SO_3Na$
AI-17	=CH-CH=CH-CH=CH-		
AI-18	=CH-CH=CH-CH=CH-		
AI-19	=CH-CH=CH-CH=CH-		
AI-20	=CH-CH=CH-CH=CH-		 $-CH_2\underset{CH_3}{CH}SO_3Na$
AI-21	=CH-CH=CH-CH=CH-		$-CH_2CH_2COOH$
AI-22	=CH-CH=CH-CH=CH-		

No.	$=L_7-(L_8=L_9)_k$	R_4, R_5	R_6, R_7
AI-23	=CH-CH=CH-CH=CH-	$-CONHCH_2CH_2OH$	
AI-24	=CH-CH=CH-CH=CH-	$-CONHCH_2CH_2OH$	
AI-25	=CH-CH=CH-CH=CH-	$-CONHCH_2CH_2OH$	
AI-26	=CH-CH=CH-CH=CH-	$-CONHCH_2CH_2OH$	
AI-27	=CH-CH=CH-CH=CH-		
AI-28	=CH-CH=CH-CH=CH-		
AI-29	=CH-CH=CH-CH=CH-		

No.	$=L_7\!-\!(L_8=L_9)_k$	R_4, R_5	R_6, R_7
AI-30	$=CH-CH=CH-CH=CH-$	-CONH- 	$-CH_2CH_2OH$
AI-31	 $=CH-CH=\overset{CH_3}{\overset{\vert}{C}}-CH=CH-$	-CONH- 	$-CH_2CH_2SO_3Na$
AI-32	 $=CH-CH=\overset{CH_3}{\overset{\vert}{C}}-CH=CH-$	-CONH- 	
AI-33	 $=CH-CH=\overset{CH_3}{\overset{\vert}{C}}-CH=CH-$	-CON 	
AI-34	$=CH-CH=CH-$	-CN	
AI-35	$=CH-CH=CH-$	-CONH- 	

These dyes having Formula AI can be synthesized in accordance with the methods described in JP O.P.I. Nos. 143342/1983 and 165656/1987.

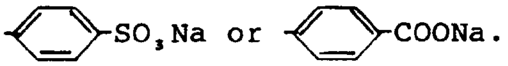
Formula AII



wherein R_{11}, R_{14}, R_{15} and R_{18} each represent a hydrogen atom, a hydroxyl group, $-OR_{19}$ or


$$-N{<}^{R'}_{R''}$$

wherein R_{19} is an alkyl group or an aryl group, and R' and R″ each represent a hydrogen atom or an alkyl or aryl group having at least one sulfo or carboxyl group; R_{12}, R_{13}, R_{16} and R_{17} each represent a hydrogen atom, a carboxyl group, a sulfo group or an alkyl or aryl group having at least one carboxyl or sulfo group. The alkyl group represented by the R_{19} for $-OR_{19}$ represented by R_{11}, R_{14}, R_{15} or R_{18} in Formula AII is, e.g., a methyl, ethyl or butyl group, and the aryl group represented by the same is, e.g., a phenyl group. The alkyl group having at least one sulfo or carboxyl group represented by the R' or R″ for -NR'R″ is, e.g., $-CH_2SO_3H$, $-(CH_2)_2SO_3H$, $-CH_2COOH$ or $-(CH_2)_2COOH$ or the sodium salt, potassium salt or ammonium salt thereof. The aryl group represented by R' or R″ is, e.g.,

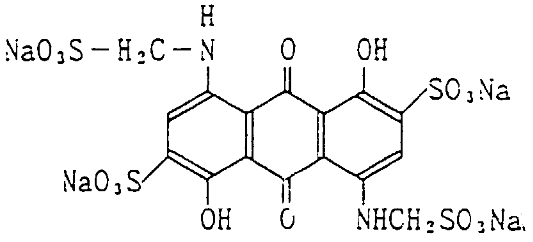


The alkyl or aryl group having at least one carboxyl or sulfo group, represented by R_{12}, R_{13}, R_{16} or R_{17} include the same groups as defined for R' and R".

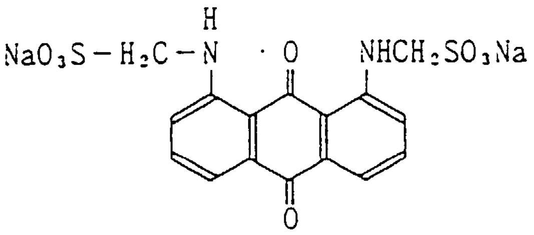
The following are the typical examples of the compound having Formula AII.

Exemplified compounds

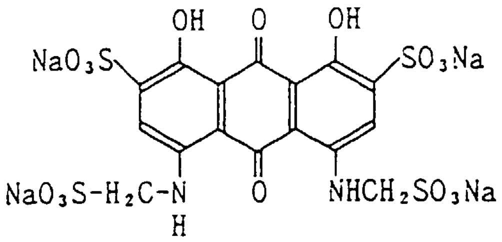
A II - 1



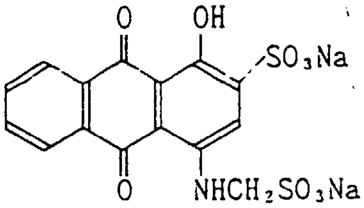
A II - 2



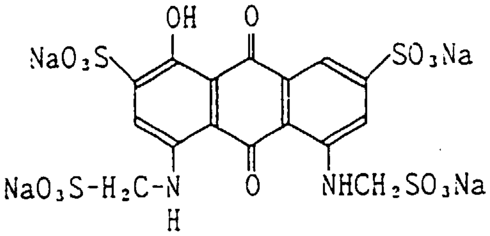
A II - 3



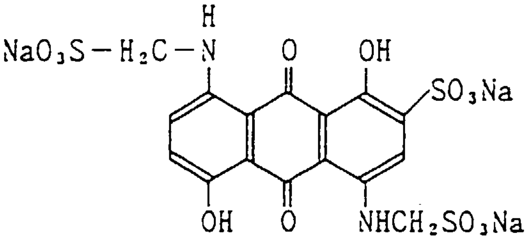
A II − 4



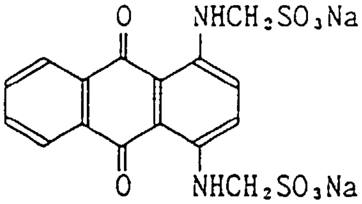
A II − 5



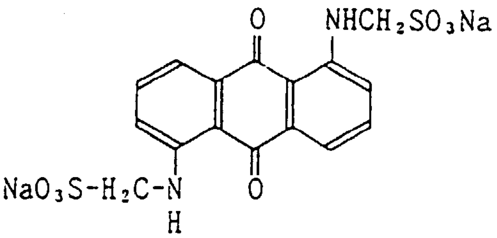
A II − 6



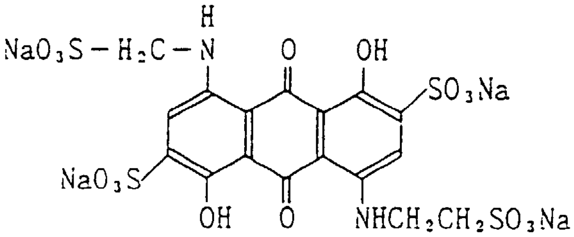
A II − 7



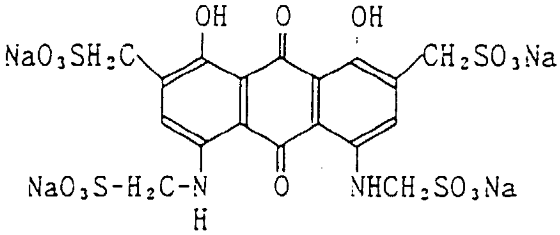
A Ⅱ - 8



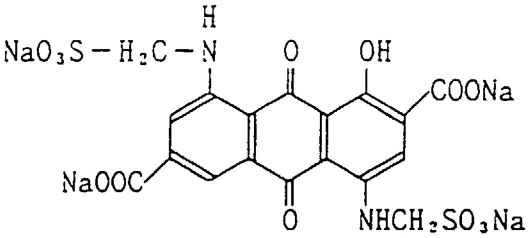
A Ⅱ - 9



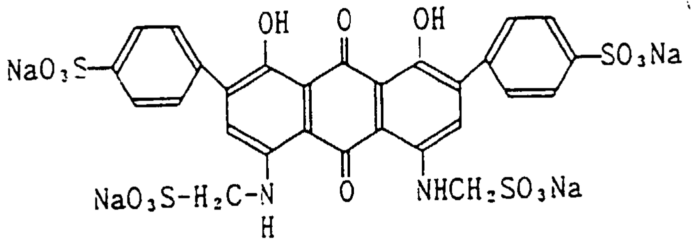
A Ⅱ - 10



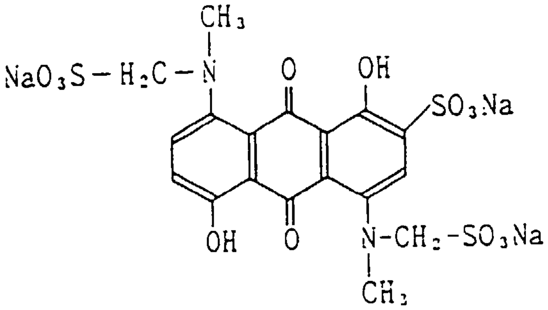
A Ⅱ - 11



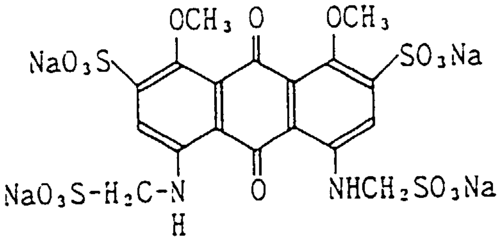
A II - 12



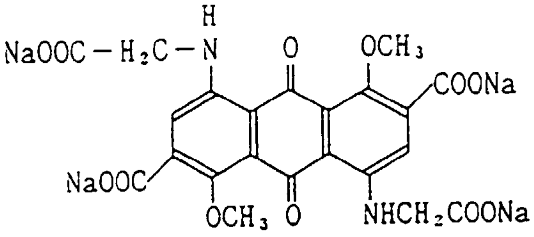
A II - 13



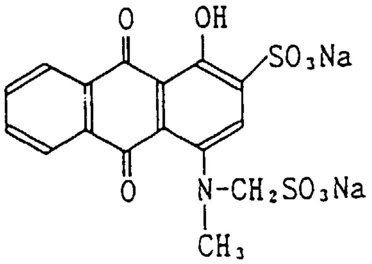
A II - 14



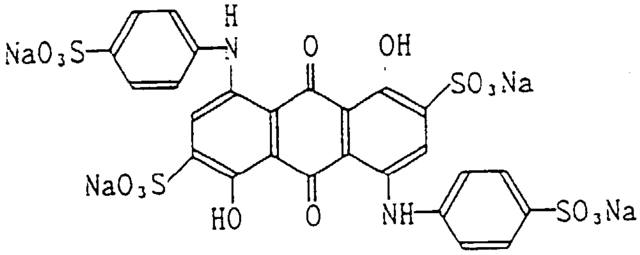
A II - 15



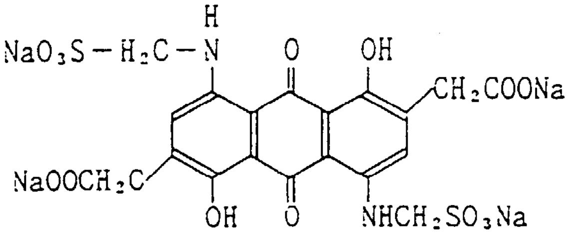
A II − 16



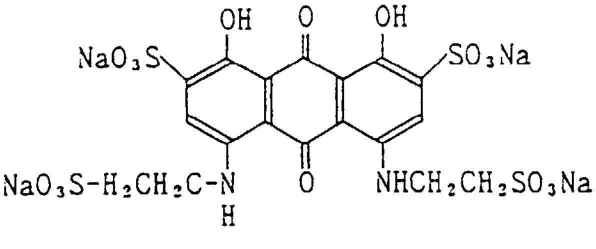
A II − 17



A II − 18



A II − 19



These compounds having Formula AII can be synthesized in accordance with the method described in U.S. Patent No. 2,865,752.

