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(54) **A method for processing silver halide colour photographic light-sensitive materials.**

(57) A method for processing a silver halide color photographic light-sensitive material (A) comprising a support having thereon a silver halide emulsion layer containing silver halide grains having a silver iodide content of not less than 0.5 mol%, said method comprising :

developing said photographic material with a color developer ;

bleaching said photographic material with a bleaching solution ; and

fixing said photographic material with a fixing solution (FA) ;

wherein the fixing solution (FA) is replenished by a fixing solution (FB) that has processed a silver halide photographic material (B) comprising a support having thereon a silver halide emulsion layer containing silver halide grains substantially not containing silver iodide.

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FIELD OF THE INVENTION

The present invention relates to a method for processing a silver halide color photographic light-sensitive material (hereinafter sometimes merely called light-sensitive material), and more particularly to a light-sensitive material processing method having an improved fixing characteristic.

BACKGROUND OF THE INVENTION

In general, the processing of a light-sensitive material to form a color image comprises a color development process and a fixing process; generally, the silver image, formed by a first development process in the case of a reversal color light-sensitive material or by a color development process in the case of a color negative film, is bleached with an oxidizing agent (bleaching agent) to be made into a soluble silver salt, which is then dissolved to be removed by a fixing process for desalting, whereby a color dye image is formed on the light-sensitive material.

The light-sensitive material is usually subjected to running processing in an automatic processor of a photofinisher, but there has lately been a demand for return of the processed film and prints to the customer within the day the D.P. order was accepted, and more recently, even its return within only several hours after the acceptance is growingly demanded, and thus it is now of urgent necessity to develop new techniques for still more rapid processing.

However, a fixer solution used in the processing, as it is continuously used to fix the light-sensitive material, has silver complex salts become accumulated therein to thereby gradually lower its fixing efficiency and, when still continuously used as it is, the solution is exhausted to become finally unable to be used. In order to revive the exhausted fixer, there is usually adopted a process of replenishing the solution with an appropriate amount of a fresh fixer solution and having the exhausted liquid overflown out. However, discharging the overflow is unacceptable from the standpoint of environmental pollution. In view of such the situation, it has lately been proposed a method for recycling the overflow, while being replenished with a fresh fixer solution.

Despite of the above method, as the frequency of using the fixer solution increases, its fixing ability gradually lowers to finally cause fixing failure. To solve this problem, there is proposed a method for increasing the concentration of or adding a fixing accelerator to the fixer solution to improve its fixing ability. However, the former, the use of a highly concentrated fixer solution, has its limit in respect of the solubility of a fixing agent, while the latter, adding a fixing accelerator such as the sulfur compound described in JP E.P. No. 35754/1970 or the polyethylene glycol compound described in JP E.P. No. 39173/1973, is not sufficient.

On the other hand, in recent years, there has been a strong demand for reducing the discharge of photographic processing waste liquid for economical reason and from the viewpoint of the protection of environment, so that various techniques therefor have now been investigated. For example, JP O.P.I. Nos. 60731/1978 and 14849/1980 describe techniques for recovering silver from a used fixer liquid to recycle the fixer liquid, but this method requires an automatic processor equipped with a silver recovery device, so that the automatic processor is necessarily bulky and costly, and therefore impracticable. JP O.P.I. Nos. 26174/1986, 251852/1986 and 251851 disclose techniques to reduce the replenishing amount to a photographic processing liquid, but when the replenishing amount is reduced, the processing liquid's renewal rate lowers. Particularly in the fixing process, there occurs an undesirable state such as fixation failure or attachment of sediment to the periphery (rollers, solutions' interface) of the fixer bath, so that the reduction in the replenishing amount has its limit.

Further, most recently, the use of small-sized automatic processors, called 'minilab', is prevalent. Consequently, the number of small-scaled photofinishing labs handling small number of processings are increasing, giving rise to such a state that, for example, there are some D.P. processings on Mondays and Tuesdays, but almost none in weekends. As a result, the previously stated fixation problem or attachment of sediment to the periphery of the fixing bath is liable to occur.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to improve the fixation problem that is liable to occur in the fixer bath or bleach-fix bath at the time of rapid processing, and to provide a method for processing a silver halide color photographic light-sensitive material, which enables a further rapid processing.

