(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 488 737 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
10.01.1996 Bulletin 1996/02

(51) Int Cl.^{6}: **G03C 1/09**, G03C 7/30

(21) Application number: **91311027.6**

(22) Date of filing: **28.11.1991**

(54) Image forming method
Bilderzeugungsverfahren
Procédé de formation d'image

(84) Designated Contracting States:
DE FR GB NL

(30) Priority: **30.11.1990 JP 339421/90**

(43) Date of publication of application:
03.06.1992 Bulletin 1992/23

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(56) References cited:
EP-A- 0 264 288
EP-A- 0 294 149
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Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

The present invention relates to an image forming method in which a photographic image is formed by color-developing a light-sensitive silver halide photographic material containing a dye image forming coupler. More particularly, it relates to an image forming method that can perform rapid color photographic processing with a low fog and in a stable state.

BACKGROUND OF THE INVENTION

Nowadays, rapid processing performance is strongly demanded in the market for reasons of improving productivity in photofinishing labs or coping with the order time for short-time finishing.

The rapid processing performance can be achieved to a reasonably high level by using as a light-sensitive silver halide emulsion a silver chloride emulsion or a silver chlorobromide emulsion with a high silver chloride content (for example, 90 mol % or more; hereinafter called "silver chloride-rich") and using processing methods exclusively used therefor, e.g., a rapid processing method as typified by the QA processing of Konica Corporation and the RA-4 processing of Eastman Kodak Co.

Nevertheless, in the above processing methods, a further improvement has become required for the following reasons (1) and (2).

(1) In the market, there is a demand for much shorter-time finishing.

(2) The silver chloride-rich emulsion must be improved because of its poor reciprocity law failure characteristics as disclosed in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as "Japanese Patent O.P.I. Publication") No. 183647/1989.

For the purpose of the improvements stated above, the present inventors made studies to reveal the following:

(1) Making the processing more rapid can be achieved by more activating the color development (for example, by raising the temperature of the processing solution, or increasing the pH). This, however, results in a deterioration of processing stability.

(2) As a technique to improve the reciprocity law failure characteristics of silver chloride-rich emulsions, it has been found effective to use an iridium compound and a compound of any metals of Group VA, VIA, VIIA or Group VIII of the periodic table, except iridium, in combination when silver halide grains are formed. This technique, on the other hand, has been found disadvantageous in that the fog characteristics are deteriorated.

Concerning the above technical problems, the following techniques are known in the art.

With regard to ultra-rapid processing (those which disclose the technique of carrying out color developing for 40 seconds or less), Japanese Patent O.P.I. Publication No. 203338/1990 discloses a technique in which an exposed light-sensitive silver halide photographic material is immersed for 1 second to 10 seconds in a solution with a pH of 1 to 8 containing a developing agent and thereafter processed for 1 second to 10 seconds in an alkali-containing solution with a pH of 10 to 14, which describes an example in which the developing is carried out for 8 seconds. The light-sensitive material used therein is a commercially available color photographic paper.

Japanese Patent O.P.I. Publications No. 71264/1990 and No. 33142/1990 disclose a technique in which a light-sensitive color photographic material containing a silver halide emulsion having a silver chloride content of not less than 80 mol % is very rapidly processed; Japanese Patent O.P.I. Publication No. 196044/1989, a technique in which a light-sensitive material containing a silver halide emulsion having a silver chloride content of not less than 90 mol % is subjected to color developing for 25 seconds or less using a color developing solution containing substantially no benzyl alcohol; Japanese Patent O.P.I. Publications No. 200252/1989 and No. 187559/1989, a technique in which a light-sensitive material containing an emulsion substantially composed of silver chloride is color-developed in 10 to 20 seconds using a color developing solution containing a hydroxyacetone; and Japanese Patent O.P.I. Publication No. 205162/1989, a technique in which a light-sensitive color photographic material containing a dye or spectral sensitizer having a specific structure is subjected to color developing for 25 seconds or less using a color developing solution containing substantially no benzyl alcohol.

With regard to a technique by which silver halide grains are doped with metal ions for the purpose of improving the reciprocity law failure characteristics, Japanese Patent O.P.I. Publication No. 135832/1980 discloses a technique in which silver halide grains containing not less than 80 mol % of silver chloride are doped with Cd, Pb, Zn and Cu; Japanese Patent Examined Publication No. 55494/1983, a technique in which silver halide grains containing not less than 50 mol % of silver chloride and not more than 10 mol % of silver iodide are doped with Co (III) and Cr (III); Japanese Patent Examined Publication No. 5419/1983, a technique in which silver halide grains are doped with Rh in an amount of 10^{-9} to 10^{-6} mol per mol of AgX and also a spectral sensitizer having an oxidation potential of not more than 0.79 V is used; Japanese Patent Examined Publication No. 22733/1983, a light-sensitive silver halide photographic material containing a Ru complex; SU-788066, a technique in which $CdCl_2$ is added to silver halide; SU-792202, a technique in which $Pb(CO_3)_2$ is added to a silver halide emulsion; Japanese Patent Examined Publication No. 25822/1982, a technique in which Rh and hydroxyazaindene are used in combination when a first ripening is carried out; Japanese Patent Examined Publication No. 23250/1982, a technique in which Rh and a mercapto compound are used in combination when a first ripening is carried out; Japanese Patent Examined Publication No. 23251/1982, a technique in which hydroxytetrazaindene and a mercapto compound are used; Ep-242190, a technique in which grains are formed in the presence of Rh (III) having 3 to 6 CN ligands; Japanese Patent O.P.I. Publication No. 184740/1988, a technique in which in which silver halide grains are doped with Ru and Ir; DE3723419 and DE3340323, a technique in which silver halide grains are doped with In (III) or La (III); USP4,933,272, silver halide grains of a face-centered cubic structure, containing any of Group 5 to 10 transition metals with a nitrosil or thionitrosil ligand; USP4,945,035, silver halide grains of a face-centered cubic lattice structure, containing not less than 50 mol % of silver chloride and not more than 5 mol % of silver iodide, the grains being formed in the presence of a complex with 6 ligands of Re, Ru, Os or Ir having 4 or more cyan ligands; USP4,937,180, silver halide grains of a face-centered cubic lattice structure, containing silver iodide, the grains being formed in the presence of a complex with 6 ligands of Re, Ru, Os or Ir having 4 or more cyan ligands; and Japanese Patent O.P.I. Publication No. 20885/1990, silver halide grains of a face-centered cubic lattice structure, containing Re ions in their insides.

None of these, however, can satisfactorily settle the technical problems discussed above.

SUMMARY OF THE INVENTION

A first object of the present invention is to provide an image forming method that enables rapid and stable color photographic processing, in a method of forming a photographic image by color-developing a light-sensitive silver halide photographic material containing a dye image forming coupler.

A second object of the present invention is to provide an image forming method that enables very rapid color photographic processing with a low fog and in a stable state, using a light-sensitive silver halide photographic material containing a dye image forming coupler and having a superior exposure illuminance dependence.

According to the invention there is provided an image forming method comprising subjecting an imagewise exposed light-sensitive silver halide color photographic material comprising a support, and a light-sensitive layer containing a dye forming coupler and a silver halide emulsion, to color developing for 40 seconds or less in the presence of an aromatic primary amine color developing agent, characterised in that the silver halide emulsion comprises grains which are formed in the presence of an iridium compound and a compound of a further metal belonging to Group VA, VIA, VIIA or Group VIII of the Periodic Table, except iridium, and have a silver chloride content of not less than 95 mol per cent.

The preferable example of the metal for the metal compounds is selected from the group consisting of iron, rhenium, osmium and ruthenium.

In the image forming method of the present invention, said color developing is preferably carried out for 30 seconds or less.

The silver halide emulsion of the present invention has been chemically sensitizied preferably using a gold compound.

In another embodiment of the present invention, the silver halide emulsion has been chemically sensitizied in the presence of at least one compound selected from the group consisting of an inorganic sulfur, an organic compound containing a polysulfide bond to which at least three sulfur atoms are linked, and an organic compound having a heterocyclic ring containing at least two thioether bonds or at least one disulfide bond.

DETAILED DESCRIPTION OF THE INVENTION

The silver halide grains of the silver halide emulsion having a silver chloride content of not less than 95 mol % and comprised of grains formed in the presence of the metal compounds described above (hereinafter "the silver halide grains of the present invention") may preferably have a silver bromide content of not more than 5 mol % and a silver iodide content of not more than 0.5 mol %. They may more preferably be silver chlorobromide grains having a silver bromide content of from 0.1 mol % to 2 mol %.

The silver halide grains of the present invention may be used alone, or may also be used in combination with other silver halide grains having different composition. They may also be used in combination with silver halide grains having a silver chloride content of not more than 95 mol %.

In the light-sensitive silver halide emulsion layer in which the silver halide grains of the present invention are contained, the silver halide grains of the present invention may be held in an amount of not less than 60 % by weight, and preferably not less than 80 % by weight, of the whole silver halide grains contained in that layer.

The composition of the silver halide grains of the present invention may be uniform throughout a grain, from its inside to its outer portion, or may be different between the inside and outer portion of a grain. In the case when the composition of the grain is different between the inside and the outer portion, the composition may change continuously or discontinuously.

There are no particular limitations on the grain size of the silver halide grains of the present invention. Taking account of the rapid processing performance and speed, and also other photographic performances, it may be preferably in the range of from 0.2 µm to 1.6 µm, and more preferably from 0.25 µm to 1.2 µm. The above grain size can be measured by various methods generally used in the present technical field. Typical methods are described in Loveland, "Grain Size Analytical Methods", A.S.T.M. Symposium on Light Microscopy, 1955, pp.94-122, or Mees and James, "The Theory of The Photographic Process", 3rd Ed., 2nd Chapter, Macmillan Publishing Co., Inc. (1966).

This grain size can be measured by use of the projected area or diameter approximate value of a grain. If the grains are of substantially uniform shape, the grain size distribution can be represented fairly accurately as the diameter or projected area.

The grain size distribution of the silver halide grains of the present invention may be polydisperse or monodisperse. Prefered are monodisperse silver halide grains wherein, in the grain size distribution of the silver halide grains, its coefficient of variation is 0.22 or less, and preferably 0.15 or less. Here, the coefficient of variation is a coefficient indicating the breadth of the grain size distribution, and can be defined by the following formula:

$$\text{Coefficient of variation } (S/\dot{r}) = \frac{\text{Standard deviation of grain size distribution}}{\text{Average grain size}}$$

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

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

Here, ri represents the grain size of the individual grains; and ni, its number. The grain size herein mentioned indicates the diameter when a silver halide grain is spherical; and, when it is cubic or of the form other than the spherical, the diameter obtained by calculating a projected image thereof as a round image having the same area.

The silver halide grains of the present invention may be those obtained by any of the acid method, the neutral method and the ammoniacal method. The grains may be grown at one time, or may be grown after making seed grains. The method of making seed grains and the method of growing them may be the same or different.

The manner by which soluble silver salts are reacted with readily soluble halogen salts may be any of those including the normal precipitation, the reverse precipitation, the double-jet precipitation, and the combination of any of these. Preferred are grains obtained by the double-jet precipitation. As one manner of the double-jet precipitation, it is also possible to use the pAg-controlled double-jet precipitation described in Japanese Patent O.P.I. Publication No. 48521/1979.

If necessary, a silver halide solvent such as thioethers may also be used. A mercapto group-containing compound, a nitrogen-containing heterocyclic compound or a compound like a spectral sensitizer may also be used by adding them at the time the silver halide grains are formed or after the formation of grains has been completed.

As the silver halide grains of the present invention, those of any shape can be used. A preferable example thereof is a cube having { 100} face as a crystal surface. It is also possible to prepare grains of the shape such as an octahedron, a tetradecahedron or a dodecahedron, according to the methods as disclosed in publications such as U.S. Patents No. 4,183,756 and No. 4,225,666, Japanese Patent O.P.I. Publication No. 26589/1980, Japanese Patent Publication No. 42737/1980, and The Journal of Photographic Science, 21, 39 (1973), and put them into use. Grains with twin planes may also be used.

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

To the silver halide grains of the present invention, metal ions may be added using a cadmium salt, a zinc salt, a lead salt or a thallium salt, in the course the grains are formed and/or in the course they are grown, whereby they can be incorporated in the insides of the grains and/or the surfaces thereof. Alternatively, the silver halide grains may be placed in a reducing atmosphere, whereby reduction sensitization nuclei can be imparted to the insides of the grains and/or the surfaces of the grains.

From the light-sensitive silver halide emulsion of the present invention having a silver chloride content of not less than 95 mol % (hereinafter "the emulsion of the present invention"), excess soluble salts may be removed after the growth of the silver halide grains has been completed, or they may remain unremoved. In the case when the slats are removed, they can be removed by the method described in Research Disclosure No. 17643.

The silver halide grains used in the emulsion of the present invention may be those in which a latent image is mainly formed on the surfaces, or those in which it is formed in the insides of grains. It is preferred to use grains in which the latent image is mainly formed on the surfaces.

The emulsion of the present invention can be chemically sensitized by conventional methods. More specifically, the sulfur sensitization making use of a compound containing sulfur capable of reacting with silver ions or an active gelatin, the selenium sensitization making use of a selenium compound, the reduction sensitization making use of a reducing substance and the noble metal sensitization making use of a compound of noble metal such as gold or the like can be used alone or in combination. This will be described later in detail.

In the present invention, the feature that silver halide grains are formed in the presence of an iridium compound and at least one compound of any metals belonging to Group VA, VIA, VIIA or Group VIII of the periodic table means that an iridium compound and at least one compound of any metals belonging to Group VA, VIA, VIIA or Group VIII of the periodic table, except an iridium compound, are each added at any stages of the formation of silver halide nuclei, the growth of grains and the physical ripening thereof.