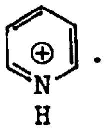
In the foregoing Formula AIII, the alkyl group represented by V_1, V_2, W_1, W_2, X_1, X_2 or R_1 to R_6 is a methyl, ethyl, propyl, isopropyl, butyl or t-butyl group, and these groups each may be substituted further by a hydroxy group, a sulfo group, a carboxyl group, a halogen atom such as fluorine, chlorine or bromine; an alkoxy group such as methoxy or ethoxy; an aryloxy group such as phenoxy, 4-sulfophenoxy or 2,4-disulfophenoxy; an aryl group such as phenyl, 4-sulfophenyl or 2,5-disulfophenyl; a cyano group; an alkoxycarbonyl group such as methoxycarbonyl or ethoxycarbonyl; or an aryloxycarbonyl group such as phenoxycarbonyl.

The aryl group represented by V_1, V_2, W_1, W_2, X_1, X_2 or R_1 to R_6 is a phenyl or naphthyl group such as 2-methoxyphenyl, 4-nitrophenyl, 3-chlorophenyl, 4-cyanophenyl, 4-hydroxy phenyl, 4-methanesulfonylphenyl, 4-sulfophenyl, 3-sulfophenyl, 2-methyl-4-sufophenyl, 2-chloro-4-sulfophenyl, 4-chloro-3-sulfophenyl, 2-chloro-5-sulfophenyl, 2-methoxy-5-sulfophenyl, 2-hydroxy-4-sulfophenyl, 2,5-dichloro-4-sulfophenyl, 2,6-diethyl-4-sulfophenyl, 2,5-disulfophenyl, 3,5-disulfophenyl, 2,4-disulfophenyl, 4-phenoxy-3-sulfophenyl, 2-chloro-6-methyl-4-sulfophenyl, 3-carboxy-2-hydroxy-5-sulfophenyl, 4-carboxyphenyl, 2,5-dicarboxyphenyl, 3,5-dicarboxyphenyl, 2,4-dicarboxyphenyl, 3,6-disulfo-α-naphthyl, 8-hydroxy-3,6-disulfo-α-naphthyl, , 5-hydroxy-7-sulfo-β-naphthyl or 6,8-disulfoβ-naphthyl.

The heterocyclic group represented by V_1, V_2, W_1, W_2, X_1, X_2 or R_1 to R_6 is a pyridyl group such as 2-pyridyl, 3-pyridyl, 4-pyridyl, 5-sulfo-2-pyridyl, 5-carboxy-2-pyridyl, 3,5-di-chloro-2-pyridyl, 4,6-dimethyl-2-pyridyl, 6-hydroxy-2-pyridyl, 2,3,5,6-tetrafluoro-4-pyridyl or 3-nitro-2-pyridyl; an oxazolyl group such as 5-sulfo-2-benzooxazolyl, 2-benzooxazolyl or 2-oxazolyl; a thiazolyl group such as 5-sulfo-2-benzothiazolyl, 2-benzothiazolyl or 2-thiazolyl; an imidazolyl group such as 1-methyl-2-imidazolyl or 1-methyl-5-sulfo-2-benzimidazolyl; a furyl group such as 3-furyl; a pyrrolyl group such as 3-pyrrolyl; a thienyl group such as 2-thienyl; a pyrazinyl group such as 2-pyrazinyl; a pyrimidinyl group such as 2-pyrimidinyl or 4-chloro-2-pyrimidinyl; a pyridazinyl group such as 2-pyridazinyl; a purinyl group such as 8-purinyl; an isooxazolinyl group such as 3-isooxazolinyl; a selenazolyl group such as 5-sulfo-2-selenazolyl; a sulforanyl group such as 3-sulforanyl; a piperidinyl group such as 1-methyl-3-piperidinyl; a pyrazolyl group such as 3-pyrazolyl; or a tetrazolyl group such as 1-tetrazolyl.

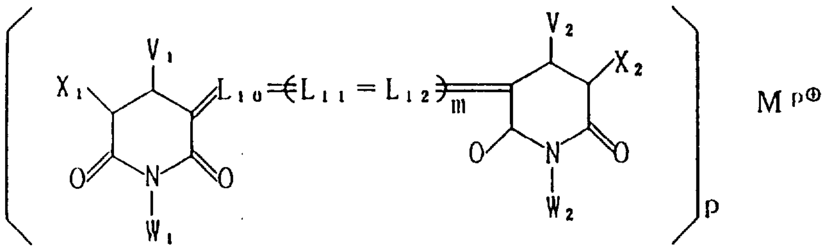
The methine group represented by L_1, L_2 and L_3 includes those having a substituent such as a methyl, ethyl or phenyl group or a chlorine atom.

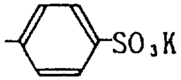
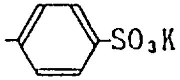
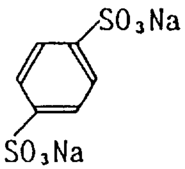
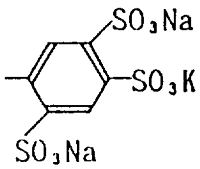
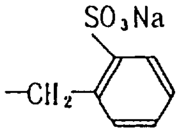
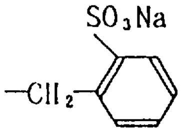
$M^{p\oplus}$ represents a p-valent cation (p is 1, 2 or 3) such as $N^{\oplus}$, $K^{\oplus}$, $Ca^{2\oplus}$, $NH_4^{\oplus}$, $NH(C_2H_5)_3^{\oplus}$ or

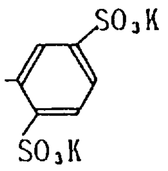
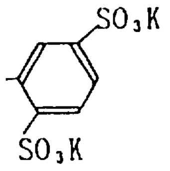
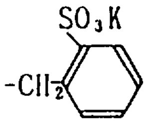
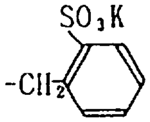
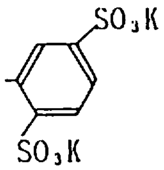
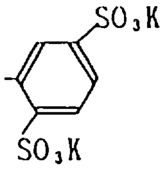


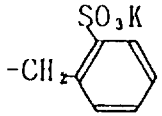
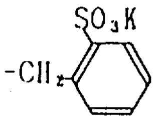
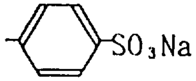
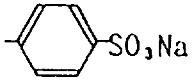
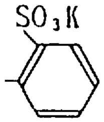
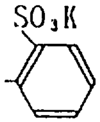
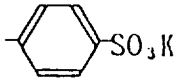
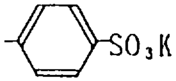
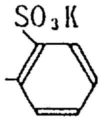
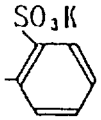
The following are the typical examples of the dyes of Formula AIII of the invention, but are not limited thereto.

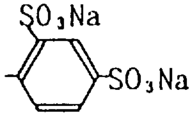
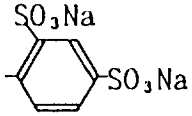
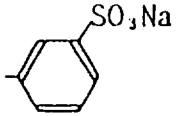
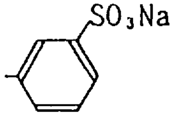
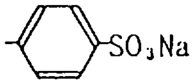
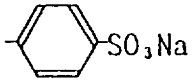
Exemplified compounds

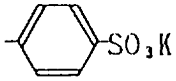
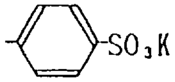
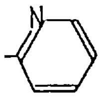
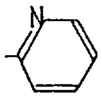
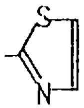
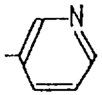
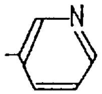


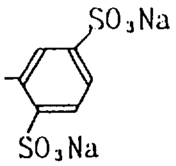
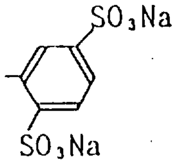
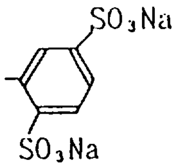
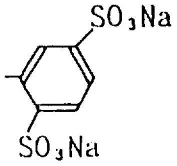
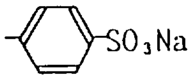
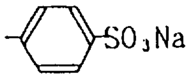
No.	$=L_{10}-(L_{11}=L_{12})_m$	V_1	V_2	X_1	X_2	W_1	W_2	$M^{p\oplus}$
A III - 1	=CH-CH=CH-CH=CH-	$-CH_3$	$-CH_3$	-CN	-CN			$H^{\oplus}$
A III - 2	=CH-CH=CH-CH=CH-	$-CH_3$	$-CH_3$	-CN	-CN			$H^{\oplus}$
A III - 3	=CH-CH=CH-CH=CH-	$-CH_3$	$-CH_3$	-CN	-CN			$H^{\oplus}$

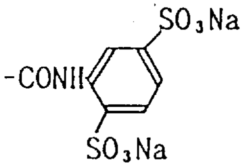
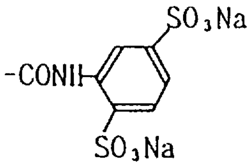
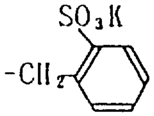
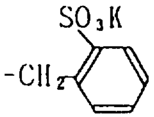
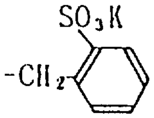
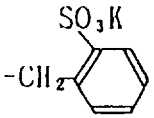
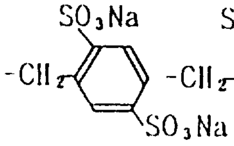
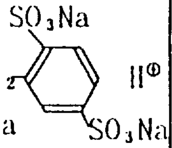
No.	$=L_{10}-(L_{11}=L_{12})_m$	V_1	V_2	X_1	X_2	W_1	W_2	$M'^{\oplus}$
A Ⅲ - 4	=CH-CH=CH-CH=CH-	$-CH_3$	$-CH_3$	-COOH	-COOH			$H^{\oplus}$
A Ⅲ - 5	=CH-CH=CH-CH=CH-	$-CH_3$	$-CH_3$	$-SO_2CH_3$	$-SO_2CH_3$	$-C_2H_5$	$-C_2H_5$	$H^{\oplus}$
A Ⅲ - 6	=CH-CH=CH-CH=CH-	$-CH_2SO_3K$	$-CH_2SO_3K$	-CN	-CN	$-C_2H_5$	$-C_2H_5$	$\overset{\oplus}{H}N(C_2H_5)_3$
A Ⅲ - 7	=CH-CH=CH-CH=CH-	$-CH_3$	$-CH_3$	$-CONHCH_2*$ $*CH_2SO_3K$	$-CONHCH_2*$ $*CH_2SO_3K$			$H^{\oplus}$
A Ⅲ - 8	=CH-CH=CH-CH=CH-	$-CH_3$	$-CH_3$	$-CONHCH_2*$ $*CH_2SO_3K$	$-CONHCH_2*$ $*CH_2SO_3K$			$H^{\oplus}$
A Ⅲ - 9	=CH-CH=CH-CH=CH-	$-CH_3$	$-CH_3$	$-CH_2SO_3K$	$-CH_2SO_3K$			$H^{\oplus}$

