

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 546 711 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **92310699.1**(51) Int. Cl.⁵: **G03C 1/775, G03C 7/30**(22) Date of filing: **23.11.92**(30) Priority: **11.12.91 JP 327798/91**(43) Date of publication of application:
16.06.93 Bulletin 93/24(84) Designated Contracting States:
DE FR GB NL(71) Applicant: **KONICA CORPORATION**
26-2, Nishi-shinjuku 1-chome Shinjuku-ku
Tokyo(JP)(72) Inventor: **Kadowaki, Takashi, c/o Konica**
Corporation
28 Horinouchi
Odawara-shi, Kanagawa-ken(JP)
Inventor: **Kajiwara, Makoto, c/o Konica**
Corporation
28 Horinouchi
Odawara-shi, Kanagawa-ken(JP)(74) Representative: **Brock, Peter William et al**
UROUHART-DYKES & LORD 91 Wimpole
Street
London W1M 8AH (GB)(54) **Method for forming dye images.**

(57) A photographic dye image forming method is disclosed. The method comprises steps of
imagewise exposing to light a silver halide color light-sensitive material, developing the exposed light-sensitive material with a color developer, in which the light-sensitive material satisfies the following requirements. (1) A surface of the support on which said silver halide emulsion layers to be provided has a roughness of not more than 1.0 μm in terms of arithmetical mean deviation of profile determined. (2) The emulsion layers each contains silver halide grains having a silver chloride content of not less than 90 mol%. (3) In the green-sensitive emulsion layer the ratio of oil component to a hydrophilic binder each contained in the green-sensitive is not less than 0.8 by weight. (4) The developing step is carried out with a color developer containing a color developing agent in an amount of not less than 1.8×10^{-2} mol/1000 ml for a time of not less than 70 seconds. Images with high sharpness and high glossiness can be easily obtained by the method.

EP 0 546 711 A1

FIELD OF THE INVENTION

The present invention relates to a method for forming dye images, more particularly, to a method for forming images capable of producing easily color prints excellent in sharpness and glossiness.

BACKGROUND OF THE INVENTION

Though a silver halide color photographic light-sensitive material (hereinafter, referred to simply as "a light-sensitive material") has a particularly excellent image quality and sensitivity, further improvement in image quality is demanded. Important factors on the above-mentioned image quality include color reproducibility capable of reproducing original colors faithfully and sharply and sharpness influencing on sharpness and cubic effect of image.

For improving color reproducibility, it is necessary to gather extremely many factors. Of them, spectral sensitivity of light-sensitive material for printing use is important. In this sense, since silver chloride has no absorption in visible region in high silver chloride color paper, its inherent sensitivity does not deteriorate separation on red light sensitivity, green light sensitivity and blue light sensitivity. Therefore, it is extremely advantageous for improving color reproducibility because so-called color mixing is not caused.

The high silver chloride color paper is normally used in combination with rapid type processing solutions and an automatic developer in order to actuate characteristics of rapid processing property. In this case, though it can conduct rapid processing, processing solutions and an automatic developing equipment must be renewed. Therefore, labor and expenses therefor becomes necessary. Against it, many attempts have been tried for obtaining a characteristic that the color reproducibility of high silver chloride color paper is superior employing an existing automatic developing machine. However, color mixture phenomenon took place, deteriorating color reproducibility remarkably. Therefore, it was far from putting into practice.

On the other hand, makers have been requested to supply users light-sensitive materials at a cheaper price. Therefore, improvement in productivity of light-sensitive material has been demanded. In order to increase productivity of light-sensitive material, manufacturers have been conducting various improvement. Of them, increasing speed for coating photographic composition layers including silver halide emulsion layers on a support, i.e., coating speed, has been desired, because increasing coating speed directly results in improvement in productivity.

However, it is difficult to coat coating layer in a high speed uniformly and without any defect. Streak defect and unevenness of coated layer are liable to occur, preventing coating in a high speed.

Recently, demand for a large-sized print has been increased. Therefore, even fine coating defect causes a serious quality problem because it is conspicuous in a large-sized print. It has been known that the above-mentioned coating property is influenced noticeably by the component of silver halide emulsion coating solution and the quality of coated support. In addition, a light-sensitive material employing a high silver chloride emulsion is easy to cause unevenness after development processing. Therefore, overall improvement has been requested.

Under the above-mentioned status, glossiness is an extremely important property among the image quality of color print. As a support, a base paper having high smoothness is preferable. The improvement in this base paper has been described in Japanese Patent Publication Open to Public Inspection (hereinafter, referred to as "Japanese Patent O.P.I. Publication") Nos. 234281/1988, 83066/1990, 93640/1990, 97942/1990, 216139/1990 and 281251/1990.

However, it turned out that coating unevenness is easy to occur at the beginning of coating when a base paper having high smoothness is used. Various investigations have been conducted for improving coating unevenness. As a result, it turned out that coating unevenness is remarkably improved when the proportion of oil to a hydrophilic binder in a green sensitive silver halide emulsion layer is reduced to 0.8 or less.

However, when applying the above-mentioned method, variation of photographic property depending upon the variation of the pH of color development processor is extremely large, causing practical problems.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a method for forming dye images capable of producing easily color print excellent in print glossiness.

The above-mentioned object of the invention is attained by a method for forming a photographic dye image comprising steps of

imagewise exposing to light a silver halide color light-sensitive material comprising a paper support,

and photographic component layers including a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer provided on the support in this order from the support,

developing the exposed light-sensitive material with a color developer,

wherein a surface of the support on which said silver halide emulsion layers to be provided has a roughness of not more than $1.0\ \mu\text{m}$ in terms of arithmetical mean deviation of profile SR_A determined by the following equation;

the emulsion layers each contains silver halide grains having a silver chloride content of not less than 90 mol%;

in the green-sensitive emulsion layer the ratio of oil component to a hydrophilic binder each contained in the green-sensitive is not less than 0.8 by weight; and

the developing step is carried out with a color developer containing a color developing agent in an amount of not less than 1.8×10^{-2} mol/1000 ml for a time of not less than 70 seconds;

$$SR_A = \frac{1}{S_A} \int_0^{L_x} \int_0^{L_y} |f(x, y)| \, dx \, dy$$

in the above equation, L_x is the length of measured area in the direction of X axis, L_y is the length of measured area in the direction of Y axis, S_A is the measured area in which $L_x = L_y = 5\ \text{mm}$ and $S_A = L_x \times L_y = 25\ \text{mm}^2$.

The above arithmetical mean deviation of the profile SR_A can be determined by, for example, roughness measuring apparatus SE-3AK manufactured by Kosaka Research Laboratory.

As a material of the raw paper relating to the invention, (KBKP), a sulfite bleached hardwood pulp (LBKP), an alkaline sulfite bleached hardwood pulp (NBSP) and an alkaline sulfite bleached hardwood pulp (LBSP) can be used solely or in combination. When the pulps are used in combination, mixing ratio of broad leaf-tree pulp to needle leaf-tree pulp is preferably 95/5 to 60/40 by weight. Furthermore, a straw pulp, esparto pulp or bamboo pulp may be combine with the above natural pulps if necessary.

The thickness of raw paper is selected depending upon its purpose and application. Ones having a base weight of 50 to 250 g/m² are conventionally employed.

It is preferable to add the following addenda to the raw paper to raise the strength thereof. As a sizing agent, for example, an fatty acid, rosin, maleated rosin, alkenyl-substituted succinate, alkyl- substituted succinate and polysaccharide are cited. The sizing agent is preferably added to the raw paper in an amount of 0.2 to 2% by weight of the pulp used.

As a dry paper strength increasing agent, a cationized starch, a cationized polyacrylamide, an anionized polyacrylamide and a calboxy-modified polyvinyl alcohol are employed.

In addition, as a wet paper strength increasing agent, a melamine resin, an urea resin and an epoxy polyamide resin are employed.

In addition, as a stabilizer, multi-value metal salts such as aluminium sulfate and aluminum chloride and cation polymers such as cationized starch are employed.

White pigment such as clay, talc, calcium carbonate, titanium oxide and barium sulfate may be contained, if necessary.

Generally, surface of the raw paper is subjected to tub-sizing or press-sizing with a solution containing a water-soluble high molecular addenda. For example, as water-soluble polymers, cationized starch, polyvinyl alcohol, carboxy-modified polyvinyl alcohol, carboxymethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, polyacrylamide and gelatin are employed.

As inorganic electrolytes, sodium chloride and sodium sulfate are employed. As moisture-absorption substances, glycerin and polyethylene glycol are employed. As pH adjusting agents, hydrochloric acid, sodium hydroxide and sodium carbonate are employed. In addition, dyes, fluorescent brightening agents, anti-static agents and foam-extinguishers are employed in combination.

A support in the present invention is laminated with polyolefin resin on both surfaces of raw paper obtained in the above method.

The above-mentioned polyolefin resin includes for example, homo-polymers of α -olefin such as polyethylene and polypropylene and mixtures of each polymer. The practically preferable polyolefins are high density polyethylene, low density polyethylene or mixtures thereof. Though there is no limitation to the molecular weight of the above-mentioned polyolefin, polyolefins having 20,000 to 200,000 molecular weight

are employed. There is no limitation in the thickness of polyolefin resin laminated layer. Normally, it is about 15 to 50 μm .

As white pigments used in a polyolefin resin laminated layer in the present invention, titanium oxide including anatase type and rutile type, barium sulfate, zinc oxide, calcium carbonate, aluminiumoxide, magnesium oxide and talc are employed. Titanium oxide is particularly preferable.

Titanium oxide may or may not be subjected to surface treatment with aluminum oxide, alcohol and surfactants. The above-mentioned white pigments are contained, on a basis of 13 to 20 weight% and preferably 15 to 18 weight% against a polyolefin resin, in the polyolefin resin laminated layer on the side of the reflective support or raw paper on which photographic emulsions to be coated.

The arithmetic mean deviation of profile SRa of the support in the present invention is not more than 1.0 μm and preferably 0.05 to 0.09 μm . In order to prepare a support having SRa of not more than 1.0 μm , methods (1) to make a laminated resin layer more thick, (2) to augment depressing pressure at the time of laminating resin layer, (3) to augment calendering pressure of machine in order to improve flatness of base paper, (4) to adjust the fiber length, die porosity, the average fiber width and the average fiber thickness of pulp forming a raw paper and (5) to employ an one side grossed paper prepared by superposing one surface of raw paper under a heating mirror surface drier are employed independently or in combination.

Silver halide grains in the present invention have silver chloride content of 90 mol% or more, silver bromide content of 10 mol% or less and silver iodide content of 0.5 mol% or less. It is more preferable to be silver chlorobromide having silver bromide content of 0.1 to 1 mol%.

The silver halide grains in the present invention may be used independently or used in combination with other silver halide grains having different composition. In addition, they may be used in combination with silver halide grains having silver chloride content ratio of less than 90 mol%.

In addition, in silver halide emulsion layers containing silver halide grains having silver chloride content ratio of 90 mol% or more, the proportion of silver halide grains having silver chloride content ratio of 90 mol% or more among the total silver halide grains contained in said emulsion layers is 60 weight% or more, or preferably 80 weight% or more.

The composition of silver halide grains in the present invention may be uniform throughout from the inside of grains to the outside thereof, or may be different between the inside of a grain and the outside of a grain. In addition, when the composition of the inside of the grains and the outside of the grains are different, the composition may change continuously or discretely.

Though there is no limitation in the grain size of silver halide grains in the present invention, it is preferably in the range of 0.2 to 1.6 μm and more preferably in the range of 0.25 to 1.2 μm considering other photographic properties such as rapid processability and sensitivity. The above-mentioned grain size can be measured by various methods normally employed in the relevant technological field.