A method therefor may specifically include a method in which the compounds are previously added in a mother liquor before the formation of nuclei, a method in which the compounds are instantaneously added on the way of the formation of silver halide grains, a method in which the compounds are previously added to a silver halide solution or soluble silver salt solution used for the formation and growth of silver halide grains, and a method in which the compounds are added after the growth has been completed and immediately before physical ripening is carried out. In a method of preparing an emulsion by feeding fine grains of silver halide before silver halide grains are formed and grown, the compounds may be added to the fine grain silver halide by the method as described above, when the fine grain silver halide is prepared, and thereafter the mixture may be charged in a reaction vessel to form silver halide grains.

The iridium compound to be added may be dividedly added at different stages. The iridium compound to be added may be used in the formed of a solution comprising a mixture of two or more kinds of different iridium compounds. Alternatively, solutions of two or more kinds of different iridium compounds may be respectively added at different stages.

The aforesaid metal compound other than the iridium compound to be added may also be dividedly added at different stages, or may be added using a solution comprising a mixture of two or more kinds of different metal compounds. Alternatively, solutions of two or more kinds of the aforesaid metal compounds may be respectively added at different stages.

There are no particular limitations on the kind of the iridium compound used in the present invention. Those which are industrially usable and preferable in view of the stability, safety and economical advantages of the compound, may include iridium (III) halides, iridium (IV) halides, and iridium complexes having a halogen, amine, oxalato or the like as a ligand.

Examples of the iridium compound are shown below. The present invention is by no means limited by these.

Iridum trichloride, iridium tribromide, potassium hexachloroiridate (III), ammonium iridium (III) sulfate, potassium iridium (III) disulfate, tripotassium iridium (III) trisulfate, iridium (III) sulfate, tiroxalatoiridium (III), potassium hexacyanoiridium (III), iridium tetrachloride, iridium tetrabromide, potassium hexachloroiridate (IV), ammonium hexachloroiridate (IV), potassium iridate (IV), trioxalatoiridium (IV), and potassium hexacyanoiridium (IV).

In the present invention, any desired one may be selected from these compounds. If necessary, they can be used in combination. These iridium compounds are often used by dissolving it in water or in a solvent compatible with water. Alternatively, it is possible to use methods widely used for stabilizing aqueous solutions of iridium compounds, that is, methods in which a hydrogen halide as exemplified by hydrochloric acid and bromic acid, an alkali halide as exemplified by potassium chloride, sodium chloride or potassium bromide, or nitric acid is added.

In the present invention, the iridium compound may be added in such an amount that the molar number of the iridium compound per mol of silver halide is not less than 10^{-11} mol, and preferably not less than 10^{-9} mol, which latter can be more effective for the present invention. From the standpoint of fog or desensitization, it may preferably be not more than 5×10^{-5} mol, and more preferably not more than 5×10^{-6} mol.

The "metals" in the compounds of metals belonging to Group VA, VIA, VIIA or Group VIII of the periodic table, except iridium, in the present invention specifically mean banadium, chromium, manganese, iron, cobalt, nickel, niobium, technetium, ruthenium, rhodium, palladium, tantalum, rhenium, osmium, and platinum.

In the present invention, compounds of any desired metals among these metals can be used. Complex salts of compounds of any of these metals can also be used. Ligands of the complex salts may include chloro, bromo, iodo, amine, cyan, thiocyan and acetylacetone, any of which can be used.

Examples thereof are given below.

Banadium oxide dichloride, banadium oxyoxide, banadium oxysulfate, banadium oxide acetyl acetate, chromium (III) chloride, chromium (III) bromide, chromium (III) nitrate, chromium (III) acetate, chromium (III) potassium sulfate, manganese (II) acetate, manganese (II) sulfate, ammonium manganese (II) sulfate, manganese (II) bromide, manganese (II) carbonate, manganese (II) chloride, iron (II) chloride, iron (III) chloride, iron (II) sulfate, iron (III) sulfate, Mohr's salt, red prussiate, yellow prussiate, iron (II) thiocyanate, iron (III) thiocyanate, iron (II) bromide, iron (III) bromide. iron (II) acetate, iron (III) acetate, pentacyanoammineferrate (II), cobalt (II) chloride, cobalt (III) chloride, cobalt (II) acetate, hexamminecobalt (II) chloride, cobalt (II) nitrate, nickel (II) chloride, nickel (II) oxalate, nickel (II) benzoate, nickel (II) cyanate, niobium (V) chloride, ruthenium (III) chloride, ruthenium (III) acetyl acetate, rhodium (III) chloride, rhodium (III) nitrate, rhodium (III) acetate, palladium (II) acetate, palladium (II) acetyl acetate, ammonium palladium (II) chloride, palladium (II) chloride, tantalum (V) chloride, hexachloroplatinate (IV), platinum (IV) chloride, potassium tetrachloroplatinate (II), osmate (VIII), potassium hexacyanatorhenium (II), potassium hexacyanatoruthenium (II), potassium hexathiocyanatoruthenium (III), potassium pentacyanochlororuthenate (III), sodium pentachloronitrosilruthenate (III), and potassium pentabromonitrosilosmate (III).

In the present invention, any desired compound may be selected from these compounds. If necessary, any compounds may be used in combination.

In the present invention, the metal compound other than the iridium compound may be added in such an amount that the molar number of the metal compound other than the iridium compound per mol of silver halide is not less than 10^{-10} mol, and preferably not less than 10^{-8} mol, which latter can be more effective for the present invention. From the standpoint of fog or desensitization, it may preferably be not more than 5×10^{-3} mol, and more preferably not more than 5×10^{-4} mol.

The iridium compound and the compound of any metals except iridium should preferably be present at the same time when silver halide grains are formed.

The compound of any metals belonging to Group VA, VIA, VIIA or Group VIII of the periodic table, except iridium, may particularly preferably include compounds of metals such as iron, rhenium, ruthenium and osmium.

In the present invention, in order to more highly achieve the objects of the present invention, the silver halide emulsion comprised of grains formed in the presence of the iridium compound and the compound of a metal selected from metals belonging to Group VA, VIA, VIIA or Group VIII of the periodic table, except iridium may preferably chemically sensitized in the presence of at least one compound previously described.

The inorganic sulfur preferably used in the present invention will be described below.

The term "inorganic sulfur" used in the present invention refers to what is called elemental sulfur, which forms no compound with other element(s). Therefore the sulfur-containing compounds known as photographic additives in the present industrial field, as exemplified by sulfides, sulfuric acid or salts thereof, sulfurous acid or salts thereof, thiosulfuric acid or salts thereof, sulfonic acid or salts thereof, thioether compounds, thiourea compounds, mercapto compounds and sulfur-containing heterocyclic compounds are not included in the "inorganic sulfur" in the present invention.

The elemental sulfur used as the "inorganic sulfur" in the present invention is known to have several allotropes. Any of such allotropes may be used.

Of the allotropes, what is stable at room temperature is α-sulfur, which belongs to a rhombic system. In the present invention, it is preferred to use this α-sulfur.

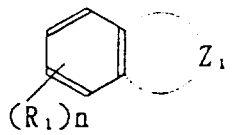
In the case when the "inorganic sulfur" according to the present invention is added, it may be added as it is in the form of a solid. It may more preferably be added in the form of a solution. The inorganic sulfur is insoluble in water, but is known to be soluble in carbon disulfide, sulfur chloride, benzene, diethyl ether, ethanol, etc. The inorganic sulfur may preferably be added after it has been dissolved in any of these solvents. Of these solvents for the inorganic sulfur, ethanol may particularlv preferably be used in view of handling properties or photographic influences.

The inorganic sulfur may be added in an appropriate amount, which may vary depending on the types of silver halide emulsions applied or the extent to which the effect of addition is expected. It may be added in an amount ranging from 1×10^{-5} mg to 10 mg, and preferably 1×10^{-3} mg to 5 mg.

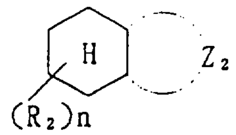
The organic compound containing a polysulfide bond to which at least three sulfur atoms are linked and the organic compound having a heterocyclic ring containing at least two thioether bonds or at least one disulfide bond (hereinafter "the sulfide compound according to the present invention") will be described below.

Of the sulfide compound according to the present invention, what can be preferably used is a compound represented by the following Formula A or B.

Formula A



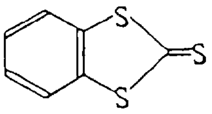
Formula B



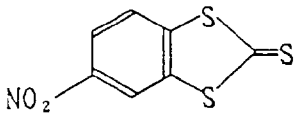
In the formulas, R_1 and R_2 each represent a group capable of being substituted on the benzene ring or hexane ring, and n represents an integer of 0 to 4. Z_1 and Z_2 each represent a group of atoms necessary to complete a heterocyclic ring of 5 to 8 members, containing at least two ether bonds or at least one disulfide bond.

Typical examples of the sulfide compound according to the present invention are shown below. These are given as examples, and by no means limited to these.

A - 1



A - 2



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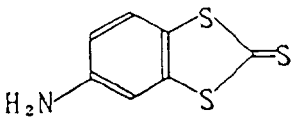

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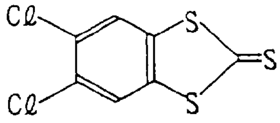

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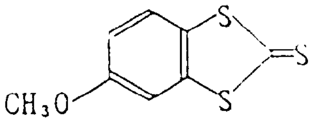

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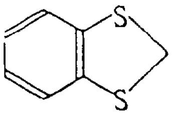

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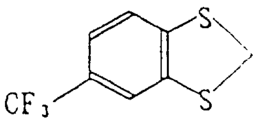

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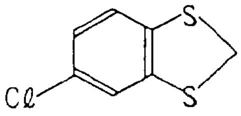

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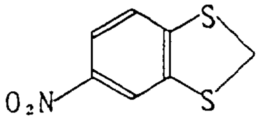

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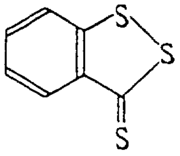

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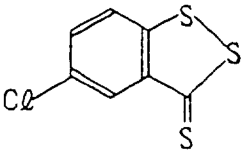

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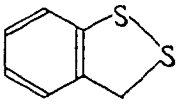

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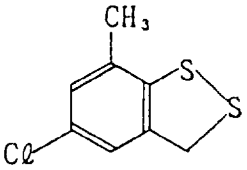
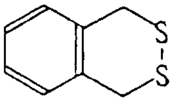
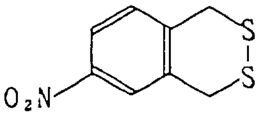


A - 14



A - 15



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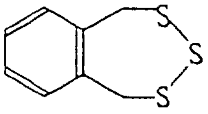

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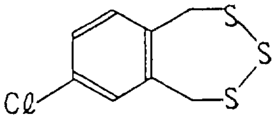

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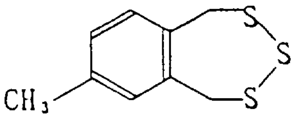

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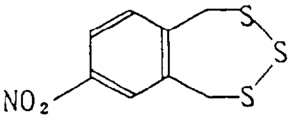

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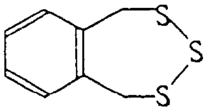

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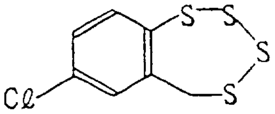

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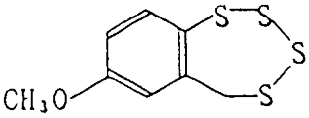

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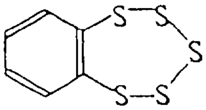

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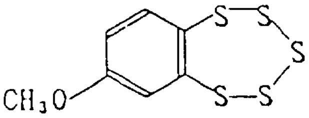

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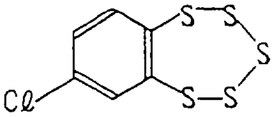

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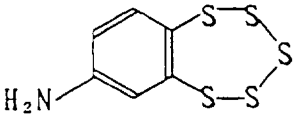

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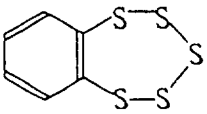

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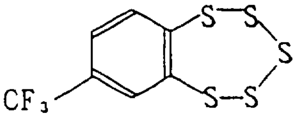

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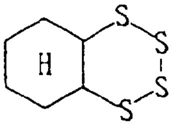

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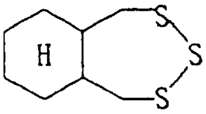

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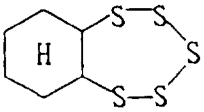

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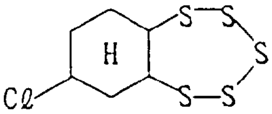

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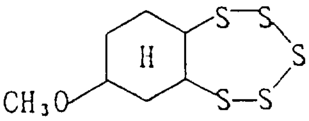

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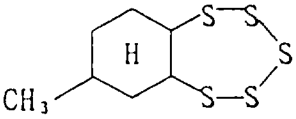

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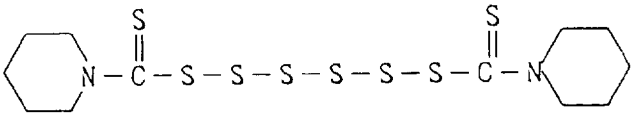

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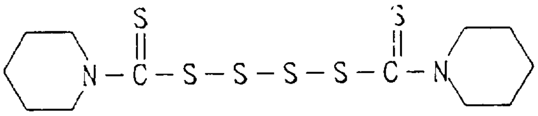

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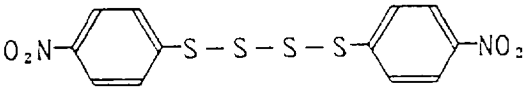

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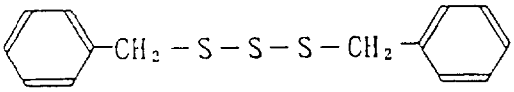

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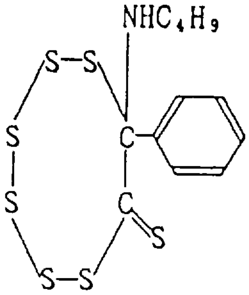

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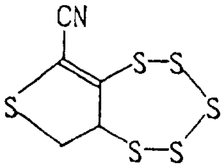

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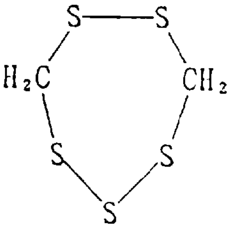

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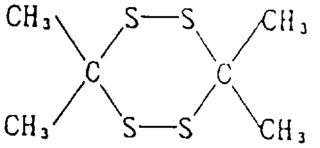

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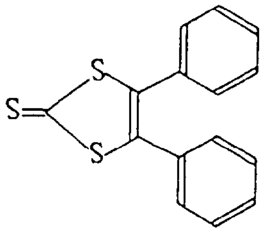

These sulfide compounds can be synthesized by the methods disclosed in Journal of the American Chemical Society (J. Am. Chem. Soc.), 104, 6045 (1982); ditto, 107, 3871 (1985); Journal of Organic Chemistry (J. Or. Chem.), 49, 1221 (1984); ditto, 37, 4196 (1972); ditto, 41, 2465 (1976); ditto, 46, 2072 (1981); Journal of the Chemical Society (J. Am. Chem. Soc.), 2901 (1965); ditto, 1582 (1929); ditto, 187 (1941); Chemistry Letters (Chem. Lett.), 349 (1986); Bulletin of the Chemical Society of Japan (Bll. Chem. Soc. Japan), 61, 1647 (1988); etc.