It is another object of the invention to provide a method for processing a silver halide color photographic light-sensitive material, which makes it possible to reduce the amount of a waste liquid, to increase the economical merit and to decrease the environmental pollution load.

It is still another object of the invention to provide a method for processing a silver halide color photographic light-sensitive material, which has little fluctuation of processing and causes little sediment to the periphery of

the fixing bath, and which can be carried out stably over a long period of time.

The above objects of the invention are accomplished by a method using a color developer solution, a bleaching ability-having solution and a fixing ability-having solution for processing each of a silver halide color photographic light-sensitive material (A) comprising a support having thereon at least one silver halide emulsion layer having a silver iodide content of 0.5 mol% or more and a silver halide color photographic light-sensitive material (B) comprising a support having thereon an emulsion substantially not containing silver iodide, in which a part or the whole of the overflow from said fixing ability-having solution that has processed said silver halide color photographic light-sensitive material (B) is used to replenish said fixing ability-having solution for fixing said silver halide color photographic light-sensitive material (A).

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 and Fig. 2 are explanatory diagrams showing the flows of the processing solutions in the processing lines of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The color developing process of the invention is a process for forming a color image; more particularly a process for forming a color dye image by the coupling reaction of a color coupler with the oxidation product of a color developing agent.

Accordingly, in the color developing process, a color developer solution usually needs to contain a color developing agent, but a color light-sensitive material containing a color developing agent may be processed either in a color developing agent-containing developer solution or in an alkali solution, called an activator solution.

The color developing agent contained in the color developer solution is an aromatic primary amine color developing agent, examples of which include aminophenol derivatives and p-phenylenediamine derivatives. These color developing agents may be used in the form of organic and inorganic acid salts, such as hydrochlorides, sulfates, p-toluenesulfonates, sulfites, oxalates and benzenesulfonates.

These compounds each may be used in an amount of preferably about 0.1g to about 30g, and more preferably about 1g to 15g per liter of a color developer solution.

If in an amount of less than 0.1g, the compound would not be able to provide any sufficient color density.

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

Examples of the above aminophenol developing agent include o-aminophenol, p-aminophenol, 5-amino-2-hydroxytoluene, 2-amino-3-hydroxytoluene and 2-hydroxy-3-amino-1,4-dimethylbenzene.

A particularly useful aromatic primary amine color developing agent is a N-N-dialkyl-p-phenylenediamine compound, wherein the alkyl group and phenyl group each may or may not have a substituent. The particularly preferred among examples of the above compound are N-N-dimethyl-p-phenylenediamine hydrochloride, N-methyl-p-phenylenediamine sulfate, N,N-dimethyl-p-phenylenediamine sulfate, 2-amino-5-(N-ethyl-N-dodecylamino)toluene, N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-amino-aniline sulfate, N-ethyl-N-β-hydroxyethylaminoaniline, 4-amino-3-methyl-N,N′-diethylamiline, and 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluene sulfonate.

The above color developing agent may be used alone or in combination of two or more kinds thereof. The above color developing agent may be incorporated into the color photographic light-sensitive material. The incorporation may be made according to any one of the following methods: the method for incorporating the color developing agent in the form of its metallic salt described in U.S. Patent No. 3,719,492; the method for incorporating the agent in the form of a Schiff's salt described in U.S. Patent No. 3,342,559 and Research Disclosure No.15159, 1976; the method for incorporating the agent in the form of a dye precursor described in JP O.P.I. Nos. 65429/1983 and 24137/1983; and the method for incorporating the agent in the form of a precursor described in U.S. Patent No. 3,342,597. In this instance, it is also possible to process the silver halide color photographic light-sensitive material in an alkali activator solution, and immediately after that, the light-sensitive material is processed in a bleach-fix bath. The color developer solution used in the invention may contain a usual alkali agent such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, potassium carbonate, sodium sulfate, sodium metaborate or borax; various additives including benzyl alcohol, a halogenated alkali metal such as potassium bromide or potassium chloride, a development control agent such as citrazinic acid, and a preservative such as hydroxylamine or a sulfite; various defoaming agents or surfactants; and organic solvents such as methanol, dimethylformamide or dimethylsulfoxide.

