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(54) **Process for processing silver halide color photographic materials.**

(57) A process for processing a silver halide color photographic material is described, which comrises processing a silver halide photographic material having on a support at least one silver halide photographic emulsion layer containing a silver bromide or silver chlorobromide emulsion in which tabular silver halide grains having main crystal planes parall to each other and a average aspect ratio of at least 5 account for at least 50% of the total projected area of the silver halide grains with a color developer containing 8 ml/liter or less of benzyl alcohol.

Croydon Printing Company Ltd.

PROCESS FOR PROCESSING SILVER HALIDE COLOR PHOTOGRAPHIC MATERIALS

FIELD OF THE INVENTION

This invention relates to a process for processing silver halide color photographic materials, and more particularly to a photographic processing process giving excellent coloring property using an improved color developer.

BACKGROUND OF THE INVENTION

Hitherto, various techniques have been proposed for increasing color developing speed. In these techniques, color developing agents for use in the color development have had a low hydrophilic properties, and hence the permeation of the color developing agent into the photographic light-sensitive material has been slow. Accordingly, for increasing the permeation thereof, various penetrating agents have been investigated, and in particular a process for increasing the color development by adding benzyl alcohol to the color developer shows a high coloring accelerating effect, and hence such process has been widely used for the processing of color photographic materials, particularly color photographic papers.

However, when benzyl alcohol has been used in an amount of from more than 10 ml/liter to 15 ml/liter, which is the amount conventionally used for processing color photographic papers, the use of diethylene glycol, triethylene glycol, or an alkanolamine is required as a solvent due to the low water-solubility. However, since benzyl alcohol, glycols, and alkanolamine show high BOD (biochemical oxygen demand) or COD (chemical oxygen demand) values, which are environmental pollution factors, it is preferred to reduce the amount of benzyl alcohol in order to reduce environmental pollution problems, and if it is possible to reduce the amount of benzyl alcohol to less than 8 ml/liter, the use of the above-described solvent becomes unnecessary, which results in greatly reducing the pollution problem, as described, for example, in Japanese Patent Application (OPI) No. 50536/83 (the term "OPI" as used herein means an "unexamined published Japanese application.").

Furthermore, when benzyl alcohol is carried in a bleach bath or a blix bath, which is a bath after a color development bath, it causes the formation of a leuco dye of a cyan coupler, which results in reducing the coloring density of cyan dye. Moreover, when benzyl alcohol is carried in water bath which is a post path to a fix bath or the bleach bath, the life of the color images formed is reduced. Accordingly, by the reasons described above, it is preferred that the concentration of benzyl alcohol in a color developer be low.

However, if the concentration of benzyl alcohol in a color developer is reduced below about 8 ml/liter, the density of colored images is reduced, and in this case, sufficient coloring density cannot be obtained even in the case of using various kinds of color development accelerators as described, for example, in U.S. Patents 2,950,970, 2,515,147, 3,496,903, 2,304,925, 4,038,075, 4,119,642, British Patents 1,430,998, 1,455,413, Japanese Patent Application (OPI) Nos. 15831/78, 62450/80, 62451/80, 62452/80, 62453/80, Japanese Patent Publication Nos. 12422/76, 49728/80, etc.).

SUMMARY OF THE INVENTION

An object of this invention is to provide a processing process for color photographic materials using a color developer containing no or very little benzyl alcohol.

A further object of this invention is to provide a processing process for color photographic materials giving very less pollution problems.

As the result of extensive investigations, the inventors have discovered that the above-described objects of this invention can be attained by processing a silver halide color photographic material comprising a support having thereon at least one silver halide emulsion layer containing a silver bromide or silver chlorobromide emulsion in which tabular silver halide grains having main crystal planes parallel to each other and an average aspect ratio of at least 5 account for at least 50 percent of the total projected area of the silver halide grains with a color developer containing 8 ml/liter or less of benzyl alcohol.

DETAILED DESCRIPTION OF THE INVENTION

Hitherto, for improving the coloring property (coloring density and/or coloring speed) of a silver halide photographic material by a color developer, it has been considered necessary to change the structure of couplers, increase the coating amount of couplers, or increase the coating amount of silver halide, and hence it is an utterly unexpected fact that the form of the crystals of the silver halide grains influences the improvement of the coloring property even if the coating amounts of silver halide and couplers are same as those of other silver halide and couplers, and the halogen composition is same as that of other silver halide grains.

Color developer for use in this invention are described below.

The color developer for use in this invention contains from 8 ml/liter or less and preferably 5 ml/liter or less of benzyl alcohol, including the case in which no benzyl alcohol is present.

The color developer for use in this invention preferably contains a known aromatic primary amine color developing agent. Preferred aromatic primary amine color developing agents are p-phenylenediamine derivatives, and specific examples are shown below, although the invention is not restricted to those specifically listed.

D - 1: N,N-Diethyl-p-phenylenediamine

D - 2: 2-Amino-5-diethylaminotoluene

D - 3: 2-Amino-5-(N-ethyl-N-laurylamino)toluene

D - 4: 4-[N-Ethyl-N-(β-hydroxyethyl)amino]aniline

D - 5: 2-Methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]-aniline

D - 6: N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline

D - 7: N-(2-Amino-5-diethylaminophenylethyl)methanesulfonamide

D - 8: N,N-Dimethyl-p-phenylenediamine

D - 9: 4-Amino-3-methyl-N-ethyl-N-methoxyethylaniline

D - 10: 4-Amino-3-methyl-N-ethyl-N-β-ethoxyethyl-aniline

D - 11: 4-Amino-3-methyl-N-ethyl-N-β-butoxyethyl-aniline

Also, the p-phenylenediamine derivatives may be in the forms of salts such as the sulfates, hydrochlorides, sulfites, p-toluenesulfonates, etc.

The amount of the aromatic primary amine developing agent for the color developer is generally from about 0.1 g to about 20 g, and preferably from about 0.5 g to about 10 g per liter of the developer.

The above-described color developing agent may exist in a silver halide color photographic material for simplifying and quickening the processing.

For using the color developing agent in the color photographic material, it is preferred to use the various precursor for the color developing agent. Examples of such precursors are the indoaniline series compounds described in U.S. Patent 3,342,597, etc.; the Sciff base-type compounds described in U.S. Patent 3,342,599, Research Disclosure, RD No. 14850 (Aug., 1976) *ibid*., RD No. 15159 (Nov., 1976), etc., the aldol compounds described in *ibid*., RD No. 13924 (Nov., 1975), the metal complexes described in U.S. Patent 3,719,492, the urethane series compounds described in Japanese Patent Application (OPI) No. 135628/78, etc., and other various salt-type precursors described in Japanese Patent Application (OPI) Nos. 6235/81, 16133/81, 59232/81, 67842/81, 83734/81, 83735/81, 83736/81, 89735/81, 81837/81, 54430/81, 106241/81, 107236/81, 97531/82, 83565/82, etc.

The silver halide color photographic material for use in this invention may, if desired, contain various 1-phenyl-3-pyrazolidones for accelerating a color development. Examples of these compounds are described in Japanese Patent Application (OPI) No. 64339/81, 144547/82, 211147/82, 50532/83, 50536/83, 50533/83, 50534/83, 50535/83, and 115438/83, etc.

The color developer for use in this invention may further contain a hydroxylamine of types known in the art.

Such a hydroxylamine may be used in the form of a free amine in the color developer but is generally used in the form of a water-soluble acid salt thereof. General examples of these salts are sulfates, oxalates, chlorides, phosphates, carbonates, acetates, etc. The hydroxylamines may be substituted or unsubstituted, and also the nitrogen atom of the hydroxylamines may be substituted by an alkyl group. In particular, the hydroxylamines substituted by a substituted or unsubstituted alkyl group are preferred.

The pH of the color developer for use in this invention is preferably from 9 to 12, and more preferably from 9 to 11.0. The color developers for use in this invention may further contain other components known as developer components.

Examples include sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium tertiary phosphate, potassium tertiary phosphate, potassium metaborate, borax, etc., as an alkali agent or a pH buffer. They can be used solely or as a combination thereof. Also, for giving buffer function to the color developer, facilitating the preparation of the color developer, or increasing the ionic strength of the color developer, various salts such as disodium hydrogenphosphate, dipotassium hydrogenphosphate, potassium dihydrogenphosphate, sodium dihydrogenphosphate, sodium hydrogencarbonate, potassium hydrogencarbonate, borates, an alkali nitrate, an alkali sulfate, etc.

Furthermore, various chelating agents may be used for the color developers as a precipitation preventing agent for calcium and magnesium. Examples of such agents are polyphosphates, aminopolycarbonates, phosphonocarbonates, aminopolyphosphonates, 1-hydroxyalkylidene-1,1-diphosphonates, etc.

The color developer may, if desired, contain a development accelerator. Examples of the development accelerator include various pyrimidium compounds and other cationic compounds, a cationic dye such as phenosafranine, and neutral salts such as thallium nitrate, potassium nitrate described in U.S. Patent 2,648,604, Japanese

Patent Publication No. 9503/69, U.S. Patent 3,171,247 etc., polyethylene glycol and derivatives thereof, and nonionic compounds such as polythioethers described in Japanese Patent Publication No. 9304/69, U.S. Patents 2,533,990, 2,531,832, 2,950,970, 2,577,127, etc., and the thioether series compounds described in U.S. Patent 3,201,242, etc.

Also, the color developer may further contain sodium sulfite, potassium sulfite, potassium bisulfite, or sodium bisulfite, which is usually used as a preservative.

The color developer for use in this invention may further contain, if desired, an antifoggant. Examples of the antifoggant are alkali metal halides such as potassium bromide, sodium bromide, potassium iodide, etc., and organic antifoggants. Examples of the organic antifoggants are nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole , 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chloro-benzotriazole, 2-thiazolylbenzimidazole, 2-thiazolylmethylbenzimidazole, hydroxyazaindrizine, etc., mercapto-substituted heterocyclic compounds such as 1-phenyl-5-mercaptotetrazole, 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, etc., and further mercapto-substituted aroamtic compounds such as thiosalicylic acid, etc. The nitrogen-containing heterocyclic compounds are particularly preferred. Such an antifoggant may be used in such a manner that it is dissolved out from a color photographic light-sensitive material and accumulates in a color developer.

The silver halide color photographic material is usually bleached after color development. The bleach process may be performed simultaneously with a fix process (blix process) or may be performed separately from a fix process. As a bleaching agent, there are, for example, compounds of polyvalent metals such as iron(III), cobalt (III), chromium(VI), copper(II), etc., peracids, quinones, nitroso compounds, etc. Examples of the bleaching agent are ferricyanides, dichromates, organic complex salts of iron(III) or cobalt(III), complex salts of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid, 1,3-diamino-2-propanoltetraacetic acid, etc., or organic acids such as citric acid, tartaric acid, malic acid, etc., persulfates, manganates, nitrosophenol, etc. In these compounds, potassium ferricyanide, ethylenediaminetetraacetic acid iron(III) sodium, ethylenediaminetetraacetic acid iron(III) ammonium, triethylenetetraaminepentaacetic acid iron(III) ammonium, persulfates, cyclohexanediaminetetraacetic acid iron(III) salt, etc., are particularly useful. Ethylenediaminetetraacetic acid iron(III) complex salts are useful in bleach solutions and in blix solutions.