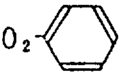
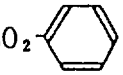
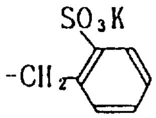
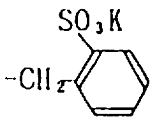
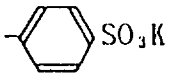
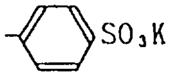
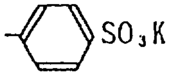
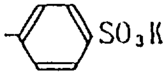
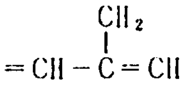
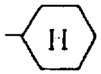
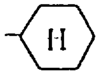
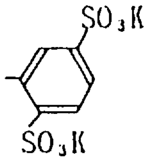
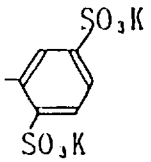
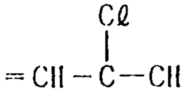
No.	$=L_{10}\!-\!(L_{11}=L_{12})_m$	V_1	V_2	X_1	X_2	W_1	W_2	$M'^{\oplus}$
A III -10	$=CH-CH=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CONH_2$	$-CONH_2$			$H^{\oplus}$
A III -11	$=CH-CH=CH-CH=CH-$	$-OH$	$-OH$	$-COOCH_3$	$-COOCH_3$			$H^{\oplus}$
A III -12	$=CH-CH=\overset{CH_3}{C}-CH=CH-$	$-CH_3$	$-CH_3$	$-COCH_3$	$-COCH_3$	$-CH_2CH_2SO_3Na$	$-CH_2CH_2SO_3Na$	$H^{\oplus}$
A III -13	$=CH-CH=\overset{CH_3}{C}-CH=CH-$	$-CH_3$	$-CH_3$	$-SO_2CH_3$	$-SO_2CH_3$			$H^{\oplus}$
A III -14	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CN$	$-CN$			$H^{\oplus}$
A III -15	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CN$	$-CN$			$H^{\oplus}$

No.	$=L_{10}\text{—}(L_{11}=L_{12})_m$	V_1	V_2	X_1	X_2	W_1	W_2	$M^{p\oplus}$
A III-16	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	-CN	-CN			$H^{\oplus}$
A III-17	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	-CN	-CN	$-C_2H_5$	$-C_2H_5$	$H^{\oplus}$
A III-18	$=CH-CH=CH-$	$-CF_3$	$-CF_3$	-CN	-CN			$H^{\oplus}$
A III-19	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	-CN	-CN	$-CH_2CH_2SO_3Na$	$-CH_2CH_2SO_3Na$	$H^{\oplus}$
A III-20	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	-CN	-CN	$-CH_2COOK$	$-CH_2COOK$	$H^{\oplus}$
A III-21	$=CH-CH=CH-$	$-CH_2SO_3Na$	$-CH_2SO_3Na$	-CN	-CN			$H^{\oplus}$
A III-22	$=CH-CH=CH-$	$-CH_2SO_3Na$	$-CH_2SO_3Na$	-CN	-CN	$-(n)C_4H_9$	$-(n)C_4H_9$	$\overset{\oplus}{N}H(C_2H_5)$
A III-23	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	-COOH	-COOH	$-CH_3$	$-CH_3$	$H^{\oplus}$

No.	$=L_{10}-(L_{11}=L_{12})_m$	V_1	V_2	X_1	X_2	W_1	W_2	$M'^{\oplus}$
A III-24	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CONH_2$	$-CONH_2$			$H^{\oplus}$
A III-25	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CH_2SO_3K$	$-CH_2SO_3K$	$-C_2H_5$	$-C_2H_5$	$H^{\oplus}$
A III-26	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CH_2SO_3K$	$-CH_2SO_3K$			$H^{\oplus}$
A III-27	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CH_2SO_3K$	$-CH_2SO_3K$			$H^{\oplus}$
A III-28	$=CH-CH=CH-$	$-OH$	$-OH$	$-CH_2SO_3K$	$-CH_2SO_3K$			$H^{\oplus}$
A III-29	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CONHCH_2CH_2OH$	$-CONHCH_2CH_2OH$	$-CH_3$	$-CH_3$	$H^{\oplus}$
A III-30	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CONHCH_2CH_2OH$	$-CONHCH_2CH_2OH$	$-CH_2CH_2OH$	$-CH_2CH_2OH$	$H^{\oplus}$

No.	$=L_{10}-(L_{11}=L_{12})_m$	V_1	V_2	X_1	X_2	W_1	W_2	$M'^{\oplus}$
A III-31	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CONHCH_2*$ $*CH_2OH$	$-CONHCH_2*$ $*CH_2OH$	$-CH_2CH_2SO_3K$	$-CH_2CH_2SO_3K$	$H^{\oplus}$
A III-32	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-CONHCH_2*$ $*CH_2OH$	$-CONHCH_2*$ $*CH_2OH$			$H^{\oplus}$
A III-33	$=CH-CH=CH-$	$-CH_2*$ $*SO_3Na$	$-CH_2*$ $*SO_3Na$	$-CONHCH_2*$ $*CH_2OH$	$-CONHCH_2*$ $*CH_2OH$			$H^{\oplus}$
A III-34	$=CH-CH=CH-$	$-CH_2*$ $*SO_3Na$	$-CH_2*$ $*SO_3Na$	$-CONHCH_2*$ $*CH_2OH$	$-CONHCH_2*$ $*CH_2OH$			$H^{\oplus}$
A III-35	$=CH-CH=CH-$	$-CH_2*$ $*SO_3Na$	$-CH_2*$ $*SO_3Na$	$-CONHCH_2*$ $*CH_2SO_3K$	$-CONHCH_2*$ $*CH_2SO_3K$	$-CH_2CH_2SO_3K$	$-CH_2CH_2SO_3K$	$H^{\oplus}$

No.	$=L_{10}\text{-}(L_{11}=L_{12})_m$	V_1	V_2	X_1	X_2	W_1	W_2	$M'^{\oplus}$
A III -36	=CH−CH=CH−	$-CH_3$	$-CH_3$			$-CH_3$	$-CH_3$	$H^{\oplus}$
A III -37	=CH−CH=CH−	$-CH_3$	$-CH_3$			$-CH_3$	$-CH_3$	$H^{\oplus}$
A III -38	=CH−CH=CH−	$-CH_3$	$-CH_3$	$-CONHCH_2CH_2OH$	$-CONHCH_2CH_2OH$			$H^{\oplus}$
A III -39	=CH−CH=CH−	$-CH_3$	$-CH_3$	$-CONH_2$	$-CONH_2$			$H^{\oplus}$
A III -40	=CH−CH=CH−	$-CH_3$	$-CH_3$	$-CONH_2$	$-CONH_2$		$-CH_2$ 	$H^{\oplus}$

No.	$=L_{10}-(L_{11}=L_{12})_m$	V_1	V_2	X_1	X_2	W_1	W_2	$M^{p\oplus}$
A III-41	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-SO_2-$ 	$-SO_2-$ 	$-CH_2CH_2SO_3K$	$-CH_2CH_2SO_3K$	$H^{\oplus}$
A III-42	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-SO_2NHCH_3$	$-SO_2NHCH_3$	$-CH_2CH_2SO_3Na$	$-CH_2CH_2SO_3Na$	$H^{\oplus}$
A III-43	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-NHCOCH_3$	$-NHCOCH_3$			$H^{\oplus}$
A III-44	$=CH-CH=CH-$	$-CH_3$	$-CH_3$	$-NHSO_2CH_3$	$-NHSO_2CH_3$			$H^{\oplus}$
A III-45	$=CH-CH=CH-$	$-COO*$ $*C_2H_5$	$-COO*$ $*C_2H_5$	$-SO_2CH_3$	$-SO_2CH_3$	$-C_2H_5$	$-C_2H_5$	$\overset{\oplus}{H}N(C_2H_5)$
A III-46	$=CH-CH=CH-$	$-OH$	$-OH$	$-COOCH_3$	$-COOCH_3$			$\overset{\oplus}{H}N(C_2H_5)$
A III-47	 $=CH-\overset{CH_2}{\overset{\mid}{C}}=CH$			$-COCH_3$	$-COCH_3$			$H^{\oplus}$
A III-48	 $=CH-\overset{Cl}{\overset{\mid}{C}}-CH$	$-CH_3$	$-CH_3$	$-CONHCH_2CH_2SO_3K$	$-CONHCH_2CH_2SO_3K$	$-CH_3$	$-CH_3$	$H^{\oplus}$

These dyes of the invention can be synthesized according to the methods described in British Patent Nos. 1,278,621, 1,512,863 and 1,579,899.

Where the present invention is applied to a color photographic light-sensitive material, there are normally used a yellow dye-forming coupler in the blue-sensitive emulsion layer, a magenta dye-forming coupler in the green-sensitive emulsion layer and a cyan dye-forming coupler in the red-sensitive emulsion layer. However, the above coupler/emulsion combinations may be altered according to purposes in preparation of a silver halide photographic light-sensitive material.

These dye-forming couplers each preferably have in the molecule thereof a group called a ballasting group having 8 or more carbon atoms, which makes the couplers nondiffusible. These dye-forming couplers each may be either a four-equivalent coupler, requiring the reduction of four molecules of silver ions for forming one molecule of a dye, or a two-equivalent coupler, requiring the reduction of 2 molecules of silver ions for forming one molecule of a dye.

As the yellow dye-forming coupler, various acylacetanilide couplers may be suitably used. Advantageous ones among these couplers are benzoylacetanilide compounds and pivaloylacetanilide compounds.

Suitably usable as the cyan dye-forming coupler are naphthol couplers and phenol couplers.

The incorporation of any of the above dye-forming couplers into the light-sensitive material of the invention is carried out in the manner that the coupler is dissolved in a high-boiling organic solvent having a boiling point of not less than 150°C, if necessary, in combination with a low-boiling water-soluble organic solvent, the solution is emulsifiedly dispersed with aid of a surfactant into a hydrophilic binder such as a gelatin aqueous solution, and then the dispersion is added to an intended hydrophilic colloid-coating liquid for the layer formation. In the above process may be inserted a step of removing the low-boiling solvent simultaneously with the dispersing procedure.

The above high-boiling organic solvent is preferably a solvent having a permittivity of not more than 6.5, including esters such as phthalates or phosphates, organic acid amides, ketones, and hydrocarbon compounds.

More preferably, the solvent is a high-boiling organic solvent having a permittivity of not more than 6.5 and not less than 1.9, and a vapor pressure of not more than 0.5mmHg. More preferred among these solvents are phthalates and phosphates, and the most preferred are dialkyl phthalates having an alkyl group of not less than 9 carbon atoms. Further, the high-boiling organic solvent may be a mixture of two or more kinds thereof. The above-mentioned permittivity is a permittivity at 30°C.

The above high-boiling organic solvent is used in an amount of from 0 to 400% by weight, and preferably 10 to 100% by weight of the coupler.

The light-sensitive material of the invention may be, e.g., a color negative film, a color positive film or a color photographic paper, and can make the most of the effect of the invention particularly when used as a color photographic paper for direct appreciation.

The light-sensitive material of the invention, mostly used as a color photographic paper, may be either for monochromatic use or multicolor use.

The silver halide emulsion of the invention may be spectrally sensitized to desired wavelength resions with use of dyes known as sensitizing dyes to the photographic field, provided, however, that the red-sensitive silver halide emulsion of the invention is preferably spectrally sensitized with the sensitizing dye having the foregoing Formula RS1 or RS2.

The binder used for the silver halide light-sensitive material of the invention is preferably gelatin.

The gelatin used in the photographic industry includes alkali(lime)-treated gelatin and acid(hydrochloric acid)-treated gelatin, both being made from cowbones, cowhide, pigskin and the like.

The manufacture and characteristics of gelatin are detailed in Arthur Veis, 'The Macromolecular Chemistry of Gelatin,' Academic Press, pp.187-217 (1964); T. H. James, 'The Theory of the Photographic Process,' 4th ed. 1977, (Macmillan), p.55; 'Kagaku-Shashin Benran' (Handbook of Scientific Photography) Vol.I, pp.72-75 (Maruzen); and 'Shashin-Kogaku no Kiso - Ginen-Shashin Hen' (Fundamental course of Photographic Technology: Silver Halide Photography), pp.119-124 (Corona).

The gelatin used in the light-sensitive material of the invention may be either lime-treated gelatin or acid-treated gelatin, made from any of cowbones, cowhide or pigskin, but is preferably lime-treated gelatin made from cowbones.

The photographic emulsion layer and other hydrophilic colloid layer of the light-sensitive material of the invention are hardened with use of a hardener or hardeners for briding the molecules of the binder (or protective colloid) to increase the strength thereof.

The light-sensitive material preferably contains the hardener in an amount good enough to need no addition of it to the processing solution therefor, but the hardener may be added also to the solution.

The hydrophilic colloid layers including the protective layer and intermediate layer of the light-sensitive material of the invention may contain an ultraviolet absorbent in order to prevent the light-sensitive material from being fogged due to the discharge of the triboelectricity caused by friction of it with others and also to prevent the resulting image from being deteriorated by ultraviolet rays.

