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(54) Method for forming color images.

(57) A method for forming a color image using a silver halide color photographic light-sensitive material is disclosed. By the method, fluctuation in sensitivity and color balance of processed light-sensitive material depending a circumstance humidity at the time of exposure is lowered. The method comprises steps of imagewise exposing a silver halide color light-sensitive material which comprises a support having thereon a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and developing the light-sensitive material by means of immersing the light-sensitive material in a color developer. In the method, at least one of the silver halide emulsion layers of the light-sensitive material comprises a silver halide emulsion formed in the presence of iridium compound and at least one of the emulsion layers contains a specified cyan coupler, and the time interval between completion of the step of exposing the light-sensitive material and the immersion of the light-sensitive material into the color developer is not more than 3 minutes.

FIELD OF THE INVENTION

The present invention relates to a method for foming color images by use of a silver halide light-sensitive material.

BACKGROUND OF THE INVENTION

With the speed-up in processing and printing of color light-sensitive materials, finished prints are usually delivered to customers within one day after acceptance of processing and printing, and even deliveries only in 40 minutes are practiced at some mini-processing laboratories which are spreading in recent years. Accordingly, requirements for rapid processing of color photographs extend not only to shortening of the processing time of color negative films and color papers, but to cutting down of the time for accepting work and loss time, namely, the time required to set a negative film on a printer, and even the exposing time of a color paper.

Under the circumstances, the time of interval between exposure of a color paper and processing thereof has been shortened. Usually, it takes at least several minutes to expose and process a color paper, including a loss time before processing to set a magazine containing color papers exposed with a printer in a processor. However, it is found that when the time interval between exposure and processing is shortened, effects of moisture during exposure on photographic characteristics such as changes in sensitivity are lessened, but on the contrary, changes in density become larger because latent images formed on a color paper are unstable for several minutes after exposure. It is also found that such phenomena are much more liable to occur in a color paper of high silver chloride content which is suitable for rapid processing.

For example, Japanese Pat. O.P.I. Pub. No. 18547/1990 describes these facts and, also, discloses density changes in a period ranging from several seconds to about 1 minute after exposure. As a measure to prevent such density changes, Japanese Pat. O.P.I. Pub. No. 18547/1990 proposes to improve the stability of latent images by forming specific areas where the silver bromide content is peculiarly high, by means of an appropriate control of silver halide composition. However, in systems where scanning exposure is practiced by use of laser beams, the exposure takes several minutes, and the balance of color is changed from initial portion to final portion of the scanning exposure as the humidity changes, thereby the quality of images is lowered. Further, studies made by the present inventors have found that a photographic light-sensitive material containing a silver halide having peculiarly high silver bromide content areas, as seen in Japanese Pat. O.P.I. Pub. No. 18547/1990, is low in contrast and, therefore, unsuitable for usual photographs.

Japanese Pat. O.P.I. Pub. No. 183647/1989 describes that the stability of latent images can be improved by use of an emulsion comprised of silver chloride rich grains having a silver bromide localized phase and containing iron ions, but the effect is unclear for lack of exemplifications. According to an examination of the present inventors made to verify the description, satisfactory images can not be necessarily obtained only by this method, and the stability of latent images cannot be improved sufficiently when iron ions alone are used as a dopant.

On the other hand, it is found by the present inventors, that iridium compounds often used in the preparation of emulsions to prevent reciprocity law failures, though worsen the humidity dependency during exposure and eventually increase the change in sensitivity, have an effect to improve the stability of latent images when a few minutes have elapsed after exposure. It is also found that when an iridium compound is used singly, the stability of latent images is not improved for a few minutes immediately after exposure; particularly, balances in density and contrast are unstable, and thereby images obtained are poor in quality.

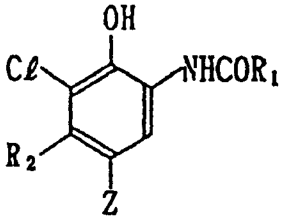
It is further found by the inventors that high-quality images satisfactory in density balance and less susceptible to moisture during exposure can be obtained, by use of a light-sensitive material containing an emulsion using an iridium compound and a cyan coupler having a specific structure, and by shortening the time interval between exposure and processing to 3 minutes and less, which takes about 5 minutes or more in a conventional method. This combination has led to an unexpected outcome; indeed, it was a surprising finding.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a method for forming color images less in sensitivity change due to the presence of moisture during exposure and capable of forming high quality images, by use of a silver halide color photographic light-sensitive material.

The object of the invention is achieved by a method for forming color images comprising steps of exposing imagewise a silver halide light-sensitive material having on a support at least one layer each of blue-sensitive layer, green-sensitive layer and red-sensitive layer and then color developing it, wherein at least one silver halide emulsion used in the light-sensitive material is prepared in the presence of an iridium compound, at least one layer of the light-sensitive material contains the coupler represented by the following Formula (I), and the time interval between completion of imagewise exposure of the light-sensitive material and dipping of it into a color developer is not more than 3 minutes.

Formula I



In the formula, R_1 represents a ballast group; R_2 represents an alkyl group having 2 or more carbon atoms; and Z represents an atom or a group of atoms capable of splitting off upon reaction with an oxidation product of a color developing agent.

In one preferable embodiment to bring out the effect of the invention fully, at least one silver halide emulsion contained in the above light-sensitive material has a silver chloride content not less than 90 mol% and is prepared in the presence of an iridium compound and a compound of a Va to VIII group metal in the periodic table; the time interval between imagewise exposure of the light-sensitive material and immersing of it into a color developer is not more than 1 minute, especially not more than 15 seconds; and the time required to expose imagewise the light-sensitive is not less than 0.01 second and not more than 30 seconds, especially not more than 2 seconds.

DETAILED DESCRIPTION OF THE INVENTION

The silver halide light-sensitive material according to the invention has at least one layer each of red-sensitive layer, green-sensitive layer and blue-sensitive layer, and each of such spectrally sensitive layers may be comprised of a single layer or a plurality of layers of the same spectral sensitivity. These layers may be configured in any order.

The silver halide grains contained in the light-sensitive material according to the invention may be any of silver bromide, silver chlorobromide, silver iodobromide, silver bromide and silver chloroiodobromide, but silver chlorobromide having a silver chloride content not less than 90 mol% or silver chloride are preferred. Though silver iodide may be contained, the content thereof is desirably not more than 1 mol% and more desirably not more than 0.5 mol%; most desirably, silver iodide is not contained at all.

The silver halide grains contained in the light-sensitive material according to the invention may be used in combination with silver halide grains extraneous to the invention. In this case, the projected area of the silver halide grains of the invention amounts to preferably not less than 50%, especially not less than 75% of the projected area of the total silver halide grains in a silver halide emulsion layer where the silver halide grains of the invention are contained.

The silver halide grains of the invention can be prepared according to the methods described, for example, in Japanese Pat. O.P.I. Pub. Nos. 162540/1984, 48754/1984, 222844/1985, 222845/1985 and 136735/1985.

The size of the silver halide grains of the invention is not particularly limited, but preferably 0.2 to 1.6 µm and especially 0.25 to 1.2 µm, in view of rapid processability, sensitivity and other photographic properties.

The grain size distribution of the silver halide grains of the invention may be of monodispersion or polydispersion, but suitable silver halide grains are those having a variation coefficient of 0.22 or less in grain size distribution and, preferably, monodispersed silver halide grains having a variation coefficient of 0.15 or less. "Variation coefficient" is a coefficient indicating an extent of grain size distribution and expressed by (standard deviation of grain size distribution)/(average grain size).