Also, the bleach solution or the blix solution may further, if desired, contain various kinds of accelerators. Examples of the bleach accelerator include thiourea series compounds as described in U.S. Patent 3,706,561, Japanese Patent Publication Nos. 8506/70 and 26586/74, Japanese Patent Application (OPI) Nos. 32735/78, 36233/78, and 37016/78, thiol series compounds as described in Japanese Patent Application (OPI) Nos. 124424/78, 95631/78, 57831/78, 32736/78, 65732/78, and 52534/79, and U.S. Patent 3,893,858, heterocyclic compounds as described in Japanese Patent Application (OPI) Nos. 59644/74, 140129/75, 28426/78, 141623/78, 104232/78, 35727/79, etc., thioether compounds as described in Japanese Patent Application (OPI) Nos. 20832/77, 25064/80, and 26506/80, quaternary amines described in Japanese Patent Application (OPI) No. 84440/73, and the thiocarbamoyls as described in Japanese Patent Application (OPI) No. 42349/74, as well as bromine ions, iodine ions, etc.

As a fixing agent for use in this invention, there are thiosulfates, thiocyanates, thioether series compounds, thioureas, a large amount of iodides, etc.

In these compounds, thiosulfates are most generally used.

As the preservatives for the blix solution or the fix solution, sulfites, bisulfites, or carbonyl-bisulfite addition products are preferably used.

After the blix process or fix process, a washing process is usually performed. In the washing process, various known compounds may be used for the purposes of precipitation prevention and of water saving. For example, for preventing precipitation, a water softener such as an organic phosphoric acid, an aminopolycarboxylic acid, an inorganic phosphoric acid, etc., can be used. Moreover, a sterilizer or an antimold agent for preventing the generation of various bacteria, algae, and molds, a hardening agent such as a magnesium salt or an aluminum salt, or a surface active agent for preventing drying load (increase of energy) or uneven drying of the surface can be used for the washing process. Also, the compounds described in L.E. West, <u>Photographic Sceince and Engineering</u>, Vol.3, No.6, p283 (1959) and Vol. 9, No. 6 (1965) may be used for the washing step. In particular, the addition of a chelating agent or an antimold is effective. Furthermore, it is possible to practice water saving by employing a multi-stage (e.g., 2 to 5 stages) countercurrent system for the washing treatment step.

Moreover, after or in place of the wash treating step, multi-stage countercurrent stabilization, as described, e.g., in Japanese Patent Application (OPI) No. 8543/82 may be applied. In this case, 2 to 9 countercurrent baths are required. In the case of employing such stabilization step, various kinds of compounds can be used for the stabilization baths for stabilizing the images formed. Examples of these compounds are buffers (e.g., borates, metaborates, borax, phosphates, carbonates, potassium hydroxide, sodium hydroxide, aqueous ammonia, monocarboxylates, dicarboxylates, polycarboxylates, etc.) and formalin for adjusting the pH of the layers. Furthermore, if desired, water softeners (e.g., inorganic phosphoric acids, aminopolycarboxylic acids, organic phosphoric acids, aminopolyphosphonic acids, phosphonocarboxylic acids, etc.), sterilizers (e.g., proxel, isothiazolone, 4-thiazolylbenzimidazole, halogenated phenolbenzotriazoles, etc.), surface active agents, fluorescent whitening agents, hardening agents, etc., may be added to the stabilizing bath(s).

Also, as a film pH adjusting agent after process, various ammonium salts such as ammonium chloride, ammonium nitrate, ammonium sulfate, ammonium phosphate, ammonium sulfite, ammonium thiosulfate, etc. can be also added to the stabilizing bath(s).

The tabular silver bromide or silver chlorobromide grains for use in this invention are more excellent in coloring property as the average aspect ratio thereof becomes higher, but the tabular grain silver bromide or silver chlorobromide emulsion wherein the tabular silver halide grains having an average aspect ratio (defined below) of at least 5 (i.e., 5/1), and preferably at least 8, account for at least 50% of the total projected area of the silver halide grains can be advantageously used in this invention with the effect of this invention as compared with ordinary silver bromide or silver chlorobromide emulsions which are used for conventional color photographic light-sensitive materials, and in particular for conventional color photographic papers.

The silver halide for use in this invention is preferably silver bromide or silver chlorobromide containing 3 mol% or less of silver iodide. The silver chloride content in the silver chlorobromide is preferably within the range of 15 mole % to 99 mole %. For the purposes of quickening the processing and reducing the replenishing amount, it is preferred that the amount of the silver chloride is more increased. The silver halide grains may differ in halogen composition between the inside and the surface layer thereof or may differ in halogen composition between the central portion and the annular peripheral portion thereof. Also, a mixture of silver halide grains having a uniform halogen composition and silver halide grains having a double layer or multilayer structure may be used.

The aspect ratio in this invention is defined as the ratio of the diameter of a circle having the same area as the projected area formed by projecting the parallel main crystal planes of the tabular grains onto a plane which is parallel to the crystal planes, to the thickness of the parallel main crystal plates of the grain.

The average diameter of the tabular silver halide grains having the average aspect ratio of at least 5 for use in this invention is preferably from 0.25 μm to 2.8 μm, and particularly preferably from 0.45 μm to 1.9 μm. Also, the thickness of the tabular grains is generally at most 0.56 μm, preferably at most 0.38 μm, more preferably at most 0.2 μm.

In the silver halide emulsion containing the tabular silver halide grains for use in this invention, the tabular silver halide grains having an average aspect ratio of at least 5 account for at least 50%, preferably at least 70%, and particularly preferably at least 90% of the total projected area of the silver halide grains.

The tabular grain silver halide emulsion in this invention can be used in a narrowed distribution about the diameter or the thickness of the tabular silver halide grains. In this invention, it is particularly preferred that the tabular silver halide grains have a distribution of thin thickness.

The tabular silver halide grain emulsion for use in this invention is usually prepared by mixing an aqueous solution of a water-soluble silver salt (e.g., silver nitrate) and an aqueous solution of water-soluble halide(s) (e.g., potassium bromide or sodium chloride alone, or a mixture thereof in the presence of an aqueous solution of a water-soluble polymer such as gelatin.

More particularly, the production of such tabular silver halide grain emulsions are described in U.S. Patents 4,434,226, 4,439,520, 4,414,310, 4,425,425, 4,399,215, 4,435,501, 4,386,156, 4,400,463, 4,414,306, and 4,425,426, European Patent 84,637A2, Japanese Patent Application (OPI) No. 99433/84, Research Disclosure, RD No. 22534 (January,1983), etc.

The silver halide grains for use in this invention may be formed or physically ripened in the presence of a cadmium salt, a zinc salt, a lead salt, a thallium salt, an iridium salt or a complex salt thereof, a rhodium salt or a complex salt thereof, an iron salt or a complex salt thereof, etc.

The silver halide emulsions for use in this invention are usually, after the formation of the silver halide grains, subjected to physical ripening, desalting, and chemical ripening before coating.

For the precipitation, physical ripening and chemical ripening of the silver halide emulsions, known silver halide solvents (e.g., ammonia, potassium rhodanide (potassium thiocyanate), and the thioethers and thione compounds described in U.S. Patent 3,271,157, Japanese Patent Application (OPI) Nos. 12360/76, 82408/78, 144319/78, 100717/79, 155828/79, etc.) can be used. For removing soluble salts from the silver halide emulsions after physical ripening, a noodle washing method, flocculation-sedimentation method, or a ultrafiltration method can be used.

The silver halide emulsions for use in this invention can be chemically sensitized by a sulfur sensitization method using active gelatin or a sulfur-containing compound capable of reacting silver (e.g., thiosulfates, thioureas, mercapto compounds, rhodanine, etc.); a reduction sensitization method using a reducing material (e.g., stannous salts, amines, hydrazine derivatives, formamidinesulfinic acid, silane compounds, etc.); a noble metal sensitizing method using a metal compound (e.g., a gold complex salt and complex salts of metals belonging to group VIII of the periodic table, such as platinum, iridium, palladium, rhodium, iron etc.), etc.

These methods may be used individually or as a combination thereof.

The silver halide photographic emulsions for use in this invention are usually spectrally sensitized by photographic sensitizing dyes. Examples of dyes which are used for the spectral sensitization are cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxonol dyes.

These sensitizing dyes may be used singly or as a combination thereof. A combination of sensitizing dyes is frequently used for the purpose of supersensitization.

The silver halide emulsion for use in this invention may contain a dye having no spectral sensitizing action by itself or a material which does not substantially absorb visible light, but which shows supersensitization when used together with the sensitizing dye(s). Examples of such compound as above, which can be incorporated in the photographic emulsion together with the sensitizing dye(s), are an aminostilbene compound substituted by a nitrogen-containing heterocyclic ring group (e.g., those described in U.S. Patents 2,933,390, 3,635,721, etc.), an aromatic organic acid-formaldehyde condensation product (e.g., those described in U.S.

Patent 3,743,510, etc.), a cadmium salt, an azaindene compound, etc.

The spectral sensitization can be performed in any stage of the preparation of the silver halide emulsion, said stage being known to be a useful stage. It is most usual to perform the spectral sensitization after completion of chemical sensitization. However, the spectral sensitization may be performed simultaneously with chemical sensitization, may be performed before performing chemical sensitization, or may be performed before the end of the precipitation formation of silver halide grains as described in U.S. Patents 3,628,960 and 4,225,666. Furthermore, a spectral sensitizing dye is introduced into a silver halide emulsion in split two portions, i.e., a part of the spectral sensitizing dye is introduced into a silver halide emulsion before chemical sensitization and the remaining portion is introduced thereto after the chemical sensitization as described in U.S. Patent 4,225,666. Also, a spectral sensitizing dye may be added to a silver halide emulsion after forming the 80% precipitation of the silver halide different from the method shown in the above-described U.S. Patent. In an preferred embodiment, a spectral sensitizing dye can be incorporated in a silver halide emulsion after the completion of the formation of the precipitation of the silver halide and before the chemical sensitization of the emulsion.

Also, for satisfying the desired gradation properties by the photographic light-sensitizing material of this invention, two or more kinds of mono-dispersed silver halide emulsions each composed of silver halide grains of a different size can be used for silver halide emulsion layers having substantially same color sensitive property as a mixture thereof in the same emulsion layer or as separate emulsion layers. Furthermore, two or more kinds of poly-dispersed silver halide emulsions or a mixture of a mono-dispersed silver halide emulsion and a poly-dispersed silver halide emulsion may be used as a mixture thereof or for separate emulsion layers.