In the case when the sulfide compound according to the present invention is added, the compound in a solid form may be added as it is. The compound may more preferably be added in the form of a solution.

The sulfide compound according to the present invention may be added in an appropriate amount, which may vary depending on the types of silver halide emulsions applied or the extent to which the effect of addition is expected. It may be added in an amount of 5×10^{-7} mol to 5×10^{-3} mol per mol of silver halide. The compound may be added at one time in its entirety, or may be dividedly added at several times.

As to the time for addition, the inorganic sulfur and the sulfide compound according to the present invention may be added at any steps until the step of stopping chemical sensitization is completed.

More specifically, they may be added at any time selected from the following: Before the formation of silver halide grains, at the start of chemical sensitization, during the formation of silver halide grains, after completion of the formation of silver halide grains and before start of chemical sensitization, at the completion of chemical sensitization, and after completion of chemical sensitization and before coating. They may preferably be added at the start of chemical sensitization, during chemical sensitization, and before completion of chemical sensitization.

The step of starting chemical sensitization refers to the step at which a chemical sensitizer is added. In this step, the time at which the chemical sensitizer is added is the time at which chemical sensitization is started.

In the present invention, as the chemical sensitizer, it is possible to use, for example, a chalcogen sensitizer. The chalcogen sensitizer is a generic term of a sulfur sensitizer, a selenium sensitizer and a tellurium sensitizer. For use in photography, the sulfur sensitizer and the selenium sensitizer are preferred. As the sulfur sensitizer, known compounds can be used. It may include, for example, thiosulfate, allylthiocarbazide, thiorurea, allylisothiocyanate, cystine, p-toluene thiosulfonate, and rhodanine. Besides, it is also possible to use the sulfur sensitizers as disclosed in U.S. Patents No.

1,574,944, No. 2,410,689, No. 2,278,947, No. 2,728,668, No. 3,501,313 and No. 3,656,955, West German Application Publication (OLS) No. 14 22 869, Japanese Patent O.P.I. Publications No. 24937/1981 and No. 45016/1980, etc. The sulfur sensitizer is added in an amount which may vary in a fairly broad range depending on various conditions such as pH, temperature and silver halide grain size. As a standard, it may preferably be added in an amount of approximately 10^{-7} mol to 10^{-1} mol per mol of silver halide.

In place of the sulfur sensitizer, the selenium sensitizer may be used. The selenium sensitizer that can be used may include aliphatic isoselenocyanates such as allyl isoselenocyanate, selenoureas, selenoketones, selenoamides, selenocarboxylic acid salts and esters, selenophosphates, and selenides such as diethyl selenide and diethyl diselenide. Specific examples thereof are disclosed in U.S. Patents No. 1,574,944, No. 1,602,592, No. 1,623,499, etc. It is also possible to use reduction sensitization in combination. There are no particular limitations on the reducing agent. It may include stannous chloride, thiourea dioxide, hydrazine and polyamine, which are known in the art. It is also possible to use a noble metal compound as exemplified by gold compounds, platinum compounds and palladium compounds.

In the present invention, the conditions for the chemical sensitization carried out may vary depending on the silver halide grains used or the photographic performance expected. As general standards, the chemical sensitization may be carried out at a temperature of 35°C to 70°C, at a pH of 5.0 to 7.5, and at a pAg of 6.0 to 8.5. The chemical sensitization may be carried out for a time which is usually set by previously inspecting photographic performances for each time step under specific conditions for chemical sensitization, and selecting the time that can give a most preferable photographic performance among them (such that fog is low, sensitivity is high and contrast is high). To set the time, however, the stability in preparation and operation efficiency in preparation steps are often taken into account. As a general standard, the chemical sensitization may be carried out for several minutes to several hours.

The chemical sensitization described above can be stopped by the method known in the present industrial field. As methods of terminating the chemical sensitization, it is known to use, e.g., a method in which the temperature is dropped, a method in which the pH is lowered, and a method in which a chemical sensitization terminator is used. Taking account of the stability of emulsions or the like, it is preferred to use the method in which a chemical sensitization terminator is used. This chemical sensitization terminator is known to include halide salts as exemplified by potassium bromide and sodium chloride, and organic compounds known as antifoggants or stabilizers as exemplified by 7-hydroxy-5-methyl-1,3,4,7a-tetrazaindene. These may each be used alone or in combination of plural compounds.

The silver halide emulsion having a silver chloride content of not less than 95 mol % and comprised of grains formed in the presence of the iridium compound and the compound of any metals belonging to Group VA, VIA, VIIA or Group VIII of the periodic table, except iridium, may be chemically sensitized using a gold compound. This is preferable for achieving the objects of the present invention on a higher level.

The gold compound that can be used may include those in which the oxidation number of gold is either +1 or +3, and many kinds of gold compounds can be used. As typical examples, the gold compound may include chloroauric acid, potassium chloroaurate, auric trichloride, potassium aurothiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate and pyridyl trichlorogold.

The gold compound is added in an amount which may vary depending on various conditions. It may preferably be added in an amount or concentration of 5×10^{-7} mol to 10^{-3} mol, and more preferably 2×10^{-6} mol to 1×10^{-4} mol, per mol of silver halide. It may still more preferably be added in an amount of 2.6×10^{-6} mol to 4×10^{-4} mol, and most preferably 2.6×10^{-6} mol to 9×10^{-6} mol.

As to the position for addition, the gold compound may be added at any stages in the course of the preparation of silver halide emulsions. It may preferably be added at any time after silver halide grains are formed and until the chemical sensitization is completed.

In instances in which the present invention is applied to light-sensitive color photographic materials, usually a yellow dye forming coupler is used in a blue-sensitive emulsion layer, a magenta dye forming coupler in a green-sensitive emulsion layer, and a cyan dye forming coupler in a red-sensitive emulsion layer. However, depending on the purpose, a light-sensitive silver halide color photographic material may also be prepared by a method in which the couplers are used in the manner different from the above combination.

These dye forming couplers should each preferably have in the molecule a group having 8 or more carbon atoms, called a ballast group, which is capable of making the coupler non-diffusible. These dye forming couplers may be either of a four-equivalent character wherein four molecules of silver ions must be reduced for the formation of one molecule of the dye, or of a two-equivalent character wherein only two molecules of silver ions may be reduced.

As the yellow dye forming coupler, various acylacetoanilide type couplers can be preferably used. Of these, it is advantageous to use benzoylacetanilide compounds and pivaloylacetanilide compounds.

As the cyan dye forming coupler, naphthol type couplers and phenol type couplers can be preferably used.

The compounds such as dye forming coupler in the light-sensitive material of the present invention may usually be dissolved in a high-boiling organic solvent having a boiling point of 150°C or more or a water-insoluble polymeric compound, optionally together with a low-boiling and/or water-soluble organic solvent to effect emulsification dispersion in a hydrophilic binder such as an aqueous gelatin solution using a surface active agent, and thereafter the resulting emulsion may be added to the intended hydrophilic colloid layer. The step of removing the low-boiling organic solvent after dispertion or at the same time of dispersion may be inserted.

The high-boiling organic solvent may preferably be a compound having a dielectric constant of not more than 6.5, which is exemplified by esters such as phthalic acid esters and phosphoric acid esters, organic amides, ketones and hydrocarbon compounds, having a dielectric constant of not more than 6.5.

The high-boiling organic solvent may more preferably those having a dielectric constant of not more than 6.5 and not less than 1.9, and a vapor pressure of not more than 0.5 mmHg at 100°C. Of these solvents, phthalic acid esters and phosphoric acid esters are more preferred. Dialkyl phthalates containing an alkyl group having 9 or more carbon atoms are most preferred. The high-boiling organic solvent may also be in the form of a mixture of two or more kinds. The dielectric constant is meant to be a dielectric constant at 30°C.

Any of these high-boiling organic solvents may be used in an amount of usually 0 % by weight to 400 % by weight based on the coupler, and preferably 10 % by weight to 100 % by weight based on the coupler.

The light-sensitive material of the present invention can be used as, for example, color negative and positive films, and also as color photographic papers or the like. In particular, the present invention can be remarkably effective when used in color photographic papers for direct viewing.

The light-sensitive material including such color photographic papers may be used for either monochromes or multicolor photography.

The silver halide emulsions used in the present invention can be optically sensitized to the desired wavelength region, using dyes known as spectral sensitizers in the photographic industrial field.

As a binder used in the light-sensitive silver halide photographic material of the present invention, it is preferred to use gelatin.

Gelatin usually used in the photographic industrial field may include alkali-treated gelatins treated with lime or the like or acid-treated gelatin treated with hydrochloric acid or the like, when gelatin is produced from collagen. Gelatin is usually produced using cattle bones, cattle hides, pigskins or the like as starting materials.

Details of the preparation method of gelatin, the properties thereof, etc. are described in Arthur Veis, "The Macromolecular Chemistry of Gelatin", American Press, pp.187-217 (1964); T.H. James, "The Theory of the Photographic Process, 4th Ed., p.55, Macmillan (1977); KAGAKU SHASHIN BENRAN (Handbook of Science Photography), 1st Vol., pp.72-75, Maruzen; SHASHIN KOGAKU NO KISO (Basic Photographic Engineering), The Volume of Silver Salt Photography, pp.119-124, Korona-sha K.K.; etc.

The gelatin used in the light-sensitive material of the present invention may be either the lime-treated gelatin or the acid-treated gelatin, and may be any of gelatins produced using cattle bones, cattle hides, pigskins or the like as starting materials. It may preferably be lime-treated gelatin produced using cattle bones as a tarting material.

Photographic emulsion layers and other hydrophilic colloid layers of the light-sensitive material according to the present invention are hardened by cross-linking binder (or protective colloid) molecules and using alone or in combination a hardening agent or agents for increasing layer strength.

The hardening agent should preferably be added in such an amount that the light-sensitive material can be hardened to the extent no additional hardening agent is required in processing solutions. It is also possible to add the hardening agent in a processing solution.

In the light-sensitive material of the present invention, the hydrophilic colloid layers such as a protective layer and an intermediate layer may contain an ultraviolet absorbent so that the light-sensitive material can be prevented from fogging because of electric discharge due to static charging caused by friction or the like or images can be prevented from its deterioration caused by ultraviolet light.

The light-sensitive material of the present invention can be provided with auxiliary layers such as a filter layer, an anti-halation layer and/or an anti-irradiation layer. In these layers and/or in the emulsion layers, a dye may be contained which is other than the dyes of the present invention as described above and is flowed out of the light-sensitive material or bleached, during photographic processing.

In the silver halide emulsion layers and/or other hydrophilic colloid layers of the light-sensitive material according to the present invention, a matting agent can be added for the purpose of decreasing the gloss of the light-sensitive material, increasing the inscribability or preventing the mutual sticking of light-sensitive materials.

In the light-sensitive material of the present invention, a lubricant can be added so that the sliding friction can be decreased.

In the light-sensitive material of the present invention, an antistatic agent can be added for the purpose of preventing the light-sensitive material from being electrostatically charged. The antistatic agent may be used in an antistatic layer on the side of a support on which no emulsions are layered, or may be used in the emulsion layers and/or the protective colloid layers other than emulsion layers on the side of a support on which the emulsion layers are provided.

In the light-sensitive material of the present invention, various surface active agents can be used in the photographic emulsion layers and/or other hyrophilic colloid layers for the purposes of improving coating properties, preventing static charge, improving sliding properties, promoting emulsification dispersion, preventing adhesion, and improving photographic performances such as development acceleration, hardening and sensitization.

The photographic emulsion layers and other layers of the light-sensitive material according to the present invention can be formed on a paper support comprising baryta paper, or paper laminated with α-olefin polymer or the like, a paper support having an α-olefin layer that can be readily separated, a flexible reflective support made of synthetic paper or the like, a film comprised of a semi-synthetic or synthetic polymer such as cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate or polyamide, a reflective support coated with white pigment, or a rigid body such as glass, metal or ceramics. Alternatively, it is also possible to use a single-weight type reflective support with a thickness of 120 μm to 160 μm.

The support used in the light-sensitive material of the present invention may be either a reflective support or a transparent support. In order to give reflecting properties, a white pigment may be incorporated into the support, or a hydrophilic colloid layer containing a white pigment may be formed on the support.

As the white pigment, an inorganic white pigment and/or an organic white pigment can be used. Preferably the inorganic white pigment can be used, which may include sulfates of alkaline earth metals as exemplified by barium sulfate, carbonates of alkaline earth metals as exemplified by calcium carbonate, or finely powdered silicic acid, silicas of synthetic silicate, calcium silicate, aluminum oxide, aluminum hydrate, titanium oxide, zinc oxide, talc and clay. The white pigment may preferably be barium sulfate or titanium oxide.