The light-sensitive material of the invention may have auxiliary layers such as a filter layer, antihalation layer and/or antiirradiation layer. These layers and/or emulsion layers may contain non-invention dyes to be dissolved out of the light-sensitive material or bleached in the course of the processing thereof in addition to the foregoing dyes of the invention. A matting agent may be added to the silver halide emulsion layer and/or other hydrophilic colloid layer in order to decrease the surface gloss, to increase the retouchability, and to prevent the mutual sticking of the light-sensitive material.

A lubricant may be added to the light-sensitive material of the invention in order to reduce its friction with others.

An antistatic agent may be added to the light-sensitive material of the invention for the purpose of preventing it from being charged. The antistatic agent may be used in either an antistatic layer on the non-emulsion side of the support or a non-emulsion protective colloid layer on the emulsion layer side of the support.

In the photographic emulsion layer and/or other hydrophilic colloid layer of the light-sensitive material of the invention, there may be used various surfactants in order to improve the coatability, antistatic characteristic, slidability, dispersibility, antiadhesion characteristic and photographic characteristics (development accelerability, hardenability and sensitizability) thereof.

The photographic emulsion layer and other layer of the invention may be coated on a baryta paper, an α-olefin-laminated paper, a paper support with an α-olefin layer easily peelable therefrom, a flexible reflective support such as synthetic paper, a film made of a semisynthetic or synthetic polymer such as cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate or polyamide, or a stiff material such as a white pigment-coated reflective support, glass, metal, earthenware, or the like. Also. a reflective support as thin as 120 to 160μm may be used.

The support for the light-sensitive material of the invention may be either a reflectiv suppor or transparent suppot. To make the support reflective, the support may contain a white pigment or may be coated thereon with a white pigment-containing hydrophilic colloid layer.

Usable as the white pigment are inorganic and/or organic white pigments, preferably an inorganic white pigment, examples of which include an alkaline earth metal sulfate such as barium sulfate, an alkaline earth metal carbonate such as calcium carbonate, particulate silicic acid, silicas, calcium silicate, alumina, alumina hydrate, titanium oxide, zinc oxide, talc and clay. The preferred white pigments are barium sulfate and titanium oxide.

The layers of the light-sensitive material of the invention may be coated directly or through a subbing layer (comprising one, two or more subbing layers for improving the adhesion characteristic, antistatic characteristic, dimensional stability, wear resistance, hardness, antihalation characteristic, friction characteristic and/or other characteristics of the support surface) on the support whose surface, as needed, is subjected to a corona discharge, UV radiation or flame treatment.

The silver halide emulsion of the invention may contain a viscosity increasing agent in order to improve its coatability.

For coating the emulsion, the extrusion coating or curtain coating method is useful, which is capable of coating two or more layers simultaneously.

The color developing agent used for color-developing the light-sensitive material of the invention includes conventionally known color developing agents extensively used in various color photographic processes.

These color developing agents include aminophenol andpphenylenediamine derivatives. These compounds are generally used in the form of salts such as hydrochlorides or sulfates, which are more stable than their free state. Any of these compounds is used in a concentration of preferably 0.1 to 30g, and more preferably 1 to 15g per liter of a color developer solution. Examples of the aminophenol developing agent include o-aminophenol, p-aminophenol, 5-amino-2-oxytoluene, 2-amino-3-oxytoluene and 2-oxy-3-amino-1,4-dimethylbenzene.

Particularly useful primary aromatic amine color developing agents are N,N-dialkyl-p-phenylenediamine compounds, whose alkyl and phenyl groups may be substituted by an arbitrary substituent. The most useful examples of such compounds are N,N-diethyl-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, and 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluene-sulfonate.

In addition to the above color developing agent, the color developer solution applied to the processing of the light-sensitive material of the invention may also contain discretional ones of known additives including alkali agents such as sodium hydroxide, sodium carbonate or potassium carbonate, alkali metal sulfites, alkali metal bisulfites, alkali metal thiocyanates, alkali metal halides, benzyl alcohol, water softener, thickener and the like.

The color developer solution is used at a pH of normally 7 or more, and most commonly about 10 to 13.

The color developer solution is used at a temperature of normally 15°C or higher, generally 20°C to 50°C, and preferably not lower than 30°C for rapid processing. The color developing time is preferably in the range of 20 to 60 seconds, and more preferably 30 to 50 seconds.

The light-sensitive material of the invention may contain in a hydrophilic colloid layer thereof the above color developing agent as it is or in the form of its precursor in order to be processed in an alkaline activator solution. The color developing agent precursor is a compound capable of producing a color developing agent under an alkaline condition, and includes a precursor of the type of Schiff's base with an aromatic aldehyde derivative, a polyvalent metallic ion complex precursor, a phthalic acid imide derivative precursor, phosphoric acid amide derivative precursor, sugaramin reaction product preccursor and urethane-type precursor. These aromatic primary amine color developing agent precursors are described in U.S. Patent Nos. 3,342,599, 2,507,114, 2,695,234 and 3,719,492; British Patent No. 803,783; JP O.P.I. Nos. 185628/1978 and 79035/1978; and Research Disclosure Nos. 15159, 12146 and 13924.

To the light-sensitive material the aromatic primary amine color developing agent or the precursor thereof needs to be added in an amount enough to carry out sufficient color formation when the light-sensitive material is processed in an activator solution. The amount depends on the kind of the light-sensitive material used, but is preferably 0.1 to

5 mols, more preferably 0.5 to 3 mols per mol of silver halide. These color developing agents or precursors thereof may be used alone or in combination.

To incorporate the color developing agent or the precursor thereof into the light-sensitive material, the compound may be added in the form of a solution of it dissolved in an appropriate solvent such as water, ethanol or acetone, or of an emulsified dispersion of it prepared with use of a high-boiling solvent such as dibutyl phthalate, dioctyl phthalate or tricresyl phthalate. Alternatively, it may be impregnated into a latex polymer to be added as described in Research Disclosure No. 14850.

The light-sensitive material of the invention, after its color developing, is subjected to bleaching and fixing. The bleaching and the fixing may be performed simultaneously.

As the bleaching agent for use in bleaching there are used a variety of compounds, the preferred among which are compounds of polyvalent metals such as iron(III), cobalt(III) and copper(II), particularly complex salts of organic acids with these polyvalent metallic cations, e.g., metallic complex salts of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, nitrilotriacetic acid and N-hydroxyethylethylenediaminediacetic acid; malonic acid, tartaric acid, malic acid, diglycolic acid, dithioglycolic acid, etc.; ferrycyanates and bichromates. These may be used alone or, in combination.

As the fixing agent there are used soluble complex-forming agents for making silver halide into a soluble complex salt. Examples of the soluble complex-forming agent include sodium thiosulfate, ammonium thiosulfate, potassium thiocyanate, thiourea and thioether.

The fixing process is followed by a washing process. The washing process may be replaced by a stabilization process, or both may be used in combination. A stabilizing solution for use in the stabilization process may contain a pH control agent, a chelating agent and a preservative.

For details about the above matter, reference can be made to JP O.P.I. No. 134636/1983.

EXAMPLES

The following are the examples of the present invention, but the invention is not limited by the examples.

Emulsion preparation example 1

Preparation of blue-sensitive silver halide emulsion

To 1000 ml of a 2% gelatin aqueous solution kept at 40°C were added spending 30 minutes the following Solution A and Solution B simultaneously with pAg and pH controlled to 6.5 and 3.0, respectively, and then spending 180 minutes the following Solution C and Solution D simultaneously with pAg and PH controlled to 7.3 and 5.5, respectively, wherein the pAg control was performed according to the method described in JP O.P.I. No. 45437/1984, and the pH control was made by use of sulfuric acid or a sodium hydroxid aqueous solution.

Solution A

Sodium chloride	3.42g
Potassium bromide	0.03g
Water to make	200 ml

Solution B

Silver nitrate	10 g
Water to make	200 ml

Solution C

Sodium chloride	102.7 g
Potassium bromide	1.0 g
Water to make	600 ml

Solution D

Silver nitrate	300 g
Water to make	600 ml

After completion of the addition, the obtained silver halide, after being desalted by use of a 5% aqueous solution of Demol N, produced by Kawo Atlas Co., and a 20% aqueous magnesium sulfate solution, was mixed with a gelatin aqueous solution, whereby a monodisperse cubic Emulsion EMP-1, having an average grain size of 0.85μm, a variation coefficient ($\sigma/\bar{r}$) of 0.07 and containing 99.5 mol% silver chloride, was obtained.

The above Emulsion EMP-1, with use of the following compounds, was then chemically ripened at 50°C for 90 minutes, whereby a blue-sensitive silver halide Emulsion EmA-1 was obtained.

Sodium thiosulfate	0.8 mol/mol of AgX
Stabilizer STAB	6×10^{-4} mol/mol of AgX
Sensitizing dye BS-1	4×10^{-4} mol/mol of AgX
Sensitizing dye BS-2	1×10^{-4} mol/mol of AgX

Emulsions EmA-2 through EmA-10 shown in Table 1 were prepared in the same manner as in Emulsion EmA-1 except that the preparation conditions of EmA-1 were changed as shown in Table 1, provided that to each of Emulsions EmA-6 to EmA-10 was additionally added chloroauric acid in an amount of 0.5mg/mol of AgX besides the above compounds at the time of the chemical ripening thereof.

Table 1

Em No.	Solutions A, B adding time (min.)	Metal dopant*	Average grain size (μm)	Variation coefficient (σ/r)	Ir content per grain (mol/grain)	Chemical ripening condition
EmA-1	30	-	0.85	0.07	0	-
EmA-2	30	K_2IrCl_6: 0.019mg	0.86	0.07	10^{-22}	-
EmA-3	23	K_2IrCl_6: 0.028mg	0.75	0.06	10^{-22}	-
EmA-4	30	K_2IrCl_6: 0.019mg $K_4Fe(CN)_6$: 0.4mg	0.85	0.07	10^{-22}	-
EmA-5	23	K_2IrCl_6: 0.028mg $K_4Fe(CN)_6$: 0.4mg	0.74	0.07	10^{-22}	-
EmA-6	23	K_2IrCl_6: 0.028mg $K_4Fe(CN)_6$: 0.4mg	0.74	0.07	10^{-22}	Chloroauric acid 0.5mg/mol AgX added in chemical ripening
EmA-7	30	K_2IrCl_6: 0.019mg $K_4Fe(CN)_6$: 0.4mg	0.85	0.07	10^{-22}	''
EmA-8	23	K_2IrCl_6: 0 mg $K_4Fe(CN)_6$: 0.4mg	0.75	0.06	0	''
EmA-9	23	K_2IrCl_6:0.0019mg $K_4Fe(CN)_6$: 0.4mg	0.75	0.07	10^{-23}	''
EmA-10	23	K_2IrCl_6: 0.19mg $K_4Fe(CN)_6$: 0.4mg	0.74	0.06	10^{-20}	''

Note: * Added to Solution C.

Preparation of Green-sensitive silver halide emulsion

A monodisperse cubic Emulsion EMP-2, having an average grain size of 0.43µm, a variation coefficient $(\sigma/\bar{r})$ of 0.08 and containing 99.5 mol% silver chloride, was prepared in the same manner as in Emulsion EMP-1 except that the adding periods of time of Solutions A and B and of Solutions C and D were altered, and to Solution C were added 0.15mg of K_2IrCl_6 and 1 mg of $K_4Fe(CN)_6$.

Emulsion EMP-2, with use of the following compounds, was chemically ripened at 55°C for 120 minutes, whereby a greensensitive silver halide Emulsion Em-G was obtained.