For the photographic light-sensitive material which is processed by the process of this invention, various color couplers can be used. The term "color coupler" in this invention means a compound capable of forming a dye by causing coupling reaction with the oxidation product of an aromatic primary amine developing agent. Typical examples of useful color couplers include naphtholic and phenolic compounds, pyrazolone and pyrazoloazole series compounds, and open chain and heterocyclic ketomethylene compounds. Specific examples of these cyan, magenta, and yellow couplers which can be used for the silver halide photographic materials are described in the patents cited in Research Disclosure, RD No. 17643 (December, 1978), VII-D, and *ibid.*, RD No. 18717 (November, 1979).

It is preferred that the color couplers contained in the silver halide photographic materials which are processed by the process of this invention are rendered non-diffusible by having a ballast group or by being polymerized. In this invention, a two-equivalent coupler having the coupling active position of which is substituted by a coupling releasable group is more preferred than a four-equivalent coupler having a hydrogen atom at the coupling active position thereof since the coating amount of silver can be reduced in the case of using the two-equivalent coupler. Furthermore, couplers capable of providing coloring dyes having a proper diffusibility, non-coloring couplers, DIR couplers, i.e., couplers releasing a development inhibitor with a coupling reaction, or couplers releasing a development accelerator with coupling reaction can be also used in this invention.

Typical examples of the yellow couplers for use in this invention include oil protect type acylamide series couplers. Specific examples of these couplers are described in U.S. Patents 2,407,210, 2,875,057, and 3,265,506. In this invention, two-equivalent yellow couplers are preferably used. Examples of the two-equivalent yellow couplers are the oxygen atom releasing type yellow couplers described in U.S. Patents 3,408,194, 3,447,928, 3,933,501, 4,022,620, etc., and the nitrogen atom releasing type yellow couplers described in Japanese Patent Publication No. 10739/83, U.S. Patents 4,401,752 and 4,326,024, Research Disclosure, RD No. 18053 (April, 1979), British Patent 1,425,020, West German Patent Application (OLS) Nos. 2,219,917, 2,261,361, 2,329,587, 2,433,812, etc. Of these yellow couplers, α-pivaloylacetanilide series couplers are excellent in fastness, in particular, light fastness of the colored dyes formed therefrom. α-Benzoylacetanilide series couplers are excellent in coloring density.

Magenta couplers for use in this invention include oil protect type indazolone series couplers, cyanoacetyl series couplers, preferably 5-pyrazolone series couplers, and pyrazoloazole series couplers such as pyrazolotriazoles. In the case of the 5-pyrazolone series couplers, it is preferred that the 3-position of the coupler is substituted by an arylamino group or an acylamino group from the viewpoint of the hue and the coloring density of the colored dyes formed therefrom. Specific examples of such 5-pyrazolone series couplers are described in U.S. Patents 2,311,082, 2,343,703, 2,600,788, 2,908,573, 3,062,653, 3,152,896, and 3,936,015. As the releasable groups for the two-equivalent 5-pyrazolone series couplers, the nitrogen atom-releasing groups described in U.S. Patent 4,310,619 and the arylthio groups described in U.S. Patent 4,351,897 are particularly preferred. Also, the 5-pyrazolone series couplers having a ballast group described in European Patent 73,636 give high coloring density.

Examples of pyrazoloazole series magenta couplers include pyrazolobenzimidazoles described in U.S. Patent 3,061,432, preferably the pyrazolo[5,1-c][1,2,4]-triazoles described in U.S. Patent 3,725,067, the pyrazolotetrazoles described in Research Disclosure, RD No. 24220 (June, 1984) and Japanese Patent Application (OPI) No. 33552/85 and the pyrazolopyrazoles described in Research Disclosure, RD No. 24230 (June, 1984), and Japanese Patent Application (OPI) No. 43659/85. The imidazo[1,2-b]pyrazoles described in U.S. Patent 4,500,630 are preferred from the view point of having less yellow side adsorption of the colored dyes formed therefrom,and light fastness. The pyrazolo[1,5-6][1,2,4]triazoles described in European Patent No. 119,860A are more preferred.

Cyan couplers for use in this invention include oil protect type naphtholic and phenolic couplers and typical examples of these cyan couplers are the naphtholic couplers described in U.S. Patent 2,474,293 and preferably the oxygen atom releasing type two-equivalent naphthalic couplers described in U.S. Patents 4,052,212, 4,146,396, 4,228,233, and 4,296,200. Also, specific examples of the phenolic cyan couplers are described in U.S. Patents 2,369,929, 2,801,171, 2,772,162, 2,895,826, etc. The cyan couplers having high fastness to humidity and temperature are preferably used in this invention and specific examples of these cyan couplers are the phenolic cyan couplers having an alkyl group having 2 or more carbon atoms at the meta-position of the phenol nucleus as described in U.S. Patent 3,772,002, the 2,5-diacylamino-substituted phenolic couplers described in U.S. Patents 2,772,162, 3,758,308, 4,126,396, 4,334,011, and 4,327,173, West German Patent Application (OLS) No. 3,329,729, European Patent 121,365, etc., and the phenolic couplers having a phenylureido group at the 2-position and an acylamino group at the 5-position thereof as described in U.S. Patents 3,446,622, 4,333,999, 4,451,559, 4,427,767, etc.

The silver halide photographic materials for use in this invention may contain a compound releasing a development inhibitor with the progress of development in place of the DIR coupler.

Two or more kinds of the above-described couplers may be used in one silver halide emulsion layer, or the same coupler may be used for two or more different silver halide emulsion layers for satisfying the characteristics required for the silver halide photographic material.

Each of the couplers described above is incorporated in a silver halide emulsion layer in an amount of generally from 2×10^{-3} mole to 5×10^{-1} mole, and preferably from 1×10^{-2} mole to 5×10^{-1} mole, per mole of silver in the emulsion layer.

The silver halide photographic materials which are processed by the process of this invention may further contain hydroquinone derivatives, aminophenol derivatives, amines, gallic acid derivatives, cathechol derivatives, ascorbic acid derivatives, non-coloring couplers, sulfonaminophenol derivatives, etc., as a color fog preventing agent or a color mixing preventing agent.

The photographic light-sensitive materials for use in this invention may further contain various fading preventing agents. Examples of organic fading-preventing agents include hindered phenols such as hydroquinones, 6-hydroxychromans, 5-hydroxycoumarans, spirochromans, p-alkoxyphenols, bisphenols, etc., gallic acid derivatives, methylenedioxybenzenes, aminophenols, hindered amines, and the ether or ester derivatives formed by silylating or alkylating the phenolic hydroxyl groups of these compounds. Also, metal complexes such as (bis-salicyclaldoxymato)nickel complex and (bis-N,N-dialkyldithiocarbamato)nickel complex can also be used as the fading-preventing agent.

Also, the use of a compound having a moiety structure of hindered amine and hindered phenol in the same molecule thereof such as those described in U.S. Patent 4,268,593, gives good results for preventing the yellow dye images from being deteriorated by heat, humidity, and light. Also, the use of spiroindanes as described in Japanese Patent Application (OPI) No. 159644/81, or chromans substituted by hydroquinone diether or mono-ether as described in Japanese Patent Application (OPI) No. 89835/80, gives good results for preventing the magenta dye images from being deteriorated, particularly by light.

The photographic light-sensitive materials for use in this invention can contain an ultraviolet absorbent in the hydrophilic colloid layers thereof.

The photographic light-sensitive materials for use in this invention may further contain in the hydrophilic colloid layers thereof water-soluble dyes as filter dyes or for irradiation prevention or halation prevention.

Also, the photographic light-sensitive materials for use in this invention may further contain stilbene series, triazine series, oxazole series or coumarin series whitening agents in the photographic emulsion layers or other hydrophilic colloid layers thereof. Such a whitening agent may be water-soluble, or a water-insoluble whitening agent may be used in the form of a dispersion thereof.

As a binder or a protective colloid which can be used for the silver halide emulsion layers and interlayers, etc., of the silver halide photographic materials for use in this invention, gelatin is advantageously used but other hydrophilic colloids can be used.

Useful gelatins include limed gelatin which is most generally used for the purpose, as well as acid-treated gelatin and enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, No. 16, p. 30 (1966). Also, hydrolyzed or enzyme-decomposition products of gelatin can also be used.

The photographic light-sensitive materials for use in this invention may further contain an inorganic or organic hardening agent in the photographic silver halide emulsion layers and other optional hydrophilic colloid layers constituting, for example, backing layers.

The photographic light-sensitive materials for use in this invention may further contain at least one kind of surface active agent as a coating aid or for preventing electrification, improving the slipping property, improving emulsification-dispersibility, preventing adhesion, and improving photographic properties (e.g., acceleration of development, increase of contrast, and increase of sensitivity).

The photographic light-sensitive materials for use in this invention may further contain various additives useful for photographic materials, such as various stabilizers, stain-preventing agents, developing agents or precursors therefor, development accelerators or precursors therefor, lubricants, mordants, matting agents, antistatic agents, plasticizers, etc., in addition to the above-described additives. Specific examples of these additives are described in Research Disclosure, RD No. 17643 (December, 1978) and *ibid.*, RD No. 18716 (November, 1979).

This invention can be applied to multilayer multicolor photographic materials having at least two silver halide emulsion layers, each having a different spectral sensitivity, on a support. A multilayer natural color photographic material usually has at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer, and at least one blue-sensitive emulsion layer on a support. The disposition order of these emulsion layers can optionally be selected according to the intended purpose. Also, each of the emulsion layers described above may be composed of at least two emulsion layers, each having a different sensitivity, and a light-insensitive layer may exist between two or more emulsion layers each having the same sensitivity.

The photographic light-sensitive material for use in this invention have a protective layer, inter-layers, a filter layer, an antihalation layer, a backing layer, etc., in addition to the above-described silver halide emulsion layers.

The photographic light-sensitive material for use in this invention is prepared by forming the photographic emulsion layers and other layers on a flexible support of a type which is usually used for photographic materials, such as a plastic film, a paper, a cloth, etc., of a solid support such as a glass plate, porcelain, a metal foil, etc.

The processing process of this invention can be applied for processing general silver halide color photographic materials such as color negative photographic films, color photographic papers, color positive photographic films, color reversal films, etc., but is particularly preferably applied for processing color photographic papers.

The invention is explained in more detail by reference to the following examples. However, the scope of the invention is not limited to these examples.

Example 1

A multilayer silver halide photographic material was prepared by forming the following layer 1 (the lowermost layer) to layer 7 (the uppermost layer) on a paper support, both of the surfaces of which were laminated with polyethylene.