In the present invention, the variation coefficient of the distribution of grain size of silver halide grains is preferably 0.22 or less, and more preferably 0.15 or less. They are mono-dispersed silver halide grains. Here, the variation coefficient means a coefficient indicating the variance of the distribution of grain size, and is represented by "Variation coefficient = (Standard deviation of the distribution of grain size)/(Average grain size).

Silver halide grains used for the emulsions in the present invention may be prepared by either of the acidic process, the neutral process or the ammoniacal process. Said grains may be grown successively or they may be grown after preparing seed grains. A method to prepare a seed grain and a method to grow may be the same or different.

In addition, as a method for reacting soluble silver salt and soluble silver halide, a normal precipitation method, a reverse precipitation method, a double jet method or combination thereof may be employed. It is preferable to employ a double jet method. In addition, as one kind of a double jet method, a pAg-controlled-double jet method disclosed in Japanese Patent O.P.I. Publication No. 48521/1979 can be employed. In addition, silver halide solvent such as thioethel may be used, if necessary.

Arbitrary form of silver halide grains can be employed. A preferable example is a cube having (100) plane as a crystal plane. In addition, it is allowed to prepare grains having a shape of octahedron, tetradecahedron or dodecahedron to employ. In addition, grains having twinned plane may be employed.

Silver halide grains in the present invention may be of a single form or a mixture of grains of various forms.

To the silver halide grain used in the present invention, metal ions may be added and contained inside and/or on the surface of the grain, employing cadmium salt, zinc salt, lead salt, thallium salt, illidium salt including complex salts thereof, rhodium salt including complex salts thereof and iron salt including complex salts thereof in the course of forming and/or growing grains. In addition, by placing grains under a reducing atmosphere, reduction sensitization nucleus can be provided inside the grain and/or the surface of

the grain.

With regard to emulsions containing silver halide grains in the present invention (hereinafter, referred to as "emulsion in the present invention"), unnecessary soluble salts may be removed after the growth of silver halide grains, or they may be kept contained.

The silver halide grain used for the emulsion in the present invention may be one wherein latent images are formed on the surface thereof mainly, or may be one wherein latent images are formed inside the grain. It is preferable to be the grain wherein latent images are formed on the surface thereof mainly.

The emulsions in the present invention are chemically sensitized employing a conventional method. Namely, a sulfur sensitization method employing compounds containing sulfur which can react with silver ions or active gelatin, a selenium sensitization method employing selenium compounds and a noble metal sensitization method employing gold and other noble metals can be used singly or in combination.

Silver halide grains in the present invention are preferable to contain gold compounds. Gold compounds preferably used for the present invention include various ones having an oxidation number of gold of + 1 or + 3. As typical examples, chloraurate, potassium chloraurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate, pyridyl trichloro gold, gold sulfide and gold selenide are cited.

Gold compounds may be used so that silver halide grains are sensitized, or may be used so that they do not substantially contribute to sensitization.

Added amount of gold varies depending upon various conditions. It is normally 10^{-8} to 10^{-1} mol and preferably 10^{-7} to 10^{-2} mol per mol of silver. The adding time of the above-mentioned compounds may be in either one of the steps of forming silver halide grains, physical ripening, chemical ripening, and after chemical ripening.

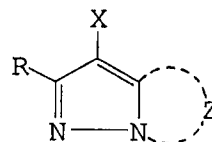
The emulsion in the present invention can be spectrally sensitized to desired wavelength region employing dyes known as sensitizing dyes in the field of photographic industry. Sensitizing dyes may be used independently, or 2 or more of them may be used in combination. Together with sensitization dyes, dyes not having spectral sensitization effect in itself and a super sensitizer which does not substantially absorb visible light and which strengthen sensitization effect of sensitization dye may be contained in an emulsion.

A color light-sensitive material in the present invention is formed by coating a blue sensitive silver halide emulsion layer containing a yellow dye forming coupler mainly, a green sensitive silver halide emulsion layer containing a magenta dye forming coupler and a red sensitive silver halide emulsion layer containing a cyan dye forming coupler in this order from the support.

Recently, coating thin layer uniformly and in a high speed without coating defect such as coating unevenness has been requested. As a coating method, a successive simultaneous multi-layer coating method employing a slide hopper apparatus is employed generally.

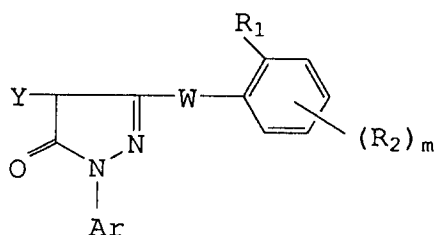
In the present invention, as a magenta dye forming coupler contained in a green sensitive silver halide emulsion layer, couplers illustrated by the following formulas M-I and M-II. can be employed.

Formula M-I



wherein Z represent a nonmetal atom group necessary for forming a nitrogen-containing heterocycle; rings formed by said Z may form a substituent; X represents a hydrogen atom or a group capable of being split off upon reaction with an oxidation product of color developer; R represents a hydrogen atom or a substituent.

Formula M-II



wherein Ar represents an aryl group; R_1 represents a hydrogen atom or a substituent; R_2 represents a substituent; Y represents a hydrogen atom or a group capable of being split off upon reaction with an oxidation product of color developer; W represents -NH-, -NHCO- which is linked with the carbon atom to the pyrazolone nucleus or -NHCONH-; m represents an integer of 1 or 2.

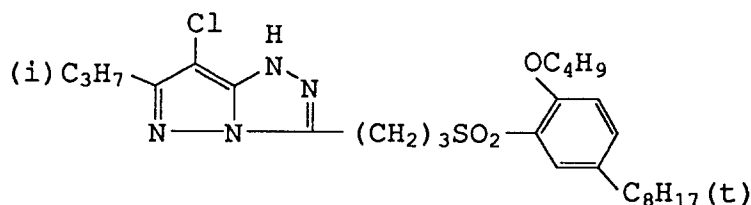
Of the above-mentioned magenta dye forming couplers, the particularly preferable coupler is one represented by formula M-I.

In a formula M-I, there is no limitation in a substituent represented by R. Typically, an alkyl group, an aryl group, an anilino group, an acylamino group, a sulfonamide group, an alkylthio group, an arylthio group, an alkenyl group and a cycloalkyl group are cited. In addition, halogen atoms, a cycloalkenyl group, an alkynyl group, a heterocycle, a sulfonyl group, a sulfinyl group, a phosphonyl group, an acyl group, a carbamoyl group, a sulfamoyl group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a siloxy group, an acyloxy group, a carbamoyloxy group, an amino group, an alkylamino group, an imido group, an ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic thio group, spiro compound residues and bridge-having hydrocarbon compound residues are cited.

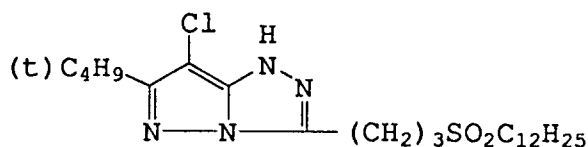
Preferable range and practical examples of substituent represented by R, groups capable of being split off through a reaction with an oxidation product of a color developer represented by X, a nitrogen-containing ring formed by Z and substituents which may be included by a ring formed by Z and preferable examples of magenta couplers represented by formula M-I are the same as those described in the line 23 of page 5 to the line 52 of page 8 of European Patent Publication EP-A-0327272.

Hereunder, we will illustrate typical examples of magenta couplers represented by formula M-I.

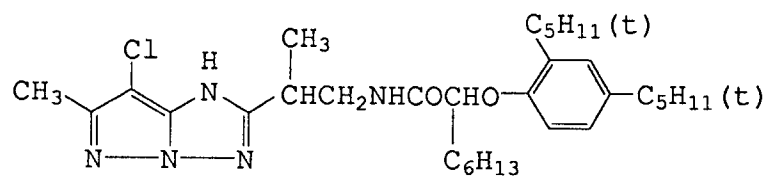
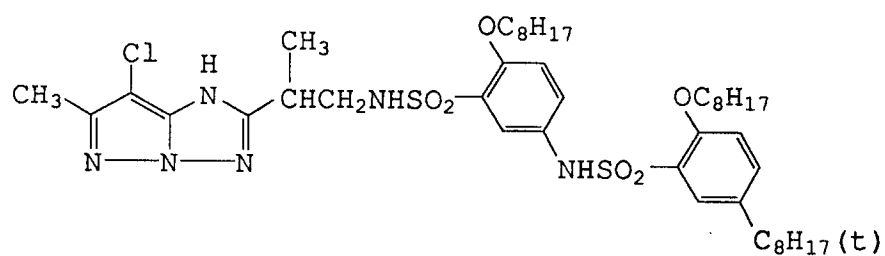
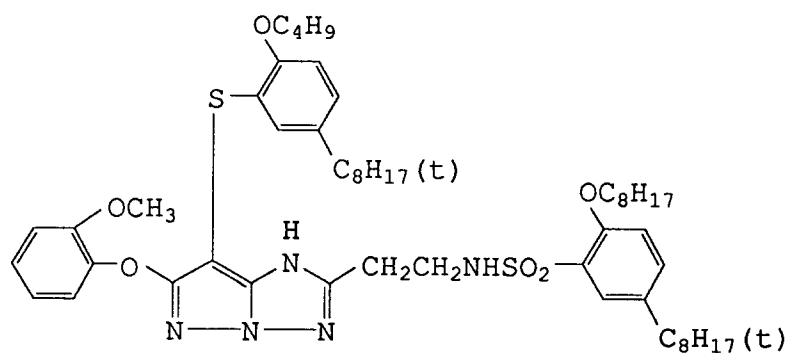
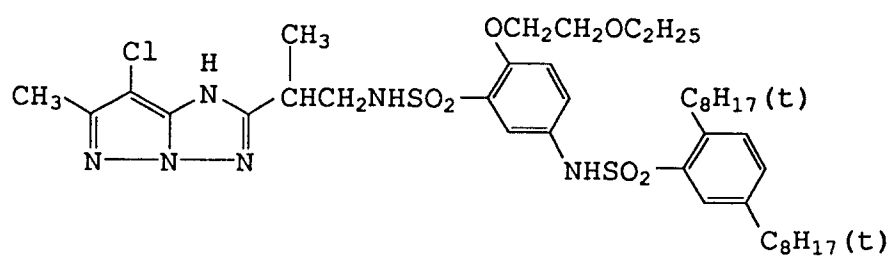
M-1