In the light-sensitive material of the present invention, the support surface may optionally be subjected to corona discharging, ultraviolet irradiation or flame treating and thereafter may be coated with emulsions directly or via an under coat layer (one or more of under coat layer(s) for improving adhesion properties of the support surface, antistatic properties, dimensional stability, friction resistance, hardness, anti-halation properties, friction characteristics and/or other characteristics).

When the silver halide emulsions of the present invention are coated, a thickening agent may be used so that the coating properties can be improved. As for coating methods, extrusion coating and curtain coating are particularly useful which can carry out simultaneous coating for two or more kinds of layers.

In the processing of the light-sensitive material of the present invention, the color developing agent used in the color developing solution may include known agents widely used in various color photographic processes.

Such color developing agents may include aminophenol derivatives and p-phenylenediamine derivatives.

Aminophenol type developing agents include, for example, o-aminophenol, p-aminophenol, 5-amino-2-oxytoluene, 2-amino-3-oxytoluene, and 2-oxy-3-amino-1,4-dimethylbenzene.

Particularly useful aromatic primary amine color developing agents are N,N-dialkyl-p-phenylenediamine compounds. The alkyl group and phenyl group therein may each have any desired substituent.

Specific examples of the color developing agent preferably used are shown below.

- Exemplary Color Developing Agent -

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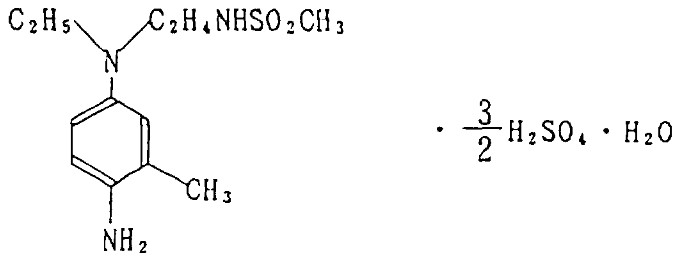

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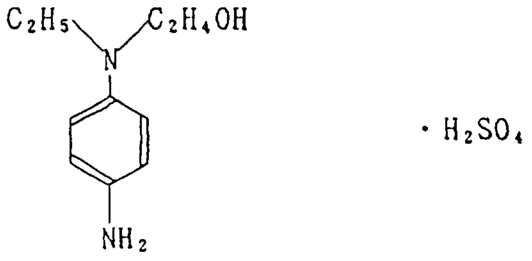

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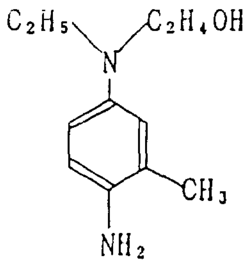
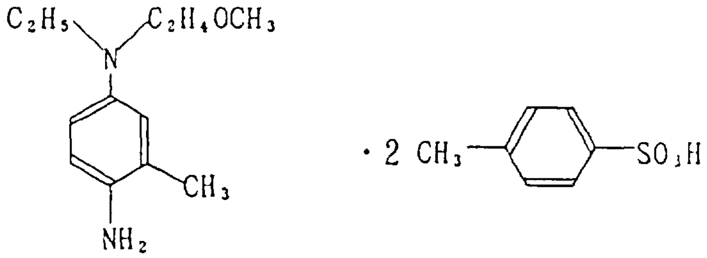


· H_2SO_4

(D-4)



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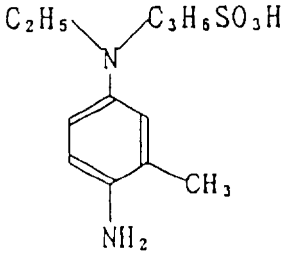

· H_2SO_4

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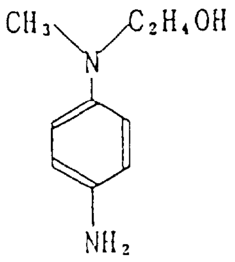

· $\frac{1}{2}H_2SO_4$

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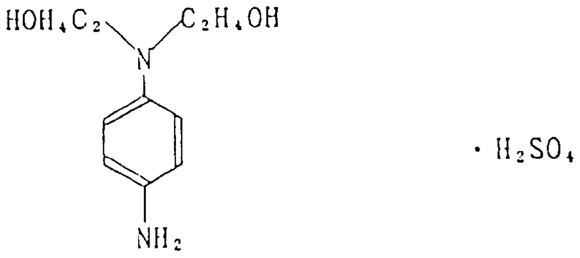
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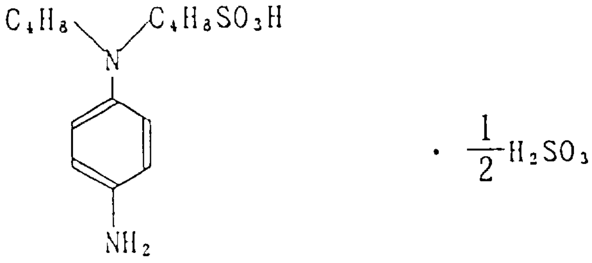
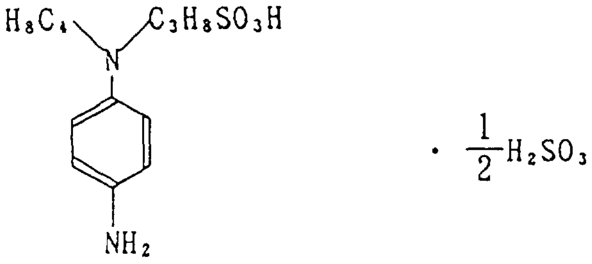
C₂H₄OH
N
NH₂
· H₂SO₄

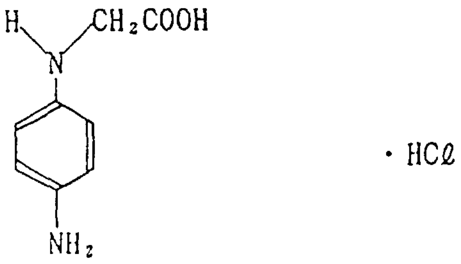
(D - 8)


C₄H₈
C₄H₈SO₃H
N
NH₂
· 1/2 H₂SO₃

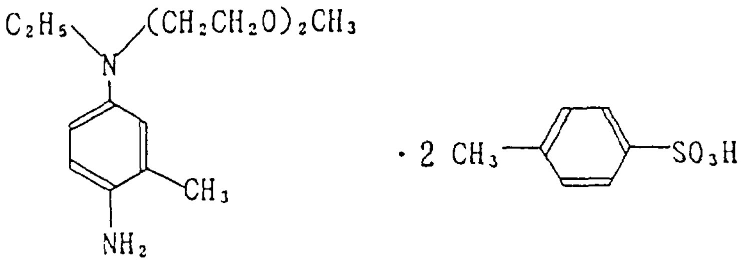
(D - 9)


H₈C₄
C₃H₈SO₃H
N
NH₂
· 1/2 H₂SO₃

(D -10)


H
CH₂COOH
N
NH₂
· HCℓ

(D-11)



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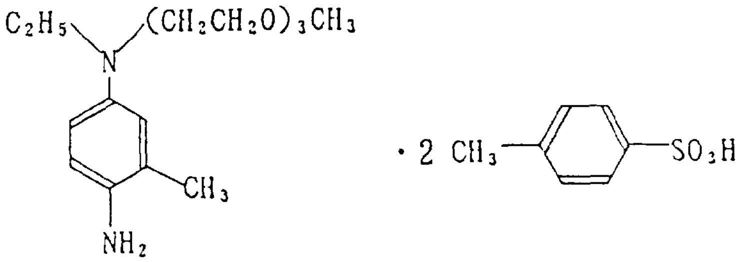

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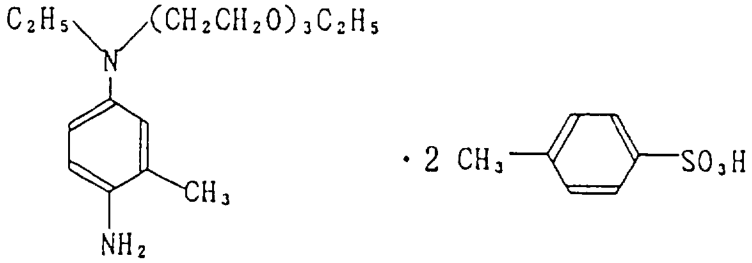

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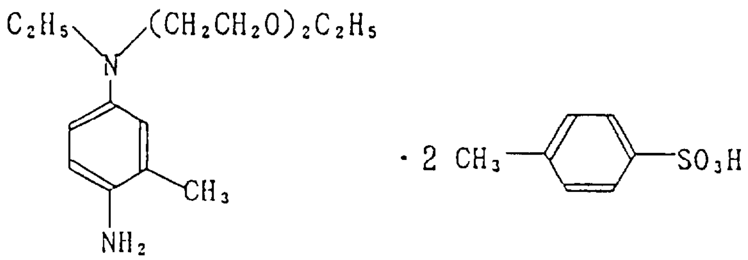

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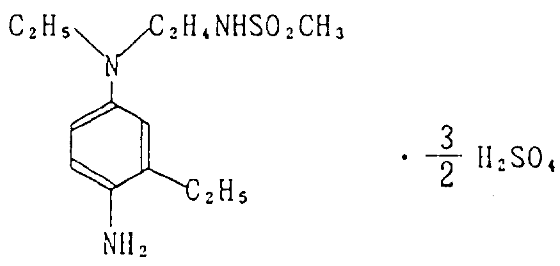

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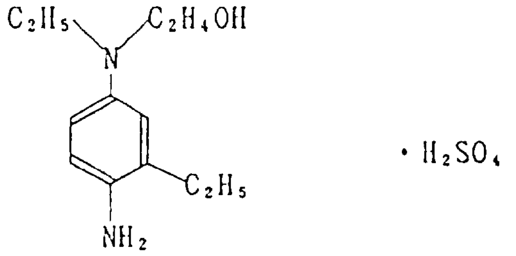


Of the above exemplary color developing agents, what are preferably used in the present invention are the compounds denoted as Exemplary Compounds No. (D-1), (D-2), (D-3), (D-4), (D-6), (D-7) and (D-15). Compound (D-1) is particularly preferred.

The above color developing agent is usually used in the form of a salt such as a hydrochloride, a sulfate or a p-toluenesulfonate.

The color developing agent may preferably be added in an amount of not less than 0.5 x 10^{-2} mol per liter of a color developing solution. It may more preferably be added in an amount ranging from 1.0 x 10^{-2} mol to 1.0 x 10^{-1} mol, and most preferably from 1.5 x 10^{-2} mol to 7.0 x 10^{-2} mol.

The color developing solution used in the step of color developing may contain an alkali agent usually used in developing solutions, as exemplified by sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, potassium carbonate, sodium sulfate, sodium metaborate or borax. It may also contain various additives as exemplified by benzyl alcohol or a halogenated alkali, potassium bromide or potassium chloride, a development regulator as exemplified by citrazinic acid, and a preservative as exemplified by hydroxylamine, a hydroxylamine derivative (e.g., diethylhydroxylamine), a hydrazine derivative (e.g., hydrazinodiacetic acid) or a sulfite.

The color developing solution may still also appropriately contain various kinds of antifoaming agent and surface active agent, and an organic solvent such as methanol, dimethylformamide or dimethylsulfoxide.

The color developing solution may optionally contain as an antioxidant, tetronic acid, tetronimide, 2-anilinoethanol, dihydroxyacetone, aromatic secondary alcohol, hydroxamic acid, pentose or hexose, pyrogallol-1,3-dimethyl ether or the like.

In the color developing solution, various kinds of chelating agent can be used in combination as a metal ion blocking agent. Such a chelating agent may include aminopolycarboxylic acids such as ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid, organic phosphonic acids such as 1-hydroxyethylidene-1,1-diphosphonic acid, aminopolyphosphonic acids such as aminotri(methylenephosphonic acid), oxycarboxylic acids such as citric acid or gluconic acid, phosphonocarboxylic acids such as 2-phosphonobutane-1,2,4-tricarboxylic acid, and polyphosphoric acids such as hexametaphosphoric acid.

In continuous processing, the color developing solution may be replenished preferably in an amount of 20 ml to 300 ml, and more preferably 30 ml to 160 ml, per 1 m^2 of a light-sensitive material.

In the present invention, the color developing is carried out for 40 seconds or less. It may preferably be carried out for 30 seconds or less, and particularly preferably 20 seconds or less in order to achieve the effect of the present invention. The color developing solution may preferably have a temperature of 30°C to 50°C. A higher temperature makes it possible to carry out the rapid processing in a shorter time, and hence is preferred. However, taking account of the stability of the processing solution, it is better for the temperature to be not so high. Thus the nrocessing may preferably be carried out in the temperature range of 33°C to 45°C.

When the color developing solution is so composed as to contain substantially no hydroxylamine and contain a hydroxylamine derivative, it is possible to achieve highly optimized rate of coupling and rate of development of silver halide.

The color developing solution may preferably have a pH value ranging from 9,5 to 13.0, and more preferably ranging from 9.8 to 12.0, from the viewpoint of rapid processing.

In the present invention, various processing methods can be used, including the monobath processing, and also other various methods as exemplified by the spray method in which the processing solution is sprayed, the web method in which a light-sensitive material is brought into contact with a carrier impregnated with a processing solution, and a developing method making use of a viscous processing solution. The processing steps may be substantially comprised of the steps of color developing, bleach-fixing (or bleaching and fixing), and washing or stabilizing.

There are no particular limitations on bleaching agents that can be used in the bleaching solution or bleach-fixing solution used in this invention. They may preferably be metal complex salts of organic acids. The complex salts are compounds formed by coordination of a metal ion such as iron, cobalt or copper with an organic acid such as polycarboxylic acid, aminopolycarboxylic acid, oxalic acid or citric acid. A most preferable organic acid used for the formation of such metal complex salts of organic acids may include aminopolycarboxylic acids. These aminopolycarboxylic acids may be in the form of alkali metal salts, ammonium salts or water soluble amine salts.