Layer 1: Blue-sensitive emulsion layer:

Silver chlorobromide emulsion shown in Table 1 below (silver coverage). (Br: 70 mol%)	0.30 g/m^2
Yellow coupler Y - 1	0.60 g/m^2
Yellow coupler solvent (dibutyl phthalate)	1.00 g/m^2
Fading-preventing agent F - 3	0.10 g/m^2

Layer 2: Interlayer:

Gelatin	1.50 g/m^2

Layer 3: Green-sensitive emulsion layer:

Silver chlorobromide emulsion shown in Table 1 (silver coverage) (Br: 70 mol%)	0.45 g/m^2
Magenta coupler M - 1	0.45 g/m^2
Magenta coupler solvent (tri-n-octyl phosphate)	0.44 g/m^2

Fading-preventing agent F - 1	0.050 g/m^2
" F - 2	0.100 g/m^2

Layer 4: Ultraviolet absorption layer:

Gelatin	2.00 g/m^2
Ultraviolet absorbent UV - 1	0.015 g/m^2
" UV - 2	0.045 g/m^2
" UV - 3	0.090 g/m^2
Solvent (dibutyl phthalate)	0.060 g/m^2

Layer 5: Red-sensitive emulsion layer:

Silver chlorobromide emulsion shown in Table 1 (silver coverage) (Br: 70 mol%)	0.300 g/m^2
Cyan coupler C - 1	0.200 g/m^2
" C - 2	0.200 g/m^2
Cyan coupler solvent (dibutyl phthalate)	0.240 g/m^2
Ultraviolet absorbent UV - 1	0.020 g/m^2
" UV - 2	0.050 g/m^2
" UV - 3	0.060 g/m^2

Layer 6: Ultraviolet absorption layer:

Gelatin	1.50 g/m^2
Ultraviolet absorbent UV - 1	0.050 g/m^2
" UV - 2	0.150 g/m^2
" UV - 3	0.300 g/m^2
Solvent (dibutyl phthalate)	0.200 g/m^2

Layer 7: Protective layer:

Gelatin	1.50 g/m^2

The coating composition for Layer 1 described above was prepared as follows. That is, 100 g of the yellow coupler Y-1 having the structure shown below was dissolved in a mixture of 166.7 ml of dibutyl phthalate (DBP) and 200 ml of ethyl acetate, the solution was dispersed by emulsification in 800 g of a 10% aqueous gelatin solution containing 80 ml of an aqueous solution of 1% sodium dodecylbenzenesulfonate, and the emulsified dispersion was mixed with 1450 g (containing 66.7 g of silver) of a blue-sensitive silver chlorobromide emulsion (Br: 80 ml % of halide content) to provide the coating composition.

The coating compositions for other layers described above were also prepared by similar manner to above.

In addition, for each layer, 2,4-dichloro-6-hydroxy-s-triazine sodium salt was used as a hardening agent.

Also, for each of the emulsion layers described above, the following spectral sensitizer was used.

Spectral sensitizer for blue-sensitive emulsion layer:

3,3'-Di-(γ-sulfopropyl)-selenacyanine sodium salt (2×10^{-4} mole per 1 mole of silver halide).

Spectral sensitizer for green-sensitive emulsion layer:

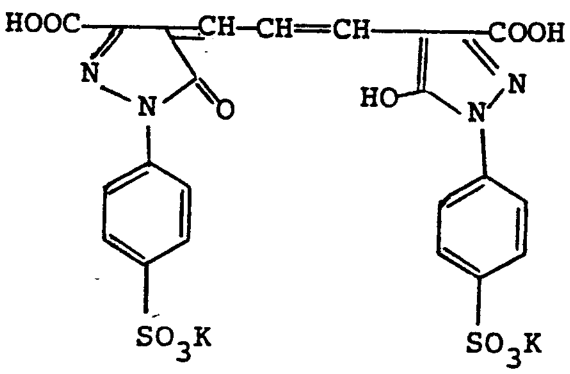
3,3'-Di-(γ-sulfopropyl)-5,5'-diphenyl-9-ethyloxacarbocyanine sodium salt (2.5 x 10^{-4} mole per 1 mole of silver halide).

Spectral sensitizer for red-sensitive emulsion layer:

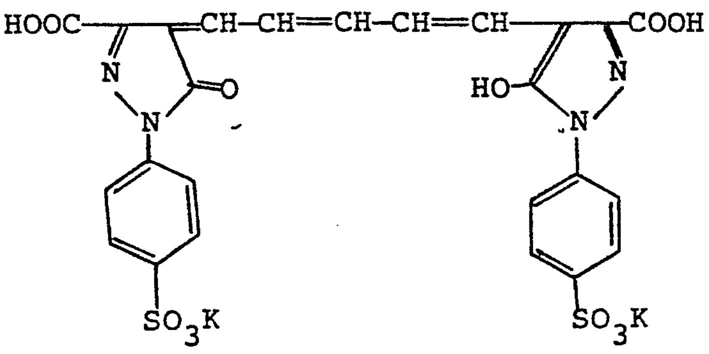
3,3'-Di-(γ-sulfopropyl)-9-methyl-thiadicarbocyanine sodium salt (2.5 x 10^{-4} mole per 1 mole of silver halide).

Also, for the green-sensitive emulsion layer and the red-sensitive emulsion layer described above, the following dyes were used as anti-irradiation dyes.

Anti-irradiation dye for green-sensitive emulsion layer:

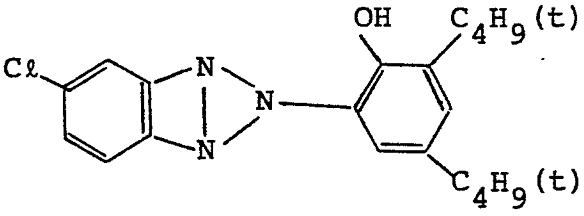


Anti-irradiation dye for red-sensitive emulsion layer:



The chemical structures of the other compounds that were used in this example are as follows.

UV - 1



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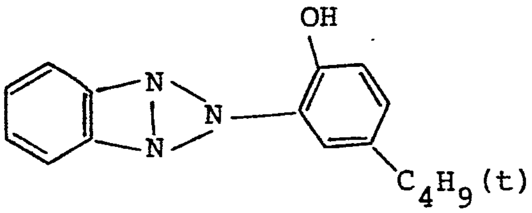
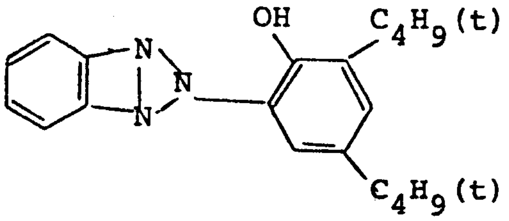


UV - 3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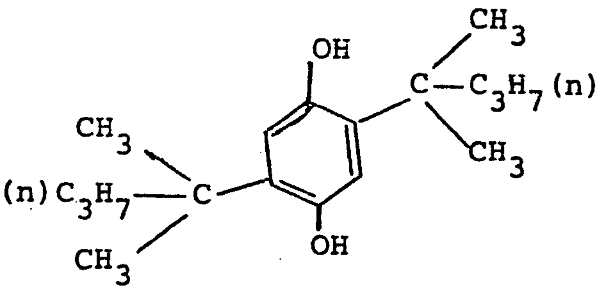
N
N
N
C4H9(t)

F - 1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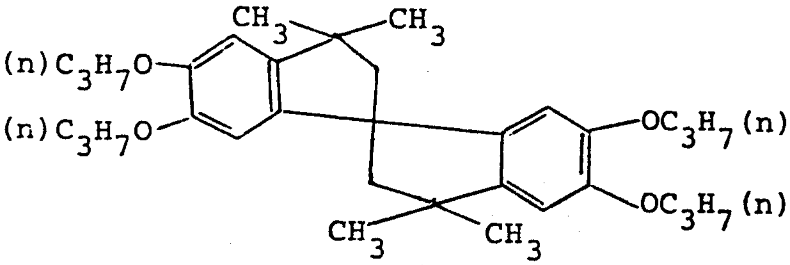
CH3
CH3
(n)C3H7—C
CH3
OH

F - 2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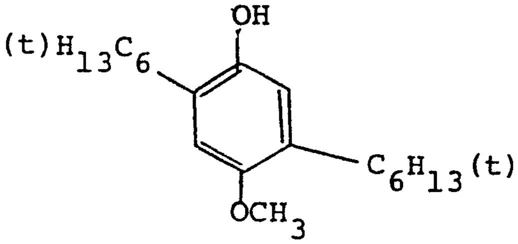
(n)C3H7O
OC3H7(n)
OC3H7(n)
CH3
CH3

F - 3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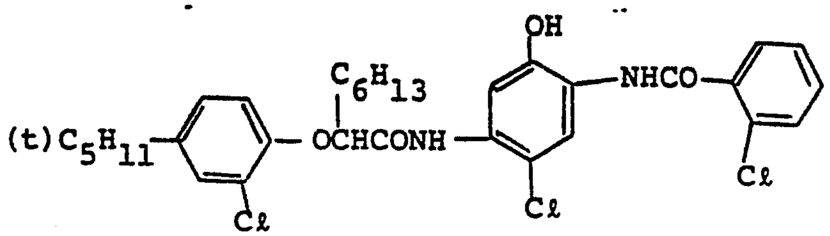
C6H13(t)
OCH3

C - 1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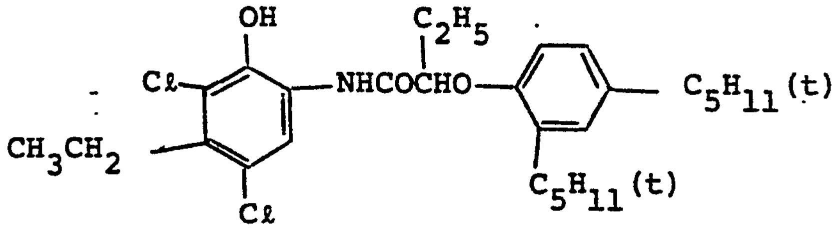
OCHCONH
Cl
Cl
Cl

C - 2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Cl
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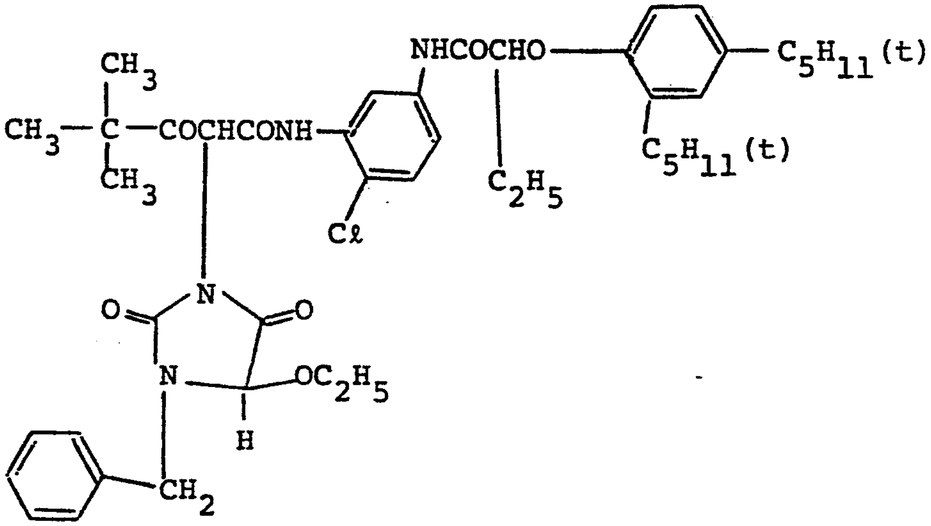
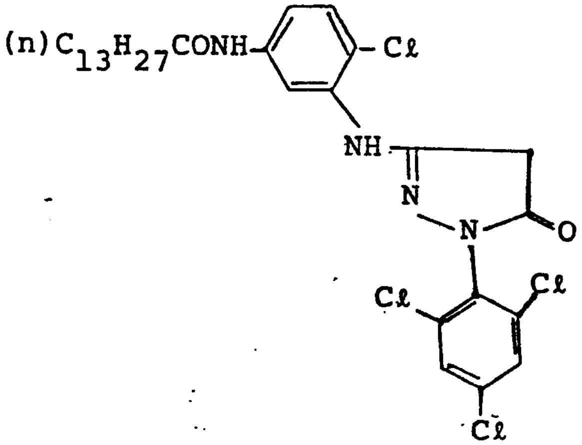
C_5H_{11}(t)
CH_3CH_2
Cl
C_5H_{11}(t)

Y - 1


NHCOCHO
C_5H_{11}(t)
CH_3
CH_3—C—COCHCONH
CH_3
Cl
C_2H_5
C_5H_{11}(t)
N
O
O
N
OC_2H_5
H
CH_2

M - 1



The silver chlorobromide grains used for the above-described emulsion layers in this example are shown in Table 1 below.