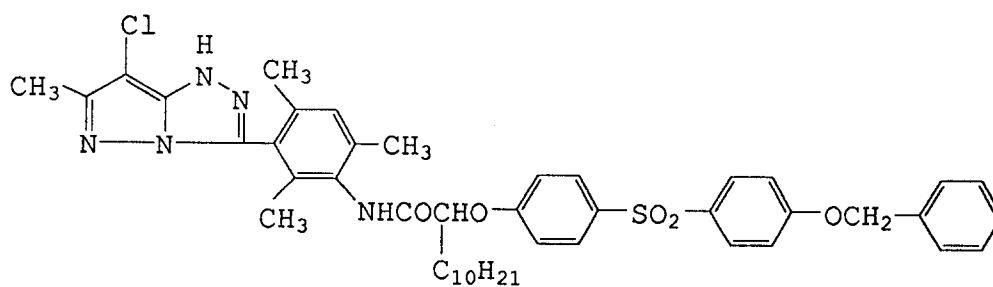


M-2

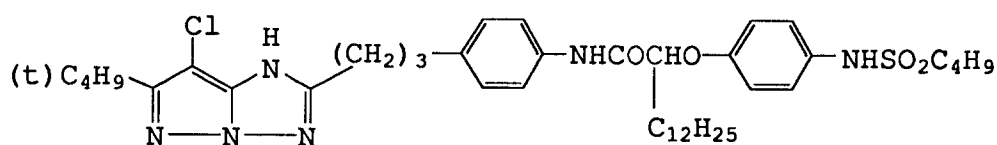


M-3

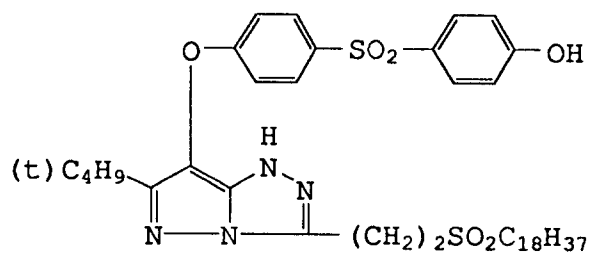




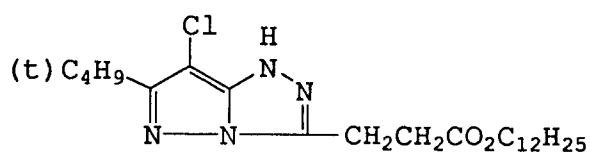
M-8



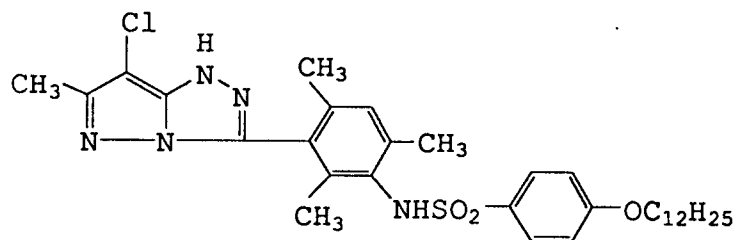
M-9



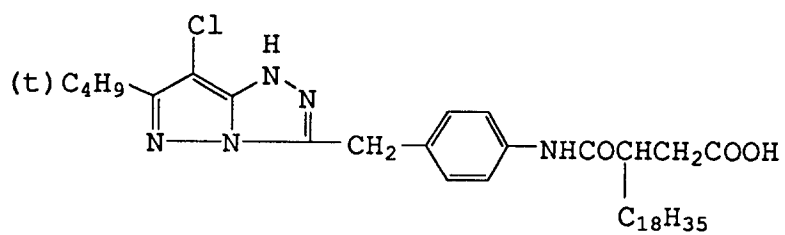
M-10



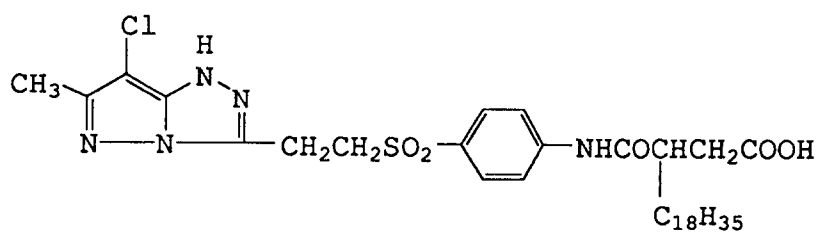
M-11



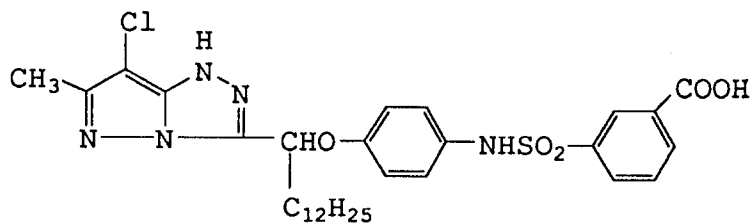
M-12



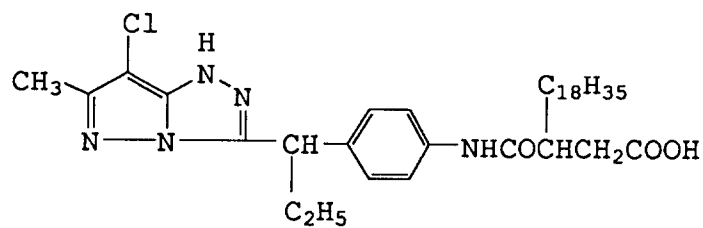
M-13



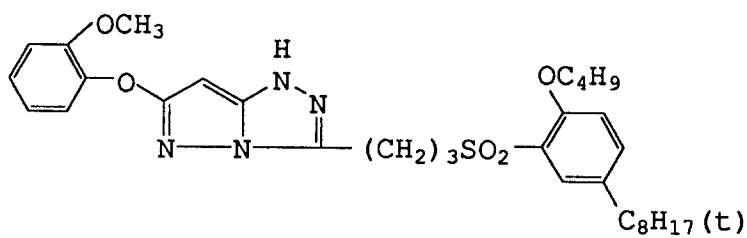
M-14



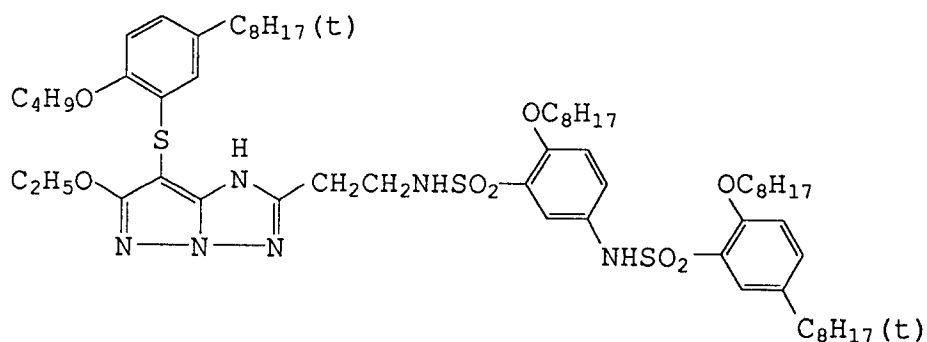
M-15



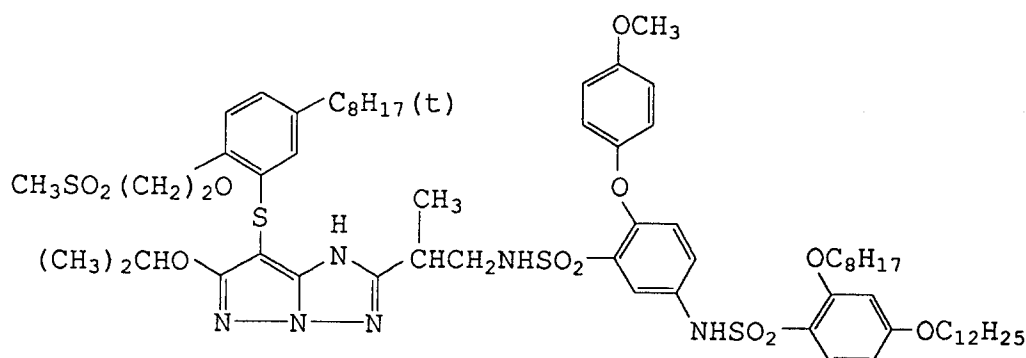
M-16



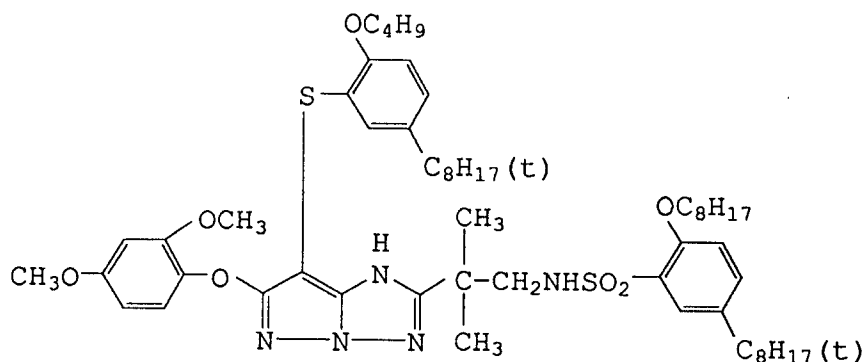
M-17



M-18



M-19



45 In addition, as other examples, compounds M-1 to M-61 described in pp. 6 to 21 of European Patent Publication EP-A-0273712 and those other than the above-mentioned typical examples among compounds 1 to 223 described in pp. 36 to 92 of European Patent Publication EP-A-0235913.

In addition, the above-mentioned couplers can be synthesized in reference to Journal of the Chemical Society, Perkin I(1977), 2047 to 2052, U.S. Patent No. 3,725,067 and Japanese Patent O.P.I. Publication Nos. 99437/1984, 42045/1983, 162548/1984, 171956/1984, 33552/1985, 43659/1985, 172982/1985, 190779/1985, 209457/1987 and 307453/1988.

The above-mentioned couplers can be used in combination with other kinds of magenta couplers. Normally, they can be employed in the range of 1×10^{-3} mol to 1 mol and preferably 1×10^{-2} mol to 8×10^{-1} mol per mol of silver halide.

As a color mixing preventing agent mainly used for a green sensitive silver halide emulsion layer in the present invention, various compounds can be employed. For example, illustrated compounds I-1 to I-32 described on pp.291 to 292 and illustrated compounds II-1 to II-18 described in page 293, of Japanese

Patent Publication Open to Public Inspection No. 66541/1990, illustrated compounds II-1 to II-30 described in pp. 605 to 606 in Japanese Patent O.P.I. Publication No. 309058/1989, illustrated compounds IIIa-1 to IIIa-15 and IIIb-1 to IIIb-12 described on pp. 387 to 388 and illustrated compounds A-1 to A-35 described on pp. 428 to 429 and illustrated compounds PH-1 to PH-20 described on pp. 430 to 431 in Japanese Patent Publication O.P.I. Publication No. 90445/1989 may be used.

As a hydrophilic binder used for color light-sensitive materials in the present invention, gelatin is useful. In addition, gelatin derivative, graft polymer of gelatin and other polymers, other proteins, sugar derivatives, cellulose derivatives and hydrophilic colloid such as synthetic hydrophilic polymer substances including homopolymers and copolymers.

It is especially preferable that the total weight of hydrophilic binder is 7.8 g/m² or less, more preferably 7.0 to 7.8 g/m².

As addition methods of photographically effective hydrophobic compounds useful such as the above-mentioned dye-forming couplers and image stabilizers to the light-sensitive materials, various methods such as a solid dispersion method, a latex dispersion method, an oil-in-water emulsification dispersion method can be employed. They can be selected appropriately depending upon chemical structure of hydrophobic compounds and so on.

The ratio by weight between an oil-phase component such as a useful hydrophobic compound useful contained in the green-sensitive silver halide emulsion layer in the present invention and a high boiling solvent dissolving thereof and the hydrophilic binder (hereinafter, called "O/B") is 0.8 or less. It is preferably 0.5 to 0.7.

Various compounds can be employed as a high boiling organic solvent used in the present invention. For example, illustrated compounds II-1 to II-9 and III-1 to III-6 described on page 503 in Japanese Patent O.P.I. Publication No. 103245/1988, illustrated compounds H-1 to H-22 described on pp. 528 to 529 in Japanese Patent O.P.I. Publication No. 196048/1989 and illustrated compounds II-1 to II-38 described on pp. 410 to 412 in Japanese Patent O.P.I. Publication No. 66646/1989 are cited.