Sodium thiosulfate	1.5mg/mol of AgX
Chloroauric acid	1.0mg/mol of AgX
Stabilizer STAB-1	$6x10^{-4}$ mol/mol of AgX
Sensitizing dye GS-1	$4x10^{-4}$ mol/mol of AgX

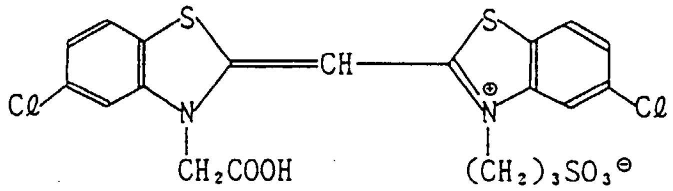
Preparation of red-sensitive silver halide emulsion

A monodisperse cubic Emulsion EMP-3, having an average grain size of 0.50µm, a variation coefficient $(\sigma/\bar{r})$ of 0.08 and containing 99.5 mol% silver chloride, was prepared in the same manner as in Emulsion EMP-1 except that the adding periods of time of Solutions A and B and of Solutions C and D were altered, and to Solution C were added 0.093mg of K_2IrCl_6 and 1 mg of $K_4Fe(CN)_6$.

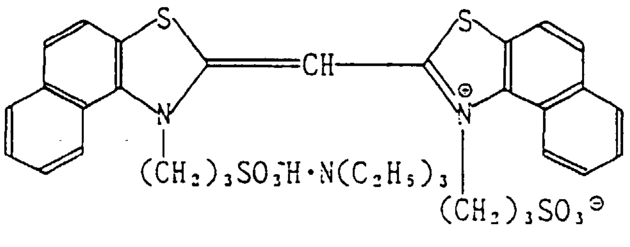
Emulsion EMP-3, with use of the following compounds, was chemically ripened at 60°C for 90 minutes, whereby a red-sensitive silver halide Emulsion Em-R was obtained.

Sodium thiosulfate	1.8mg/mol of AgX
Chloroauric acid	2.0mg/mol of AgX
Stabilizer STAB-1	$6x10^{-4}$ mol/mol of AgX
Sensitizing dye RS-1	$1x10^{-4}$ mol/mol of AgX

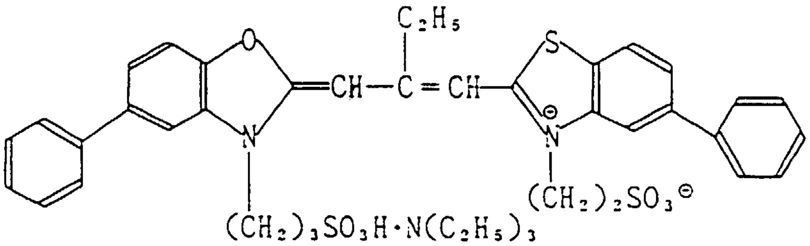
BS-1



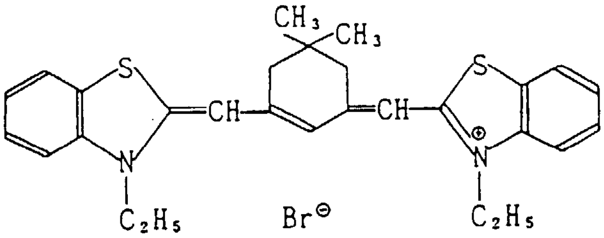
BS-2



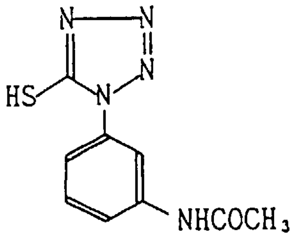
GS-1



RS-1



STAB-1



Emulsion preparation example 2

Preparation of blue-sensitive silver halide emulsion

Emulsion EmB-1 was prepared in quite the same manner as in the Emulsion EmA-1 of Emulsion preparation example 2.

On the other hand, a monodisperse cubic Emulsion EMP-1′, having an average grain size of 0.65μm, a variation coefficient of 0.07 and containing 99.5 mol% silver chloride, was obtained, following the preparation method of Emulsion EmA-1. The Emulsion EMP-1′ was chemically ripened in the same manner as in Emulsion EmA-1, whereby a blue-sensitive silver halide Emulsion EmC-1, having a speed lower than that of EmA-1, was obtained.

Subsequently, Emulsions EmB-2 to EmB-7 and EmC-2 to EmC-7 were prepared in the same manner as in Emulsions EmB-1 and EmC-1 except that the following metallic compounds were added as shown in Table 2.

Table 2

Em No.	Added amt of $K_3Ir(CN)_6$ (mol/mol AgX)	Added amt of $K_4Fe(CN)_6$ (mol/mol AgX)
EmB-1	0	0
EmB-2	$4x10^{-8}$	0
EmB-3	0	$1x10^{-5}$
EmB-4	$4x10^{-8}$	$1x10^{-5}$
EmB-5	$6x10^{-8}$	$1x10^{-5}$
EmB-6	$7x10^{-8}$	$1x10^{-5}$
EmB-7	$7x10^{-8}$	$1x10^{-9}$

Table 2 (continued)

Em No.	Added amt of $K_3Ir(CN)_6$ (mol/mol AgX)	Added amt of $K_4Fe(CN)_6$ (mol/mol AgX)
EmC-1	0	0
EmC-2	4×10^{-8}	0
EmC-3	0	1×10^{-5}
EmC-4	4×10^{-8}	1×10^{-5}
EmC-5	6×10^{-8}	1×10^{-5}
EmC-6	7×10^{-8}	1×10^{-5}
EmC-7	7×10^{-8}	1×10^{-9}

Example 1

A paper support having one side thereof laminated with polyethylene and the other side thereof laminated with titanium oxide-containing polyethylene was used, and the following compositions-having layers were coated on the titanium oxide-containing polyethylene layer side, whereby a multilayer silver halide color photographic light-sensitive material sample was prepared. The coating liquids were prepared as follows.

Layer 1 coating liquid

Twenty-six point seven grams of an yellow coupler Y-1, 10.0g of a dye image stabilizer ST-1, 6.67g of a dye image stabilizer ST-2 and 0.67g of an additive HQ-1 were dissolved in 6.67g of high-boiling organic solvent DNP and 60 ml of ethyl acetate, and this solution was emulsifiedly dispersed by using an ultrasonic homogenizer into 220 ml of a 10% gelatin aqueous solution containing a 20% surfactant SU-1, whereby a yellow coupler-dispersed liquid was prepared. This dispersion was mixed with a blue-sensitive silver halide emulsion (containing 10g of silver) that was prepared under the following conditions, whereby a coating liquid for Layer 1 was prepared.

Coating liquids for Layers 2 to 7 were prepared in similar manner to the above coating liquid for Layer 1, provided that a hardener H-1 was added to Layers 2 and 4, a hardener H-2 was added to Layer 7, and to all the layers were added surfactants SU-2 and SU-3 as coating aids for surface tension adjustment.

Layer	Composition	Adding amt (g/m²)
Layer 7 (Protective layer)	Gelatin	1.00
	Antistain agent HQ-2	0.002
	Antistain agent HQ-3	0.002
	Antistain agent HQ-4	0.004
	Antistain agent HQ-5	0.02
	DIDP	0.005
	Compound F-1	0.002
Layer 6 (UV absorbing layer)	Gelatin	0.40
	UV absorbent UV-1	0.10
	UV absorbent UV-2	0.04
	UV absorbent UV-3	0.16
	Antistain agent HQ-5	0.04
	DNP	0.20
	PVP	0.03
	Antiirradiation dye AI-2	0.02
	Antiirradiation dye AI-4	0.01
Layer 5 (Red-sensitive layer)	Gelatin	1.30
	Red-sensitive silver chlorobromide emulsion Em-R	0.21
	Cyan coupler C-1	0.17
	Cyan coupler C-2	0.25
	Dye image stabilizer	0.20
	Antistain agent HQ-1	0.01
	HBS-1	0.20
	DOP	0.20
Layer 4 (UV absorbing layer)	Gelatin	0.94
	UV absorbent UV-1	0.28
	UV absorbent UV-2	0.09

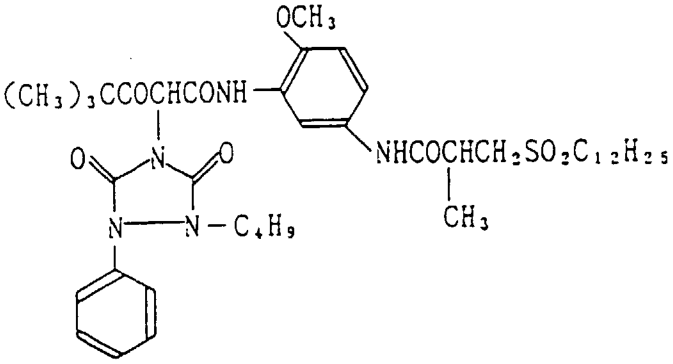
(Continued)

(Continued)

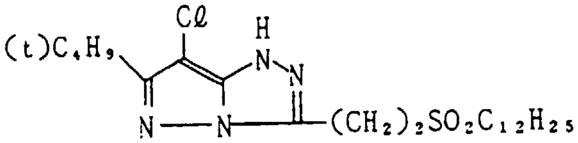
	UV absorbent UV-3	0.38
	Antistain Agent HQ-5	0.10
	DNP	0.40
Layer 3 (Green-sensitive layer)	Gelatin	1.40
	Green-sensitive silver chlorobromide emulsion Em-G	0.17
	Magenta coupler M-1	0.23
	Dye image stabilizer ST-3	0.20
	Dye image stabilizer ST-4	0.17
	DIDP	0.13
	DBP	0.13
	Antiirradiation dye AI-1	0.01
Layer 2 (Inter-layer)	Gelatin	1.20
	Antistain agent HQ-2	0.03
	Antistain agent HQ-3	0.03
	Antistain agent HQ-4	0.05
	Antistain agent HQ-5	0.23
	DIDP	0.06
	Compound F-1	0.002
Layer 1 (Blue-sensitive layer)	Gelatin	1.20
	Blue-sensitive silver chlorobromide emulsion (shown in Table 3)	0.26
	Yellow coupler Y-1	0.80
	Dye image stabilizer ST-1	0.30
	Dye image stabilizer ST-2	0.20
	Antistain agent HQ-1	0.02
	Antiirradation agent AI-3	0.01
	DNP	0.20
Support	Polyethylene-laminated paper	

* Added amount of the silver halide emulsion is shown in silver equivalent.