The silver halide grains of the invention are preferably formed under acid conditions. The term "under acid conditions" means the pH at which grains are formed is not more than 7, preferably not more than 5 and especially not more than 4.

The pH may be controlled by any method, but use of an inorganic acid such as sulfuric acid, hydrochloric acid or nitric acid or an organic acid such as acetic acid or citric acid is preferred.

To react a soluble silver salt and a soluble halide, there may be used any of the single jet method, the reverse jet method, the double jet method and combinations thereof, but use of the double jet method is preferred. Further, the pAg-controlled double jet method described, for example, in Japanese Pat. O.P.I. Pub. No. 48521/1978, a modification of the double jet method, can also be used.

In the invention, the form of the silver halide grains may be arbitrarily selected. One preferable example is a cube having (100) faces as crystal faces.

There may also be employed octahedral, tetradecahedral or dodecahedral grains, which are prepared according to the methods described, for example, in U.S. Pat. Nos. 4,183,756, 4,225,666, Japanese Pat. O.P.I. Pub. No. 26589/1980, Japanese Pat. Exam. Pub. No. 42737/1980 and The Journal of Photographic Science, 21, 39 (1973). In addition, grains having twin faces and grains of irregular forms may also be used.

The wording "silver halides are formed in the presence of an iridium compound" used in the invention means that an iridium compound is added in one of steps of nucleus formation, growth and physical ripening of silver halide grains.

The addition of an iridium compound can be practiced by various methods, such as a method of adding it to a mother liquid before nucleus formation, a method of adding it with a rush in the course of silver halide formation, a method of adding it in advance to a halide solution or a soluble silver salt solution each used for formation or growth of silver halide grains, and a method of adding it immediately before physical ripening to a liquid in which growth of grains is completed. Further, in a method for preparing an emulsion by feeding silver halide fine grains to form and grow silver halide grains, an iridium compound may be added to silver halide fine grains by one of the above methods during formation of such silver halide fine grains, the fine grains thus formed are added in a reaction vessel to form silver halide grains.

Such an iridium compound may be added by lots in different stages. Such an iridium compound may be added in combination of two or more kinds in the form of a solution dissolving a mixture thereof, there may also be added in different stages two or more solutions respectively dissolving different types of iridium compounds.

The iridium compound used in the invention is not particularly limited; but, in view of stability, safety, economy and availability of the compound, suitable ones are iridium(III) halide compounds, iridium(IV) halide compounds, and iridium complex salts having a ligand selected from halogens, amines and oxalates. The following are typical examples thereof, but ones usable in the invention are not limited to them.

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

In the invention, suitable ones can be arbitrarily selected from these compounds and may be used in combination according to a specific requirement. In many cases, these iridium compounds are used in the form of aqueous solutions or solutions of solvents miscible with water, and these iridium compound solutions can be stabilized in the well-known manner, that is, the addition of a hydrogen halide such as hydrochloric acid or hydrobromic acid, a alkali halide such as potassium chloride, sodium chloride or potassium bromide or nitric acid.

In the invention, the addition amount of the iridium compound is usually not less than 10^{-11} mol, preferably not less than 10^{-9} mol per mol of silver halide, in order to bring out the effect of the invention fully. And, in view of fogging and desensitization, it is usually not more than $5 \text{ X } 10^{-6}$ mol, preferably not more than 5×10^{-6} mol.

Further, in forming silver halide grains according to the invention, it is preferable that the formation of grains be carried out in the presence of a compound of metal selected from Va, VIa, VIIa and VIII groups in addition to the iridium compound. The compound of a metal selected from Va, VIa, VIIa and VIII groups other than iridium can be added, together with the iridium compound or independently, in the same manner, and at the same addition time, as those for the iridium compound.

In the term "compound of a metal selected from Va, VIa, VIIa and VIII groups other than iridium", "metal" means vanadium, chromium, manganese, iron, cobalt, nickel, niobium, technetium, ruthenium, rhodium, palladium, tantalum, rhenium, osmium or platinum. Hiereinafter these metals are referred simply a "metal other than iridium" In the invention, a compound of any of these metals can be used. A complex salt thereof can also be used. As a ligand, any of chlorine, bromine, iodine, amines, cyan, thiocyan and acetylacetone can be used. The following are examples thereof, but usable ones are not limited to them.

Oxodichlororanadate, oxovanadate, oxosulfatovanadate oxoacetylacetatovanadate, chromium(III) chloride, chromium(III) bromide, chromium(III) nitrate, chromium(III) acetate, potassium chromium(III) sulfate, manganese(II) acetate, 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, potassium ferrocyanate, potassium ferrocyanate , iron(II) thiocyanate, iron(III) thiocyanate, iron(II) bromide, iron(III) bromide, iron(II) acetate, iron(III) acetate, penacyanoammineferrate(II), cobalt(II) chloride, cobalt (III) chloride, cobalt(II) acetate, hexamminecobalt (III), chlonide, cobalt(II) nitrate, nickel(II) chloride, nickel(II) oxalate, nickel(II) benzoate, nickel(II) cyanide, niobium(V) chloride, ruthenium(III) chloride, ruthenium(III) acetylacetate, rhodium(III) chloride, rhodium(III) nitrate, rhodium(III) acetate, palladium(II) acetate, palladium-(II) acetylacetate, ammonium palladium(II) chloride, palladium(II) chloride, tantalum(V) chloride, chloroplatinic(IV) acid, platinum(IV) chloride, potassium tetrachloroplatinate(II), osmic(VIII) acid, potassium hexacyanothenate(II), potassium hexacyanoruthenate(II), potassium hexacyanoruthenate(III), potassium pentacyanochlororuthenate(II), sodium pentachloronitrosylruthenate(III) and potassium pentabromonitrosylosmate(IV).

In the invention, suitable ones can be arbitrarily selected from these compounds and used in an appropriate combination according to a specific requirement.

In the invention, the addition amount of the metal compound other than the iridium compound is preferably not less than 10^{-10} mol, especially not less than 10^{-8} mol per mol of silver halide, in order to bring out the effect of the invention fully. On the other hand, from the viewpoint of fogging and desensitization, it is preferably not more than 5×10^{-3} mol, especially not more than 5×10^{-4} mol.

It is particularly preferable that the iridium compound and the compound of a metal other than iridium be present concurrently during silver halide grain formation.

The silver halide emulsion according to the invention may, or may not, be subjected to desalting after the growth of silver halide grains in order to remove useless soluble salts.

The silver halide emulsion according to the invention is chemically sensitized by a method known in the art. Usable chemical sensitizers may be chalcogen compounds, precious metal compounds. Typical examples thereof include thiosulfates, thioureas, allyl isothiocyanate, cystine, rhodanine, potassium chloroaurate, auric trichloride, and platinum compounds, palladium compounds. These chemical sensitizers may be appropriately selected and combined according to a specific requirement.

The silver halide emulsion according to the invention may be spectrally sensitized to a desired wavelength region by use of dyes known as sensitizing dyes in the art. Sensitizing dyes may be used singly or in combination. There may also be employed, together with a sensitizing dye, a supersensitizer, a dye having no spectrally sensitizing function by itself or a compound which absorbs substantially no visible light, in order to enhance the sensitizing function of a sensitizing dye.

The light-sensitive material according to the invention contains the cyan coupler represented by the above Formula I at least in one layer.