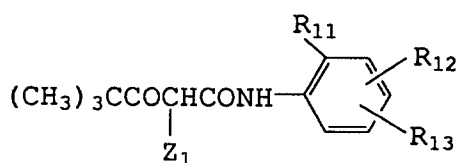
An oil-phase component contained in the present invention means as follows:

Normally, the oil-phase component exists in the form of oil drop in photographic constituting layers. When hydrophobic compounds such as a dye forming coupler, an image stabilizer, a color-mixture preventing agent and a UV absorber are contained in the drop, the total weight of oil drops means a weight totalling the weights of organic solvents and the above-mentioned hydrophobic compounds entirely. In addition, when other kind of oil-drops such as oil drops composed of merely an organic solvent without hydrophobic compound, oil drops containing different hydrophobic compounds and drops of a hydrophobic compounds such as a UV absorber oily at room temperature without being dissolved in an organic solvent are exist, the total weight of entire oil drops mean the total weight of oil phase components in the invention.

As a cyan dye forming coupler used in the present invention, a phenol type, naphthol type or an imidazole type 4-equivalent or 2-equivalent cyan forming couplers are cited. Of them, a 2-acylamino-5-alkylphenol type compound and a 2,5-diacylaminophenol type compound are preferable.

As yellow dye forming couplers, conventional acylacetoanilide type couplers can preferably be employed. Of them, a benzoylacetoanilide type and a pivaloylacetoanilide compound are advantageous. Of them, a pivaloylacetoanilide compound represented by the following Formula Y-I is preferable.

Formula Y-I



wherein R₁₁ represents a halogen atom or an alkoxy group; R₁₂ represents a hydrogen atom, a halogen atom or an alkoxy group which may have a substituent; R₁₃ represents an acylamino group, an alkoxycarbonyl group, an alkylsulfamoyl group, an arylsulfamoyl group, an arylsulfonamido group, an alkylureido group, an arylureido group, a succinimido group, an alkoxy group or an aryloxy group, the above groups may have a substituent; Z₁ represents a group capable of being split off upon coupling reaction with an oxidation product of color developing agent.

In the color light-sensitive materials in the present invention, various conventional additives for photographic use can be contained. Practically, UV absorbers, i.e., benzophenones and benzotriazoles type compound, anti-stain agents, i.e., hydroquinone derivatives, surfactant, i.e., sodium alkylnaphthalenesulfonate, sodium alkylbenzenesulfonate, alkyl sodium sulfosuccinate and polyalkylene glycol, water-soluble anti-irradiation dyes, i.e., an azo type, a styryl type, a triphenylmethane type, an oxonol type and an antraquinone type compound, hardeners, i.e., a halogen-s-triazine type, a vinylsulfon type, an acryloil type, an ethyleneimine type, an N-methylol type and an epoxy type compound and water-soluble aluminum salt, improvers for physical properties of layer, i.e., glycelin, aliphatic multi-value alcohol, polymer dispersants or latex, solid or liquid parafin and colloidal silica, brightening agents, i.e., diaminostylbene type compound and various oil-soluble dyes can be cited.

As photographic layers constituting the color light-sensitive material in the present invention, in addition to each emulsion layer, subbing layers, intermediate layers, yellow filter layers, UV absorbing layers, protective layers and anti-halation layers can be provided appropriately, if necessary.

Color developing agents used for the color developer in the present invention include conventional ones used for various color photography processing widely. The above-mentioned developing agents include aminophenol derivatives and p-phenylenediamine derivatives. Since the above-mentioned compounds are more stable than free state, they are normally employed in the form of salt such as hydrochlorate and sulfate. In addition, the above-mentioned compounds are preferably employed in the concentration of 1.8×10^{-2} or more and more preferably 2×10^{-2} to 1×10^{-1} mol per 1000 ml of color developer.

As 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 primary aromatic amine type color developing agents are N,N-dialkyl-p-phenylenediamine type compounds. Their alkyl group and phenyl group may be substituted with arbitrary substituents. Of them, as especially useful compounds, N-methyl-p-phenylenediamine hydrochloride, N,N-dimethyl-p-phenylenediamine hydrochloride, N,N-dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-(N-ethyl-N-dodecylamino)toluene, N-ethyl-N- β -methanesulfonamidoethyl-3-ethyl-4-aminoaniline sulfate, N-ethyl-N- β -hydroxyethylaminoaniline, 4-amino-3-methyl-N,N-diethylaniline and 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluene sulfonate are cited.

To developers, applied to processing of the color light-sensitive materials in the present invention, conventional developer-component compounds can be added in addition to the above-mentioned developing agent. For example, alkali agents such as sodium hydroxide and potassium carbonate, alkali metal sulfite, alkali metal bi sulfite, alkali metal thiocyanate, alkali metal halide compounds, benzyl alcohol, water-softening agents and thickeners can be contained arbitrarily. The temperature of development may be 15 °C or more, normally 20 to 50 °C, preferably 30 to 45 °C. The developing time is preferably 70 seconds or more, more preferably 70 to 210 seconds, most preferably 90 to 150 seconds.

The pH value of developer is normally 7 or more, and most normally about 10 to about 13.

As the above-mentioned color developers for high silver chloride light-sensitive material, Process CPK-20QA (produced by Konica) and Process RA-4 (produced by Eastman Kodak) available in the market are cited. In the present invention, they can be employed as they are. However, it is preferable to employ them after reducing the activity of developer slightly. Therefore, it is preferable to employ them after reducing the temperature of developer and enhancing the concentration of halide compounds.

Color light-sensitive materials in the present invention are subjected to bleaching processing and fixing processing after color developing. Bleaching may be conducted concurrently with fixing processing.

As bleachers, many kinds of compounds are employed. Of them, polyvalent metal compounds such as iron (III), cobalt (III) and copper (II), especially metal complex salts of polyvalent metal cation with organic acids including aminopolycarbonic acid such as ethylenediaminetetraacetic acid, nitrilotriacetic acid, N-hydroxyethylethylenediaminediacetic acid and aminopolycarbonic acid, malonic acid, tartaric acid, malic acid, diglycolic acid, dithioglycolic acid, ferricyanate and heavy chromate are employed singly or in combination.

As fixing agents, soluble complexing agents wherein silver halide is dissolved as a complex salt are employed. As the above-mentioned soluble complexing agents, for example, sodium thiosulfate, ammonium thiosulfate, potassium thiocyanate, thiourea and thioether are cited.

After fixing processing, washing step is normally conducted. In addition, in place of washing step, stabilizing step may be conducted and both may be employed in combination. To a stabilizer employed in the stabilizing step, a pH adjusting agent, a chelate agent and an antimold agents can be contained. Japanese Patent O.P.I. Publication No. 134636/1983 can be helpful for practical conditions thereof.

EXAMPLE

Example 1

To prepare a raw material of paper, 20% of dry weight of NBSP and 80% by dry weight of LBSP were each beaten by 250 ml and 280 ml in terms of Canadian Standard Freeness by a refiner, respectively.

Additives for paper making was employed in the following amount against the absolute dry weight of pulp.

Cationized starch	2.0%
Alkylketenedimer resin	0.4%
Anionic polyacrylamido resin	0.1%
Polyamidopolyamineepichlorohydrin resin	0.7%
Sodium hydroxide	Adjusted to pH 7.5

The above materials of paper were made to paper by a Fort-linear paper machine after addition of the above listed addenda. The paper was subjected to press-sizing and machine calendering. As a press-sizing solution, a solution containing 3.3% by weight of a carboxyl-modified PVA and 1.7% by weight of sodium chloride was used. The solution was coated on both surfaces of the paper by 2.2 g/m². Four kinds of raw papers were prepared having a basic weight of 170 g/m², a bulk density of 1.0 and a moisture of 8%. The surface roughness SRa of the each raw papers were adjusted by controlling the pressure for machine calendering to 1.2, 0.85, 0.6 or 0.4.

Both surfaces of the raw paper were subjected to corona discharge. On the surface thereof, a layer laminated with polyolefin resin having the thickness of 35 μ m composed of high-density polyethylene (specific gravity of 0.94 and MI=6.8) containing 15% by weight of anatase type titanium dioxide, by means of an extrusion coating method. On rear surface thereof, by means of an extrusion coating method, a layer laminated with polyethylene resin was formed. The prepared laminated-layer was pressed on a cleaning roll having a smooth surface at 20 °C. Thus, a support for photographic paper shown in Table 1 was prepared.

Table 1

Sample No.	Support SRa (μ m)	Green-sensitive emulsion layer				Color developing condition	
		Magenta* Coupler	Silver* halide	Gelatin	O/G	Processing condition	Color developer
1(Comparative)	1.20	M-2 0.23	0.17	1.60	0.68	B	2
2(Comparative)	0.85	M-2 0.23	0.17	1.00	1.09	B	2
3(Comparative)	0.85	M-2 0.23	0.17	1.60	0.68	A	1
4(Comparative)	0.85	M-2 0.23	0.17	1.60	0.68	A	2
5(Comparative)	0.85	M-2 0.23	0.17	1.60	0.68	B	1
6(Invention)	0.85	M-2 0.23	0.17	1.60	0.68	B	2
7(Invention)	0.60	M-2 0.23	0.17	1.60	0.68	B	2
8(Invention)	0.40	M-2 0.23	0.17	1.60	0.68	B	2
9(Invention)	0.85	M-a 0.23	0.30	1.60	0.68	B	2
10(Invention)	0.85	M-a 0.23	0.30	1.60	0.68	C	2
11(Invention)	0.85	M-a 0.23	0.30	1.60	0.68	D	2
12(Invention)	0.85	M-2 0.23	0.17	1.40	0.77	B	2
13(Invention)	0.85	M-2 0.23	0.17	2.18	0.55	B	2
14(Invention)	0.85	M-2 0.23	0.17	2.42	0.45	B	2
15(Invention)	0.85	M-2 0.23	0.17	1.60	0.68	C	2
16(Invention)	0.85	M-2 0.23	0.17	1.60	0.68	D	2

* Added amounts in each case are shown by g/m².

On a support thus prepared, each layer having compositions as shown in Tables 2 and 3 were coated by means of a continuous simultaneous multi-layer coating method employing a slide hopper. Thus, multi-

layer silver halide color photographic light-sensitive materials were prepared. The coating solutions were prepared as follows:

Coating solution for the first layer

To 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 an additive (HQ-1) and 6.67 g of high boiling organic solvent (DNP), 60 ml of ethyl acetate was added to be dissolved. The solution was dispersed into 220 ml of 10% aqueous gelatin solution containing 7 ml of 20% surfactant (SU-1) employing a supersonic homogenizer. Thus, a dispersion of yellow coupler was prepared.

The above-mentioned dispersion was mixed with a blue sensitive silver halide emulsion containing 10 g of silver prepared under the conditions mentioned later. Thus, the coating solution for the first layer was prepared.

The coating solutions for the second and fourth layers to the seventh layer were prepared in the similar manner to the coating solution for the first layer.

As hardeners, (H-1) was added to the second layer and (H-2) was added to the seventh layer. As coating aids, surfactants (SU-2) and (SU-3) were added for adjusting surface tension.