The color developer solution of the invention is used preferably at a pH of 7 or more, and more preferably

at a pH of about 9 to 13.

The color developer solution of the invention may, if necessary, contain an antioxidant such as diethylhydroxylamine, tetronic acid, tetronimide, 2-anilinoethanol, dihydroxyacetone, aromatic secondary alcohol, hydroxamic acid, hydrazinoacetic acid, pentose, hexose or pyrogallol-1,3-dimethyl-ether. In the color developer solution used in the invention, various chelating agents may be used in combination as metallic ion chelating agents, including aminepolycarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminopentaacetic acid; organic phosphonic acids such as 1-hydroxyethylidene-1,1′-diphosphonic acid; aminopolyphosphonic acids such as aminotri(methylenephosphonic acid) or ethylenediaminetetraphosphoric aic; oxycarboxylic acids such as citric acid or gluconic acid; phosphonocarboxylic acids such as 2-phosphonobutane-1,2,4-tricarboxylic acid; polyphosphoric acids such as tripolyphosphoric acid or hexametaphosphoric acid; or polyhydroxy compounds.

The water-soluble surfactant described in Japanese Patent Application No. 341357/1989 may be preferably used in the color developer solution for increasing the effect of the invention.

In the invention, the bleaching ability-having solution means a bleaching solution or bleach-fix solution. A bleaching solution is more preferable in respect of the effect of the invention.

The bleaching agent preferably usable in the bleaching ability-having solution of the invention is an organic acid metallic complex salt, in which metallic ions such as of iron, cobalt or copper is coordinated to an organic acid such as an aminopolycarboxylic acid, oxalic acid or citric acid. The most preferred organic acid for use in forming such organic acid metallic complex salts is a polycarboxylic acid or aminopolycarboxylic acid, which may be in the form of an alkali metallic salt, ammonium salt or water-soluble amine salt. Examples of these are listed below:

1-1 Ethylenediaminetetraacetic acid
1-2 Diethylenetriaminepentaacetic acid
1-3 Ethylenediamine-N-(β-hydroxyethyl)-N,N′,N′-triacetic acid
1-4 1,3-Propylenediaminetetraacetic acid
1-5 Nitrilotriacetic acid
1-6 Cyclohexanediaminetetraacetic acid
1-7 Iminodiacetic acid
1-8 Dihydroxyethylglycinecitric (or -tartaric) acid
1-9 Ethyl ether diaminetetraacetic acid
1-10 Glycol ether diaminetetraacetic acid
1-11 Ethylenediaminetetrapropioneacetic acid
1-12 Phenylenediaminetetraacetic acid
1-13 Sodium ethylenediaminetetraacetate
1-14 Trimethylammonium ethylenediaminetetraacetate
1-15 Tetrasodium ethylenediaminetetraacetate
1-16 Pentasodium diethylenetriaminepentaacetate
1-17 Sodium ethylenediamine-N-(β-hydroxyethyl)-N,N′,N′-triacetate
1-18 Ammonium 1,3-propylenediaminetetraacetate
1-19 Sodium nitrilotriacetate
1-20 Sodium cyclohexanediaminetetraacetate

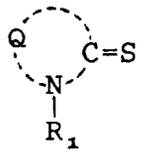
Among the above bleaching agents the particularly useful for the effect of the invention and rapid-processability are ethylenediaminetetraacetatic acid ferric complex salt, 1,3-propylenediaminetetraacetic acid ferric complex salt, diethylenetriaminepentaacetic acid ferric complex salt and glycol ether diaminetetraacetic acid ferric complex salt. Especially, 1,3-diaminopropanetetraacetic acid ferric complex salt is preferred. These complex salts are used in the form of ammonium salts, sodium salts, triethanolammonium salts, potassium salts, trimethylammonium salts or monoethanolammonium salts. From the viewpoint of solubility and processability, the ammonium salts are especially useful.

These bleaching agents may be used in an amount of preferably 20 to 400g/liter, more preferably 30 to 250g/liter, and most preferably 50 to 180g/liter.