TABLE 1

Sample No.	Emulsion Layer	Grain Form	Average Grain size* (μm)	Average Aspect Ratio	Projected Area (%)	Halogen Composition**
101 (Comparison)	Blue-sensitive Layer	Irregular	0.82	-	-	80/20
	Green-sensitive Layer	Spherical	0.56	-	-	70/30
	Red-sensitive Layer	Spherical	0.56	-	-	70/30
102 (Comparison)	Blue-sensitive Layer	Irregular	0.82	-	-	80/20
	Green-sensitive Layer	Cubic	0.45	-	-	70/30
	Red-sensitive Layer	Cubic	0.45	-	-	70/30
103 (This Invention)	Blue-sensitive Layer	Tabular	1.01	7.0	63	80/20
	Green-sensitive Layer	Tabular	0.76	6.1	56	70/30
	Red-sensitive Layer	Tabular	0.76	6.1	56	70/30
104 (This Invention)	Blue-sensitive Layer	Tabular	1.01	7.0	63	80/20
	Green-sensitive Layer	Tabular	0.82	9.3	71	70/30
	Red-sensitive Layer	Tabular	0.82	9.3	71	70/30
105 (This Invention)	Blue-sensitive Layer	Tabular	1.20	8.0	70	80/20
	Green-sensitive Layer	Tabular	0.60	6.3	60	70/30
	Red-sensitive Layer	Tabular	0.60	6.3	60	70/30
106 (Comparison)	Blue-sensitive Layer	Tabular	0.99	4.0	65	80/20
	Green-sensitive Layer	Tabular	0.74	4.1	58	70/30
	Red-sensitive Layer	Tabular	0.74	4.2	58	70/30
107 (Comparison)	Blue-sensitive Layer	Tabular	0.85	7.0	40	80/20
	Green-sensitive Layer	Tabular	0.63	6.0	45	70/30
	Red-sensitive Layer	Tabular	0.64	5.9	45	70/30

(*): The average grain size is based on a sphere-calculated diameter for non-tabular grains, and on a circle-calculated diameter of the projected area for tabular grains.

(**): [AgBr mol%/AgCl mol%]

Each of the photographic silver halide materials thus prepared was light-exposed through an optical wedge and then processed in the following steps.

Processing Step	Temperature	Time
Color Development	37°C	3 min. 30 sec.
Blix	33°C	1 min. 30 sec.
Wash	24-34°C	3 min.
Drying	80°C	1 min.

The compositions of the processing solutions are as follows.

Color Developer

Water	800 ml
Diethylenetriaminepentaacetic acid	1.0 g
Benzyl alcohol	Table 2
Diethylene glycol	Table 2
Sodium sulfite	2.0 g
Sodium bromide	1.0 g
Sodium carbonate	30.0 g
N-Ethyl-N-(p-methanesulfonamido-ethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
Hydroxylamine sulfate	4.0 g
Fluorescent whitening agent (4,4'-diaminostilbene series)	1.0 g
Water to make	1000 ml.
pH (25°C)	10.10

Blix Solution

Water	400 ml
Ammonium thiosulfate (70%)	150 ml
Sodium sulfite	18 g
Ethylenediaminetetraacetic acid iron(III) ammonium	55 g
Ethylenediaminetetraacetic acid di-sodium	5 g
Water to make	1000 ml
pH (25°C)	6.70

After processing as above using various color developers each having changed concentrations of benzyl alcohol and diethylene glycol, three-color reflection densities of each sample were measured. The results obtained are shown in Table 2 below. In the table, the relative sensitivity of each sample is shown based on the case of the benzyl alcohol concentration of 15 ml/liter being taken as 100.

TABLE 2

Color Developer		A		B		C		D		E		F	
Benzyl Alcohol (ml/l)		0		2		4		8		10		15	
Diethylene Glycol (ml/l)		0		0		0		0		5		10	
Photographic Properties		1*	D_{max}	1*	D_{max}	1*	D_{max}	1*	D_{max}	1*	D_{max}	1*	D_{max}
101 (Comparison)	B	31	0.90	42	1.12	53	1.34	60	1.59	83	1.75	100	1.90
	G	45	1.60	51	1.80	65	2.00	75	2.25	90	2.30	100	2.35
	R	50	1.80	59	1.95	64	2.10	80	2.20	92	2.25	100	2.30
102 (Comparison)	B	31	0.89	42	1.13	52	1.32	61	1.57	82	1.71	100	1.89
	G	42	1.49	48	1.70	61	1.92	70	2.18	88	2.24	100	2.29
	R	45	1.75	61	1.90	67	2.05	85	2.17	90	2.21	100	2.25
103 (This Invention)	B	98	1.85	100	1.90	100	1.95	100	1.95	100	1.95	100	1.95
	G	99	2.28	100	2.30	100	2.29	100	2.31	100	2.30	100	2.30
	R	99	2.20	100	2.23	100	2.25	100	2.25	100	2.25	100	2.25
104 (This Invention)	B	98	1.84	100	1.91	100	1.94	100	1.94	100	1.94	100	1.94
	G	99	2.29	100	2.30	100	2.31	100	2.33	100	2.33	100	2.33
	R	99	2.25	100	2.27	100	2.31	100	2.30	100	2.30	100	2.30
105 (This Invention)	B	97	1.90	99	1.95	100	1.99	100	2.00	100	2.01	100	2.01
	G	99	2.24	100	2.26	100	2.28	100	2.27	100	2.26	100	2.27
	R	99	2.09	100	2.12	100	2.15	100	2.18	100	2.20	100	2.20

Note: 1*: Relative Sensitivity

TABLE 2 (cont'd)

Color Developer		A		B		C		D		E		F	
Benzyl Alcohol (ml/l)		0		2		4		8		10		15	
Diethylene Glycol (ml/l)		0		0		0		0		5		10	
Photographic Properties		1*	D_{max}	1*	D_{max}	1*	D_{max}	1*	D_{max}	1*	D_{max}	1*	D_{max}
106	B	41	0.94	52	1.15	63	1.35	73	1.61	84	1.80	100	1.90
(Comparison)	G	45	1.63	53	1.82	69	1.99	78	2.26	89	2.30	100	2.36
	R	46	1.83	55	1.95	70	2.13	80	2.21	90	2.27	100	2.31
107	B	43	0.95	55	1.18	65	1.40	77	1.65	88	1.83	100	1.91
(Comparison)	G	49	1.61	60	1.80	70	2.01	83	2.28	91	2.31	100	2.34
	R	50	1.85	61	1.96	72	2.15	87	2.20	92	2.25	100	2.29

Note: 1*: Relative Sensitivity

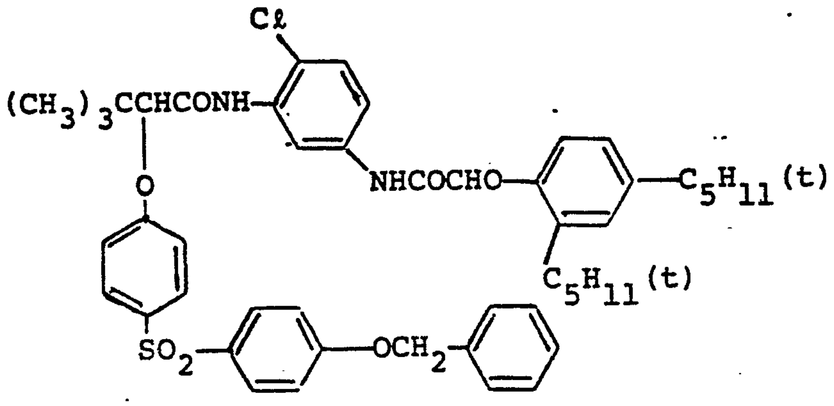
As shown in the above table, it can be seen that according to this invention, the reductions in sensitivity and density are quite low even when the concentration of benzyl alcohol in the color developer becomes less than 8 ml/liter, and the reduction of the concentration of benzyl alcohol thus causes no problem in the photographic performance. This effect is particularly large for the blue-sensitive emulsion layer.

Example 2

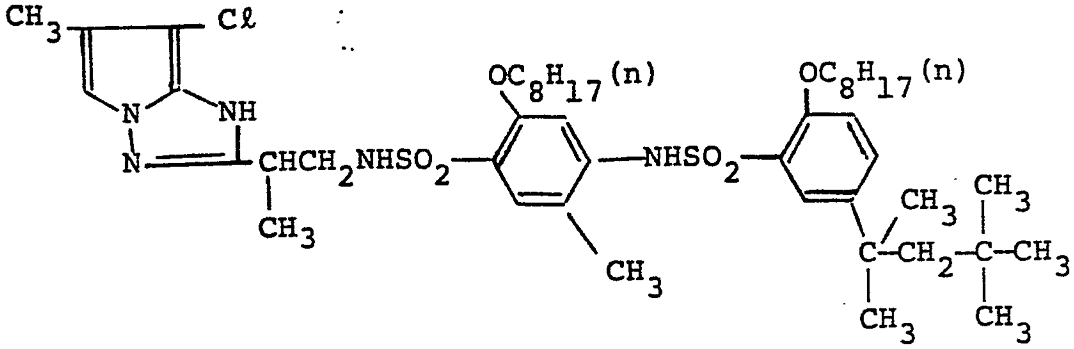
By following the same procedure as in Example 1 except that the yellow, magenta, and cyan couplers shown below were used in place of the couplers in Example 1, samples 201 to 205 of photographic light-sensitive materials were prepared.

When these samples were processed as above using the five kinds of color developers, samples 203 to 205 using the silver halide emulsions containing the tabular silver halide grains in this invention showed less dependence on the concentration of benzyl alcohol in the color developers, as in the case of Example 1.