Table 2

Layer	Constitution	Added amount (g/m ²)
Seventh layer (Protective layer)	Gelatin Anti-stain agent (HQ-2) Anti-stain agent (HQ-3) Anti-stain agent (HQ-4) Anti-stain agent (HQ-5) DIDP Antimold agent (F-1)	1.20 0.002 0.002 0.004 0.02 0.01 0.002
Sixth layer (UV absorber)	Gelatin UV absorber (UV-1) UV absorber (UV-2) UV absorber (UV-3) Anti-stain agent (HQ-5) DNP PVP Anti-irradiation dye (AI-2) Anti-irradiation dye (AI-4)	0.60 0.10 0.04 0.16 0.04 0.45 0.03 0.02 0.01
Fifth layer (Red sensitive layer)	Gelatin Red sensitive silver chlorobromide emulsion (Em-R) Cyan coupler (C-1) Cyan coupler (C-2) Dye image stabilizer (ST-1) Anti-stain agent (HQ-1) HBS-1 DOP	0.30 0.21 0.17 0.25 0.20 0.01 0.40 0.40

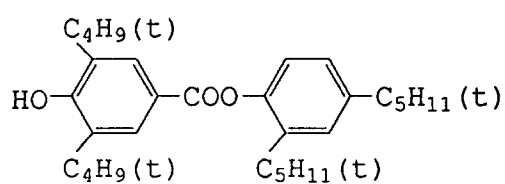
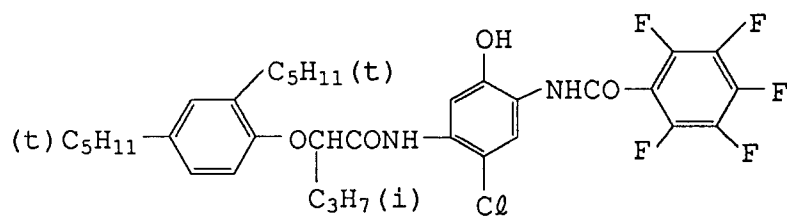
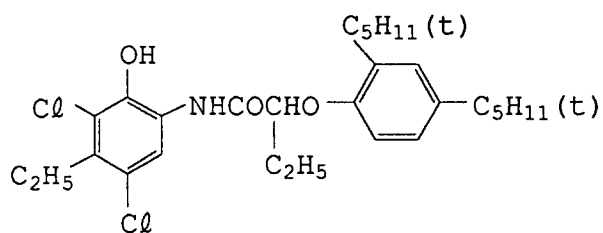
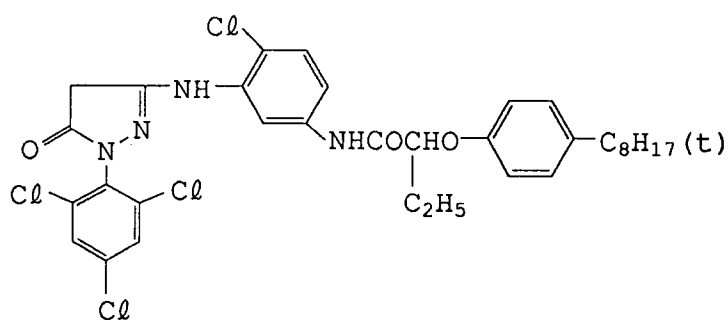
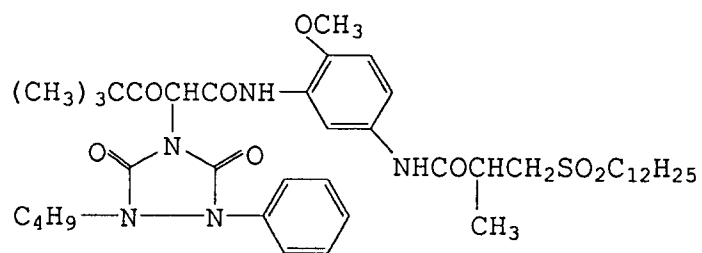
Table 3

Layer	Constitution	Added amount (g/m ²)
Fourth layer (UV absorber)	Gelatin UV absorber (UV-1) UV absorber (UV-2) UV absorber (UV-3) Anti-stain agent (HQ-5) DNP	1.10 0.28 0.09 0.38 0.10 0.80
Third layer (Green sensitive layer)	Gelatin Green sensitive silver chlorobromide emulsion (Em-G) Magenta coupler (Table 1) Dye image stabilizer (ST-3) Dye image stabilizer (ST-4) DIDP DBP Anti-irradiation dye (AI-1)	Table 1 Table 1 Table 1 0.20 0.17 0.13 0.15 0.01
Second layer (Intermediate layer)	Gelatin Anti-stain agent (HQ-2) Anti-stain agent (HQ-3) Anti-stain agent (HQ-4) Anti-stain agent (HQ-5) DIDP Antimold agent (F-1)	1.30 0.03 0.03 0.05 0.23 0.20 0.002
First 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) Anti-stain agent (HQ-1) Anti-irradiation dye (AI-3) DNP	1.20 0.26 0.80 0.30 0.20 0.02 0.01 0.40
Support	Paper laminated with polyethylene	
Added amount of silver halide emulsion was shown in terms of silver.		

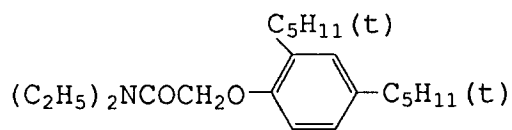
Additives employed for preparing the light-sensitive materials are shown as follows:

- DBP : dibutyl phthalate
- DOP : dioctyl phthalate
- DNP : dinonyl phthalate
- DIDP : di-i-decyl phthalate
- PVP : polyvinylpyrrolidone
- HQ-1 : 2,5-di-t-octylhydroquinone
- HQ-2 : 2,5-di-sec-dodecylhydroquinone
- HQ-3 : 2,5-di-sec-tetradecylhydroquinone
- HQ-4 : 2-sec-dodecyl-5-sec-tetradecylhydroquinone
- HQ-5 : 2,5-di(1,1-dimethyl-4-hexyloxycarbonylbutyl) hydroquinone
- SU-1 : sodium tri-i-propylnaphthalenesulfonate
- SU-2 : di(2-ethylhexyl) sodium sulfosuccinate
- SU-3 : di(2,2,3,3,4,4,5,5-octafluoropentyl) sodium sulfosuccinate
- H-1 : tetra(vinylsulfonylmethyl)methane
- H-2 : sodium 2,4-dichloro-6-hydroxy-s-triazine
- F-1 : 2-methyl-5-chloroisothiazoline-3-on

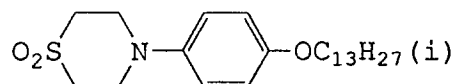
Y-1



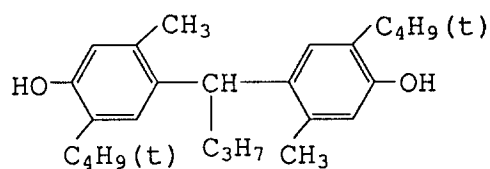
ST-2



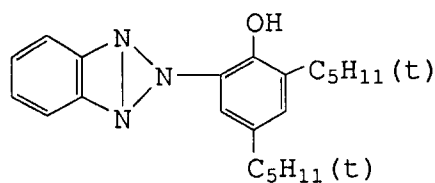
10 ST-3



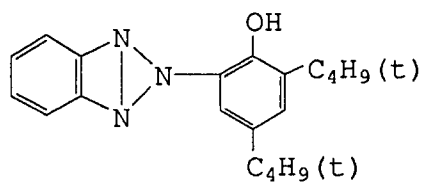
ST-4



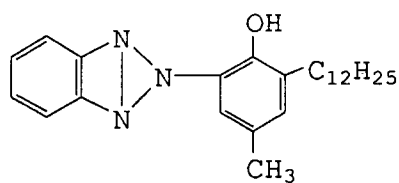
25 UV-1



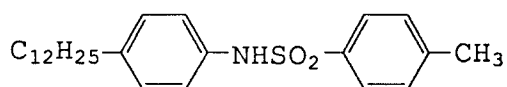
35 UV-2



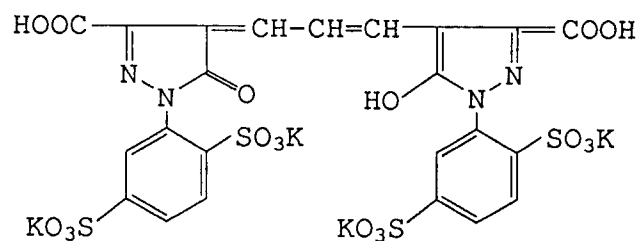
45 UV-3



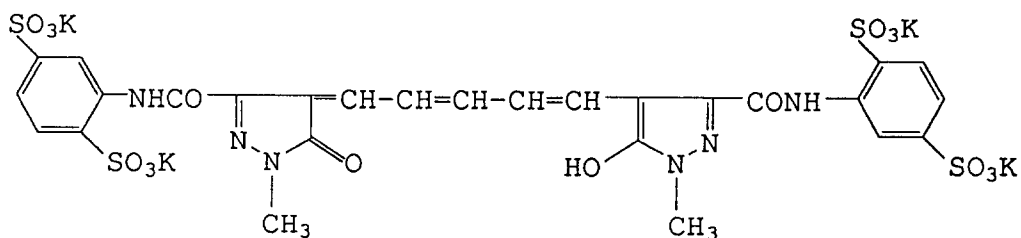
55 HBS-1



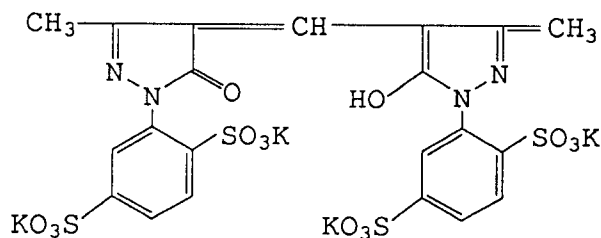
Al-1



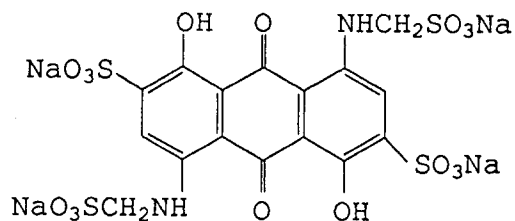
Al-2



Al-3



Al-4



(Preparation of blue sensitive silver halide emulsion)

To 1000 ml of 2% aqueous gelatin solution kept at 40°C, the following solutions A and B were added simultaneously for 30 minutes while controlling pAg at 6.5 and pH at 3.0. In addition, the following solutions C and D were added for 180 minutes while controlling pAg at 7.3 and pH at 5.5. In these occasions, pAg

EP 0 546 711 A1

was controlled by a method described in Japanese Patent O.P.I. Publication No. 45437/1984 and pH was controlled employing aqueous solution of sulfuric acid or sodium hydroxide.

5

(Solution A)	
Sodium chloride	3.42 g
Potassium bromide	0.03 g
Add water to make 200 ml.	

10

(Solution B)	
Silver nitrate	10 g
Add water to make 200 ml	

15

20

(Solution C)	
Sodium chloride	102.7 g
Potassium bromide	1.0 g
Add water to make 600 ml.	

25

30

(Solution D)	
Silver nitrate	300 g
Add water to make 600 ml	

35

After addition is completed, desalting is conducted employing 5% aqueous solution of Demol N produced by Kao Atlas and 20% aqueous solution of magnesium sulfate. Then, the solution was mixed with gelatin aqueous solution to prepare a mono-dispersed cubic grain emulsion EMP-1 having average grain size of 0.85 μm , the variation coefficient of 0.07 and silver chloride content ratio of 99.5 mol%.

EMP-1 was subjected to chemical ripening for 90 minutes at 50 °C employing the following compounds to prepare a blue sensitive silver halide emulsion (Em-B).

40

Sodium thiosulfate	0.8 mg/mol AgX
Chloro aurate	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

45

(Preparation of green sensitive silver halide emulsion)

50

A mono-dispersed cubic grain emulsion EMP-2 having the average grain size of 0.43 μm , the variation coefficient of 0.08 and silver chloride content ratio of 99.5 mol% was obtained in the same manner as EMP-1 except that the addition times of Solutions A and B and Solutions C and D were varied.

EMP-2 was subjected to chemical ripening for 120 minutes at 55 °C employing the following compounds to prepare a green sensitive silver halide emulsion (Em-G).