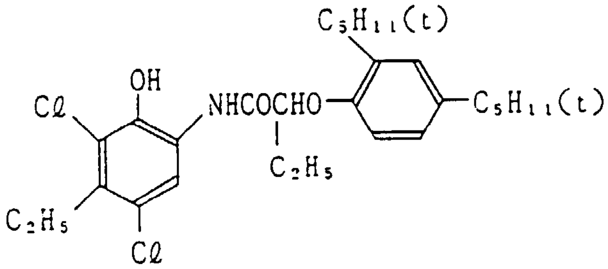
Y - 1


OCH₃
(CH₃)₃CCOCHCONH
NHCOCHCH₂SO₂C₁₂H₂₅
CH₃
O
N
O
N
N-C₄H₉

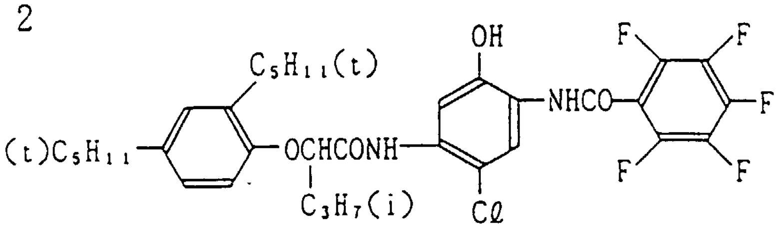
M - 1


Cl
H
(t)C₄H₉
N
N
N
N
(CH₂)₂SO₂C₁₂H₂₅

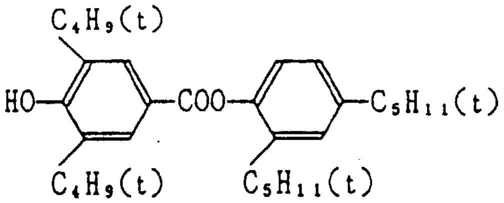
C - 1


C₅H₁₁(t)
OH
Cl
NHCOCHO
C₅H₁₁(t)
C₂H₅
C₂H₅
Cl

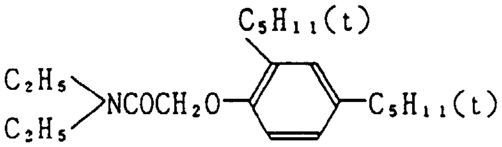
C - 2


OH
F
F
C₅H₁₁(t)
NHCO
F
(t)C₅H₁₁
OCHCONH
F
F
C₃H₇(i)
Cl

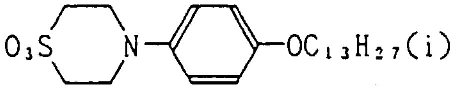
ST-1



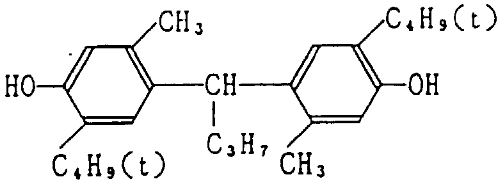
ST-2



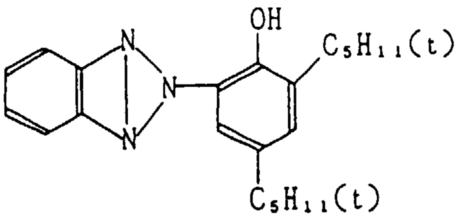
ST-3



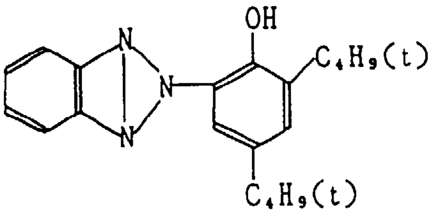
ST-4



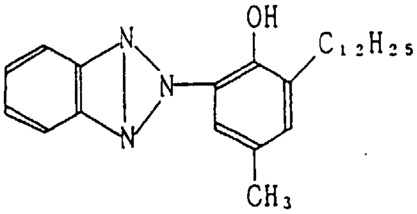
UV-1



UV-2

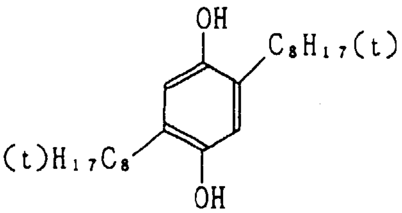


UV-3

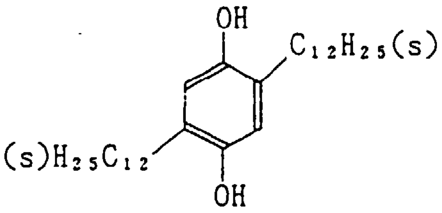


DBP	Dibutyl phthalate
DOP	Dioctyl phthalate
DNP	Dinonyl phthalate
DIDP	Diisodecyl phthalate
PVP	Polyvinyl pyrrolidone

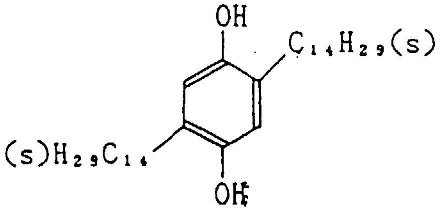
HQ-1



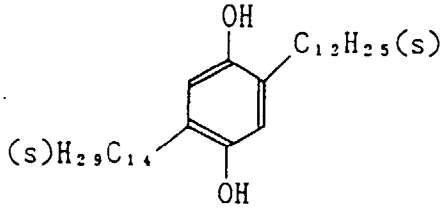
HQ-2



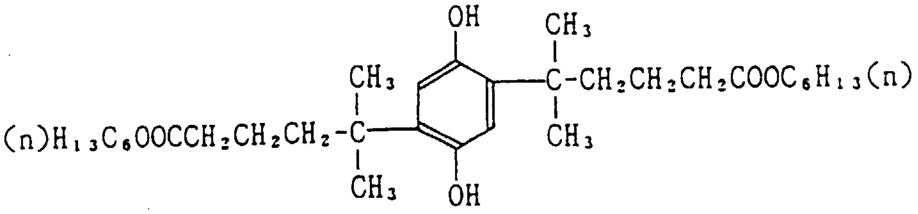
HQ-3



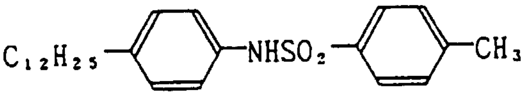
HQ-4



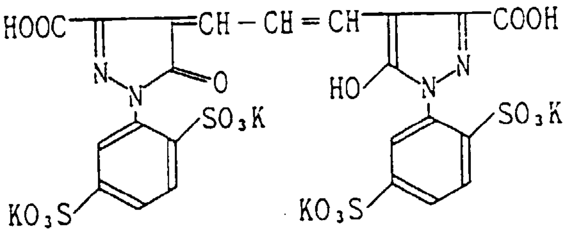
HQ-5



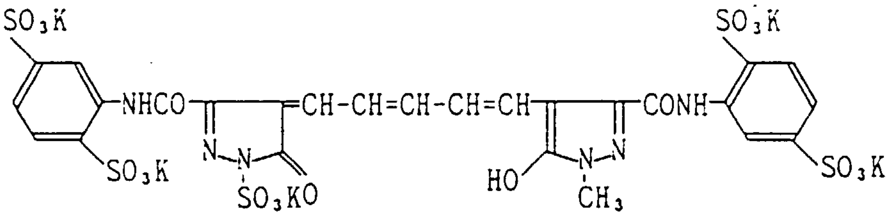
HBS-1



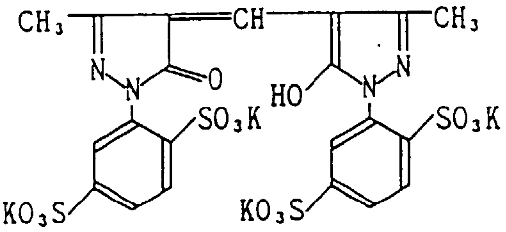
AI-1



AI-2



AI-3



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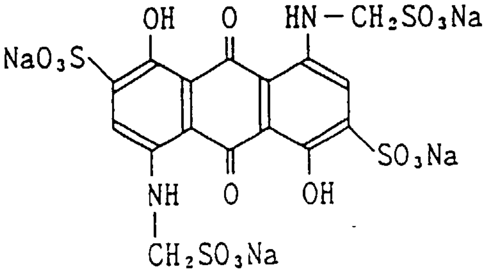
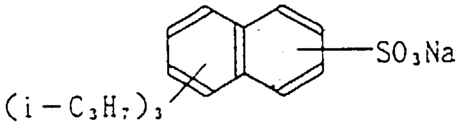


SU-1



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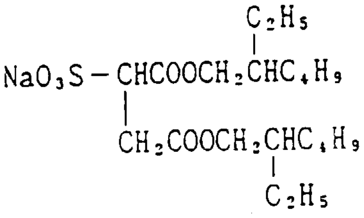
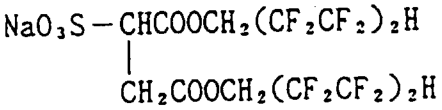


$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\quad C_2H_5 \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ NaO_3S-CHCOOCH_2CHC_4H_9 \\ \qquad\quad\;\; | \\ \qquad\quad\;\; CH_2COOCH_2CHC_4H_9 \\ \qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad\quad C_2H_5 \end{array}$$

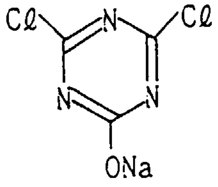
SU-3



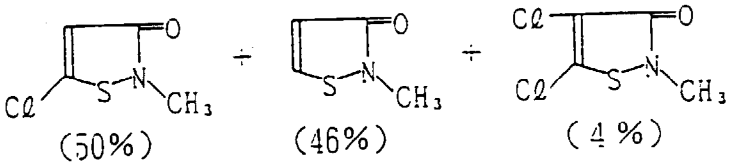
$$\begin{array}{l} NaO_3S-CHCOOCH_2(CF_2CF_2)_2H \\ \qquad\qquad\; | \\ \qquad\qquad\; CH_2COOCH_2(CF_2CF_2)_2H \end{array}$$

H-1 $C(CH_2SO_2CH=CH_2)_4$

H-2



F − 1



Molar ratio

Table 3

Emulsion No.	Blue-sensitive layer's EM combination
1 (Comparative)	EmA-3 (100%)
2 (Comparative)	EmA-2 (50%) + EmA-3 (50%)
3 (Invention)	EmA-2 (45%) + EmA-5 (55%)
4 (Invention)	EmA-4 (50%) + EmA-5 (55%)
5 (Invention)	EmA-6 (45%) + EmA-7 (55%)

Each of the above samples was exposed in the usual manner and then subjected to the following processing for sensitometry tests.

The sensitivity evaluation of each sample was made with the relative value of the reciprocal of the exposure amount necessary to obtain a reflection density of 0.8.

As for the dependence of the sensitivity and that of the gradation upon illuminace, one piece of each sample was exposed for 0.05 second (high-intensity exposure) and another for 10 seconds (low-intensity exposure) through an optical wedge so that both pieces undergo the same exposure amount, and the variations of the sensitivity and gradation thereof were examined. The gradation evaluation was made with the inclination between densities of 0.8 and 1.2, and its variation was indicated with the relative value of the low-intensity exposure condition to the high-intensity exposure condition.

The exposure's dependence on-humididy was indicated with the relative value of the sensitivity at 20°C/85%RH to the sensitivity at 20°C/18% RH.

The results are shown in Table 4.

Processing step	Temperature	Time
Color developing	35.0 ± 0.3°C	45 seconds
Bleach-fix	35.0 ± 0.5°C	45 seconds
Stabilizing	30 to 34°C	90 seconds
Drying	60 to 80°C	60 seconds

<u>Color developer</u>

Pure water	800 ml
Triethanolamine	10 g
N,N-diethylhydroxylamine	5 g
Potassium bromide	0.02g
Potassium chloride	2 g
Potassium sulfite	0.3 g
1-Hydroxylethylidene-1,1-diphosphonic acid	1.0 g

(continued)

Ethylenediaminetetraacetic acid	1.0 g
Disodium catechol-3,5-diphosphonate	1.0 g
N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Brightening agent, 4,4'-diaminostilbenesulfonic acid derivative	1.0 g
Potassium carbonate	27 g
Water to make 1 liter. Adjust pH to 10.10.	

Bleach-fix bath

Ferric-ammonium ethylenediaminetetraacetate, dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (70% aqueous solution)	100 ml
Ammonium sulfite (40% aqueous solution)	27.5 ml
Water to make 1 liter. Adjust pH to 5.7 with potassium carbonate or glacial acetic acid.	

Stabilizing bath

5-Chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Ethylenediaminetetraacetic acid	1.0 g
Ammonium hydroxide (20% aqueous solution)	3.0 g
Brightening agent, 4,4-diaminostilbenesulfonic acid derivative	1.5 g
Water to make 1 liter. Adjust pH to 7.0 with sulfuric acid or potassium hydroxide.	

Table 4

Emulsion No.	Blue-sensitive layer			
	Sensitivity (%)*1	Sensitivity's dependence on illuminance*2 (%)	Gradation's dependence on illuminance*3 (%)	Sensitivity's dependence on humidity *4(%)
1 (Comp.)	100	53	138	119
2 (Comp.)	110	69	112	116
3 (Inv.)	112	79	110	109
4 (Inv.)	122	84	111	105
5 (Inv.)	140	85	99	101

Note: *1: The larger the value, the more excellent.
*2, *3 and *4: The closer to 100%, the more excellent.

As is apparent from Table 4, Samples 1 and 2, comprising the emulsions in which the iridium compound alone was present at the time of growing grains thereof, have larger dependence of the sensitivity upon humidity than the samples of the invention. Samples 3, 4 and 5 of the invention, comprising the emulsion in which the iridium compound and the compound of iron, one of the elements belonging to Group VIII of the periodic table, were present together at the time of growing grains, are excellent in the sensitivity's dependence upon humidity, and also improved in the sensitivity/gradation's dependence upon illuminance.

Further, Sample 5, in which the gold compound was used at the time of the chemical ripening thereof, shows exceptionally excellent characteristics.