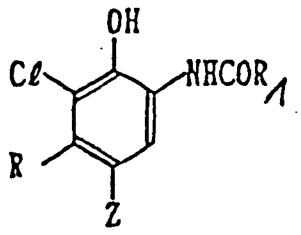
In Formula I, the alkyl group represented by R_2 may be straight-chained or branched and includes ones having a substituent. The number of carbon atoms in R_2 is preferably 2 to 6.

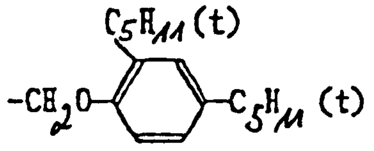
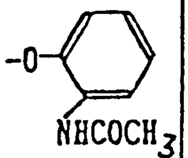
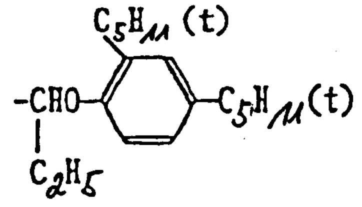
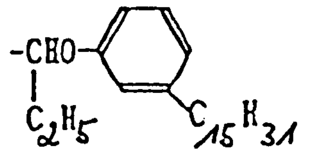
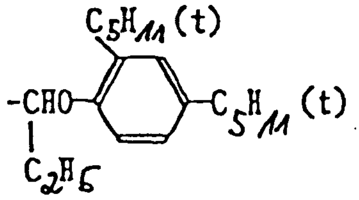
The ballast group represented by R_1 is an organic group having a size and a form necessary to give to the coupler a bulkiness large enough to substantially prevent the coupler from diffusing from the layer in which it is contained to other layers. Preferable ballast groups are those represented by the following Formula Ia:

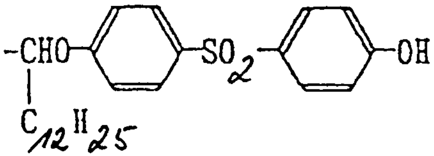
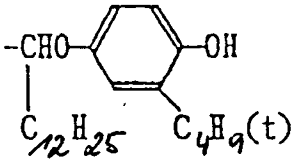
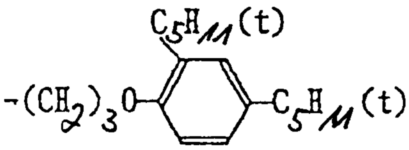
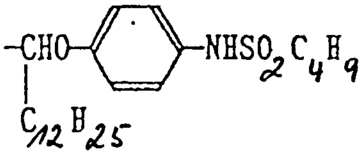
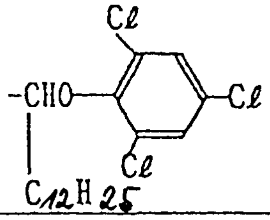
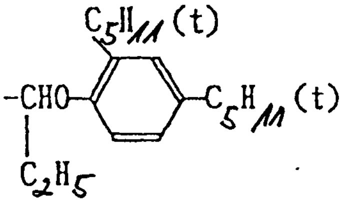
Formula Ia $-CH(R_3)OAr$

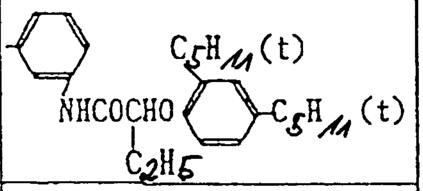
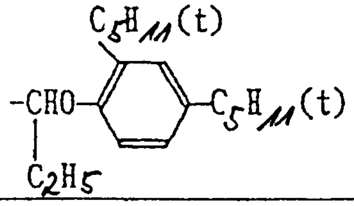
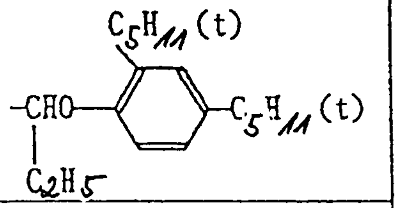
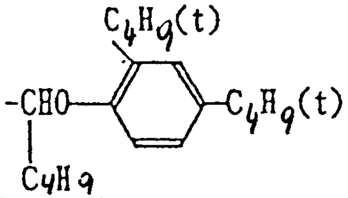
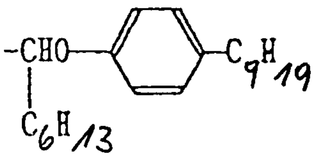
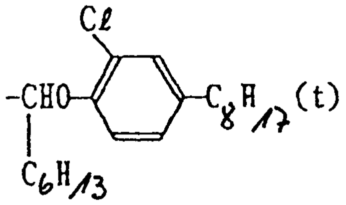
where R_3 represents an alkyl group having 1 to 12 carbon atoms, Ar represents an aryl group such as phenyl group, this aryl group may have a substituent.

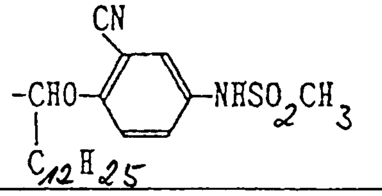
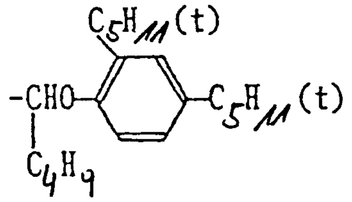
Typical examples of the coupler represented by Formula (I) are shown below, but usable ones are not limited to them.



No.	R_2	Z	R_1
I − 1	$-C_2H_5$	$-Cl$	
I − 2	$-C_2H_5$		
I − 3	$-C_3H_7(i)$	$-Cl$	
I − 4	$-C_2H_5$	$-Cl$	

	R_2	Z	R_1
I – 5	$-C_4H_9$	-F	
I – 6	$-C_2H_5$	-F	
I – 7	$-C_2H_5$	-Cl	
I – 8	$-C_2H_5$	-Cl	
I – 9	$-C_2H_5$	-Cl	
I –10	$-C_6H_{13}$	-Cl	

	R_2	Z	R_1
I −11	$-C_3H_7$	$-Cl$	
I −12	$-CH_2CH_2*$ $*NHCOCH_3$	$-Cl$	
I −13	$-CH_2CH_2*$ $*OCH_3$	$-Cl$	
I −14	$-C_2H_5$	$-Cl$	
I −15	$-C_4H_9(t)$	$-CH_2CH_2*$ $*SO_2CH_3$	
I −16	$-C_2H_5$	$-Cl$	

	R_2	Z	R_1
I −17	$-C_2H_5$	$-Cl$	
I −18	$-C_2H_5$	$-Cl$	
I −19	$-C_2H_5$	$-Cl$	$-C_{15}H_{31}$

Including these compounds, examples of cyan couplers usable in the invention can be seen, for example, in Japanese Pat. Exam. Pub. No. 11572/1974, Japanese Pat. O.P.I. Pub. Nos. 3142/1986, 9652/1986, 9653/1986, 39045/1986, 50136/1986, 99141/1986 and 105545/1986.

The cyan coupler of the invention represented by Formula (I) can be used in an amount of usually 1×10^{-3} mol, preferably 1×10^{-2} to 8×10^{-1} mol per mol of silver halide.

The light-sensitive material according to the invention may contain a cyan coupler other than the cyan coupler represented by Formula I. Such jointly usable cyan couplers are those described in Japanese Pat. O.P.I. Pub. Nos. 247365/1987, 246051/1987, 129342/1988, 118132/1984 and 136855/1990. The effect of the invention is clearly revealed when cyan couplers other than those of Formula (I) are jointly used in an amount not more than 50%, preferably not more than 25% of the total coupler amount.