Specific examples of these organic acids may include the following:

[1] Ethylenediaminetetraacetic acid

[2] Diethylenetriaminepentaacetic acid

[3] Ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetic acid

[4] 1,3-Propoylenediaminetetraacetic acid

[5] Nitrilotriacetic acid

[6] Cyclohexanediaminetetraacetic acid

[7] Iminodiacetic acid

[8] 1,2-Propylenediaminetetraacetic acid

[9] Ethyl ether diaminetetraacetic acid

[10] Glycol ether diaminetetraacetic acid

[11] Ethylenediaminetetrapropionic acid

[12] Ammonium ethylenediaminetetraacetate

[13] Disodium ethylenediaminetetraacetate

[14] Tetra(trimethyl ammonium) ethylenediaminetetraacetate

[15] Tetrasodium ethylenediaminetetraacetate

[16] Pentasodium diethylenetriaminepentaacetate

[17] Sodium ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate

[18] Sodium propylenediaminetetraacetate

[19] Sodium nitrilotriacetate

[20] Sodium cyclohexanediaminetetraacetate

Any of these bleaching agents may be used in an amount of 5 g/lit. to 450 g/lit., and more preferably 20 g/lit. to 250 g/lit. A solution so composed as to contain, in addition to the bleaching agent described above, a silver halide fixing agent and optionally a sulfite as a preservative is applied to the bleach-fixing solution. It is also possible to use a special bleach-fixing solution so composed as to be in combination of an iron (III) ethylenediaminetetraacetic acid complex bleaching agent and a large quantity of silver halide such as ammonium bromide.

As the above silver halide, besides the ammonium bromide, it is also possible to use hydrochloric acid, hydrobromic acid, lithium bromide, sodium bromide, potassium bromide, sodium iodide, potassium iodide, ammonium iodide, etc.

The above silver halide fixing agent contained in the fixing solution and bleach-fixing solution is a compound capable of forming a water-soluble complex salt as a result of reaction with a silver halide, as used in usual fixing, which is typically exemplified by thiosulfates such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate, thiocyanates such as potassium thiocyanate, sodium thiocyanate and ammonium thiocyanate, thioureas, and thioethers. Any of these fixing agents may be used in an amount not less than 5 g/lit. and within the range it can be dissolved. In usual instances, the fixing agent is used in an amount of 70 g/lit. to 250 g/lit.

In the fixing solution and bleach-fixing solution, it is also possible to incorporate, alone or in combination, various pH adjusters such as boric acid, borax, sodium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide. It is still also possible to incorporate various kinds of fluorescent brightening agents, antifoaming agents or surface active agents. It is also possible to appropriately incorporate a preservative such as hydroxylamine, hydrazine or an addition product of a bisulfite addition compound of an aldehyde compound, an organic chelating agent such as aminocarboxylic acid, a stabilizer such as nitroalcohol or a sulfate, and an organic solvent such as methanol, dimethylsulfonamide or dimethylsulfoxide.

To the fixing solution and bleach-fixing solution used in the present invention, various bleach-accelerators can be added, including those disclosed in Japanese Patent O.P.I. Publication No. 280/1971, Japanese Patent Examined Publications No. 8506/1970 and No. 556/1971, Belgian Patent No. 770,910, Japanese Patent Examined Publications No. 8836/1970 and No. 9854/1978, Japanese Patent O.P.I. Publications No. 71634/1979 and No. 42394/1974, etc.

The fixing solution and bleach-fixing solution are used at a pH of not less than 4.0. They may usually be used at a pH of not less than 4.0 and not more than 9.5, and should preferably be used at a pH of not less than 4.5 and not more than 8.5. Stated more strictly, the processing is carried out most preferably at a pH of not less than 5.0 and not more than 8.0. The processing may be carried out at a processing temperature of not lower than 80°C, and preferably not lower than 55°C, under control of evaporation or the like. The processing time for bleach fixing may preferably be 2 seconds to 50 seconds, more preferably 3 seconds to 40 seconds, and most preferably 5 seconds to 30 seconds.

The bleaching solution can be used at a pH of 0.2 to 8.0, preferably not less than 2.0 and not more than 7.0, and more preferably, not less than 4.0 and not more than 6.5. It may be used at a processing temperature of 20°C to 45°C, and preferably 25°C to 42°C.

The bleaching solution is used usually with addition of a halide such as ammonium bromide.

In the bleaching solution, it is also possible to incorporate, alone or in combination, various pH adjusters comprised of various salts such as boric acid, borax, sodium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide. It is still also possible to incorporate various kinds of fluorescent brightening agents, antifoaming agents, surface active agents or mildewproofing agents.

As a compound preferably used in the stabilizing solution may include chelating agents having a chelate stability constant with respect to iron ions, of not less than 8. These are preferably used for the purpose of achieving the object of the present invention.

Here, the chelate stability constant refers to the constant commonly known from L.G. Sillen and A.E. Martell, "Stability Constants of Metal-ion Complexes", The Chemical Society, London (1964), and S. Chaberek and A.E. Martell, "Organic Seqestering Agents", Wiley (1959).

The chelating agent preferablv used in the stabilizing solution, having a chelate stability constant with respect to iron ions, of not less than 8 may include organic carboxylic acid chelating agents, organic phosphoric acid chelating agents, inorganic phosphoric acid chelating agents and polyhydroxyl compounds. The above iron ions are meant by ferric irons (Fe^{3+}).

Specific chelating agents having a chelate stability constant with respect to iron ions, of not less than 8 can be exemplified by the following compounds, without limitation thereto. That is, they are ethylenediaminediorthohydroxyphenylacetic acid, diaminopropanetetraacetic acid, nitrilotriacetic acid, hydroxyethylethylenediaminetetraacetic acid, dihydroxyethylglycine, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, iminodiacetic acid, diethylenetriaminepentaacetic acid, hydroxyiminodiacetic acid, diaminopropanoltetraacetic acid, transcyclohexanediaminetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediaminetetrakismethylenephosphonic acid, nitrilotrimethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, 1,1-diphosphonoethane-2-carboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxy-1-phosphonopropane-1,2,3-tricarboxylic acid, catechol-3,5-diphosphonic acid, sodium pyrophosphate, sodium tetrapolyphosphate, and sodium hexametaphosphate. Particularly preferred are diethylenetriaminepentaacetic acid, nitrilotriacetic acid, nitrilotrimethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, etc. In particular, 1-hydroxyethylidene-1,1-diphosphonic acid is most preferably used.

The above chelating agent may be used preferably in an amount of 0.01 g to 50 g, and more preferably 0.05 g to 20 g, per liter of the stabilizing solution, within the range of which good results can be obtained.

A particularly preferred compound that can be added to the stabilizing solution may include ammonium compounds.

These are fed by ammonium salts of various inorganic compounds, specifically including ammonium hydroxide, ammonium bromide, ammonium carbonate, ammonium chloride and ammonium acetate.

In the present invention, a stabilizing solution treated with an ion-exchanged resin may also be used.

The pH of the stabilizing solution applicable to the present invention may be in the range of 5.5 to 10.0. The pH adjusters that can be contained in the stabilizing solution applicable to the present invention may include commonly known alkali agents or acid agents, any of which can be used.

In the stabilizing, the processing temperature may preferably range from 15°C to 60°C, and more preferably from 20°C to 45°C. The processing time may preferably be as short as possible from the viewpoint of effectively achieving the objects of the present invention. It may preferably be 3 seconds to 50 seconds, and most preferably 5 seconds to 40 seconds. When the stabilizing is carried out using a plurality of tanks, it is preferred to carry out the processing in a shorter time in pre-baths and in a longer time in post-baths. In particular, the stabilizing should be successively carried out in the processing time that is 20 % to 50 % longer than that in each pre-bath.

A stabilizing replenishing solution in the stabilizing step that can be applied to the present invention may be supplied, in the case of a multiple tank counter current system, by supplying the solution to a post-bath and allowing it to overflow to the pre-bath. It is of course possible to carry out the stabilizing in a monobath system. The compounds described above can be added by various methods such that the compounds are added to the stabilizing tank in the form of a concentrated solution, or that the compounds described above and other additives are added to the stabilizing solution supplied to the stabilizing tank and the resulting solution is used as a solution to be supplied to the stabilizing replenishing solution. Any of the methods may be used for their addition.

The amount of the stabilizing solution in the stabilizing step of the present invention may preferably be 0.1 time to 50 times, and preferably 0.5 time to 30 times, the amount of carry-in from a pre-bath (the bleach-fixing solution), per unit area of the light-sensitive material. In the present invention, however, it is preferred to employ the batch throw-away system.

The stabilizing that can be applied to the present invention may preferably be carried out using 1 stabilizing tank to 5 stabilizing tanks, particularly preferably 1 tank to 3 tanks, and most preferably 1 tank.

The total processing steps in the present invention, comprised of the steps of color developing, bleach-fixing (or bleaching and fixing) and stabilizing, are carried out in a processing time of 90 seconds or less, preferably ranging from 6 seconds to 75 seconds, more preferably ranging from 9 seconds to 60 seconds, and most preferably ranging from 15 seconds to 50 seconds.

EXAMPLES

The present invention will be described below in greater detail by giving Examples.

Example 1

On a paper support one side of which was laminated with polyethylene and the other side of which was laminated with polyethylene containing titanium oxide, each layer with the constitution shown below was provided by coating on the side on which the polyethylene layer containing titanium oxide was formed, to produce a multilayer light-sensitive silver halide color photographic material.

Coating solutions were prepared in the following way:

First layer coating solution:

To 26.7 g of a yellow coupler (Y-1), 10.0 g of a dye image stabilizer (ST-1), 6.67 g of a dye image stabilizer (ST-2), 0.67 g of an antistain agent (HQ-2) and 6.67 g of a high-boiling organic solvent (DNP), 60 ml of ethyl acetate was added to effect dissolution. The resulting solution was emulsifyingly dispersed using a homogenizer, in 220 ml of an aqueous 10 % gelatin solution containing 7 ml of a 20 % surface active agent (SU-1). Thus a yellow coupler dispersion was prepared. This dispersion was mixed with a blue-sensitive silver halide emulsion prepared under the conditions described later to give a first layer coating solution.

Second layer to seventh layer coating solutions were also prepared in the same procedure as the first layer coating solution.

As hardening agents, (H-1) was added to the second and fourth layers, and (H-2) to the seventh layer. As coating aids, surface active agents (SU-2) and (SU-3) were added to adjust the surface tension.

Layer	Constitution	Amount
Seventh layer: (Protective layer)		(g/m^2)
	Gelatin	1.00
	Anti-stain agent (HQ-2)	0.002
	Anti-stain agent (HQ-3)	0.002
	Anti-stain agent (HQ-4)	0.004
	Anti-stain agent (HQ-5)	0.02

DIDP	0.005
compound (F-1)	0.002
Sixth layer: (Ultraviolet absorbing layer)	
Gelatin	0.40
Ultraviolet absorbent (UV-1)	0.10
Ultraviolet absorbent (UV-2)	0.04
Ultraviolet absorbent (UV-3)	0.16
Anti-stain agent (HQ-5)	0.04
DNP	0.20
PVP	0.03
Anti-irradiation dye (AI-2)	0.02
Anti-irradiation dye (AI-4)	0.01
Fifth layer (Red-sensitive layer)	
Gelatin	1.30
Red-sensitive emulsion	0.21
Cyan coupler (C-1)	0.17
Cyan coupler (C-2)	0.25
Dye image stabilizer (ST-1)	0.2
Anti-stain agent (HQ-1)	0.01
HBS-1	0.20
DOP	0.20
Fourth layer: (Ultraviolet absorbing layer)	
Gelatin	0.94
Ultraviolet absorbent (UV-1)	0.28
Ultraviolet absorbent (UV-2)	0.09

Ultraviolet absorbent (UV-3)	0.38
Anti-stain agent (HQ-5)	0.10
DNP	0.40

Third layer (Green-sensitive layer)

Gelatin	1.40
Green-sensitive emulsion	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
Anti-irradiation dye (AI-1)	0.01

Second layer: (Intermediate layer)

Gelatin	1.20
Anti-stain agent (HQ-2)	0.03
Anti-stain agent (HQ-3)	0.03
Anti-stain agent (HQ-4)	0.05
Anti-stain agent (HQ-5)	0.23
DIDP	0.06
Compound (F-1)	0.002

First layer: (Blue-sensitive layer)

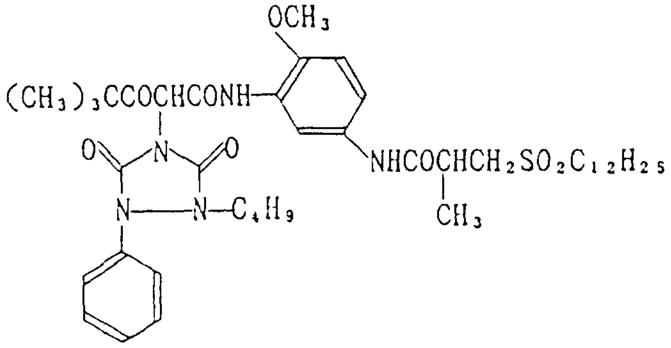
Gelatin	1.20
Blue-sensitive emulsion	0.26
Yellow coupler (Y-1)	0.80
Dye image stabilizer (ST-1)	0.30

Dye image stabilizer (ST-2)	0.20
Anti-stain agent (HQ-1)	0.02
Anti-irradiation dye (AI-3)	0.01
DNP	0.20

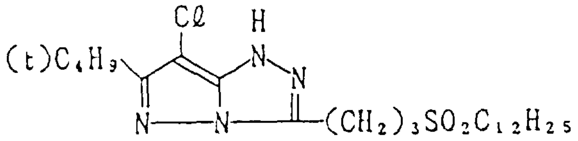
Support: Polyethylene-laminated paper

The amounts of silver halide emulsions added are each indicated in terms of silver weight.