Example 2

The blue-sensitive emulsion of Sample 5 of Example 1 was altered as shown in Table 5 to thereby prepare the samples given in Table 5, and the samples were evaluated in the same manner as in Example 1.

Table 5

Sample No.	Blue-sensitive layer's EM combination
5 (Invention)	EmA-6 (45%) + EmA-7 (55%)
6 (Comparative)	EmA-8 (45%) + EmA-7 (55%)
7 (Invention)	EmA-9 (45%) + EmA-7 (55%)
8 (Invention)	EmA-10 (45%) + EmA-7 (55%)

The results are shown in Table 6.

Table 6

Emulsion No.	Blue-sensitive layer			
	Sensitivity (%)	Sensitivity's dependence on illuminance (%)	Gradation's dependence on illuminance (%)	Sensitivity's dependence on humidity (%)
5 (Inv.)	140	85	99	101
6 (Comp.)	112	44	149	121
7 (Inv.)	144	82	116	106
8 (Inv.)	132	87	115	109

From Table 6 it is understood that Sample 6, having the blue-sensitiv layer containing no iridium compound at all, is badly inferior in the dependence of its sensitivity/gradation upon illuminance, while Samples 5 and 7, whose iridium compound content is from 10^{-21} to 10^{-23} mol per grain, are excellent in any characteristics.

Example 3

Samples 9 to 18 given in Table 7 were prepared in the same manner as in Sample 5 of Example 1 except that the metallic dopant to EmA-6 and EmA-7 of the layer thereof was altered as shown in Table 7. The respective dopants were added in equivalent molar amounts to EmA-6 and EmA-7 except the one whose amount is given in the table.

Table 7

Sample No.	Iridium compound	Metallic compound Va, VIa, VIIa, VIII
9 (Inv.)	K_2IrCl_6	$K_3Fe(CN)_6$
10 (Inv.)	K_2IrCl_6	$RhCl_3$ (added amt: 1/10)
11 (Inv.)	K_2IrCl_6	$K_3[Ru(SCN)_6]$
12 (Inv.)	K_2IrCl_6	$K_2[Re(SCN)_6]$
13 (Inv.)	K_2IrCl_6	$K_3[Os(CN)_6]$
14 (Inv.)	K_2IrCl_6	$[Co(NH_3)_6]Cl_3$
15 (Inv.)	$K_2[Ir(CN)_6$	$K_4Fe(CN)_6$
16 (Inv.)	K_3IrCl_6	$K_4Fe(CN)_6$
17 (Comp.)	K_2IrCl_6	$PbCl_2$
18 (Comp.)	K_2IrCl_6	$Cu(NH_3)_4SO_4$

The results are shown in Table 8.

Table 8

Emulsion No.	Blue-sensitive layer			
	Sensitivity (%)	Sensitivity's dependence on illuminance (%)	Gradation's dependence on illuminance (%)	Sensitivity's dependence on humidity (%)
9 (Inv.)	137	84	102	100
10 (Inv.)	120	81	95	99
11 (Inv.)	135	84	107	102
12 (Inv.)	129	83	105	103
13 (Inv.)	141	80	100	103
14 (Inv.)	124	87	101	101
15 (Inv.)	138	86	99	100
16 (Inv.)	139	84	102	102
17 (Comp.)	98	111	119	118
18 (Comp.)	101	108	136	115

As is apparent from Table 8, the effect of the invention appears due to some of the metals belonging to Groups Va, VIa, VIIa and VIII of the periodic table, but cannot be obtained with compounds of other metals (Pb and Cu in the table).

Example 4

Emulsions EmA-1 to EmA-7 and EmB-1 to EmB-7 were singly used and blended in the ratio of 1:1 as shown in Table 9 for the following coating.

Further, a papar support laminated on one side thereof with titanium oxide-containing polyethylene and on the other with polyethylene was used, and the following layers were coated on the titanium oxide-containing polyethylene side thereof, whereby Samples 21 to 97, having the following construction, were prepared.

Protective layer:	Gelatin
	Hardener H-2
Emulsion layer:	Blue-sensitive emulsion (above emulsion)
	Yellow coupler Y-1
	High-boiling organic solvent DNP
	Gelatin
Support:	Polyethylene-laminated paper

The characteristics of each of these samples were evaluated as follows:

(1) Sensitometry

Each sample was exposed through an optical wedge to a blue light for 0.5 second (standard exposure), and processed for color formation in the same manner as in Example 1 to thereby obtain the sensitivity, provided that the sensitivity is expressed in terms of the logarithm of the reciprocal of the exposure amount necessary to obtain a fog + 0.8 density.

(2) Reciprocity law failure characteristic

Each sample was exposed through a wedge to a blue light for 0.5 second (standard exposure), 0.04 second (high-intensity exposure) and 8 seconds (low-intensity exposure) with the illuminance adjusted so as to make the exposure amount constant, and then processed likewise for density measurement in sensitometry. The results are shown in Table 9, where the respective sensitivities of each sample are indicated with relative values in 0.04-second exposure and 8-second exposure to the sensitivity in 0.5-second exposure set at 100.

Table 9 (1)

Sample No.	Single Em No. Blended Em Nos.	Sensitivity S_2(log E)	Reciprocity law failure characteristic (ΔS_2)	
			High-intensity exposure	Low-intensity exposure
21	A-1	2.58	150	25
22	A-2	2.59	150	35
23	A-3	2.62	140	25
24	A-4	2.60	140	35
25	A-5	2.59	140	37
26	A-6	2.58	141	37
27	A-7	2.58	140	38
28	A-1/A-2	2.59	150	50
29	A-1/A-3	2.60	140	26
30	A-1/A-4	2.63	136	53
31	A-1/A-5	2.64	136	54
32	A-1/A-6	2.63	136	56
33	A-1/A-7	2.62	145	56
34	A-2/A-3	2.58	145	36
35	A-2/A-4	2.60	140	53
36	A-2/A-5	2.62	143	54
37	A-2/A-6	2.61	144	56
38	A-2/A-7	2.71	140	56
39	A-3/A-4	2.60	140	53
40	A-3/A-5	2.63	143	57
41	A-3/A-6	2.70	140	53

Table 9 (2)

Sample No.	Blended emulsion Nos.	Sensitivity S_2(log E)	Reciprocidy law failure characteristic (ΔS_2)	
			High-intensity exposure	Low-intensity exposure
42	A-3/A-7	2.65	135	54
43	A-4/A-5	2.60	110	86
44	A-4/A-6	2.57	109	84
45	A-4/A-7	2.56	109	84
46	A-5/A-6	2.62	108	84
47	A-5/A-7	2.60	107	85
48	A-6/A-7	2.60	121	69
49	B-1/A-1	2.36	150	26
50	B-1/A-2	2.34	150	49
51	B-1/A-3	2.35	140	29
52	B-1/A-4	2.40	135	35
53	B-1/A-5	2.43	133	38
54	B-1/A-6	2.42	132	39
55	B-1/A-7	2.41	129	35
56	B-2/A-1	2.36	150	48
57	B-2/A-2	2.34	150	59
58	B-2/A-3	2.40	140	49
59	B-2/A-4	2.36	135	56
60	B-2/A-5	2.38	136	58
61	B-2/A-6	2.38	135	60
62	B-2/A-7	2.38	133	58

Table 9 (3)

Sample No.	Blended emulsion Nos.	Sensitivity S_2(log E)	Reciprocity law failure characteristic (ΔS_2)	
			High-intensity exposure	Low-intensity exposure
63	B-3/A-1	2.44	140	45
64	B-3/A-2	2.43	140	50
65	B-3/A-3	2.50	130	45
66	B-3/A-4	2.43	132	52
67	B-3/A-5	2.44	132	54
68	B-3/A-6	2.42	130	57
69	B-3/A-7	2.43	128	57
70	B-4/A-1	2.42	136	52
71	B-4/A-2	2.44	136	57
72	B-4/A-3	2.46	132	52
73	B-4/A-4	2.46	109	85
74	B-4/A-5	2.44	120	63
75	B-4/A-6	2.45	110	88
76	B-4/A-7	2.45	108	87
77	B-5/A-1	2.44	136	54
78	B-5/A-2	2.43	136	60
79	B-5/A-3	2.46	132	54
80	B-5/A-4	2.44	109	87
81	B-5/A-5	2.42	120	66
82	B-5/A-6	2.43	110	89
83	B-5/A-7	2.45	108	89

Table 9 (4)

Sample No.	Blended emulsion Nos.	Sensitivity S_2(log E)	Reciprocity law failure characteristic (ΔS_2)	
			High-intensity exposure	Low-intensity exposure
84	B-6/A-1	2.41	128	55
85	B-6/A-2	2.43	133	60
86	B-6/A-3	2.42	130	54
87	B-6/A-4	2.42	108	90
88	B-6/A-5	2.42	109	88
89	B-6/A-6	2.45	118	75
90	B-6/A-7	2.43	120	75
91	B-7/A-1	2.41	130	55
92	B-7/A-2	2.42	136	60
93	B-7/A-3	2.41	132	54
94	B-7/A-4	2.43	108	91
95	B-7/A-5	2.45	107	90
96	B-7/A-6	2.43	119	73
97	B-7/A-7	2.45	121	74

As is apparent from the results shown in Table 9, the samples (Samples 23 to 27, 54 to 56, 60, 62, 63, 67, 68, 74 and 75) in which both emulsions blended are doped with $K_2Fe(CN)_6$ and $K_3Ir(CN)_6$ show higher sensitivities and better improved reciprocity law failure characteristic than those in which either one emulsion alone or both emulsions blended contains $K_2Fe(CN)_6$.

Further, in the case of a blend of emulsions different in the sensitivity as in the blend of the high-sensitivity emulsion (EmA-1 to A-7) and the low-sensitivity emulsion (EmB-1 to B-7), the use of a larger amount of the Ir compound in the low-sensitivity emulsion (EmB-1 to B-7) has a better effect upon the reciprocity law failure characteristic (as in Samples 67 and 68).

Also, it is understood from the results that the using amount of $K_2Fe(CN)_6$ for doping these emulsions is preferably 1×10^{-8} to 1×10^{-4} mol per mol of silver halide, and that of $K_3Ir(CN)_6$ is preferably 1×10^{-9} to 1×10^{-6} mole per mol of silver halide.

Example 5

A paper support laminated on one side thereof with polyethylene and on the other with titanium oxide-containing polyethylene was used, and similar layers to those of Example 1 were coated on the titanium oxide-containing polyethylene-laminated side to thereby prepare multilayer silver halide color photographic light-sensitive material samples, provided as the blue-sensitive silver halide emulsion thereof there were used Emulsions EmB-1 to EmB-7 and EmC-1 to EmC-7 of Example 4, and Emulsions EmD-1 to EmD-7 and EmE-1 to EmE-7 which were obtained by adding chloroauric acid in an amount of 0.5 mg per mol of silver halide to the emulsions EmB-1 to EmB-7 and EmC-1 to EmC-

7 at the time of the chemical ripening thereof.

The above samples were subjected to sensitometric and reciprocity law failure characteristic evaluations in the same manner as in Example 4. The results are shown in Table 10.

Table 10 (1)

Sample No.	Single Em No. Blended Em Nos.	Sensitivity S_2(log E)	Reciprocity law failure characteristic (ΔS_2)	
			High-intensity exposure	Low-intensity exposure
98	B-4	2.60	140	35
99	B-5	2.59	140	37
100	B-6	2.58	141	37
101	D-4	3.08	135	51
102	D-5	3.07	134	50
103	D-6	3.05	135	52
104	C-1/C-4	2.63	136	53
105	B-1/B-5	2.64	136	54
106	D-1/D-4	3.05	125	60
107	D-1/D-5	3.01	126	62
108	B-4/B-5	2.60	110	86
109	B-4/B-6	2.57	109	84
110	B-4/B-7	2.56	109	84
111	D-4/D-5	3.00	104	96
112	D-4/D-6	2.98	104	94
113	D-4/D-7	2.98	107	94
114	C-5/B-1	2.44	136	54
115	C-5/B-2	2.43	136	60
116	C-5/B-3	2.46	132	54
117	C-5/B-4	2.44	109	87
118	C-5/B-5	2.42	120	66

Table 10 (2)

Sample No.	Blended Emulsion Nos.	Sensitivity S_2(log E)	Reciprocity law failure characteristic (ΔS_2)	
			High-intensity exposure	Low-intensity exposure
119	C-5/B-6	2.43	110	89
120	C-5/B-7	2.45	108	89
121	E-5/D-1	2.82	125	60
122	E-5/D-2	2.81	125	65
123	E-5/D-3	2.84	120	61
124	E-5/D-4	2.84	104	96
125	E-5/D-5	2.83	114	78
126	E-5/D-6	2.85	104	94
127	E-5/D-7	2.86	107	94

As is apparent from Table 10, the samples to which was added chloroauric acid at the time of ripeing show better results than those to which no chloroauric acid was added.