The light-sensitive material according to the invention may use any magenta coupler and any yellow coupler. Examples of usable yellow couplers include those yellow couplers which are described in Japanese Pat. O.P.I. Pub. Nos. 85631/1988, 97951/1988, 298943/1990 and 156748/1989. Examples of usable magenta couplers can be seen in Japanese Pat. O.P.I. Pub. Nos. 166339/1987 and 100048/1990. Although, in the light-sensitive material, the silver halide emulsion formed in the presence of iridium compound on the coupler of formula may be contained in the same layer or in different layers, it is preferable that they are contained in the same layer.

The light-sensitive material of the invention is subjected to imagewise exposure and then dipped in a color developer for color development.

The term "imagewise exposure" used here means to expose a light-sensitive material to one picture at a time, like an exposure with a printer through an ordinary negative film, and does not contain a method of exposing like a scanning exposure using laser beams. The time necessary for this imagewise exposure is preferably not less than 0.01 second in order to prevent low contrasts due to reciprocity law failures. Further, in order to minimize the effect of moisture during exposure, the exposing time is usually not more than 30 seconds, preferably not more than 2 seconds.

In the invention, a silver halide light-sensitive material subjected to the imagewise exposure is immersed, within 3 minutes after the exposure, in a color developer to be color-developed. The effect of the invention can be demonstrated much more clearly when a light-sensitive material is immersed into a color developer within 1 minute, preferably within 15 seconds after exposure. In developing, when a silver halide light-sensitive material takes a long time to finish soaking into a color developer starting with its head and ending with its tail, the stability of latent images is affected to cause uneven color images. To prevent this, it is preferable to convey a light-sensitive material at a speed not less than 10 mm/sec.

In the color developer, an aromatic primary amine color developing agent is used. Usable developing agents include aminophenol derivatives and p-phenylenediamine derivatives, and p-phenylenediamine derivatives are particularly preferred. These color developing agents can be used in the form of salts of organic acids or inorganic acids, such as hydrochlorides, sulfates, p-toluenesulfonates, sulfites, oxalates or benzensulfonates.

These compounds are used in a concentration of usually about 0.1 to 30 g, preferably about 1 to 15 g per liter of color developer.

The processing temperature of the color developer is 10 to 65 ° C, preferably 25 to 45 ° C.

Usable aminophenol type developing agents include, for example, o-aminophenol, p-aminophenol, 5-amino-2-hydroxytoluene, 2-amino-3-hydroxytoluene and 2-hydroxy-3-amino-1,4-dimethylbenzene.

Particularly useful aromatic primary amine color developing agents are N,N-dialkyl-p-phenylenediamine compounds, of which alkyl groups and phenyl group may have a substituent. Of these compounds, particularly preferred ones are N,N-diethyl-p-phenylenediamine hydrochloride, N-methyl-p-phenylenediamine hydrochloride, N,N-dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-(N-ethyl-N-dodecylamino)toluene, N-ethyl-N-β-methanesulsonamidoethyl-3-methyl-4-aminoaniline sulfate, N-ethyl-N-β-hydroxyethylaminoaniline, 4-amino-3-methyl-N,N-diethylaniline and 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluenesulfonate.

The above color developing agents may be used singly or in combination. Further, these color developing agents may be contained in color photographic light-sensitive materials.

To prepare light-sensitive materials containing a color developing agent, there can be used, for example, a method for incorporating a color developing agent in the form of a metal salt as disclosed in U.S. Pat. No. 3,719,492, a method for incorporating a color developing agent in the form of a Schiff's salt as disclosed in U.S. Pat. No. 3,342,559 and Research Disclosure No. 15159 (1976), a method for incorporating it in the form of a dye precursor as disclosed in Japanese Pat. O.P.I. Pub. Nos. 65429/1983, 24137/1983, and a method for incorporating in the form of a color developing agent precursor as disclosed in U.S. Pat. No. 3,342,597. Such silver halide color photographic light-sensitive materials can be processed with an aqueous alkali, solution, an activator solution, instead of a color developer. When the processing with an aqueous alkali is finished, these light-sensitive materials are subjected to bleach-fixing at once.

The color developer used in the invention may contain, besides the above color developing agent, an alkali agent, a development accelerator, a development control agent, a preservative, a defoamer, a surfactant and an organic solvent.

The pH of the color developer is usually not less than 7, preferably about 9 to 13.

After color development, color light-sensitive materials are usually subjected to bleaching. Bleaching may be carried out concurrently with fixing (bleach-fixing) or independently. But preferably, light-sensitive materials are subjected to bleach-fixing which performs bleaching and fixing in one bath. The pH of the bleach-fixer used in the invention is preferably in a range of 4.5 to 6.8.

Bleaching agents used in the bleach-fixer are metal complexes of organic acids. Such metal complexes have functions to oxidize metal silver formed on developing to silver halide and to make a coupler remaining uncolored states develop a color, and have the structure where a metal ion such as iron, cobalt or copper is coordinated with an organic acid such as an aminopolycarboxylic acid, oxalic acid or citric acid. Preferable organic acids to form such metal complexes include polycarboxylic acids and aminopolycarboxylic acids. These polycarboxylic acids and aminopolycarboxylic acids may be alkali metal salts, ammonium salts or water-soluble amine salts.

Typical examples thereof include the following compounds:

(1) Ethylenediaminetetraacetic acid
(2) Nitrilotriacetic acid
(3) Iminodiacetic acid
(4) Disodium ethylenediaminetetracetate
(5) Tetra(trimethylammonium) ethylenediaminetetracetate
(6) Tetrasodium ethylenediaminetetracetate
(7) Sodium nitrilotriacetate

The bleaching solution used in the invention contains a metal complex of the above organic acid as a bleaching agent. In addition, it may also contain various compounds known as additives for a bleaching solution, such as rehalogenation agents, metal salts, chelating agents, pH buffers, alkyl amines and polyethylene oxides.

Further, the fixer and the bleach-fixer may contain sulfites and pH buffers singly or in combination.

When the processing of the invention is performed while replenishing a bleach-fixing agent to a bleach-fixer, the bleach-fixer may contain thiocyanates or sulfites, or these salts may be fed to a bleach-fixing bath by being dissolved in a bleach-fixing replenisher.

In the invention, there may be blown, if desired, air or oxygen into a bleach-fixing bath and a bleach-fixing replenisher storage tank in order to raise the activity of a bleach-fixing solution, or, there may be added an oxidizing agent such as hydrogen peroxide, a bromate or a persulfate.

The process of the invention substantially comprises the steps of color developing, bleach-fixing, and washing or stabilizing as the alternative thereto, i,e, washing-substituting stabilizing.

The processing temperature with a washing-substituting stabilizer is usually 15 to 60 ° C, preferably 20 to 45 ° C.

EXAMPLES

Example 1

Sample 101, a multilayered color light-sensitive material, was prepared by forming the layers shown in Table 1 on the titanium-oxide-containing polyethylene side of a paper support laminated with titanium-oxide-containing polyethylene on one side and with plain polyethylene on the other side. The coating solutions were prepared as follows:

Preparation of 1st coating solution

A mixture of 26.7 g of yellow coupler (Y-1), 10.0 g of dye image stabilizer (ST-1), 6.67 g of dye image stabilizer (ST-2), 0.67 g of additive (HQ-1) and 6.67 g of high boiling solvent (DNP) was dissolved by adding 60 ml of ethyl acetate to the mixture. This solution was dispersed with a supersonic homogenizer in 220 ml of 10% aqueous solution of gelatin containing 7 ml of 20% surfactant (SU-1) to obtain a yellow coupler dispersion. Then, the dispersion was mixed with a blue-sensitive silver halide emulsion prepared as described later, so that a coating solution for the 1st layer was obtained.