55

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

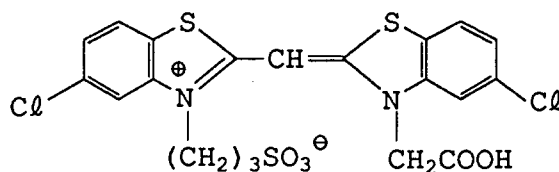
(Preparation of red sensitive silver halide emulsion)

A mono-dispersed cubic emulsion EMP-3 having the average grain size of $0.50 \mu\text{m}$, the variation coefficient of 0.08 and silver chloride content ratio of 99.5 mol% was obtained in the same manner as EMP-1 except that the addition times of Solutions A and B and Solutions C and D were varied.

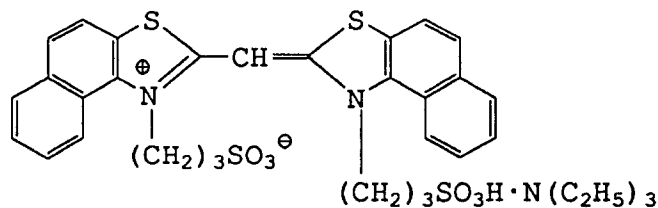
EMP-3 was subjected to chemical ripening for 90 minutes at 60°C employing the following compounds to prepare a red sensitive silver halide emulsion (Em-R).

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

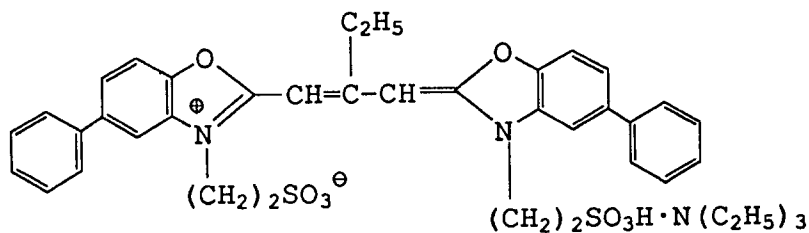
STAB-1 : 1-(3-acetoamido)phenyl-5-mercaptotetrazole
BS-1



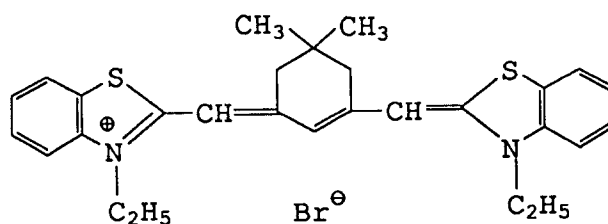
BS-2



GS-1



PS-1



The above-mentioned samples were subjected to the evaluation of the following photographic properties. The results are shown in Table 4.

〈Coating unevenness at the initial stage of coating〉

After inserting a color separation filter to a white light, coating samples were exposed to it uniformly under the conditions so as to obtain the gray image density of about 1.0 after processing. They were developed and processed under the following conditions of color development. Then, coating unevenness was checked visually.

- A --- The layers were coated uniformly any ununiformity could not be observed in the imaged of uniformly exposed area.
- B --- Though it is slightly inferior, it is within the allowance practically.
- C --- The layers were coated with an unevenness an ununiformity was observed in the image formed by the uniform exposure and the quality of the image was degraded.

〈Color mixing〉

After the samples were subjected to exposure to light through a color separation green filter and an optical wedge, they were processed under the following conditions. On the other hand a standard sample was prepared in the same manner as in Sample 3 except that the 7th, 4th and 3rd layers were coated. In this standard sample, the color mixing cannot be formed. The standard sample was exposed and processed in the same manner as in each test samples.

A blue density, i.e., a density measured by blue-light, of image at an area of processed sample having a green density, i.e., a density measured by green-light, of 1.5. Thus obtained blue density of the image was compared with a blue density of image formed on the standard sample which processed and measured under the condition the same as that for the sample to be compared. The color mixing was evaluated by the difference between the blue densities of the image of the standard sample and the sample to be tested.

Increase of blue density from the standard is 0.05 or less	--- favorable
Increase of blue density from the standard is 0.06 to 0.14	--- at the marginal level
Increase of blue density from the standard is 0.15 or more	--- not allowable

〈Glossiness〉

The samples were subjected to uniform exposure and development and processing. Then, samples of black background were prepared under each of the following color developing conditions. Their glossinesses were evaluated visually.

- A --- The print was flat and the surface of it had a high glossiness without claud such as glass surface.
- B --- Though it is slightly inferior, it is within the allowance practically.
- C --- The print not flat and the surface of it had lowered glossiness with claud.

〈Stability to pH variation of color development processing solution〉

After the samples were subjected to exposure to light through a color separation green filter and an optical wedge. Then the samples were each divided to two parts and one of them were processed under

EP 0 546 711 A1

each of the following conditions. The other part of the samples were processed identically except that pHs developers were reduced to 9.5. The maximum densities of images formed in the samples were measured with green light employing Konica color densitometer PDA-65. Decreasing of the maximum density caused by lowering pH value in developer was evaluated for each sample.

Decrease of maximum density from the standard is 0.05 or less	-- favorable
Decrease of maximum density from the standard is 0.06 to 0.09	-- at the marginal level
Decrease of maximum density from the standard is 0.10 or more	-- not allowable

The processing conditions were as follows:

	Temperature	Time
Processing step A	35 ° C	45 sec.
Processing step B	35 ° C	90 sec.
Processing step C	33 ° C	2 min. and 30 sec.
Processing step D	30 ° C	3 min. and 30 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 - 1

Pure water	800 ml
Triethanolamine	10 g
N,N-diethylhydroxylamine	5 g
Potassium bromide	0.02 g
Potassium chloride	2 g
Potassium sulfide	0.3 g
1-hydroxyethylidene-1,1-diphosphonic acid	1.0 g
Ethylenediaminetetraacetate	1.0 g
Disodium cathecol-3,5-diphosphate	1.0 g
N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Brightening agent (4,4'-diaminostyrbendisulfonic acid derivative)	1.0 g
Potassium carbonate	27 g
Add water to make 1000 ml, and adjust pH to 10.10.	

Color developer - 2

In the color developer-1, the amount of N-ethyl-N-β-methanesulfonamideethyl-3-methyl-4-aminoaniline sulfate was changed to 6.0 g.

Bleach-fixer

Ferric ammonium ethylenediaminetetraacetate dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (70% aqueous solution)	100 ml
Ammonium sulfite (40% aqueous solution)	27.5 ml
Add water to make 1000 ml, and adjust pH to 5.7 with potassium carbonate or glacial acetate.	

5-chloro-2-methyl-4-isothiazoline-3-on	1.0 g
Ethylene glycol	1.0 g
1-hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Ethylenediaminetetraacetic acid	1.0 g
Ammonium hydroxide (20% aqueous solution)	3.0 g
Brightening agent (4,4'-diaminostybenzulfonic acid derivative)	1.5 g
Add water to make 1000 ml, and adjust pH to 7.0 with sulfuric acid or potassium hydroxide.	

Table 4

Sample No.	Coating unevenness	Color mixture	Glossiness	Dmax varied caused by pH fluctuation
1(Comparative)	A	0.10	C	0.04
2(Comparative)	C	0.21	A	0.05
3(Comparative)	A	0.04	A	0.18
4(Comparative)	A	0.03	A	0.15
5(Comparative)	A	0.02	A	0.23
6(Invention)	A	0.03	A	0.03
7(Invention)	A	0.03	A	0.04
8(Invention)	B	0.03	A	0.04
9(Invention)	A	0.04	A	0.07
10(Invention)	A	0.05	A	0.07
11(Invention)	A	0.05	A	0.09
12(Invention)	A	0.05	A	0.03
13(Invention)	A	0.03	A	0.04
14(Invention)	A	0.03	A	0.08
15(Invention)	A	0.03	A	0.04
16(Invention)	A	0.04	A	0.05

From the results shown in Table 4, it turned out that the samples 6 to 16 in the present invention are favorable in terms of all evaluation items in all.

Example 2

Four kinds of papers were prepared using paper materials the same as in Example 1 having a basic weight of 170 g/m² and moisture of 8%, and the surface roughness of each were adjusted to 1.1, 0.9, 0.7 or 0.5 by controlling pressure of calendering.

On a support for photographic paper prepared in the same manner as Example 1, each layer having constitutions as shown in Tables 5 and 6 were coated on the surface of polyethylene layer containing titanium dioxide to prepare a multi-layer silver halide color photographic light-sensitive material. The coating solutions were prepared in the following manner:

Coating solution for the first layer

To 19.1 g of the yellow coupler (Y-2), 4.4 g of a dye image stabilizer (ST-5), 27.2 ml of ethylacetate and 7.7 ml of a high boiling organic solvent (solv-1) were added to be dissolved. Then, the solution was dispersed into 185 ml of 10% gelatin aqueous solution containing 8 ml of 10% sodium dodecylbenzenesulfonate so that a yellow coupler dispersion was prepared.

The above-mentioned dispersant was mixed with a blue sensitive silver halide emulsion prepared under the following conditions so that the coating solution for the first layer was prepared.

Coating solutions for the second layer to the seventh layer were prepared in the similar manner to the coating solution for the first layer. In addition, as a hardener of gelatin in each layer, H-2 was employed.

Table 5

	Layer	Constitution	Added amount (g/m ²)
5	The seventh layer (Protective layer)	Gelatin	1.06
		Acryl-modified copolymer of polyvinyl alcohol (Modifying degree 17%)	0.17
		Fluid paraffin	0.03
10	The sixth layer	Gelatin	0.42
		UV absorbent (UV-4)	0.21
		High boiling point organic solvent (solv-3)	0.08
15	The fifth layer (Red sensitive layer)	Gelatin	1.06
		Red sensitive silver bromochloride emulsion (silver chloride content: 99.5 mol%)	0.20
		Cyan coupler (C-1)	0.07
		Cyan coupler (C-3)	0.07
		Cyan coupler (C-4)	0.14
		Cyan coupler (C-5)	0.07
20		Dye image stabilizer (ST-6)	0.17
		Polymer (Ply-1)	0.40
		High boiling organic solvent (solv-4)	0.23
		Anti-irradiation dye (AI-6)	0.02
		Anti-irradiation dye (AI-7)	0.02
25	The fourth layer (UV absorption layer)	Gelatin	1.25
		UV absorbent (UV-4)	0.62
		Anti-stain agent (HQ-1)	0.05
		High boiling organic solvent (solv-3)	0.24

30

35

40

45

50

55

Table 6

	layer	Constitution	Added amount (g/m ²)
5	The third layer (Green sensitive layer)	Gelatin	Table 7
		Green sensitive silver chlorobromide emulsion (silver chloride content: 98.5 mol%)	0.13
		Magenta coupler (M-6)	0.32
10		Dye image stabilizer (ST-7)	0.20
		Dye image stabilizer (ST-8)	0.02
		Dye image stabilizer (ST-9)	0.03
		Dye image stabilizer (ST-10)	0.01
		High boiling organic solvent (solv-2)	0.65
15		Anti-irradiation dye (AI-5)	0.01
	The second layer (Intermediate layer)	Gelatin	0.79
		Anti-stain agent (HQ-5)	0.08
		High boiling organic solvent (DBP)	0.08
20	The first layer (Blue sensitive layer)	Gelatin	1.45
		Blue sensitive silver chlorobromide emulsion (silver chloride content: 99.6 mol%)	0.26
		Yellow coupler (Y-2)	0.83
		Dye image stabilizer (ST-5)	0.19
25		High boiling organic solvent (solv-1)	0.35
		Anti-irradiation dye (AI-4)	0.01
	Support	Paper laminated with polyethylene	
30	Added amount of silver halide was indicated in terms of silver.		