To the bleaching ability-having solution of the invention may be added various bleaching accelerators as described in JP O.P.I. Nos. 280/1971, 71643/1979 and 42349/1974, JP E.P. Nos. 8506/1970, 556/1971, 8836/1970 and 9854/1978, Belgian Patent No. 770,910.

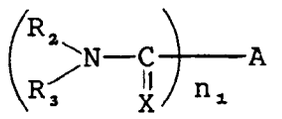
The bleaching solution of the invention, when containing at least one of imidazoles and derivatives thereof or compounds represented by the following Formulas I to IX, well exhibits the effect of the invention and also another effect of preventing the precipitate attributable to the silver in the bleaching solution.

Formula I

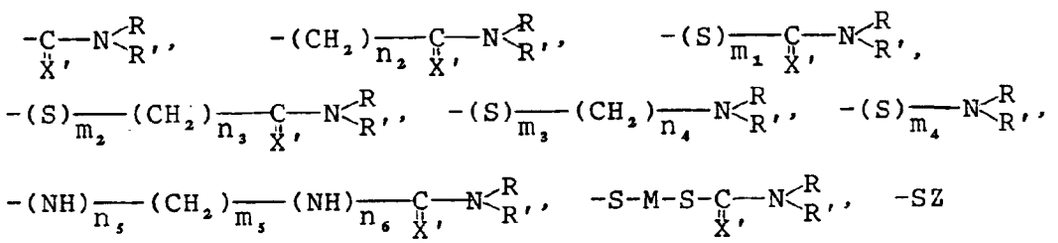


wherein Q represents a group of atoms necessary to form a nitrogen-containing heterocyclic ring, including 5 or 6-member unsaturated ring-condensed one; R_1 is a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group, an aryl group, a heterocyclic group, including 5 or 6-member unsaturated ring-condensed one, or an amino group.

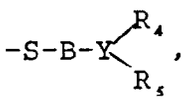
Formula II



wherein R_2, R_3 and R_4 each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxy group, a carboxy group, an amino group, an acyl group having 1 to 3 carbon atoms, an aryl group or an alkenyl group; A represents

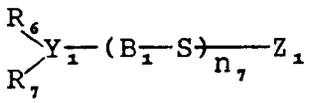


or n_1-valent heterocyclic residue, including 5 or 6-member unsaturated ring-condensed one; X is =S, =O or =NR", wherein R and R' are as defined for R_2 and R_3, respectively, X' is as defined for X, Z is a hydrogen atom, an alkali metal atom, an ammonium group, an amino group, a nitrogen-containing heterocyclic residue, an alkyl group or



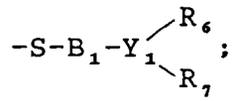
M is a divalent metal atom, R" is a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group, an aryl group, a heterocyclic residue, including 5 or 6-member unsaturated ring-condensed one, or an amino group, and n_1 to n_6 and m_1 to m_5 each represent an integer of 1 to 6. B is an alkylene group having 1 to 6 carbon atoms, Y is -N<, >C- or -CH<, and R_4 and R_5 are as defined for R_2 and R_3, respectively, provided that R_4 and R_5 each may represent -B-SZ, and R_2 and R_3, R and R', and R_4 and R_5 may combined with each other to form the respective rings. The compounds represented by the above formula include those phenolated compounds and salts thereof.

Formula III



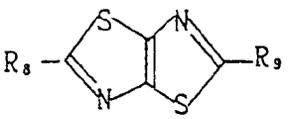
wherein R_5 and R_7 each is a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a hydroxy group, a carboxy group, an amino group, an acyl group having 1 to 3 carbon atoms, an aryl group, an alkenyl group or $-B_1-S-Z_1$, provided that R_5 and R_7 may combine with each other to form a ring; Y_1 is >N- or >CH-; B_1 is an alkylene group having 1 to 6 carbon atoms; Z, is a hydrogen atom, an alkali metal atom, an ammonium group, an amino

group, a nitrogen-containing heterocyclic residue or

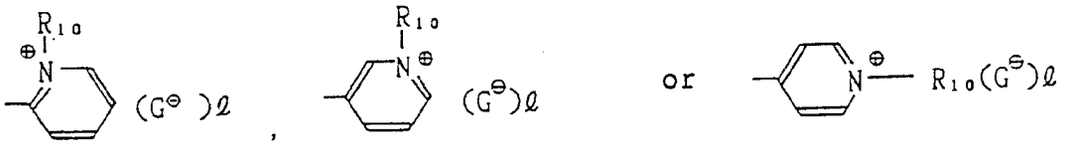


and n_7 is an integer of 1 to 6.