Coating solutions for the 2nd to 7th layers were prepared in similar procedures as the above.

In addition, hardener (H-1) was added to the 2nd and 4th layers, and hardener (H-2) to the 7th layer. As coating aids, surfactants (SU-2) and (SU-3) were added to reduce the surface tension.

H-1: Tetra(vinylsulfonylmethyl)methane
H-2: Sodium 2,4-dichloro-6-hydroxytriazine
Su-1: Sodium tri-i-propylnaphthalenesulfonate
SU-2: Sodium (2-ethylhexyl)sulfosuccinate
SU-3: Sodium (2,2,3,3,4,4,5,5-octafluoropentyl) sulfosuccinate

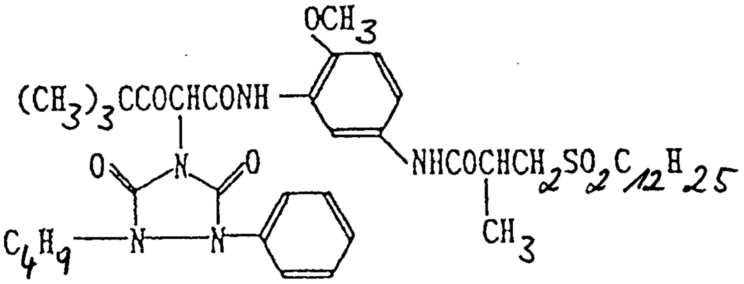
Layer	Composition	Amount Added (g/m²)
6th layer (UV absorbing layer)	Gelatin UV absorbent (UV-1) UV absorbent (UV-2) UV absorbent (UV-3) Antistain agent (HQ-5) DNP PVP Anti-irradiation dye (II-2)	0.40 0.10 0.04 0.16 0.01 0.20 0.03 0.02
5th layer (red-sensitive layer)	Gelatin Red-sensitive silver chlorobromide emulsion (Em-R) Cyan coupler (C-1) Dye image stabilizer (ST-1) Antistain agent (HQ-1) HBS-1 DOP	1.30 0.21 0.42 0.20 0.01 0.20 0.20

Layer	Composition	Amount Added (g/m²)
4th layer (UV absorbing layer)	Gelatin UV absorbent (UV-1) UV absorbent (UV-2) UV absorbent (UV-3) Antistain agent (HQ-1) DNP	0.94 0.28 0.09 0.38 0.03 0.40
3rd layer (green-sensitive layer)	Gelatin Green-sensitive silver chlorobromide emulsion (Em-G) Magenta coupler (M-1) Dye image stabilizer (ST-3) Dye image stabilizer (ST-4) Dye image stabilizer (ST-5) DNP Anti-irradiation dye (AI-1)	1.40 0.17 0.35 0.15 0.15 0.15 0.20 0.01
2nd layer (intermediate layer)	Gelatin Antistain agent (HQ-2) DIDP	1.20 0.12 0.15

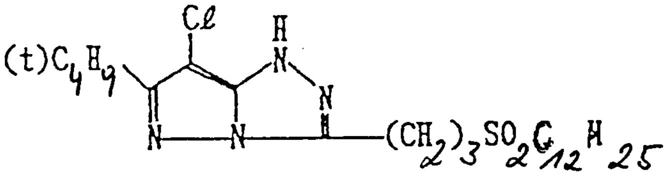
Layer	Composition	Amount Added (g/m²)
1st layer (blue-sensitive layer)	Gelatin Blue-sensitive silver chlorobromide emulsion (Em-B) Yellow coupler (Y-1) Dye image stabilizer (ST-1) Dye image stabilizer (ST-2) Antistain agent (HQ-1) Anti-irradiation dye (AI-3) DNP	1.20 0.26 0.80 0.30 0.20 0.02 0.01 0.20
Support	Polyethylene laminated paper	

The addition amounts of silver halide emulsions are shown in amounts of silver present.