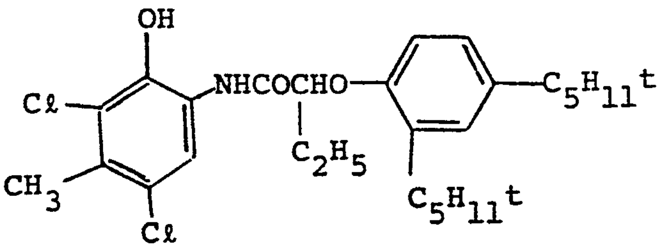
Y - 2



M - 2



C - 3



Example 3

A multilayer color photographic paper was prepared by forming the layers 1 to 7 having the following coating compsitions on paper support, both of the surfaces of which were laminated with polyethylene. In the polyethylene laminated on the first layer side of the support, white pigment (TiO_2) and bluing dye (ultramarine blue) were contained.

Layer 1: Blue-sensitive emulsion layer:

Silver chlorobromide emulsion (silver coverage) (silver bromide: 1.0 mole%)	0.30 g/m^2
Gelatin	1.86 g/m^2
Yellow coupler (a)	0.82 g/m^2
Color image stabilizer (b)	0.19 g/m^2
Solvent (c)	0.34 cc/m^2

Layer 2: Color mixing preventing layer:

Gelatin	0.99 g/m^2
Color-mixing preventing agent (d)	0.08 g/m^2

Layer 3: Green-sensitive emulsion layer:

Silver chlorobromide emulsion (silver coverage) (silver bromide: 0.5 mole%)	0.16 g/m^2
Gelatin	1.80 g/m^2
Magenta coupler (m)	0.34 g/m^2
Color image stabilizer (f)	0.20 g/m^2
Solvent (g)	0.68 cc/m^2

Layer 4: Ultraviolet absorption layer:

Gelatin	1.60 g/m^2
Ultraviolet absorbent (h)	0.62 g/m^2
Color-mixing preventing agent (i)	0.05 g/m^2
Solvent (j)	0.26 cc/m^2

Layer 5: Red-sensitive emulsion layer:

Silver chlorobromide emulsion (silver coverage) (silver bromide: 1.0 mole%)	0.26 g/m^2
Gelatin	0.98 g/m^2
Cyan coupler (k)	0.38 g/m^2
Color image stabilizer (l)	0.17 g/m^2
Solvent (e)	0.23 cc/m^2

Layer 6: Ultraviolet absorption layer:

Gelatin	0.54 g/m^2
Ultraviolet absorbent (h)	0.21 g/m^2
Solvent (j)	0.09 cc/m^2

Layer 7: Protective layer:

Gelatin	1.33 g/m^2
Acryl-modified copolymer of polyvinyl alcohol (a modification degree: 17%)	0.17 g/m^2

The coating composition for the first layer described above was prepared as follows. That is, 19.1 g of the yellow coupler (a) shown below and 4.4 g of the color image stabilizer (b) shown below were dissolved in a mixture of 27.2 mℓ of ethyl acetate and 7.9 mℓ of the solvent (c) shown below. The resulting solution was dispersed by emulsification in 185 mℓ of 10% aqueous gelatin solution containing 8 mℓ of 10% sodium dodecylbenzenesulfonate.

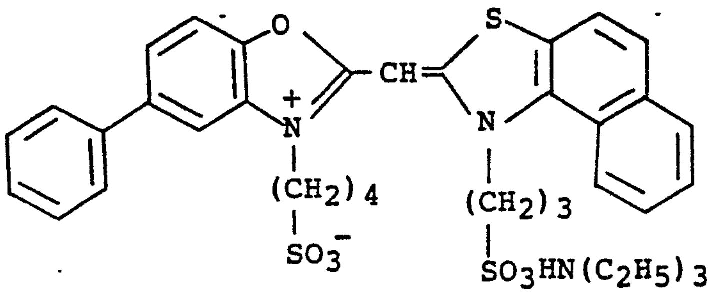
The sensitizing dye shown below for blue-sensitive emulsion layer was added to the silver chlorobromide emulsion (silver bromide: 1.0 mole%, containing 70 g/kg of silver) in an amount of 5.0×10^{-4} mole per 1 mole of silver chlorobromide to provide 90 g of the blue-sensitive emulsion.

Then, the above emulsified dispersion was mixed with the above emulsion, and the gelatin density in the mixed solution was adjusted so as to obtain the coating compositions shown above.

The coating compositions for the other second to seventh layers were also prepared in the same manner as in the above first layer coating composition. In addition, for each layer, 1-oxy-3,5-dichloro-s-triazine sodium salt was used as a hardening agent.

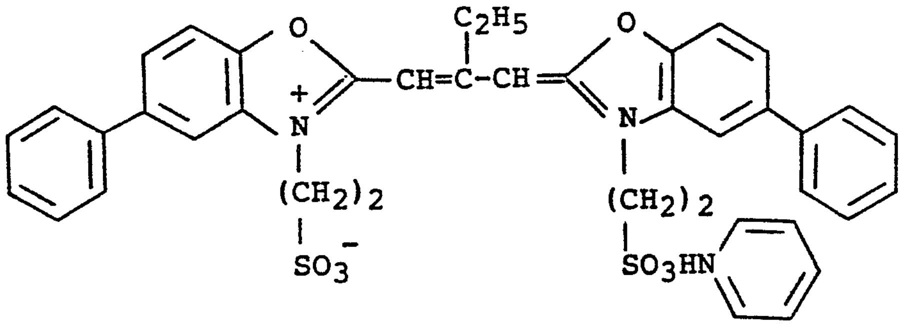
Also, for each of the emulsion layer described above, the following spectral sensitizer was used.

Spectral sensitizer for blue-sensitive emulsion layer



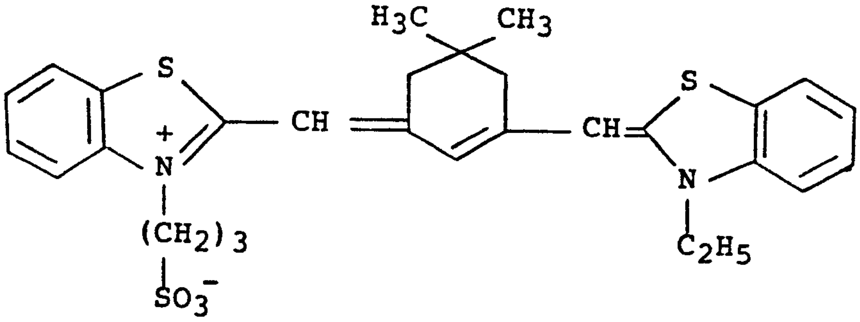
(7×10^{-4} mole per 1 mole of silver halide)

Spectral sensitizer for green-sensitive emulsion layer



(4×10^{-4} mole per 1 mole of silver halide)

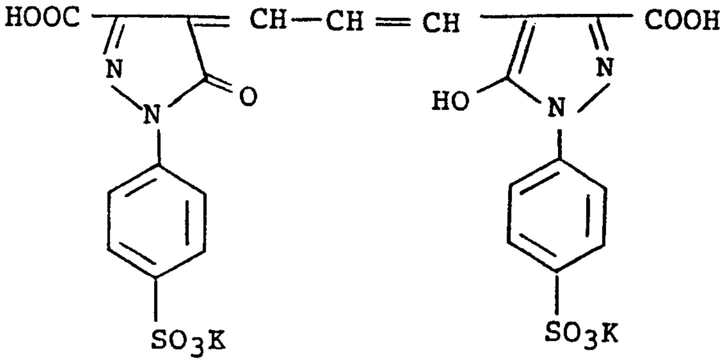
Spectral sensitizer for red-sensitive emulsion layer



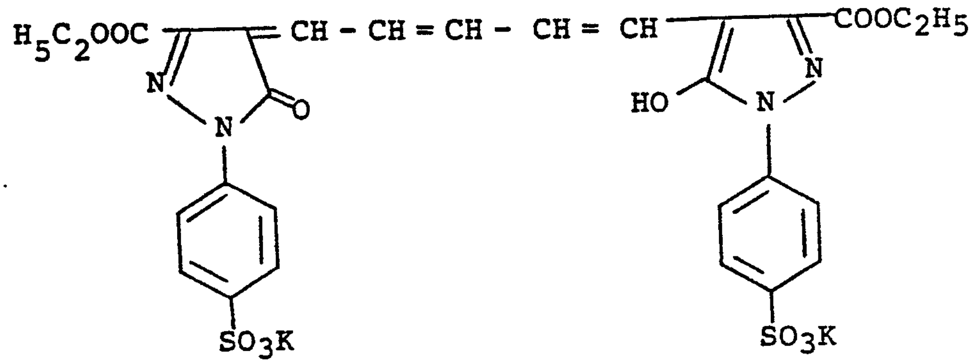
(2 x 10^{-4} mole per 1 mole of silver halide)

Also, for the green-sensitive emulsion layer and the red-sensitive emulsion layer described above, the following dyes were used as anti-irradiation dyes.

Anti-irradiation dye for green-sensitive emulsion layer:

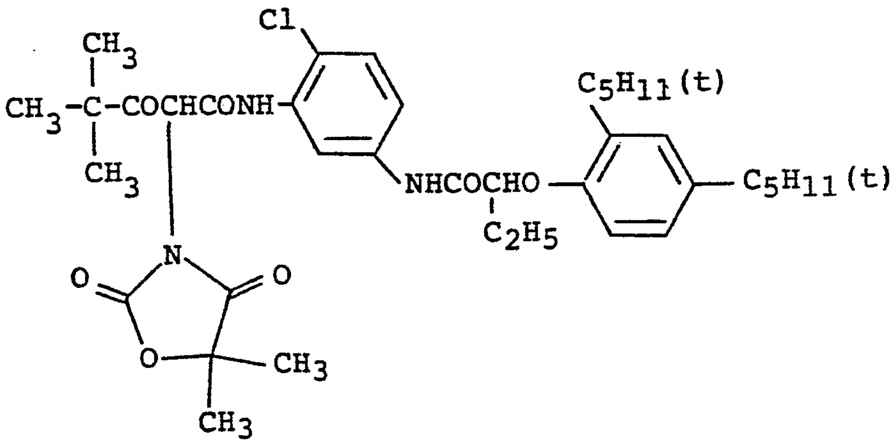


Anti-irradiation dye for red-sensitive emulsion layer:

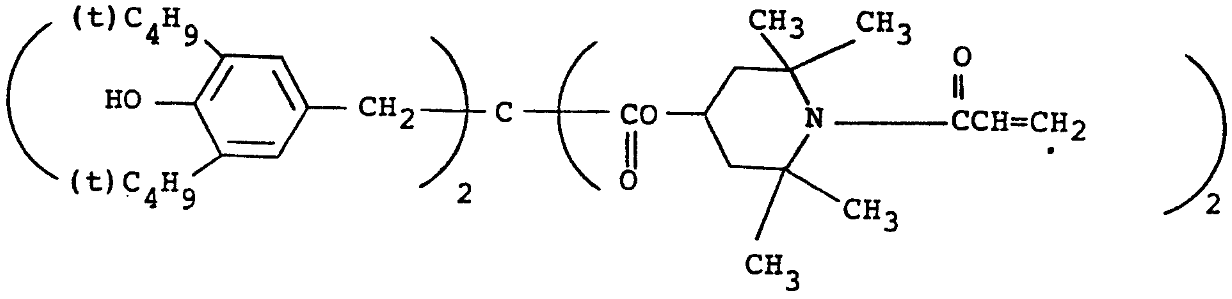


The chemical structures of the other compounds that were used in this example are as follows.