(Preparation of blue sensitive silver halide emulsion)

Into 1000 ml of 2.5% gelatin aqueous solution kept at 58°C, Solutions A and B were added. Then, Solutions C and D were added simultaneously for 45 seconds. After 10 minutes, Solutions E and F were added for 15 minutes. In addition, Solution G was added. After 10 minutes, Solutions H and I were added simultaneously for 20 minutes. After 5 minutes of adding, the temperature was reduced to be desalted. The desaltation was carried out by flocculation method. To the flocculate thus obtained, water and dispersing gelatin were added and pH was adjusted to 6.2. Thus, a mono-dispersed silver chlorobromide emulsion EMP-4 having an average grain size of 0.92 μm the variation coefficient of 0.10 and the silver chloride content of 99.6 mol% was prepared.

	(Solution A)	
45	1N sulfuric acid	20 ml

	(Solution B)	
50	1% solution of 1,3-dimethylimidazolizine-2-thion (AgX solvent)	2 ml

55

EP 0 546 711 A1

(Solution C)	
Sodium chloride	1.7 g
Add water to make 140 ml.	

(Solution D)	
Silver nitrate	5.0 g
Add water to make 140 ml.	

(Solution E)	
Sodium chloride	41.1 g
Add water to make 320 ml.	

(Solution F)	
Silver nitrate	119.5 g
Add water to make 320 ml.	

(Solution G)	
BS-3	4×10^{-4} mol
Ethyl alcohol	20 ml

(Solution H)	
Potassium bromide	0.35 g
K_2IrCl_6	0.012 g
Add water to make 50 ml.	

(Solution I)	
Silver nitrate	0.5 g
Add water to make 50 ml.	

The above-mentioned EMP-4 was subjected to chemical ripening at 58°C most appropriately employing the following compounds so that a blue sensitive silver halide emulsion (Em-B') was prepared.

Triethylthiourea	1 mg/mol AgX
Stabilizer STAB-2	3.8×10^{-4} mol/mol AgX

EP 0 546 711 A1

(Preparation of green sensitive silver halide emulsion)

A mono-dispersed silver chlorobromide emulsion EMP-5 having an average grain size of 0.51 μm , the variation coefficient of 0.78 and silver chloride content of 98.5 mol% was prepared in the same manner as EMP-4 except that the addition time of Solutions C and D were varied and the solutions E, F, G, H and I were replaced with the solutions J, K, L, M and N.

(Solution J)	
Sodium chloride	40.6 g
Add water to make 320 ml.	

(Solution K)	
Silver nitrate	118.1 g
Add water to make 320 ml.	

(Solution L)	
GS-2	3×10^{-4} mol
GS-3	5×10^{-5} mol
Ethyl alcohol	20 ml

(Solution M)	
Potassium bromide	1.3 g
K_2IrCl_6	0.024 g
Ad water to make 50 ml.	

(Solution N)	
Silver nitrate	1.9 g
Add water to make 50 ml.	

The above-mentioned EMP-5 was subjected to chemical ripening at 58°C most appropriately employing the following compounds so that a blue sensitive silver halide emulsion (Em-G') was prepared.

Triethyl thiourea	1 mg/mol AgX
Stabilizer STAB-2	5.3×10^{-4} mol/mol AgX

(Preparation of red sensitive silver halide emulsion)

A mono-dispersed silver chlorobromide emulsion EMP-6 having an average grain size of 0.60 μm , the variation coefficient of 0.72 and silver chloride content of 99.5 mol% was prepared in the same manner as EMP-4 except that the addition time of Solutions C and D were changed and the solutions E, F, G, H and I were replaced with the solutions O, P, Q, R and S.

EP 0 546 711 A1

(Solution O)	
Sodium chloride	41.06 g
Add water to make 320 ml.	

(Solution P)	
Silver nitrate	119.4 g
Add water to make 320 ml.	

(Solution Q)	
RS-2	7×10^{-5} mol
Ethyl alcohol	20 ml

(Solution R)	
Potassium bromide	0.44 g
K_2IrCl_6	0.10 g
Ad water to make 50 ml.	

(Solution S)	
Silver nitrate	0.63 g
Add water to make 50 ml.	

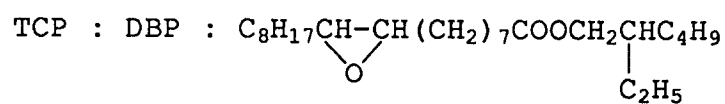
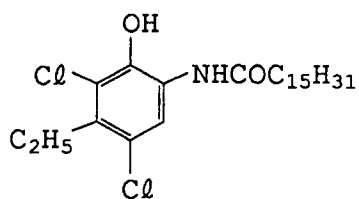
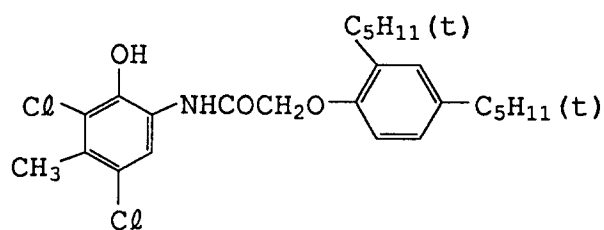
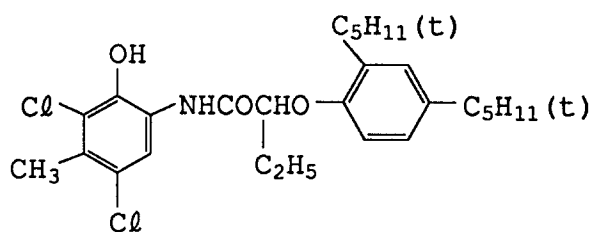
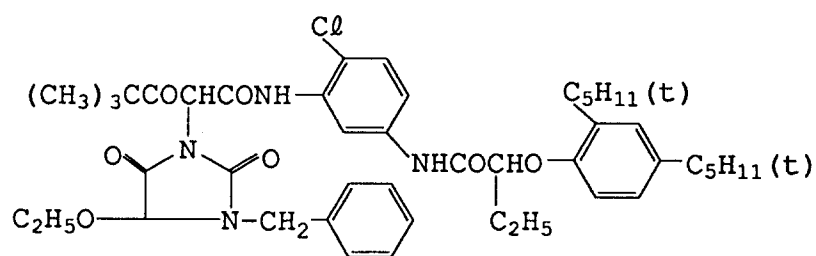
The above-mentioned EMP-6 was subjected to chemical ripening at 60 °C most appropriately employing the following compounds so that a red sensitive silver halide emulsion (Em-R') was prepared.

Triethyl thiourea	1 mg/mol AgX
Stabilizer STAB-2	5.3×10^{-4} mol/mol AgX
Super sensitizer SS-1	2.6×10^{-3} mol/mol AgX

Each emulsion and additives used for preparing color light-sensitive materials are shown as follows:

STAB : 1-{2-(3-methylureido)phenyl}-5-mercaptotetrazole
 HQ-5 : 2,5-di-sec-octylhydroquinone
 TCP : Tricresyl phosphate
 TEHP : Tri(2-ethylhexyl) phosphate
 TCHP : Tri(cyclohexyl) phosphate
 ST-10: 2-sulfo-5-pentadecylhydroquinone

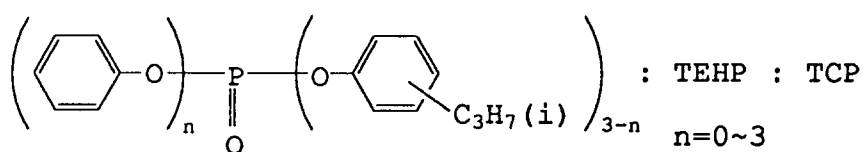
Y-2



by the ratio (weight ratio) of 1:1:2

55 solv-2

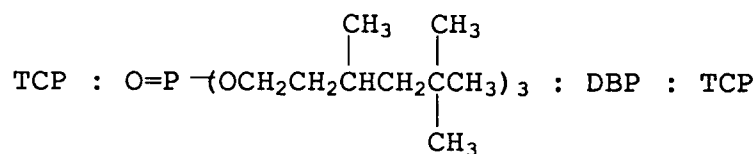
The mixture compound of



by the ratio (weight ratio) of 2:1:1

solv-3

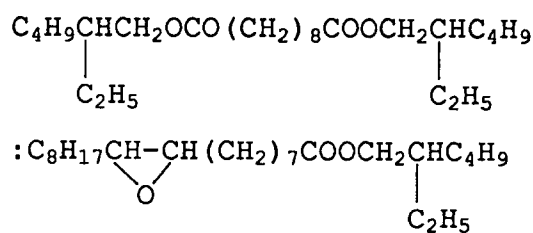
The mixture compound of



by the ratio (weight ratio) of 5:3:1:1

solv-4

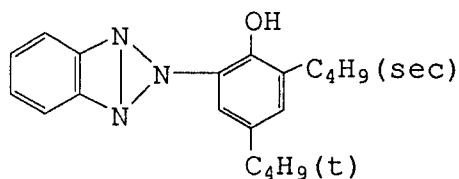
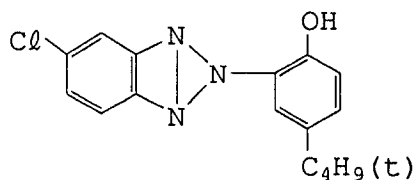
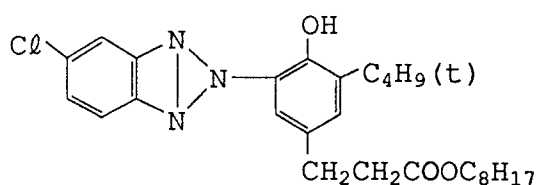
The mixture compound of



by the ratio (weight ratio) of 3:2

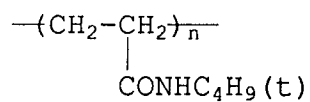
UV-4

The mixture compound of

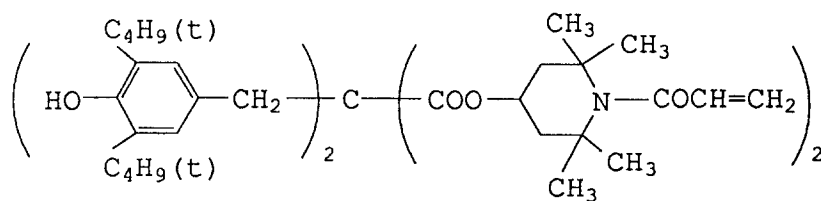


by the ratio (weight ratio) of 2:9:8

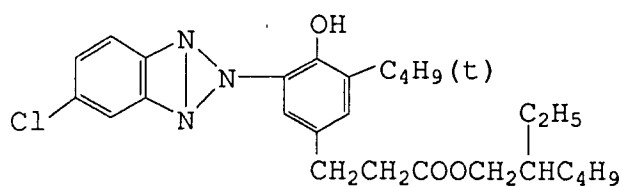
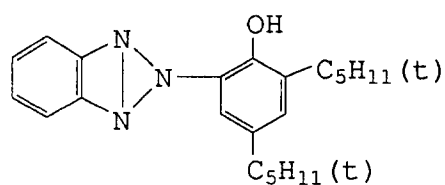
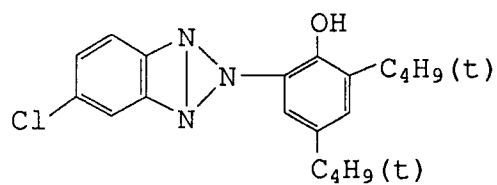
Ply-1