Formula IV

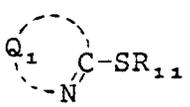


wherein R_8 and R_9 each represent

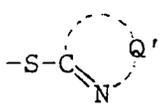


R_{10} is an alkyl group or $-(CH_2)_{n8}SO_3^{\ominus}$, provided that when R_{10} is $-(CH_2)_{n8}SO_3^{\ominus}$, 1 representsd 0 and when an alkyl group, 1 represents 1; $G^{\ominus}$ is an anion: and n_8 is an integer of 1 to 6.

Formula V

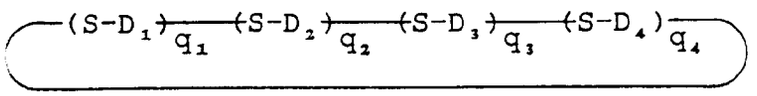


wherein Q_1 is a group of atoms necessary to form a nitrogen-containing heterocyclic ring, including 5 or 6-member unsaturated or saturated ring-condensed one; and R_{11} is hydrogen atom, an alkali metal atom,



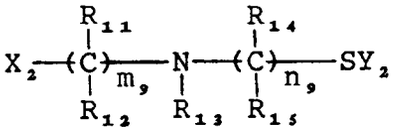
or an alkyl group, provided that Q′ is as defined for Q_1.

Formula VI

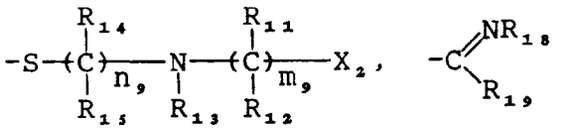


wherein D_1, D_2, D_3 and D_4 each are a mere bond, an alkylene group having 1 to 8 carbon atoms or a vinylene group; and q_1, q_2, q_3 and q_4 each represent an integer of 0, 1 or 2. The ring formed with the sulfur atom may be condensed with a 5 or 6-member saturated or unsaturated ring.

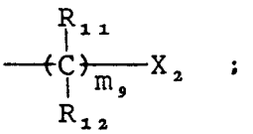
Formula VII



wherein X_2 represents -COOM′, -OH, $-SO_3M'$, $-CONH_2$, $-SO_2NH_2$, $-NH_2$, -SH, -CN, $-CO_2R_{16}$, $-SO_2R_{16}$, $-OR_{16}$, $-NR_{16}R_{17}$, $-SR_{16}$, $-SO_3R_{16}$, $-NHCOR_{16}$, $-NHSO_2R_{16}$, $-OCOR_{16}$ or $-SO_2R_{16}$; Y_2 is



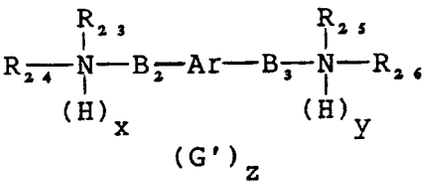
or a hydrogen atom; m_9 and n_9 each are an integer of 1 to 10; R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{17} and R_{18} each are a hydrogen atom, a lower alkyl group, an acyl group or



;

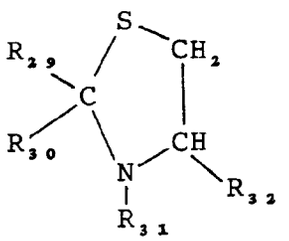
R_{16} is a lower alkyl group; R_{19} is $-NR_{20}R_{21}$, $-OR_{22}$ or $-SR_{22}$, wherein R_{20} and R_{21} each are a hydrogen atom or a lower alkyl group, and R_{22} is a group of atoms necessary to form a ring by combining with R_{18}, provided that R_{20} or R_{11} may combine with R_{18} to form a ring, and M′ is a hydrogen atom or cation.