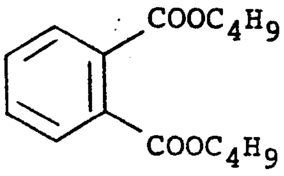
(a) Yellow coupler



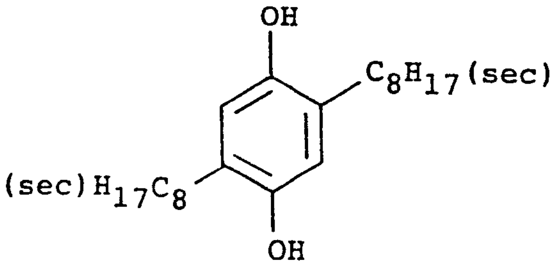
(b) Color image stabilizer



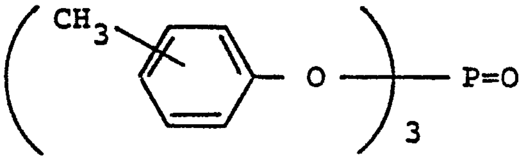
(c) Solvent



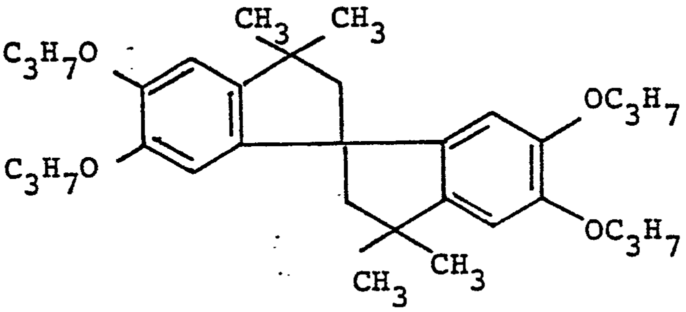
(d) Color-mixing preventing agent



(e) Solvent



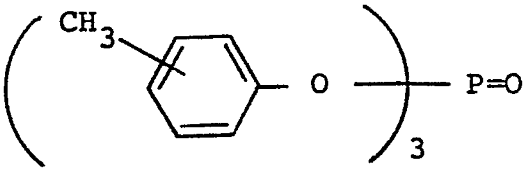
(f) Color image stabilizer



(g) Solvent

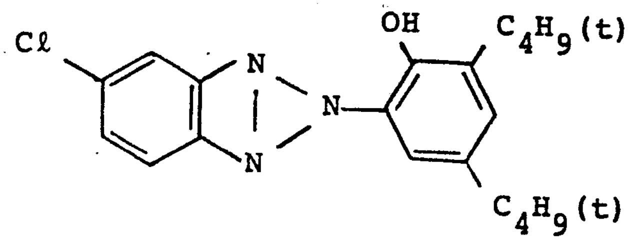
2:1 by weight mixture of

$(C_8H_{17}O)_3$—P=O and

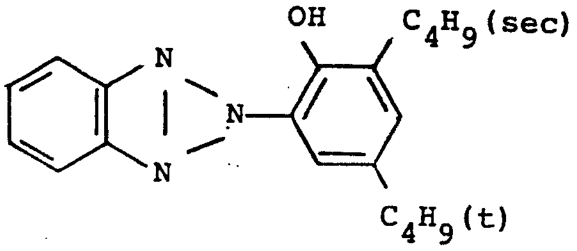


(h) Ultraviolet absorbent

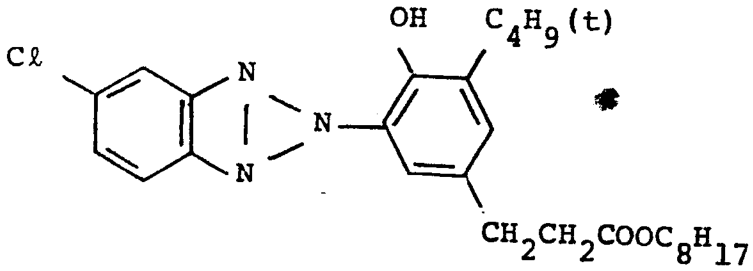
1:5:3 by mole mixture of



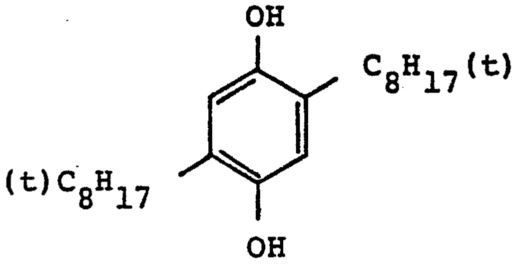
,



and



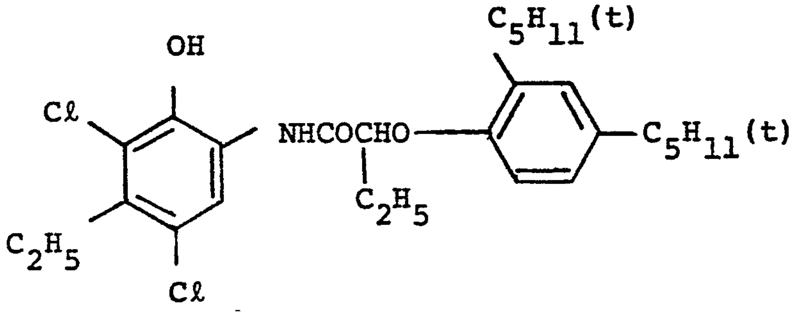
(i) Color-mixing preventing agent



(j) Solvent

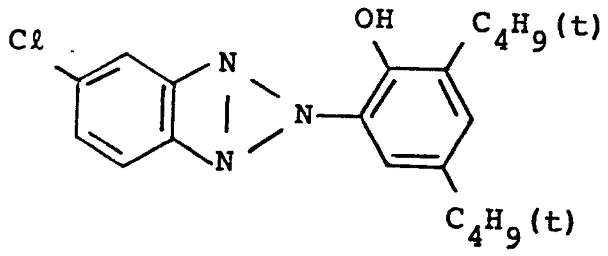
$(\text{iso-}C_9H_{18}O \rightarrow_3 P{=}O$

(k) Cyan coupler

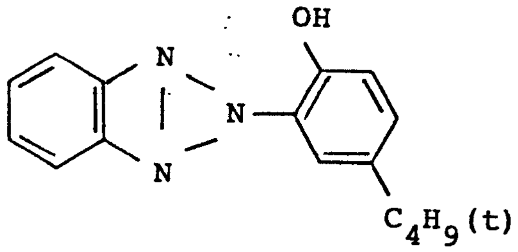


(1) Color image stabilizer

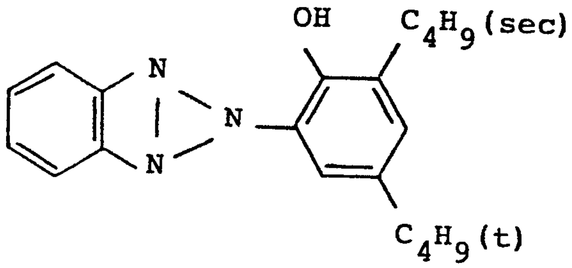
1:3:3 by mole mixture of



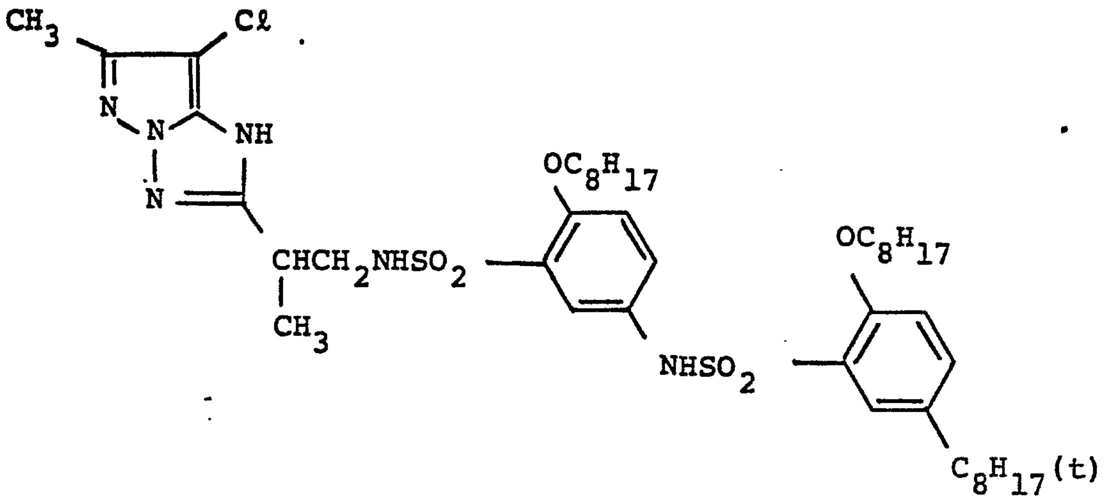
,



and



(m) Magenta coupler



The silver chlorobromide grains used for the above-described emulsion layers in this example are shown in Tabel 3 below.

TABLE 3

Sample No.	Emulsion Layer	Grain Form	Average Grain size* (μm)	Average Aspect Ratio	Projected Area (%)
106 (Comparison)	Blue-sensitive Layer	Spherical	0.60	-	-
	Green-sensitive Layer	Spherical	0.60	-	-
	Red-sensitive Layer	Spherical	0.60	-	-
107 (Comparison)	Blue-sensitive Layer	Spherical-Tabular	0.72	3.5	40
	Green-sensitive Layer	Spherical-Tabular	0.72	3.5	40
	Red-sensitive Layer	Spherical-Tabular	0.72	3.5	40
108 (Comparison)	Blue-sensitive Layer	Spherical-Tabular	0.80	4.0	50
	Green-sensitive Layer	Spherical-Tabular	0.80	4.0	50
	Red-sensitive Layer	Spherical-Tabular	0.80	4.0	50
109 (This Invention)	Blue-sensitive Layer	Tabular	0.95	7.0	65
	Green-sensitive Layer	Tabular	0.75	6.0	58
	Red-sensitive Layer	Tabular	0.75	6.0	58
110 (This Invention)	Blue-sensitive Layer	Tabular	0.95	7.0	65
	Green-sensitive Layer	Tabular	0.85	9.1	73
	Red-sensitive Layer	Tabular	0.85	9.1	73
111 (This Invention)	Blue-sensitive Layer	Tabular	1.01	8.0	70
	Green-sensitive Layer	Tabular	0.77	6.5	60
	Red-sensitive Layer	Tabular	0.77	6.5	60

(*): The average grain size is based on a sphere-calculated diameter for non-tabular grains, and on a circle-calculated diameter of the projected area for tabular grains.