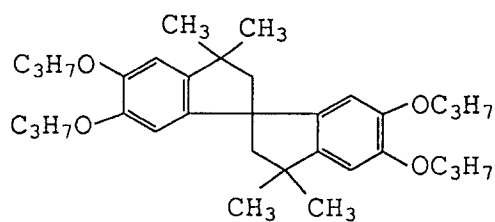
Average molecular weight 80,000
ST-5



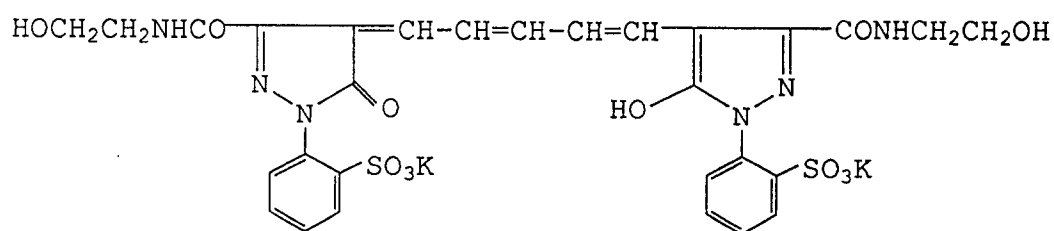
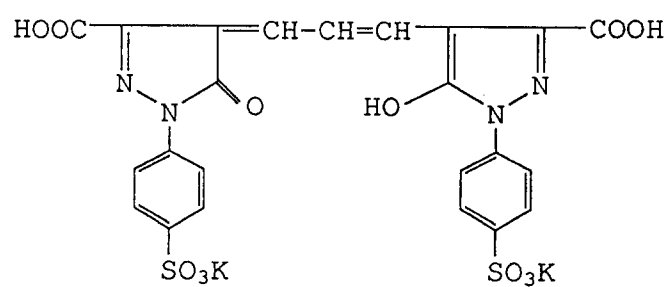
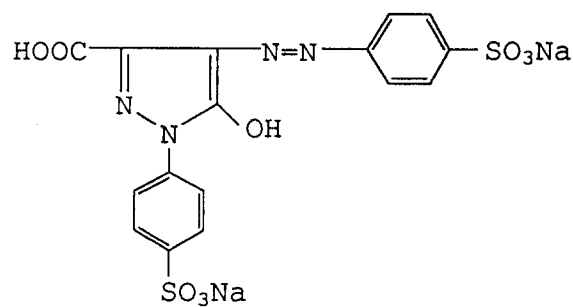
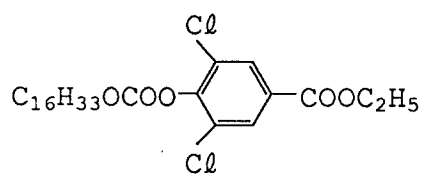
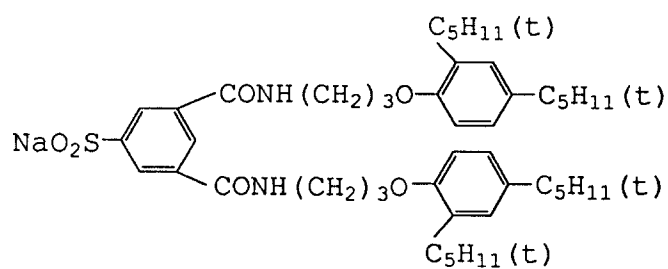
ST-6
The mixture compound of



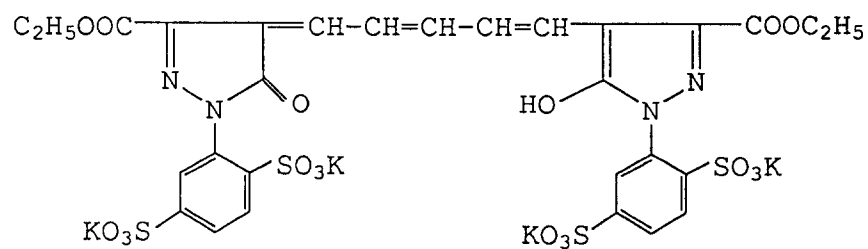
by the ratio (weight ratio) of 8:9:5
ST-7



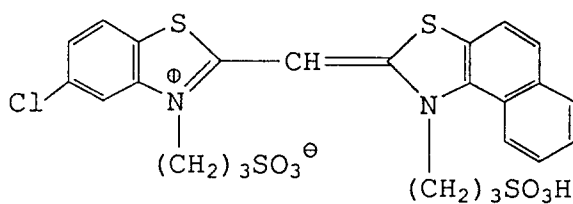
ST-8



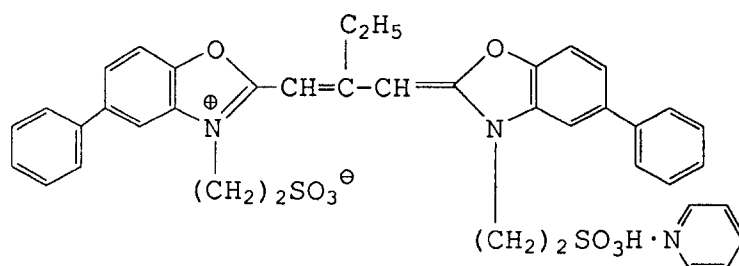
Al-7



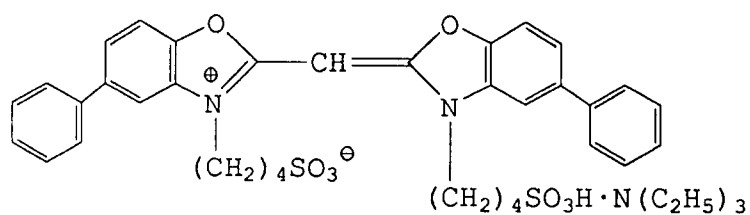
BS-3



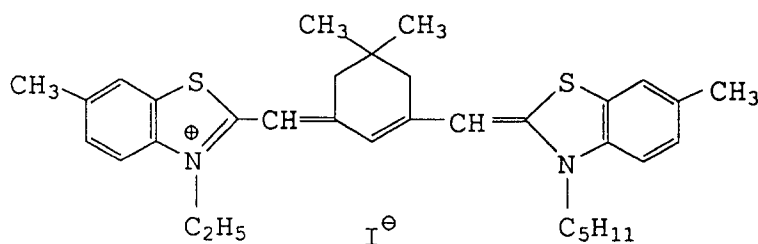
GS-2



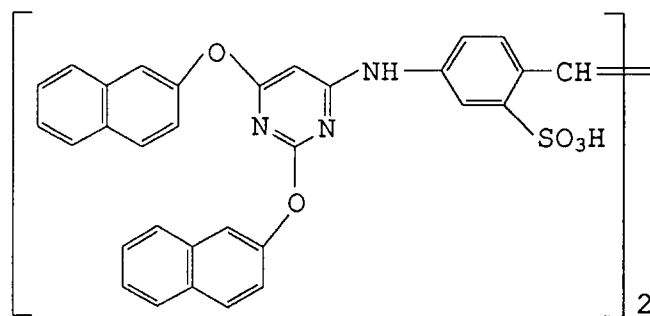
GS-3



RS-2



SS-1



In the same manner as Example 1, the above-mentioned samples were subjected to exposure to light and development processing, and the photographic properties of each of them were evaluated. As the standard sample for evaluation of color mixing a sample having the above 7th, 4th and 3rd layers was used.

Constitutions of samples 17 to 27 are shown in Table 7, and the evaluation results of photographic properties thereof are shown in Table 8.

Table 7

Sample No.	Support SRa(μm)	Green sensitive emulsion layer		Conditions of color developing	
		Gelatin*	O/G	Developing condition	Color developer
17(Comparative)	1.1	1.76	0.7	B	2
18(Comparative)	0.9	1.37	0.9	B	2
19(Comparative)	0.9	1.76	0.7	A	2
20(Comparative)	0.9	1.76	0.7	B	1
21(Invention)	0.9	1.76	0.7	B	2
22(Invention)	0.9	1.76	0.7	C	2
23(Invention)	0.9	1.76	0.7	D	2
24(Invention)	0.9	2.27	0.55	B	2
25(Invention)	0.9	3.08	0.4	B	2
26(Invention)	0.7	1.76	0.7	B	2
27(Invention)	0.5	1.76	0.7	B	2

* Added amount is indicated in terms of g/m^2 .

Table 8

Sample No.	Coating unevenness	Color mixing	Glossiness	Dmax variation caused by pH fluctuation
17(Comparative)	A	0.11	C	0.05
18(Comparative)	C	0.24	A	0.05
19(Comparative)	A	0.04	A	0.18
20(Comparative)	A	0.03	A	0.28
21(Invention)	A	0.04	A	0.04
22(Invention)	A	0.04	A	0.05
23(Invention)	A	0.05	A	0.05
24(Invention)	A	0.04	A	0.06
25(Invention)	A	0.04	A	0.09
26(Invention)	A	0.04	A	0.04
27(Invention)	B	0.04	A	0.04

As shown in Table 8, it is apparent that the samples of the present invention 21 to 27 are excellent in terms of each property.

Claims

1. A method of forming a photographic dye image comprising steps of
 imagewise exposing to light a silver halide color light-sensitive material comprising a paper support, and photographic component layers including a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer provided on said support in this order from the support,
 developing said exposed light-sensitive material with a color developer,
 wherein a surface of said support on which said silver halide emulsion layers to be provided has a roughness of not more than $1.0\ \mu\text{m}$ in terms of arithmetical mean deviation of profile SR_A determined by the following equation;
 said emulsion layers each contains silver halide grains having a silver chloride content of not less than 90 mol%;
 in said green-sensitive emulsion layer the ratio of oil component to a hydrophilic binder each contained in said green-sensitive is not less than 0.8 by weight; and
 said developing step is carried out with a color developer containing a color developing agent in an amount of not less than 1.8×10^{-2} mol/1000 ml for a time of not less than 70 seconds;

$$SR_A = \frac{1}{S_A} \int_0^{L_x} \int_0^{L_y} |f(x, y)| dx, dy$$

in the above equation, L_x is the length of measured area in the direction of X axis, L_y is the length of measured area in the direction of Y axis, S_A is the measured area in which $L_x = L_y = 5\text{mm}$ and $S_A = L_x \times L_y = 25\text{ mm}^2$.

2. The method of claim 1, wherein said roughness SR_A is within the range of from $0.05\ \mu\text{m}$ to $0.09\ \mu\text{m}$.
3. The method of claim 1, wherein the total amount of a hydrophilic binder contained in said photographic component layers is not more than 7.8 g/m^2 .
4. The method of claim 1, wherein the total amount of a hydrophilic binder contained in said photographic component layers is within the range of from 7.0 g/m^2 to 7.8 g/m^2 .
5. The method of claim 1, wherein said ratio of said oil component to hydrophilic binder in said green-sensitive emulsion layer is within the range of from 0.5 to 0.7.

6. The method of claim 1, wherein said developing step is carried out for a time of from 70 seconds to 210 seconds.
7. The method of claim 6, wherein said developing step is carried out for a time of from 90 seconds to 150 seconds.

5

10

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 31 0699

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	WO-A-9 114 046 (KODAK) * page 7, line 6 - line 18 * * page 11, line 18 - page 12, line 15 * ---	1-7	G03C1/775 G03C7/30
Y	EP-A-0 307 868 (KONICA) * page 31, line 44 - line 49 * ---	1-7	
Y	US-A-4 923 790 (KATO ET AL.) * column 37, line 32 - column 38, line 44 * * column 47, line 50 * * column 48, line 6 - line 7 * -----	1-7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26 JANUARY 1993	Examiner MAGRIZOS S.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	