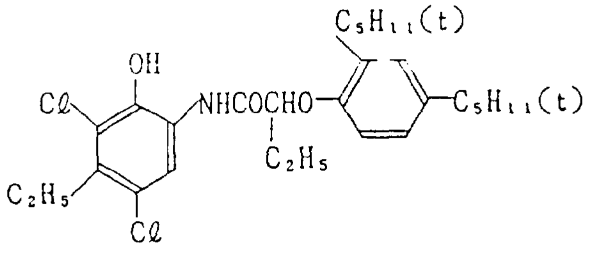
Y - 1



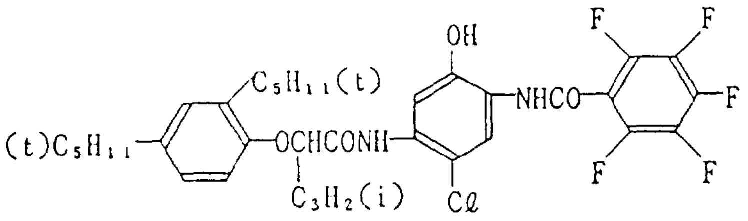
M - 1



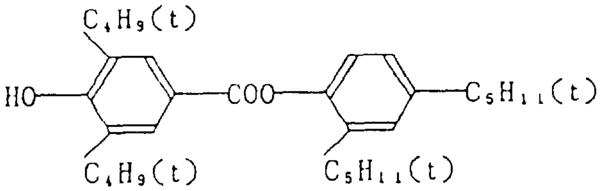
C - 1



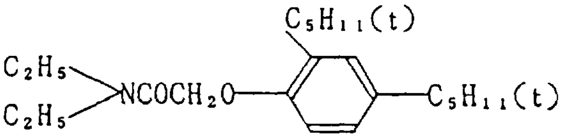
C - 2



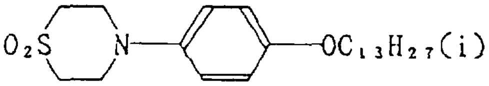
ST－1



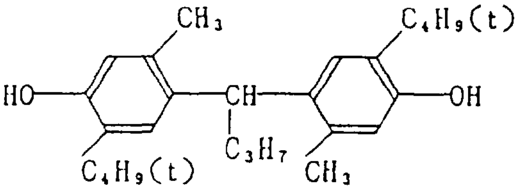
ST－2



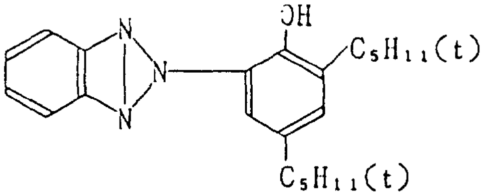
ST－3



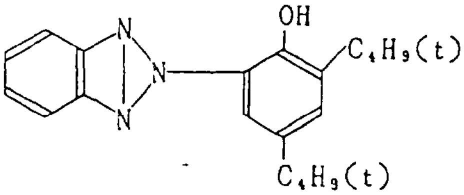
ST－4



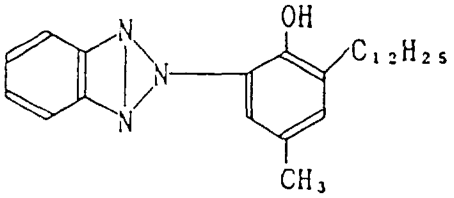
UV－1



UV－2

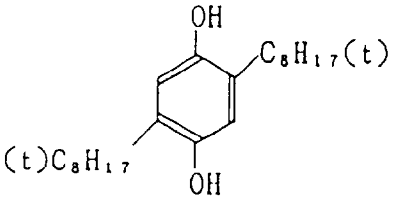


UV-3

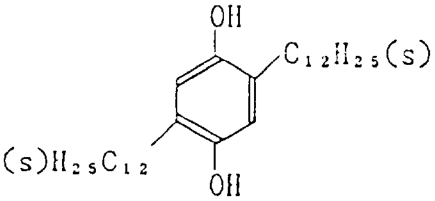


DBP	Dibutyl phthalate
DOP	Dioctyl phthalate
DNP	Dinonyl phthalate
DIDP	Diisodecyl phthalate
PVP	Polyvinyl pyrrolidone

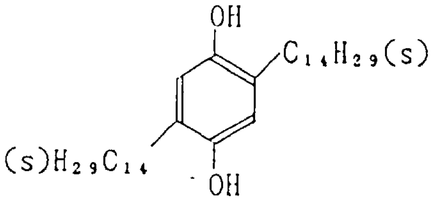
HQ-1



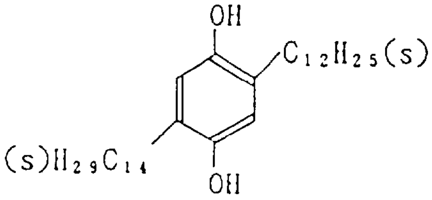
HQ-2



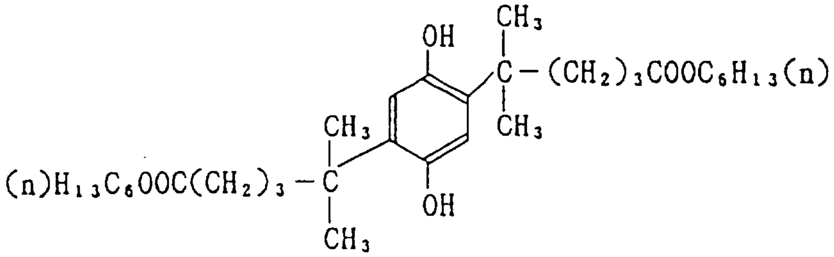
HQ-3



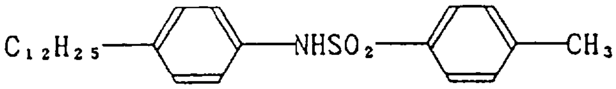
HQ-4



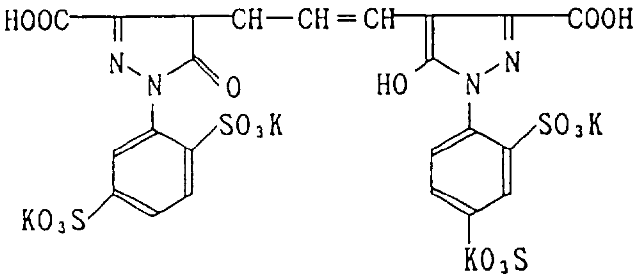
HQ-5



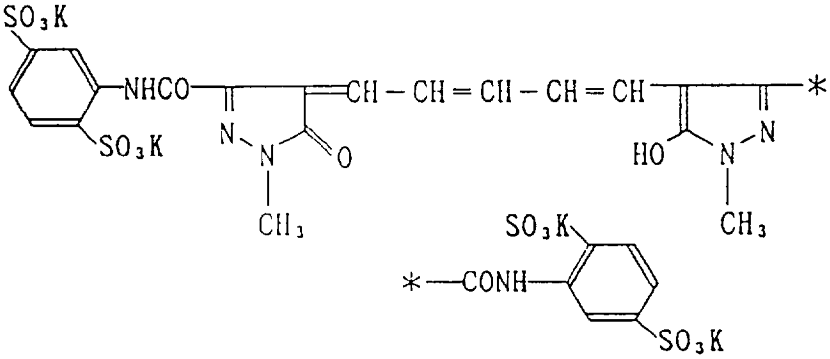
HBS-1



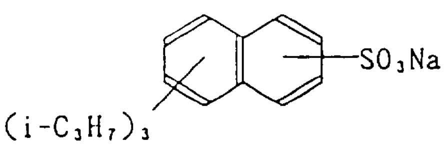
AI-1



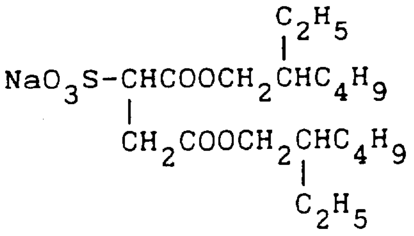
AI-2



SU-1

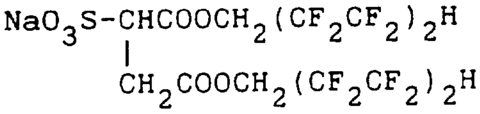


SU-2



$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad C_2H_5 \\ \qquad\qquad\qquad\qquad\quad | \\ NaO_3S-\underset{|}{C}HCOOCH_2CHC_4H_9 \\ \qquad\quad CH_2COOCH_2\underset{|}{C}HC_4H_9 \\ \qquad\qquad\qquad\qquad\quad C_2H_5 \end{array}$$

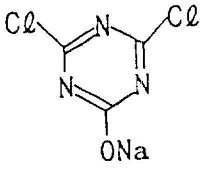
SU-3



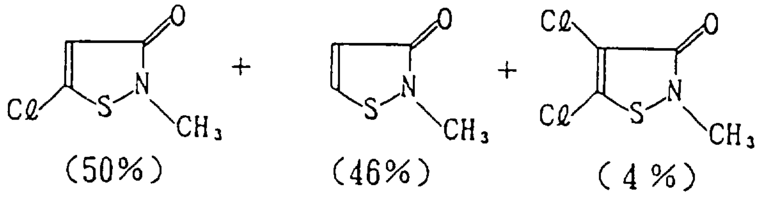
$$\begin{array}{l} NaO_3S-\underset{|}{C}HCOOCH_2(CF_2CF_2)_2H \\ \qquad\quad CH_2COOCH_2(CF_2CF_2)_2H \end{array}$$

H-1 $C(CH_2SO_3H{=}CH_2)_4$

H-2



F-1



Molar ratio

Preparation of blue-sensitive silver halide emulsion:

In 1,000 ml of an aqueous 2 % gelatin solution kept at a temperature of 40°C, the following solution A and solution B were simultaneously added in 30 minutes while controlling the pAg and pH to be 7.3 and 3.0, respectively, and the following solution C and solution D were further simultaneously added in 180 minutes while controlling the pAg and pH to be 7.3 and 5.5, respectively. At this time, the pAg was controlled by the method disclosed in Japanese Patent O.P.I. Publication No. 45437/1984 and the pH was controlled using an aqueous solution of sulfuric acid or sodium hydroxide.

Solution A:

Sodium chloride	3.42 g
Potassium bromide	0.03 g
By adding water, made up to	200 ml

Solution B:

Silver nitrate	10 g
By adding water, made up to	200 ml

Solution C:

Sodium chloride	102.7 g
Potassium bromide	1.0 g
By adding water, made up to	600 ml

Solution D:

Silver nitrate	300 g
By adding water, made up to	600 ml

After completion of the addition, the emulsion was desalted using an aqueous 5 % solution of Demol-N, produced by Kao Atlas Co. and an aqueous 20 % solution of magnesium sulfate, and then mixed with an aqueous gelatin solution to give a monodisperse cubic emulsion EMP-1 having an average grain size of 0.85 μm, a variation coefficient ($\sigma/\bar{r}$) of 0.07 and a silver chloride content of 99.5 mol %.

The above emulsion EMP-1 was subjected to chemical sensitization at 50°C to an optimum, using the following compounds to give a blue-sensitive silver halide emulsion for comparison (EnB-1).

Sodium thiosulfate	0.8 mg/mol·AgX
Chloroauric acid	0.5 mg/mol·AgX
Stabilizer STAB-1	8×10^{-4} mg/mol·AgX
Stabilizer STAB-2	4×10^{-4} mg/mol·AgX
Stabilizer STAB-3	4×10^{-4} mg/mol·AgX
Spectral sensitizer BS-1	4×10^{-4} mg/mol·AgX
Spectral sensitizer BS-1	1×10^{-4} mg/mol·AgX

Preparation of green-sensitive silver halide emulsion:

The procedure for the preparation of EMP-1 was repeated except that the addition time of the solutions A and B and the addition time of the solutions C and D were changed, to give a monodisperse cubic emulsion EMP-2 having an average grain size of 0.43 μm, a variation coefficient (σ/r) of 0.08 and a silver chloride content of 99.5 mol %.

The emulsion EMP-2 was subjected to chemical sensitization at 55°C to an optimum, using the following compounds to give a green-sensitive silver halide emulsion (EmG-1).

Sodium thiosulfate	1.5 mg/mol·AgX

Continuation of the Table on the next page

(continued)

Chloroauric acid	1.0 mg/mol·AgX
Stabilizer STAB-1	6 x 10^{-4} mg/mol·AgX
Stabilizer STAB-2	3 x 10^{-4} mg/mol·AgX
Spectral sensitizer GS-1	4 x 10^{-4} mg/mol·AgX

Preparation of red-sensitive silver halide emulsion:

The procedure for the preparation of EMP-1 was repeated except that the addition time of the solutions A and B and the addition time of the solutions C and D were changed, to give a monodisperse cubic emulsion EMP-3 having an average grain size of 0.50 µm, a variation coefficient (σ/r) of 0.08 and a silver chloride content of 99.5 mol %.

The emulsion EMP-3 was subjected to chemical sensitization at 60°C to an optimum, using the following compounds to give a red-sensitive silver halide emulsion (EmR-1).

Sodium thiosulfate	1.8 mg/mol·AgX
Chloroauric acid	2.0 mg/mol·AgX
Stabilizer STAB-1	6 x 10^{-4} mg/mol·AgX
Stabilizer STAB-2	3 x 10^{-4} mg/mol·AgX
Spectral sensitizer RS-1	1 x 10^{-4} mg/mol·AgX

The comparative sample thus obtained was designated as Sample 101.

Next, the procedure used for the preparation of the blue-sensitive emulsion EMP-1 was repeated except that the metal compound as shown in Table 1 was added to Solution C, to give EMP-4 to EMP-16.

The emulsions EMP-4 to EMP-16 were subjected to chemical sensitization under the same conditions as those for EmB-1, to give EmB-2 to EmB-14, respectively.