Each of six color photographic papers thus prepared was light-exposed through an optical wedge and then processed in the following steps.

Processing Step	Temperature	Time
Color Development	35°C	30 sec.
Blix	35°C	30 sec.
Rinse 1	35°C	20 sec.
Rinse 2	35°C	20 sec.
Rinse 3	35°C	20 sec.
Drying	80°C	1 min.

The compositions of the processing solutions are as follows.

Color Developer

Benzyl Alcohol	Table 4
N,N-diethylhydroxylamine	4 g
Triethanolamine	10 g
Potassium carbonate	30 g
EDTA·2Na·$2H_2O$	2 g
Sodium chloride	2.0 g
4-Amino-3-methyl-N-ethyl-N-[β-(methanesulfonamide)ethyl]-p-phenylenediamine sulfate	5.0 g
Fluorescent whitening agent (4,4'-diaminostilbene series)	3.0 g

1,2-Dihydroxybenzene-3,4,6-triphosphonic acid		300 mg
Water to make		1000 mℓ
	pH	10.10

<u>Blix Solution</u>

EDTA·Fe(III)·NH_4·$2H_2O$		60 g
EDTA·2Na·$2H_2O$		4 g
Ammonium thiosulfate (70%)		120 mℓ
Sodium sulfite		16 g
Glacial acetic acid		7 g
Water to make		1000 mℓ
	pH	5.5

<u>Rinse Solution</u>

1-Hydroxyethylidene-1,1'-diphosphonic acid (60%)		1.6 mℓ
Bismuth chloride		0.35 g
Polyvinyl pyrrolidone		0.25 g
Aqueous ammonia (26%)		2.5 mℓ
Nitrilo triacetic acid·3Na		1.0 g
EDTA·4H		0.5 g
Sodium sulfite		1.0 g
5-Chloro-2-methyl-4-isothiazoline-3-one		50 mg
Formalin (37%)		0.1 mℓ
Water to make		1000 mℓ
	pH(25°C)	7.0

After processing as above using various color developers each having changed concentrations of benzyl alcohol, three-color reflection densities of each sample were measured. The results obtained are shown in Table 4 below (D_{min}: Minimum density, D_{max}: Maximum density).

TABLE 4

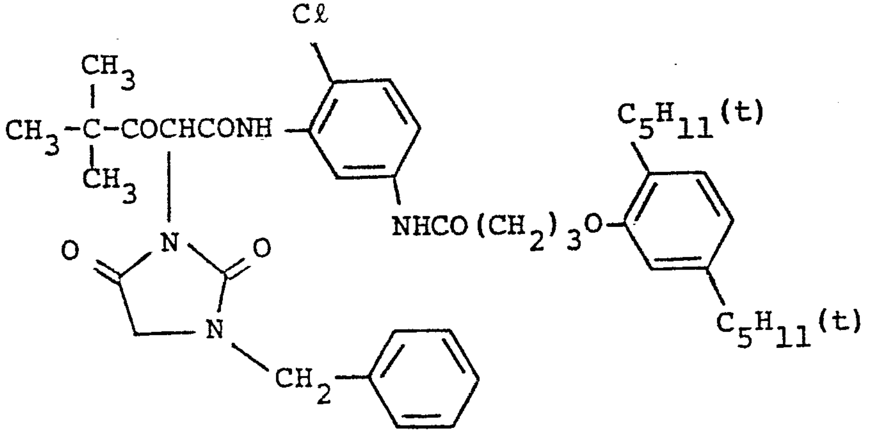
Benzyl Alcohol (ml/l)		0 (Invention)		2 (Invention)		5 (Invention)		10(Comparison)		15(Comparison)	
Photographic Properties		D_{min}	D_{max}	D_{min}	D_{max}	D_{min}	D_{max}	D_{min}	D_{max}	D_{min}	D_{max}
106	B	0.10	0.92	0.10	1.10	0.10	1.54	0.10	1.90	0.11	1.95
(Comparison)	G	0.15	1.54	0.15	1.73	0.15	2.01	0.15	2.21	0.16	2.33
	R	0.12	1.60	0.12	1.81	0.12	2.05	0.12	2.25	0.12	2.30
107	B	0.10	0.95	0.10	1.15	0.10	1.60	0.11	1.91	0.12	1.99
(Comparison)	G	0.15	1.63	0.15	1.75	0.15	2.10	0.17	2.21	0.18	2.35
	R	0.12	1.70	0.12	1.85	0.12	2.13	0.12	2.23	0.13	2.33
108	B	0.10	1.05	0.10	1.20	0.10	1.66	0.11	1.95	0.12	1.97
(Comparison)	G	0.15	1.68	0.15	1.77	0.15	2.13	0.16	2.25	0.18	2.35
	R	0.12	1.72	0.12	1.80	0.12	2.15	0.12	2.30	0.13	2.35
109	B	0.10	1.75	0.10	1.80	0.10	1.85	0.12	1.90	0.13	1.92
(This Invention)	G	0.15	2.21	0.15	2.24	0.15	2.30	0.16	2.33	0.19	2.35
	R	0.12	2.17	0.12	2.25	0.12	2.27	0.12	2.30	0.13	2.30
110	B	0.10	1.88	0.10	1.93	0.10	1.96	0.12	1.97	0.13	1.98
(This Invention)	G	0.15	2.25	0.15	2.28	0.15	2.30	0.17	2.31	0.19	2.35
	R	0.12	2.20	0.12	2.25	0.12	2.27	0.12	2.29	0.13	2.31
111	B	0.10	1.80	0.10	1.85	0.10	1.90	0.12	1.93	0.13	1.95
(This Invention)	G	0.15	2.18	0.15	2.25	0.15	2.30	0.17	2.31	0.20	2.32
	R	0.12	2.15	0.12	2.20	0.12	2.23	0.12	2.28	0.13	2.30

As shown in the above Table 4, it can be seen that when the silver-halide color photographic emulsion according to the present invention is used under the condition such that the concentration of benzyl alcohol in the color developer is within the range of not more than 8 mℓ/liter, a fog is reduced and a satisfactory coloring property can be obtained, whereby good photographic performance can be obtained.

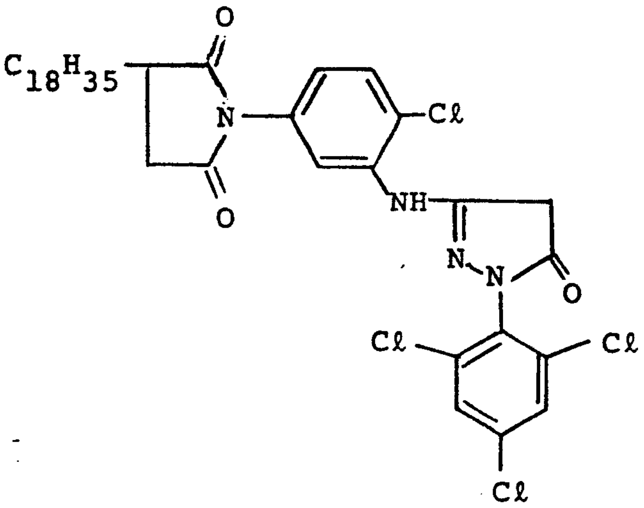
Example 4

The color photographic materials were prepared in the same procedure as in Example 3 except that the yellow, magenta, and cyan couplers shown below were used in place of the couplers in Example 3. As a result, according to the present invention, good photographic performance can be obtained.

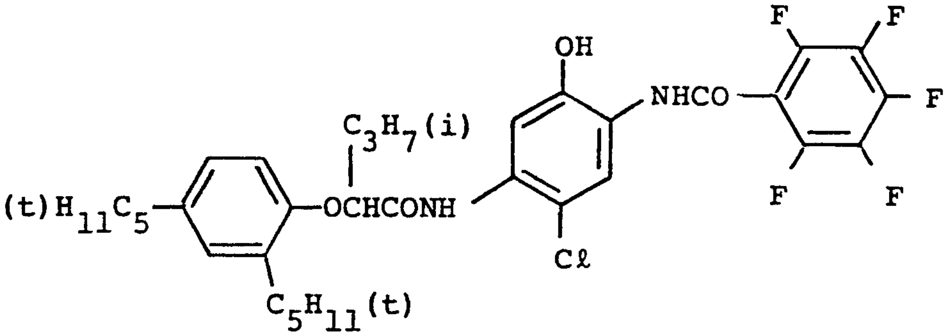
Yellow Coupler:



Magenta Coupler:



Cyan Coupler:



While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

WHAT IS CLAIMED IS:

1. A process for processing a silver halide color photographic material which comprises processing a silver halide photographic material having on a support at least one silver halide photographic emulsion layer containing a silver bromide or silver chlorobromide emulsion in which tabular silver halide grains having main crystal planes parall to each other and an average aspect ratio of at least 5 account for at least 50% of the total projected area of the silver halide grains with a color developer containing 8 ml/liter or less of benzyl alcohol.

2. A process for processing a silver halide color photographic material as in claim 1, wherein said color developer contains 5 ml/liter or less of benzyl alcohol.

3. A process for processing a silver halide color photographic material as in claim 1, wherein said color developer contains an aromatic primary amine color developing agent.

4. A process for processing a silver halide color photographic material as in claim 3, wherein said aromatic primary amine color developing agent is present in an amount of from 0.5 g to about 10 g per liter of the developer.

5. A process for processing a silver halide color photographic material as in claim 1, wherein the pH is from 9 to 12.

6. A process for processing a silver halide color photographic material as in claim 4, wherein the pH is from 9 to 11.0.

7. A process for processing a silver halide color photographic material as in claim 1, wherein the average aspect ratio is at least 8.

8. A process for processing a silver halide color photographic material as in claim 1, wherein the silver bromide or silver chlorobromide contains 3 mol% or less of silver iodide.

9. A process for processing a silver halide color photographic material as in claim 1, wherein the average diameter of the tabular silver halide grains is from 0.25 μm to 2.8 μm and the thickness of the grains is at most 0.38 μm.

10. A process for processing a silver halide color photographic material as in claim 1, wherein the average diameter of the tabular silver halide grains is from 0.45 μm to 1.9 μm and the thickness of the grains is at most 0.2 μm.

11. A process for processing a silver halide color photographic material as in claim 1, wherein said

tabular silver halide grains account for at least 70% of the total projected area of the silver halide grains.

12. A process for processing a silver halide color photographic material as in claim 1, wherein said tabular silver halide grains account for at least 90% of the total projected area of the silver halide grains.

13. A process for processing a silver halide color photographic material as in claim 6, wherein the average diameter of the tabular silver halide grains is from 0.45 μm to 1.9 μm and the thickness of the grains is at most 0.2 μm.

14. A process for processing a silver halide color photographic material as in claim 13, wherein said tabular silver halide grains account for at least 70% of the total projected area of the silver halide grains.