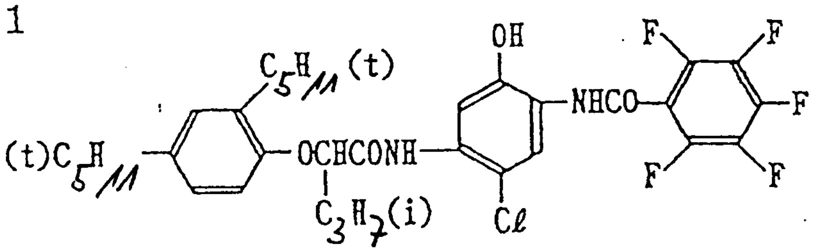
Y - 1



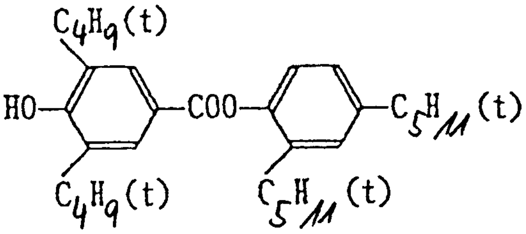
M - 1



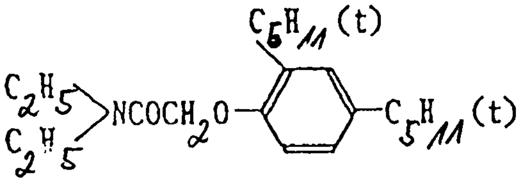
C - 1



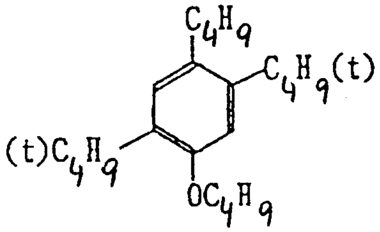
S T - 1



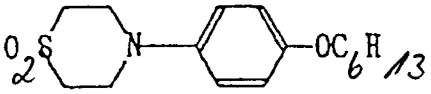
S T - 2



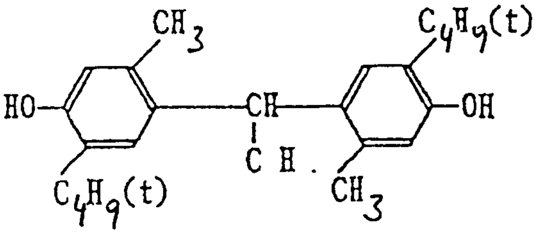
ST-3



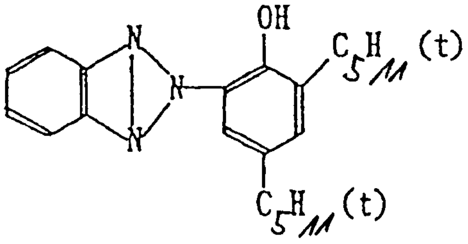
ST-4



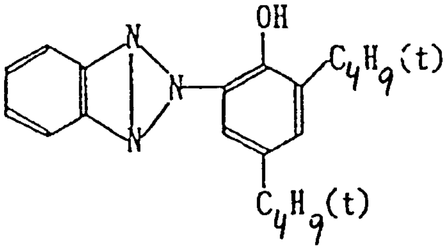
ST-5



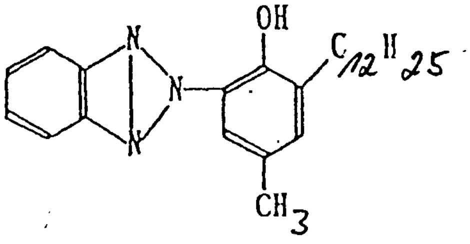
UV-1



UV-2



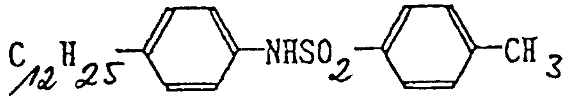
UV-3



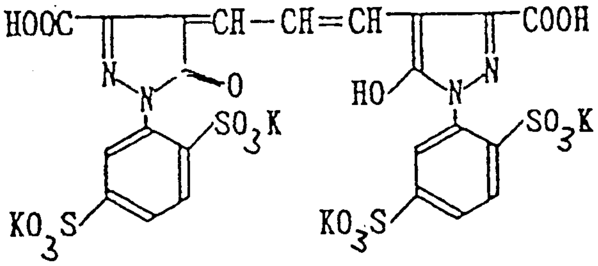
DOP :	Dioctyl phthalate
DNP :	Dinonyl phthalate
DIDP:	Diisodecyl phthalate
PVP :	Polyvinyl pyrrolidone
HQ-1:	2,5-Di-t-octylhydroquinone

HQ-2: 2-Hexadecyl-5-methylhydroquinone

HBS-1



AI-1



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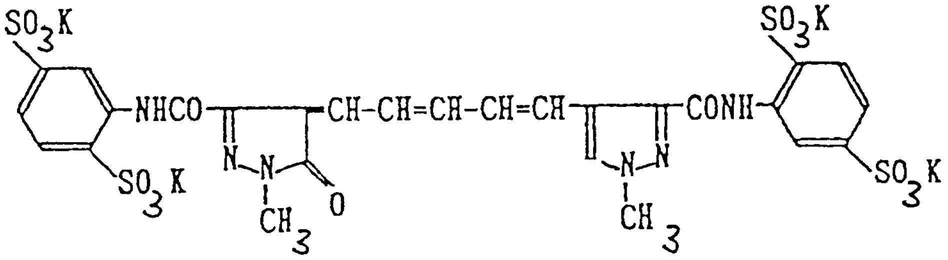
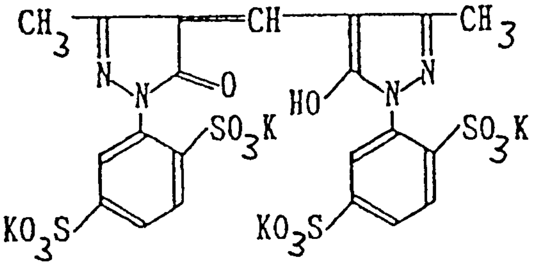


AI-3



Preparation of blue-sesitive silver halide emulsion

The following solutions (A) and (B) were simultaneously added over a period of 30 minutes to 1000 ml of 2% aqueous solution of gelatin kept at 40 ° C, while keeping the liquor pAg 6.5 and pH 3.0. Then, the following solutions (C) and (D) were simultaneously added over a period of 180 minutes, maintaining the liquor pAg 7.3 and pH 5.5. During the addition, control of the pAg was made according to the method described in Japanese Pat. O.P.I. Pub. No. 45437/1984, the pH was controlled with sulfuric acid or an aqueous sodium hydroxide.

Solution (A)	
Sodium chloride Water was added to make	3.43 g 200 ml

Solution (B)	
Silver nitrate	10 g
Water was added to make	200 ml

Solution (C)	
Sodium chloride	102.7 g
Potassium bromide	1.08 g
Water was added to make	600 ml

Solution (D)	
Silver nitrate	300 g
Water was added to make	600 ml

After completion of the addition, silver chloride grains obtained were desalted using 5% aqueous solution of Demol N made by Kao Atlas Co. and 20% aqueous solution of magnesium sulfate and, then, mixed with an aqueous solution of gelatin. Emulsion EMP-1 thus prepared was comprised of monodispersed cubic silver chloride grains having an average grain size of 0.85 µm, a grain size distribution variation coefficient of 0.07, and a silver chloride content of 99.5 mol%.

The above emulsion EMP-1 was chemically sensitized at 50 ° C for 90 minutes by use of the following compounds to obtain a blue-sensitive silver halide emulsion (Em-B).

Sodium thiosulfate	0.8 mg/mol AgX
Chloroauric acid	0.5 mg/mol AgX
Stabilizer STAB-1	6×10^{-4} mol/mol AgX
Sensitizing dye BS-1	4×10^{-4} mol/mol AgX
Sensitizing dye BS-2	1×10^{-4} mol/mol AgX

Preparation of green-sesitive silver halide emulsion

Emulsion EMP-2 was prepared in the same manner as with emulsion EMP-1, except that the addition time of solutions (A) and (B) and that of solutions (C) and (D) were changed. Emulsion EPM-2 was comprised of monodispersed cubic silver chloride grains having an average grain size of 0.43 µm, a grain size distribution variation coefficient of 0.08, and a silver chloride content of 99.5 mol%.

Emulsion EMP-2 was chemically sensitized at 55 ° C for 120 minutes by use of the following compounds to obtain a green-sensitive silver halide emulsion (Em-G).

Sodium thiosulfate	1.5 mg/mol AgX
Chloroauric acid	1.0 mg/mol AgX
Stabilizer STAB-1	6×10^{-4} mol/mol AgX
Sensitizing dye GS-1	4×10^{-4} mol/mol AgX

Preparation of red-sesitive silver halide emulsion

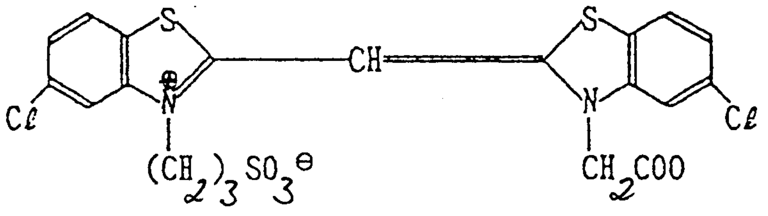
Emulsion EMP-3 was prepared in the same manner as with emulsion EMP-1, except that the addition time of solutions (A) and (B) and that of solutions (C) and (D) were changed. Emulsion EPM-3 was comprised of monodispersed cubic silver chloride grains having an average grain size of 0.50 µm, a grain size distribution variation coefficient of 0.08, and a silver chloride content of 99.5 mol%.

Emulsion EMP-3 was chemically sensitized at 60 ° C for 90 minutes by use of the following compounds to obtain a red-sensitive silver halide emulsion (Em-R).