Next, the procedure used for the preparation of Sample 101 was repeated except that EmB-2 to EmB-14 were used, to give Samples 102 to 114.

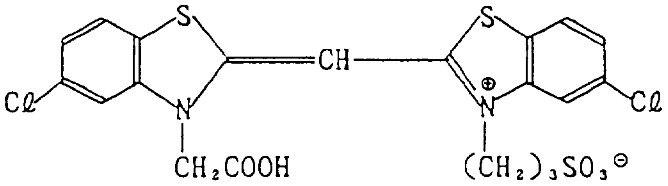
Samples 101 to 114 thus obtained were evaluated on their rapid processing suitability and exposure illuminance dependence according to the methods described later.

Tests results obtained are shown in Table 2. Here, the evaluation was made only on blue density.

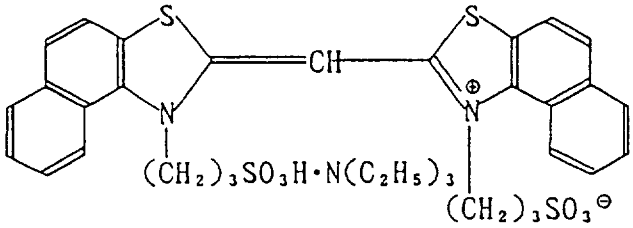
Table 1

Blue-sensitive emulsion	Emulsion No.	Iridium compound (mol/mol·AgX)		Other metal compound (mol/mol·AgX)	
EmB-1	EMP-1	-			-
EmB-2	EMP-4	K_2IrCl_6	$2x10^{-8}$	-	
EmB-3	EMP-5	-		$K_4Fe(CN)_6$	$1x10^{-5}$
EmB-4	EMP-6	K_2IrCl_6	$2x10^{-8}$	$K_4Fe(CN)_6$	$1x10^{-5}$
EmB-5	EMP-7	K_2IrCl_6	$2x10^{-8}$	$PbCl_2$	$1x10^{-5}$
EmB-6	EMP-8	K_2IrCl_6	$2x10^{-8}$	$CdCl_2$	$1x10^{-5}$
EmB-7	EMP-9	K_2IrCl_6	$2x10^{-8}$	$RhCl_3$	$1x10^{-5}$
EmB-8	EMP-10	K_2IrCl_6	$2x10^{-8}$	$K_3Rh(CN)_6$	$1x10^{-5}$
EmB-9	EMP-11	K_2IrCl_6	$2x10^{-8}$	$K_4Re(CN)_6$	$1x10^{-5}$
EmB-10	EMP-12	K_2IrCl_6	$2x10^{-8}$	$K_4Re(SCN)_6$	$1x10^{-5}$
EmB-11	EMP-13	K_2IrCl_6	$2x10^{-8}$	$K_3Rh(CN)_6$	$1x10^{-5}$
EmB-12	EMP-14	K_2IrCl_6	$2x10^{-8}$	$K_2Os(CN)_6$	$1x10^{-5}$
EmB-13	EMP-15	K_3IrCl_6	$2x10^{-8}$	$K_2Os(CN)_6$	$1x10^{-5}$
EmB-14	EMP-16	K_3IrCl_6	$2x10^{-8}$	$K_3Fe(CN)_6$	$1x10^{-5}$

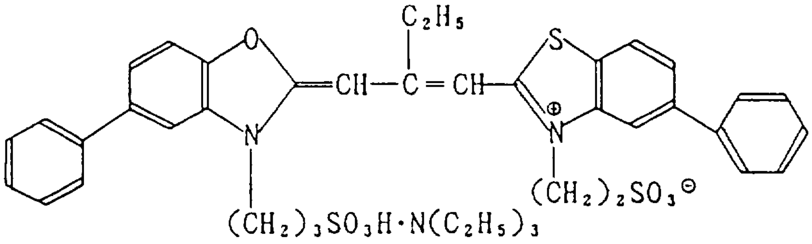
B S - 1



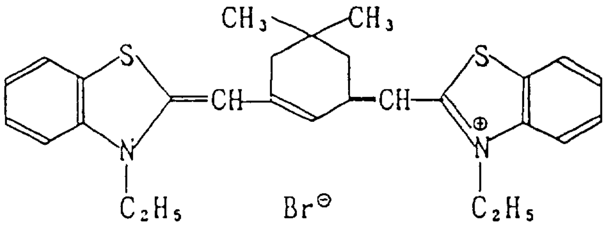
B S - 2



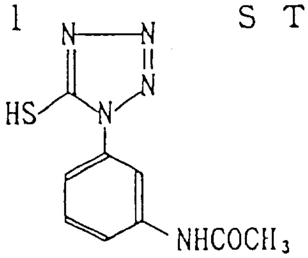
G S - 1



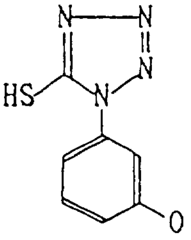
R S - 1



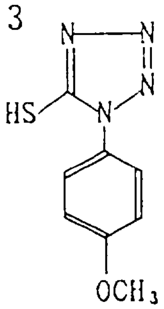
STAB-1



STAB-2



STAB-3



Evaluation of rapid processing suitability:

The samples prepared by the method described above were exposed to light by a conventional method, and then processed according to the following processing steps and using the following processing solutions.

Processing step	Temperature	Processing time
(1) Color developing	35°C to 55°C	As shown in Table 2
(2) Bleach-fixing	35°C	20 seconds
(3) Stabilizing	35°C	1st tank: 20 seconds 2nd tank: 20 seconds
(4) Drying	60 to 80°C	30 seconds

Color developing tank solution

Benzyl alcohol	5 g
Diethylene glycol	10 g
Potassium bromide	0.01 g
Potassium chloride	2.3 g
Potassium sulfite (aqueous 50 % solution)	0.5 ml
Color developing agent (3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate)	5.5 g
Diethylhydroxylamine (85 %)	5.0 g
Triethanolamine	10.0 g
Potassium carbonate	30 g
Sodium ethylenediaminetetraacetate	2.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid (aqueous 60 % solution)	3.0 g
$BiCl_3$ (aqueous 45 % solution)	0.65 g
$MgSO_4{\cdot}7H_2O$	0.2 g

Continuation of the Table on the next page

(continued)

PVD (polyvinyl pyrrolidone)	1.0 g
Ammonia water (aqueous 25 % ammonium hydroxide solution)	2.5 g
Trisodium nitrilotriacetate	1.5 g

Made up to 1 liter using water, and adjusted to pH 7.5 with ammonia water and sulfuric acid.

In each processing step, the processing was carried out for the time as shown in Table 2. The developing in which the color developing time was 8 seconds, 15 seconds, 25 seconds, 35 to 45 seconds, was carried out at a processing temperature of 55°C, 45°C, 38°C, 35°C, respectively.

Evaluation of processing stability:

Evaluated on the basis of a density variation AD (standard density: 1.0) in developing time variations of ±10 % of the color developing time shown in Table 2. Here, the temperature of the developing solution was made constant.

The smaller the ΔD is, the better the processing stability is and hence the better the rapid processing suitability is.

Evaluation of fog resistance:

Evaluated on the basis of the density (Dmin) at the non-image portion when the color developing was carried out for the time as shown in Table 2.

The smaller the value of Dmin is, the better the fog resistance is and hence the better the rapid processing suitability is.

Evaluation of exposure illuminance dependence:

The samples were subjected to wedge exposure by a conventional method (where the exposure time was set to 0.1 second and 30 seconds), and thereafter processed according to the same processing steps as used in the evaluation of rapid processing suitability.

Next, on the samples thus obtained, reflection density was measured using a densitometer PDA-65 (trade name), manufactured by Konica Corporation, to determine the sensitivity (S) defined as follows:

Sensitivity (S) = Reciprocal of the amount of exposure necessary for giving reflection density 0.8

The illuminance dependence was evaluated on the basis of the sensitivity variation (ΔS) defined as follows:

$$\text{Sensitivity variation } (\Delta S) = \frac{\text{Sensitivity in exposure time of 30 seconds}}{\text{Sensitivity in exposure time of 0.1 second}} \times 100$$

The closer to 100 the value of ΔS is, the smaller the sensitivity variations are with respect to changes in exposure illuminance and hence the better the illuminance dependence is.

Results obtained are shown in Table 2.

Table 2

Experiment No.	Sample No.	Blue-sensitive emulsion			Color developing time (sec)	Rapid processing suitability		Exposure illuminance dependence (ΔS)
		Emulsion No.	Iridium compound	Other metal compound		Processing stability (ΔD)	Fog resistance (Dmin)	
Ex-101(X)	101	EmB-1	-	-	45	0.07	0.025	43
Ex-102(")	102	EmB-2	K_2IrCl_6	-	45	0.07	0.027	62
Ex-103(")	103	EmB-3	-	$K_4Fe(CN)_6$	45	0.08	0.030	44
Ex-104(")	104	EmB-4	K_2IrCl_6	$K_4Fe(CN)_6$	45	0.07	0.033	79
Ex-105(")	101	EmB-1	-	-	15	0.10	0.023	44
Ex-106(")	102	EmB-2	K_2IrCl_6	-	15	0.11	0.024	61
Ex-107(")	103	EmB-3	-	$K_4Fe(CN)_6$	15	0.12	0.027	43
Ex-108(Y)	104	EmB-4	K_2IrCl_6	"	15	0.04	0.019	85
Ex-109(")	"	"	"	"	35	0.06	0.021	81
Ex-110(")	"	"	"	"	25	0.05	0.020	83
Ex-111(")	"	"	"	"	8	0.04	0.019	85

X: Comparative Example, Y: Present Invention

Table 2 (cont'd)

Experiment No.	Sample No.	Blue-sensitive emulsion			Color developing time (sec)	Rapid processing suitability		Exposure illuminance dependence (ΔS)
		Emulsion No.	Iridium compound	Other metal compound		Processing stability (ΔD)	Fog resistance (Dmin)	
Ex-112(X)	105	EmB-5	"	$PbCl_2$	15	0.12	0.022	60
Ex-113(")	106	EmB-6	"	$CdCl_2$	"	0.14	0.022	62
Ex-114(Y)	107	EmB-7	"	$RhCl_3$	"	0.06	0.019	80
Ex-115(")	108	EmB-8	"	$K_3Rh(CN)_6$	"	0.06	0.018	81
Ex-116(")	109	EmB-9	"	$K_4Re(CN)_6$	"	0.04	0.019	85
Ex-117(")	110	EmB-10	"	$K_4Re(SCN)_6$	"	0.05	0.019	86
Ex-118(")	111	EmB-11	"	$K_3RU(CN)_6$	"	0.04	0.018	84
Ex-119(")	112	EmB-12	"	$K_2Os(CN)_6$	"	0.03	0.019	85
Ex-120(")	113	EmB-13	K_3IrCl_6	"	"	0.05	0.019	85
Ex-121(")	114	EmB-14	"	$K_3Fe(CN)_6$	"	0.04	0.018	84

X: Comparative Example, Y: Present Invention

Table 2 shows the following:

Even if the emulsion constitution is in accordance with the present invention, the processing stability is insufficient and also the fog resistance is poor although the exposure illuminance dependence is good, when the color developing time is outside the present invention.

Even if the color developing time is in accordance with the present invention, the processing stability and the exposure illuminance dependence are poor when the emulsion constitution is outside the present invention.

The processing stability, the fog resistance and the exposure illuminance dependence have been improved at the same time only in the constitution of the present invention. The present invention is more effective when the color developing time is 15 seconds or 8 seconds than when it is 35 seconds.

The metal compound used in combination with the iridium compound contributes the achievement of the effect of the present invention when it falls under the scope of the present invention, even if the metal or ligand is changed. However, the samples (105 and 106) making use of the metal compound outside the present invention have not achieved the effect of the present invention.

Example 2

EmG-2 to EmG-4 were prepared in the same manner as EmG-1 in Example 1 except that the metal compounds as shown in Table 3 were respectively added.

Samples 201 to 203 were prepared in the same manner as Sample 101 in Example 1 except that, as green-sensitive emulsions, EmG-2 to EmG-4 were used, respectively.

On Samples 201 to 203 thus obtained and Sample 101 prepared in Example 1, the same evaluation as in Example 1 was made. Results obtained are shown in Table 4. Here, the evaluation was made only in respect of green density.

Table 4 shows that the effect of the present invention can be obtained in the same way as in Example 1 also when the present invention is applied to green-sensitive emulsions.

Table 3

Green-sensitive emulsion	Iridium compound (mol/mol·AgX)		Other metal compound (mol/mol·AgX)	
EmG-1	-		-	
EmG-2	K_3IrCl_6	$5x10^{-8}$	-	
EmG-3	-		$K_4Re(SCN)_6$	$2x10^{-5}$
EmG-4	K_3IrCl_6	$5x10^{-8}$	$K_4Re(SCN)_6$	$2x10^{-5}$

Table 4

Experiment No.	Sample No.	Green-sensitive emulsion			Color developing time (sec)	Rapid processing suitability		Exposure illuminance dependence (ΔS)
		Emulsion No.	Iridium compound	Other metal compound		Processing stability (ΔD)	Fog resistance (Dmin)	
Ex-201(X)	101	EmG-1	-	-	45	0.06	0.023	45
Ex-202(")	201	EmG-2	K_3IrCl_6	-	"	0.06	0.025	65
Ex-203(")	202	EmG-3	-	$K_4Re(SCN)_6$	"	0.06	0.029	43
Ex-204(")	203	EmG-4	K_3IrCl_6	"	"	0.05	0.031	81
Ex-205(")	101	EmG-1	-	-	15	0.10	0.022	44
Ex-206(")	201	EmG-2	K_3IrCl_6	-	"	0.10	0.023	62
Ex-207(")	202	EmG-3	-	$K_4Re(SCN)_6$	"	0.11	0.027	44
Ex-208(Y)	203	EmG-4	K_3IrCl_6	"	"	0.03	0.018	86
Ex-209(")	"	"	"	"	35	0.04	0.021	82
Ex-210(")	"	"	"	"	25	0.03	0.020	84
Ex-211(")	"	"	"	"	8	0.03	0.018	87

X: Comparative Example, Y: Present Invention

Example 3

EmR-2 to EmR-4 were prepared in the same manner as EmR-1 in Example 1 except that the metal compounds as shown in Table 5 were added to Solution C.