Example 6

Samples having the same component layers as those of Example 5 were prepared in the same manner except that the blending ratio of the Emulsions EmE-5 and EmD-4 of Example 5 was changed as shown in Table 11, and the resulting characteristics thereof were evaluated. The results are shown in Table 11.

Table 11

Sample No.	Blended emulsion Nos.	Blending ratio	Sensitivity S_2 (log E)	Reciprocity law High-intensity exposure	failure (ΔS_2) low-intensity exposure
128	E-5/D-4	1/9	3.08	109	89
129	E-5/D-4	2/8	3.04	105	90
130	E-5/D-4	3/7	2.96	106	92
131	E-5/D-4	4/6	2.90	105	92
132	E-5/D-4	5/5	2.84	104	96
133	E-5/D-4	6/4	2.78	103	98
134	E-5/D-4	7/3	2.71	100	100
135	E-5/D-4	8/2	2.65	100	101
136	E-5/D-4	9/1	2.60	100	100

As is apparent from Table 11, the use of a larger amount of the Ir compound in the low-sensitivity emulsion and a less amount of the Ir compound in the high-sensitivity emulsion has a good effect upon the reciprocity law failure characteristic, and the best results can be obtained when the ratio of the low-sensitivity emulsion with a larger amont of Ir compound/high-sensitivity emulsion with a less amount of Ir compound is 7/3, 8/2 or 9/1.

Example 7

The blue-sensitive emulsions EmD-5 and EmE-6 prepared in Example 5 are emulsions spectrally sensitized with Sensitizing dye A-27, but one or two different sensitizing dyes other than A-27 were used to prepare various blue-sensitive emulsions.

The obtained emulsions are as shown in Table 12.

Table 12

Emulsion No.	Sensitizing dye used	Remarks
EmD-5-a	A-27	The same as EmD-5
EmD-5-b	A-29	
EmD-5-c	A-30	
EmD-5-d	A-27, A-3	
EmD-5-e	A-27, A-6	
EmD-5-f	A-27, A-29	
EmD-5-g	A-27, A-30	
EmE-6-a	A-27	The same as EmD-6
EmE-6-b	A-29	
EmE-6-c	A-30	
EmE-6-d	A-27, A-3	
EmE-6-e	A-27, A-6	
EmE-6-f	A-27, A-29	
EmE-6-g	A-27, A-30	

These emulsions were blended in the D-5/E-6 ratio of 3/7 and coated in the same manner as in Example 5 to thereby prepare the samples shown in Table 13. The samples were processed for the sensitometric and reciprocity law failure characteristic evaluations in the same manner as in Example 5. The results are shown in Table 13.

Table 13

Sample No.	Single Em No. Blended Em Nos.	Sensitivity S_2(log E)	Reciprocity law failure characteristic (ΔS_2)	
			High-intensity exposure	Low-intensity exposure
137	D-5-a	3.07	125	50
138	D-5-b	3.05	124	55
139	D-5-c	3.06	126	49
140	D-5-d	3.08	125	58
141	D-5-e	3.08	123	60
142	D-5-f	3.09	120	60
143	D-5-g	3.08	126	50
144	E-6-a	2.57	125	50
145	E-6-b	2.61	127	55
146	E-6-c	2.62	126	50
147	E-6-d	2.62	123	61
148	E-6-e	2.60	121	62
149	E-6-f	2.57	120	60
150	E-6-g	2.62	125	51
151	D-5-a/E-6-a	2.82	105	89
152	D-5-b/E-6-b	2.83	104	90
153	D-5-c/E-6-c	2.84	104	92
154	D-5-d/E-6-d	2.85	101	98
155	D-5-e/E-6-e	2.84	100	101

Table 13 (continued)

Sample No.	Single Em No. Blended Em Nos.	Sensitivity S_2(log E)	Reciprocity law failure characteristic (ΔS_2)	
			High-intensity exposure	Low-intensity exposure
156	D-5-f/E-6-f	2.83	100	101
157	D-5-g/E-6-g	2.85	103	98

As is apparent from Table 13, the reciprocity law failure characteristic of the emulsion can be more improved by using two or more different sensitizing dyes than by using a single sensitizing dye alone.

It is also understood that the preferred among the blue-sensitizing dyes are monomethinethiacyanine dyes, and more preferred are those having Formula A-1 in which Y_1 and Y_2 are naphtho rings.

Example 8

The adding amont of $K_2IrCl_6$to EMP-2 and EMP-3 was varied to prepare therefrom samples having blended emulsions containing different amounts of the iridium compound as in the blue-sensitive layer of Example 1, and the samples were evaluated in the same manner as in Example 1. As a result, there were obtained excellent light-sensitive materials not only realizing the effect of the invention but also having well-balanced sensitivity/gradation's dependence upon illuminance and sensitivity's dependence upon humidity.

Example 9

A light-sensitive material sample having a silver chlorobromide emulsion containing 30 mol% silver chloride was prepared in the same manner as in Example 1 except that the compositions and adding time of the Solutions A to D were altered. This sample was processed by using EP-2 processing solutions, produced by Eastman kodak Company, and evaluated in like manner. Consequently, it has been found that even the light-sensitive material having a silver chlorobromide emulsion containing 30 mol% silver chloride enable to obtain the effect of the invention.

Claims

1. A silver halide photographic light-sensitive material comprising a support having thereon a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red- sensitive silver halide emulsion layer, wherein at least one of said color-sensitive layers comprises two or more kinds of iridium-containing silver halides having different iridium contents; and at least one of said silver halides is prepared in the presence of an iridium compound and a compound of a metal selected from metals, other than iridium, belonging to Groups Va, VIa, VIIa and VIII of the periodic table.

2. The silver halide photographic material of claim 1, wherein at least one of said silver halides is chemically sensitized with a gold compound.

3. The silver halide photographic material of claim 1, wherein iridium is contained in an amount of not more than 10^{-21} mol per silver halide grain.

4. The silver halide photographic material of claim 1, wherein said iridium compound and said compound of a metal selected from metals, other than iridium, belonging to Groups Va, VIa, VIIa and VIII are added at the same stage during the course of formation of the silver halide grain.

5. The silver halide photographic material of claim 4, wherein said compound of a metal selected from metals, other than iridium, is added in an amount of not less than 1 X 10^{-10} mol per mol of silver halide.

6. The silver halide photographic material of claim 1, characterised in that said metals, other than iridium, are vanadium, chromium, manganese, iron, cobalt, nickel, niobium, technetium, ruthenium, rhodium, palladium, tantalum, rhenium, osmium and platinum.

7. The silver halide photographic material of claim 1, characterised in that said silver halides each have a silver chloride content of not less than 99 mol%.

8. The silver halide photographic material of claim 7, characterised in that said silver halides are monodispersed, having a variation coefficient of not more than 0.22.

Patentansprüche

1. Lichtempfindliches photographisches Silberhalogenid-Aufzeichnungsmaterial mit einem Schichtträger und je einer darauf aufgetragenen blauempfindlichen, grünempfindlichen und rotempfindlichen Silberhalogenidemulsionsschicht, wobei mindestens eine der farbempfindlichen Schichten zwei oder mehrere Arten iridiumhaltiger Silberhalogenide unterschiedlicher Iridiumgehalte umfaßt und mindestens eines der Silberhalogenide in Gegenwart einer Iridiumverbindung und einer Verbindung eines Metalls, ausgewählt aus von Iridium verschiedenen Metallen der Gruppen Va, VIa, VIIa und VIII des Periodensystems, hergestellt wurde.

2. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 1, wobei mindestens eines der Silberhalogenide chemisch mit einer Goldverbindung sensibilisiert wurde.

3. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 1, wobei der Iridiumgehalt nicht mehr als 10^{-21} Mol pro Silberhalogenidkorn beträgt.

4. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 1, wobei die Iridiumverbindung und die Verbindung eines Metalls, ausgewählt aus von Iridium verschiedenen Metallen der Gruppen Va, VIa, VIIa und VIII, in derselben Stufe während der Silberhalogenidkornbildung zugesetzt wurden.

5. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 4, wobei die Verbindung eines Metalls, ausgewählt aus von Iridium verschiedenen Metallen, in einer Menge von nicht weniger als 1×10^{-10} Mol/Mol Silberhalogenid zugesetzt wurde.

6. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die von Iridium verschiedenen Metalle aus Vanadium, Chrom, Mangan, Eisen, Kobalt, Nickel, Niob, Technetium, Ruthenium, Rhodium, Palladium, Tantal, Rhenium, Osmium und Platin bestehen.

7. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die Silberhalogenide jeweils einen Silberchloridgehalt von nicht weniger als 99 Mol-% aufweisen.

8. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 7, dadurch gekennzeichnet, daß die Silberhalogenide aus monodispersen Silberhalogeniden einer prozentualen quadratischen Streuung von nicht mehr als 0,22 bestehen.

Revendications

1. Une substance photographique sensible à la lumière à base d'halogénure d'argent comprenant un support portant une couche d'émulsion d'halogénure d'argent sensible au bleu, une couche d'émulsion d'halogénure d'argent sensible au vert et une couche d'émulsion d'halogénure d'argent sensible au rouge, substance dans laquelle au moins une desdites couches sensibles aux couleurs comprend deux ou plus de deux types d'halogénure d'argent contenant de l'iridium à teneurs en iridium différentes; et au moins l'un desdits halogénures d'argent est préparé à partir d'un dérivé d'iridium et d'un dérivé d'un métal choisi parmi les métaux, autres que l'iridium, appartenant aux groupes Va, VIa, VIIa et VIII du tableau périodique.

2. La substance photographique à base d'halogénure d'argent selon la revendication 1, dans laquelle au moins l'un desdits halogénures d'argent est sensibilisé chimiquement à l'aide d'un dérivé à base d'or.

3. La substance photographique à base d'halogénure d'argent selon la revendication 1, dans laquelle l'iridium se trouve en une quantité ne dépassant pas 10^{-21} mol par grain d'halogénure d'argent.

4. La substance photographique à base d'halogénure d'argent selon la revendication 1, dans laquelle ledit dérivé d'iridium et ledit dérivé de métal, choisi parmi les métaux autres que l'iridium, appartenant aux groupes Va, VIa, VIIa et VIII sont ajoutés au même moment au cours de la formation du grain d'halogénure d'argent.

5. La substance photographique à base d'halogénure d'argent selon la revendication 4, dans laquelle ledit dérivé d'un métal choisi parmi les métaux, autres que l'iridium, est ajouté en une quantité ne dépassant pas 10-10 mol par mol d'halogénure d'argent.

6. La substance photographique à base d'halogénure d'argent selon la revendication 1, caractérisée en ce que lesdits métaux, autres que l'iridium, sont choisis dans le groupe comprenant le vanadium, le chrome, le manganèse, le fer, le cobalt, le nickel, le niobium, le technétium, le ruthénium, le rhodium, le palladium, le tantale, le rhénium, l'osmium et le platine.

7. La substance photographique à base d'halogénure d'argent selon la revendication 1, caractérisée en ce que chacun desdits halogénures d'argent présente une teneur en chlorure d'argent ne dépassant pas 99 mol %.

8. La substance photographique à base d'halogénure d'argent selon la revendication 7, caractérisée en ce que lesdits halogénures d'argent sont mono-dispersés, et présente un coefficient de variation inférieur à 0,22.