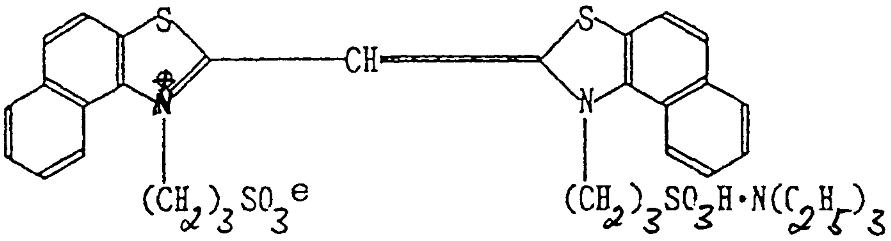
Sodium thiosulfate	1.8 mg/mol AgX
Chloroauric acid	2.0 mg/mol AgX
Stabilizer STAB-1	6×10^{-4} mol/mol AgX
Sensitizing dye RS-1	1×10^{-4} mol/mol AgX

SYAB-1: 1-(3-Acetamino)phenyl-5-mercaptotetrazole

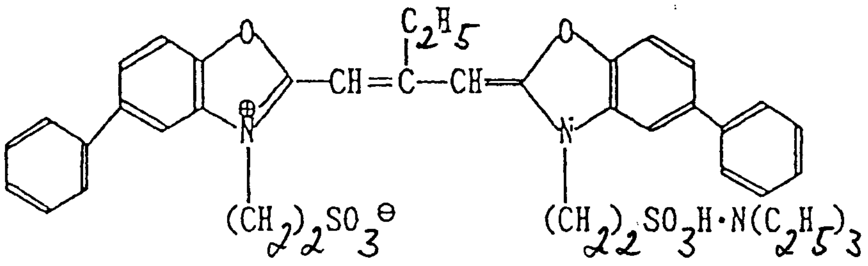
BS－1



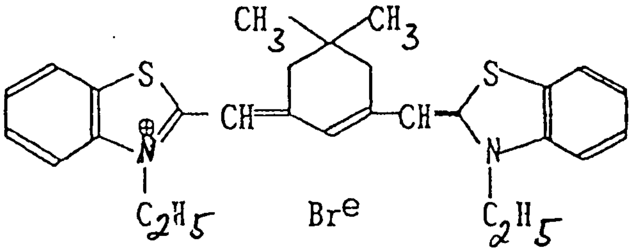
BS－2



GS－1



RS－1



The following samples 102 to 106 were prepared by changing the emulsion and coupler used in the 3rd layer of sample 101.

Sample No	Red-sensitive Emulsion	Cyan Coupler	Amount Added (g/m^2)
101	Em-R	C-1	0.42
102	Em-R	I-4	0.42
103	Em-R, but solution C_1 was used instead of solution C	C-1	0.42
104	Em-R, but solution C_1 was used instead of solution C	I-4	0.42
105	Em-R, but solution C_2 was used instead of solution C	C-1	0.35
106	Em-R, but solution C_2 was used instead of solution C	C-1	0.35
		I-4	0.07
107	Em-R, but solution C_3 was used instead of solution C	C-1	0.25

Solution (C_1)	
Sodium chloride	102.7 g
Sodium bromide	1.0 g
Water was added to make	600 ml

Solution (C_2)	
Sodium chloride	102.7 g
Sodium bromide	1.0 g
Potassium iridium hexachloride	0.035 mg
Water was added to make	600 ml

Solution (C_3)	
Sodium chloride	90.7 g
Sodium bromide	32.6 g
Potassium iridium hexachloride	0.035 mg
Water was added to make	600 ml

The light-sensitive materials obtained as above were subjected wedgewise exposure for 0.5 second in environments of 15% relative humidity and 85% relative humidity, and 10 seconds after the exposure, these were immersed into a color developer to develop colors. The conditions of the color development were as follows:

Process	Temperature	Time
Color developing	35.0 ± 0.3 ° C	45 sec
Bleach-fixing	35.0 ± 0.5 ° C	45 sec
Stabilizing	30 to 34 ° C	90 sec
Drying	60 to 80 ° C	60 sec

Color developer	
Deionized water	800 ml
Triethanolamine	10 g
N,N-Diethylhydroxylamine	5 g
Potassium bromide	0.02 g
Potassium chloride	2 g
Potassium sulfite	0.3 g
1-Hydroxyethylidene-1,1-diphosphonic acid	1.0 g
Ethylenediaminetetraacetic acid	1.0 g
Disodium catechol-3,5-disulfonate	1.0 g
N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate.	4.5 g
Optical whitening agent (4,4'-diaminostilbene-sulfonate derivative)	1.0 g
Potassium carbonate	27 g
Water is added to make 1000 ml, and the pH is adjusted to 10.10	

Bleach-fixer	
Ammonium ferric ethylenediaminetetracetate dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (70% aqueous solution)	100 ml
Ammonium sulfite (40% aqueous solution)	27.5 ml
Water is added to make 1000 ml, then the pH is adjusted to 5.7 with potassium carbonate or glacial acetic acid.	

Stabilizer	
5-Chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Ethylenediaminetetraacetic acid	1.0 g
Ammonium hydroxide (20% aqueous solution)	3.0 g
Optical whitening agent (4,4'-diaminostilbene-sulfonate derivative)	1.5 g
Water is added to make 1000 ml, then the pH is adjusted to 7.0 with sulfuric acid or potassium hydroxide.	

Each processed sample was evaluated for a change in sensitivity by comparing the sensitivity at 15% RH with that at 85% RH. The results are as follows: (in values relative to the sensitivities at 15% which are set at 100)

Sample No.	B	R	G	Change in Color Balance
101 (comparison)	88	82	94	D
102 (comparison)	87	84	94	D
103 (comparison)	89	80	102	E
104 (invention)	98	96	99	A
105 (invention)	95	93	94	A
106 (invention)	102	101	102	A
107 (invention)	104	107	101	B

Change in color balance was visually judged by a 5-grade rating.

A: No change in color balance is visually observed.

B: Only skilled persons can find a change in color balance.

C: Changes in color balance are observed in some scenes, but image quality is on an acceptable level.
D: Changes in color balance are observed, image quality is poor.
E: The color balance is entirely changed.

As apparent from the above result, only a combination of the cyan coupler of Formula (I) and an emulsion prepared in the presence of the iridium compound could minimize the moisture dependency during exposure and lessen the change in color balance. It can also be understood, from the results on samples 104, 105 and 107, that the effect of the invention became larger as the silver chloride content of the emulsion increased.

Further, samples 105 and 106 indicate that the effect of the invention could be brought out even when cyan couplers other than those represented by Formula (I) were used.

Example 2

The samples prepared in Example 1 were exposed for 0.5 second at 40% relative humidity and subjected to color development. Before the color development, the time interval between exposure and immersing into the color developer was varied as shown in Table 2. Each processed sample was subjected to sensitometry to evaluate the sensitivity of the red-sensitive layer S^R and the color balance. The results are shown in Table 2.

In the table, sensitivities are shown by values relative to the sensitivity of each sample when its time interval between exposure and processing is 3 seconds, which is set at 100. Further, the exposing conditions were adjusted in order that a time interval of 3 seconds gives the best color balance (CB) to each sample.

Table 2

Time Interval between Exposure and Color Development (sec)	Sample 101		Sample 102		Sample 103		Sample 104		Sample 105		Sample 106		Sample 107	
	S^R	CB	S^R	CB	S^R	CB	S^R	CB	S^R	CB	S^R	CB	S^R	CB
3	100	A	100	A	100	A	100	A	100	A	100	A	100	A
12	99	C	98	B	93	C	99	A	100	A	99	A	99	B
18	97	C	98	C	91	D	97	A	98	B	97	A	96	B
50	97	D	96	D	90	D	96	B	98	B	97	B	96	B
65	96	D	96	D	89	D	94	B	97	B	94	B	93	B
100	95	D	96	D	87	E	92	B	97	B	94	B	92	B
150	95	D	94	D	86	E	92	B	96	B	94	B	92	B
200	95	E	94	E	86	E	92	C	96	C	93	B	92	D
300	94	E	93	E	86	E	92	D	95	C	93	C	91	D
600	92	E	91	E	86	E	91	D	95	C	93	D	89	D

*The area enclosed with dotted lines is in the scope of the invention. CB: color balance

As apparent from Table 2, samples 101 and 102 using emulsions prepared in the absence of the iridium compound showed large color balance changes attributable to degradation of latent images. Further, sample 103 using a cyan coupler other than that of Formula (I) showed large changes in both initial sensitivity and color balance, though it used an emulsion prepared in the presence of the iridium compound.