Samples 301 to 303 were prepared in the same manner as Sample 101 in Example 1 except that, as red-sensitive emulsions, EmR-2 to EmR-4 were used, respectively.

On Samples 301 to 303 thus obtained and Sample 101 prepared in Example 1, the same evaluation as in Example 1 was made. Results obtained are shown in Table 6. Here, the evaluation was made only in resect of red density.

Table 6 shows that the effect of the present invention can be obtained in the same way as in Example 1 also when the present invention is applied to red-sensitive emulsions.

Table 5

Red-sensitive emulsion	Iridium compound (mol/mol·AgX)		Other metal compound (mol/mol·AgX)	
EmR-1	-		-	
EmR-2	K_2IrCl_6	$4x10^{-8}$	-	
EmR-3	-		$K_2Fe(CN)_6$	$3x10^{-5}$
EmR-4	K_2IrCl_6	$4x10^{-8}$	$K_2Fe(CN)_6$	$3x10^{-5}$

Table 6

Experiment No.	Sample No.	Red-sensitive emulsion			Color developing time (sec)	Rapid processing suitability		Exposure illuminance dependence (ΔS)
		Emulsion No.	Iridium compound	Other metal compound		Processing stability (ΔD)	Fog resistance (Dmin)	
Ex-301	101	EmR-1	-	-	45	0.08	0.028	41
Ex-302	301	EmR-2	K_2IrCl_6	-	45	0.07	0.029	60
Ex-303	302	EmR-3	-	$K_2Fe(CN)_6$	45	0.08	0.030	42
Ex-304	303	EmR-4	K_2IrCl_6	"	45	0.08	0.034	77
Ex-305	101	EmR-1	-	-	15	0.10	0.026	40
Ex-306	301	EmR-2	K_2IrCl_6	-	15	0.10	0.024	58
Ex-307	302	EmR-3	-	$K_2Fe(CN)_6$	15	0.09	0.027	40
Ex-308	303	EmR-4	K_2IrCl_6	"	15	0.04	0.019	85
Ex-309	"	"	"	"	35	0.06	0.021	81
Ex-310	"	"	"	"	25	0.05	0.020	83
Ex-311	"	"	"	"	8	0.04	0.019	86

Example 4

EmB-15 and EmB-16 were prepared in the same manner as EmB-1 in Example 1 except that the metal compounds as shown in Table 7 were added to Solution C.

EmG-5 and EmG-6 were prepared in the same manner as EmG-1 in Example 1 except that the metal compounds as shown in Table 7 were added to Solution C.

EmR-5 to EmR-10 were prepared in the same manner as EmR-1 in Example 1 except that the metal compounds as shown in Table 7 were added to Solution C.

With regard to EmR-8 to EmR-10, the compounds of Group A preferably used in the present invention were added as shown in Table 7, at the time the chemical sensitization was started.

Samples 401 to 406 were respectively prepared in the same manner as Sample 101 in Example 1 except that the blue-sensitive emulsions, green-sensitive emulsions and red-sensitive emulsions were used in combination as shown in Table 8.

On Samples 401 to 406 thus obtained, the same evaluation as in Example 1 was made. Here, the evaluation was made in respect of blue density (B), green density (G) and red density (R). Results obtained are shown in Table 8.

Table 8 shows more preferred embodiments in which the present invention has been applied to the blue-sensitive emulsion, green-sensitive emulsion and red-sensitive emulsion at the same time, and also shows the effect of the present invention thereby obtained. The table still also shows that use of gold sensitization and use of the compound of Group A at the time of chemical sensitization can more highly achieve the effect of the invention, which are thus preferred.

Table 7

Emulsion No.	Iridium compound (mol/mol·AgX)		Other metal compound (mol/mol·AgX)		Chloroauric acid (mg/mol·AgX)	Compound of Group A (mol/mol·AgX)	
EmB-15 (Blue-sensitive)	K_2IrCl_6	$1.5x10^{-8}$	-		-	-	
EmB-16 (")	"	"	$K_3Ru(CN)_6$	$1.2x10^{-5}$	0.5	-	
EmG-5 (Green-sensitive)	"	$4x10^{-8}$	-		-	-	
EmG-6 (")	"	"	$K_2Os(CN)_6$	$3x10^{-5}$	1.0	-	
EmR-5 (Red-sensitive)	"	$4.5x10^{-8}$	-		-	-	
EmR-6 (")	"	"	$K_4Fe(CN)_6$	$4x10^{-5}$	-	-	
EmR-7 (")	"	"	"	"	1.5	-	
EmR-8 (")	"	"	"	"	"	α-Sulfur	$5x10^{-6}$
EmR-9 (")	"	"	"	"	"	A-25	"
EmR-10 (")	"	"	"	"	"	A-36	"

Table 8

Experiment No.	Sample No.	Blue-sensitive emulsion	Green-sensitive emulsion	Red-sensitive emulsion	(1) (sec)	Processing stability (ΔD)			Fog resistance (Dmin)			Exposure illuminance dependence (ΔS)		
						B	G	R	B	G	R	B	G	R
Ex-401	401	EmB-15	EmG-5	EmR-5	45	0.11	0.10	0.13	0.033	0.030	0.030	72	73	69
Ex-402	402	" -16	" -6	" -6	45	0.09	0.09	0.12	0.034	0.031	0.033	80	82	78
Ex-403	401	" -15	" -5	" -5	15	0.15	0.14	0.16	0.032	0.029	0.028	71	72	68
Ex-404	402	" -16	" -6	" -6	15	0.04	0.05	0.09	0.018	0.019	0.021	84	84	86
Ex-405	403	"	"	" -7	15	0.05	0.04	0.06	0.019	0.019	0.018	85	84	84
Ex-406	404	"	"	" -8	15	0.04	0.04	0.03	0.019	0.019	0.018	85	85	84
Ex-407	405	"	"	" -9	15	0.04	0.05	0.04	0.018	0.019	0.017	84	84	85
Ex-408	406	"	"	" -10	15	0.04	0.04	0.04	0.020	0.018	0.018	84	85	85

(1): Color developing time

According to the present invention, rapid and stable processing is feasible, in the image forming method comprising subjecting a light-sensitive silver halide photographic material containing a dye image forming coupler, to color developing to form a dye image. According to the present invention, color photographic processing can be carried out very rapidly, with a low fog and in a stable state, using the light-sensitive silver halide photographic material having a superior exposure illuminance dependence.

Claims

1. An image forming method comprising subjecting an imagewise exposed light-sensitive silver halide color photographic material comprising a support, and a light-sensitive layer containing a dye forming coupler and a silver halide emulsion, to color developing for 40 seconds or less in the presence of an aromatic primary amine color developing agent, characterised in that the silver halide emulsion comprises grains which are formed in the presence of an iridium compound and a compound of a further metal belonging to Group VA, VIA, VIIA or Group VIII of the Periodic Table, except iridium, and have a silver chloride content of not less than 95 mol per cent.

2. An image forming method as claimed in claim 1, characterised in that the further metal is selected from the group consisting of iron, rhenium, osmium and ruthenium.

3. An image forming method as claimed in claim 1, characterised in that the silver halide emulsion is chemically sensitized with a gold compound.

4. An image forming method as claimed in claim 1, characterised in that the silver halide emulsion is chemically sensitized using an inorganic sulfur, an organic compound containing a polysulfide bond to which at least three sulfur atoms are linked or an organic compound having a heterocyclic ring containing at least two thioether bonds or at least one disulfide bond.

5. An image forming method as claimed in claim 1, characterised in that the grains of the silver halide emulsion are silver chlorobromide grains having a silver bromide content of 0.1 to 2 mol per cent.

6. An image forming method as claimed in claim 1, characterised in that the color developing is carried out for 30 seconds or less.

7. An image forming method as claimed in claim 1, characterised in that the amount of the iridium compound is 10^{-11} to 5×10^{-5} mol per mol of silver halide.

8. An image forming method as claimed in claim 7, characterised in that the amount of the iridium compound is 10^{-9} to 5×10^{-6} mol per mol of silver halide.

9. An image forming method as claimed in claim 1, characterised in that the amount of the compound of a metal is 10^{-18} to 5×10^{-3} mol per mol of silver halide.

10. An image forming method as claimed in claim 9, characterised in that the amount of the compound of a metal is 10^{-8} to 5×10^{-4} mol per mol of silver halide.

Patentansprüche

1. Bilderzeugungsverfahren, umfassend eine 40 s oder weniger dauernde Farbentwicklung eines bildgerecht belichteten lichtempfindlichen farbphotographischen Silberhalogenid-Aufzeichnungsmaterials mit einem Schichtträger und einer lichtempfindlichen Schicht mit einem einen Farbstoff bildenden Kuppler und einer Silberhalogenidemulsion in Gegenwart einer aromatischen primären Aminfarbentwicklerverbindung, dadurch gekennzeichnet, daß die Silberhalogenidemulsion Körnchen enthält, die in Gegenwart einer Iridiumverbindung und einer Verbindung eines weiteren zur Gruppe VA, VIA, VIIA oder VIII des Periodensystems gehörenden Metalls mit Ausnahme von Iridium gebildet wurden und einen Silberchloridgehalt von nicht weniger als 95 Mol-% aufweisen.

2. Bilderzeugungsverfahren nach Anspruch 1, dadurch gekennzeichnet, daß das weitere Metall aus der Gruppe Eisen, Rhenium, Osmium und Ruthenium ausgewählt ist.

3. Bilderzeugungsverfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Silberhalogenidemulsion mit einer

Goldverbindung chemisch sensibilisiert wurde.

4. Bilderzeugungsverfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Silberhalogenidemulsion mit anorganischem Schwefel, einer organischen Verbindung mit einer Polysulfidbindung, bei der mindestens drei Schwefelatome miteinander verknüpft sind, oder einer organischen Verbindung mit einem heterocyclischen Ring mit mindestens zwei Thioetherbindungen oder mindestens einer Disulfidbindung chemisch sensibilisiert wurde.

5. Bilderzeugungsverfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Körnchen der Silberhalogenidemulsion aus Silberchlorbromidkörnchen eines Silberbromidgehalts von 0,1 - 2 Mol-% bestehen.

6. Bilderzeugungsverfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Farbentwicklung 30 s oder weniger dauert.

7. Bilderzeugungsverfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Menge der Iridiumverbindung 10^{-11} bis 5×10^{-5} Mol pro Mol Silberhalogenid beträgt.

8. Bilderzeugungsverfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Menge der Iridiumverbindung 10^{-9} bis 5×10^{-6} Mol pro Mol Silberhalogenid beträgt.

9. Bilderzeugungsverfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Megne der Verbindung eines Metalls 10^{-18} bis 5×10^{-3} Mol pro Mol Silberhalogenid beträgt.

10. Bilderzeugungsverfahren nach Anspruch 9, dadurch gekennzeichnet, daß die Menge der Verbindung eines Metalls 10^{-8} bis 5×10^{-4} Mol pro Mol Silberhalogenid beträgt.

Revendications

1. Un procédé de formation d'images comprenant le développement de la couleur d'un matériau photographique couleur à base d'halogénure d'argent sensible à la lumière exposé à la manière dont on forme une image, comprenant un support et une couche photosensible comportant un coupleur formant un colorant et une émulsion d'halogénure d'argent, pendant 40 secondes ou moins, en présence d'un agent de développement de couleur à base d'amine primaire aromatique, caractérisé en ce que l'émulsion d'halogénure d'argent comprend des grains qui sont formés en présence d'un dérivé d'iridium et d'un dérivé d'un autre métal appartenant au groupe VA, VIA, VIA ou VIII du tableau périodique, sauf l'iridium, et présentent une teneur en chlorure d'argent non inférieure à 95 % en moles.

2. Un procédé de formation d'images selon la revendication 1, caractérisé en ce que l'autre métal est choisi dans le groupe consistant en fer, rhénium, osmium et ruthénium.

3. Un procédé de formation d'images selon la revendication 1, caractérisé en ce que l'émulsion d'halogénure d'argent est chimiquement sensibilisée à l'aide d'un dérivé d'or.

4. Un procédé de formation d'images selon la revendication 1, caractérisé en ce que l'émulsion d'halogénure d'argent est chimiquement sensibilisée par utilisation d'un sulfure inorganique, d'un dérivé organique contenant une liaison polysulfure à laquelle sont liés au moins trois atomes de soufre ou d'un dérivé organique comportant un noyau hétérocyclique contenant au moins deux liaisons thioéther ou au moins une liaison disulfure.

5. Un procédé de formation d'images selon la revendication 1, caractérisé en ce que les grains de l'émulsion d'halogénure d'argent sont des grains de chlorobromure d'argent présentant une teneur en bromure d'argent de 0,1 à 2 en % moles.

6. Un procédé de formation d'images selon la revendication 1, caractérisé en ce que le développement de la couleur est effectué pendant 30 secondes ou moins.

7. Un procédé de formation d'images selon la revendication 1, caractérisé en ce que la quantité du dérivé d'iridium est de 10^{-11} à 5×10^{-5} mole par mole d'halogénure d'argent.

8. Un procédé de formation d'images selon la revendication 7, caractérisé en ce que la quantité du dérivé d'iridium

est de 10^{-9} à 5 x 10^{-6} mole par mole d'halogénure d'argent.

9. Un procédé de formation d'images selon la revendication 1, caractérisé en ce que la quantité du dérivé d'un métal est comprise entre 10^{-18} et 5 x 10^{-3} mole par mole d'halogénure d'argent.

10. Un procédé de formation d'images selon la revendication 9, caractérisé en ce que la quantité du dérivé d'un métal est comprise entre 10^{-8} et 5 x 10^{-4} mole par mole d'halogénure d'argent.