On the contrary, samples 104 to 107, which employed the cyan coupler of Formula (I) as well as emulsions prepared in the presence of the iridium compound, were less in color balance change attributable to degradation of latent images, less in sensitivity change and excellent in image quality, as long as these were processed within 3 minutes after exposure. In these samples, both the color balance change and the sensitivity change became smaller as the time interval between exposure and color development became shorter, and remarkably high quality images were obtained when the time interval was within 1 minute, particularly within 15 seconds.

Example 3

Samples 301 to 308 were prepared by changing solution C_2 of the red-sensitive emulsion Em-R in sample 105 of Example 1 as follows:

Sample No.	Red-sensitive Emulsion
301 (invention)	0.01 g of potassium ferrocyanate was added to solution C_2.
302 (invention)	0.005 g of ruthenium(II) chloride was added to solution C_2.
303 (invention)	0.01 g of potassium hexathiocyanatorhenate(II) was added to solution C_2.
304 (invention)	0.02 g of potassium dichromate was added to solution C_2.
305 (comparison)	0.01 g of potassium ferrocyanate was added to solution C.
306 (comparison)	0.005 g of ruthenium(II) chloride was added to solution C.
307 (comparison)	0.01 g of potassium hexathiocyanatorhenate(II) was added to solution C.
308 (comparison)	0.02 g of potassium dichromate was added to solution C.

Each of the samples prepared was evaluated for the moisture-depending sensitivity change of the red-sensitive layer as well as the color balance change, in the same manner as in Example 1.

Sample No.	Metal Dopant	Sensitivity Change	CB change
101 (comparison)		94	D
105 (invention)	Ir	94	A
301 (invention)	Ir + Fe	98	A
302 (invention)	Ir + Ru	96	A
303 (invention)	Ir + Re	97	A
304 (invention)	Ir + Cr	96	A
305 (comparison)	Fe	94	D
306 (comparison)	Ru	92	D
307 (comparison)	Re	92	C
308 (comparison)	Cr	95	D

As apparent from the above results, the absence of the iridium compound in an emulsion preparation did not bring out the effect of the invention, even when other dopants were used. In addition, it can also be seen that the moisture dependency during exposure could be lessened by jointly using the iridium compound and the compound of Va to VIII group metal.

Example 4

Samples 301 to 308 were evaluated for the sensitivity change and the color balance change by comparing the results for a time interval of 3 seconds with those for a time interval of 65 seconds.

Sample No.	Sensitivity Change	CB change
101 (comparison)	96	D
105 (invention)	97	B
301 (invention)	100	A
302 (invention)	99	A
303 (invention)	98	B
304 (invention)	98	B
305 (comparison)	95	D
306 (comparison)	94	D
307 (comparison)	94	D
308 (comparison)	93	D

It is understood from the above results that the absence of the iridium compound in emulsion preparation did not produce the effect of the invention, even when other dopants were used. It is also apparent that the sensitivity change owing to degradation of latent images as well as the color balance change could be lessened by the joint use of the iridium compound and the compound of Va to VIII group metal.

Example 5

Using sample 106 in Example 1, the sensitivity change of the red-sensitive layer as well as the color balance change were evaluated by varying the time interval between exposure and development. The results are shown in Table 3.

Table 3

Time Interval between Exposure and Color Development (sec)	0.002 S^R CB	0.02 S^R CB	0.5 S^R CB	1.5 S^R CB	5 S^R CB	20 S^R CB	40 S^R CB
3	100 A	100 A	100 A	100 A	100 A	100 A	100 A
12	98 A	99 A	99 A	99 A	98 A	98 A	98 B
18	96 A	98 A	97 A	97 A	97 B	98 B	97 B
50	94 B	98 A	97 B	96 B	96 B	96 B	97 B
65	93 B	96 B	94 B	94 B	94 B	94 B	94 B
100	93 B	96 B	94 B	93 B	93 B	93 B	93 B
150	92 B	95 B	94 B	93 B	93 B	93 B	93 B
200	91 C	94 B	93 B	93 B	92 C	93 C	92 C
300	91 C	93 B	93 C	92 C	92 C	92 D	92 D
600	90 D	91 C	93 D	92 D	92 D	92 D	92 D

CB: color balance

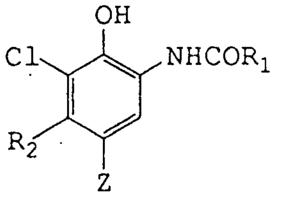
As apparent from Table 3, the effect of the invention was not lost by a prolonged exposure, it was revealed more clearly in sensitivity change, when the exposing time was at least 0.1 second and it was revealed more clearly in color balance, when the exposing time was not more than 30 seconds, especially not more than 2 seconds.

Claims

1. A method for forming color images comprising steps of imagewise exposing a silver halide color light-sensitive material which comprises a support having thereon a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and

   developing said light-sensitive material by means of immersing said light-sensitive material in a color developer,

   wherein at least one of said silver halide emulsion layers comprises silver halide emulsion formed in the presence of iridium compound and at least one of said emulsion layer contains a coupler represented by the following Formula I, and the time interval between completion of the step of exposing said light-sensitive material and the immersion of said light-sensitive material into said color developer is not more than 3 minutes,

   (I)

   wherein R_1 is a ballast group; R_2 is an alkyl group having 2 or more carbon atoms; and Z is a substituent capable of splitting off upon reaction with an oxidation product of a color developing agent.

2. The method of claim 1, wherein said silver halide emulsion formed in the presence of iridium compound comprises silver halide having a silver chloride content of not less than 90 mol%.

3. The method of claim 1 or 2, wherein said silver halide emulsion is formed in the presence of a iridium compound and a compound of vanadium, chromium, manganese, iron, cobalt, nickel, niobium, technetium, ruthenium, rhodium, palladium; tantalum, rhenium, osmium or platinum.

4. The method of claim 1, 2 or 3, wherein said time of interval between completion of exposing step and said immersion is not more than 1 minute.

5. The method of claim 4, wherein said time of interval between completion of exposing step and said immersion is not more than 15 seconds.

6. The method of claims 1 or 2 to 5, wherein a time for imagewise exposure of said light-sensitive material is 0.01 seconds to 30 seconds.

7. The method of claim 6, wherein a time for imagewise exposure of said light-sensitive material is 0.01 seconds to 2 seconds.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 11 3939

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 294 149 (KONICA) * page 7, line 13 - line 17 * * page 8, line 20 - line 57 * * page 41, line 45 - line 63 * ---	1-7	G03C7/30 G03C7/407 G03C5/08 G03C1/09
Y	PHOTOGRAPHIC SCIENCE AND ENGINEERING vol. 5, no. 5, November 1961, WASHINGTON US pages 311 - 312 J.S.GOLDHAMMER 'Rapid Processor for the KA-30 Camera' * the whole document * ---	1-7	
Y	US-A-4 619 889 (YUYAMA ET AL.) * claim 1 * ---	6,7	
Y	US-A-3 854 816 (FUJIMURA) * claim 1 * -----	6,7	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 NOVEMBER 1992	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

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