Formula VIII



wherein Ar represents a divalent arylene group or a divalent organic group in combination of an aryl group with an oxygen atom and/or an alkylene group; B_2 and B_3 each represent a lower alkylene group; R_{23}, R_{24}, R_{25} and R_{26} each represent a hydroxy group-substituted lower alkyl group; x and y each represent an integer of 0 or 1; G′ is an anion; and z is an integer of 0, 1 or 2.

Formula IX



wherein R_{29} and R_{30} each represent a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group; R_{31} is a hydrogen atom or an alkyl group; and R_{32} is a hydrogen atom or a carboxy group.

Typical examples of the compounds represented by the foregoing Formulas I to IX and the imidazoles and derivatives thereof include the exemplified compounds I-1 to I-10, II-1 to II-27, III-1 to III-15, IV-1 to IV-3, V-1

to V-23, VI-1 to VI-17, VII-1 to VII-15, VIII-1 to VIII-7, IX-1 to IX-5, and A-1 to A-8 described at pages 17 to 39 of Japanese Patent Application No. 32501/1988.

These compounds are ones generally used as bleaching accelerators, which are hereinafter referred to as the bleaching accelerator of the invention.

These bleaching accelerators may be used alone or in combination, and used in an amount of preferably 0.01 to 100g per liter of the bleaching solution. However, when the adding amount of the bleaching accelerator is too small, the bleaching acceleration effect is small, while when the amount is larger than is necessary, precipitation may occur to stain the silver halide color light-sensitive material, so that the adding amount is preferably 0.05 to 50g/liter, and more preferably 0.05 to 15g/liter.

The bleaching accelerator may be added and dissolved as it is, but generally dissolved in advance in an organic acid, if necessary, in combination with an organic solvent such as methanol, ethanol or acetone, prior to its addition to the bleaching solution.

The bleaching solution of the invention is used at a pH of preferably 2.0 to 5.5, and more preferably 2.5 to 5.0. The bleaching solution, when used at a pH exceeding 5.5, may be unable to sufficiently prevent the light-sensitive material from bleaching fog, and, when at a pH of lower than 2, can prevent the bleaching fog, but is liable to affect the photographic characteristics of the light-sensitive material. The bleaching solution is used at a temperature of preferably 20° to 45°C, and more preferably 25° to 42°C.

To the bleaching solution of the invention is usually added a halide such as ammonium bromide or potassium bromide.

The bleaching solution of the invention may contain a single one of or two or more kinds of pH buffers such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, acetic acid, sodium acetate and ammonium hydroxide, and may also contain various additives such as a brightening agent, defoaming agent, surfactant, surfactant and fungicide.

The replenishing amount of a replenisher to the bleaching solution of the invention, where the silver halide color photographic light-sensitive material processed is for camera exposure, is 20ml to 400ml/m^2, preferably 30ml to 350ml/m^2, more preferably 40ml to 300ml/m^2 and most preferably 50ml to 250ml.

Where the color light-sensitive material is for making color prints, the replenishing amount is preferably 5 to 200ml /m^2, and more preferably 10ml to 100ml/m^2.

In the invention, the light-sensitive material's processing in the bleaching solution of the invention is following by fixation in a fixing bath from the viewpoint of rapid processing.

In the invention, the fixing ability-having solution means a fixer, stop-fixer, bleach-fixer or hardening-fixer. For the effect of the invention, the fixer and/or bleach-fixer is suitable. Particularly, the fixer bath is most useful for the effect of the invention.

The fixer bath and bleach-fix bath of the invention contain a silver halide fixing agent and may, if necessary, also contain a sulfite as a preservative. Suitably usable as the silver halide fixing agent is a compound that reacts with silver halide to form a water-soluble complex salt, typical examples of which include thiosulfates such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate: thiocyanates such as potassium thiocyanate, sodium thiocyanate and ammonium thiocyanate; thiourea and thioether. The combined use of the thiocyanate and thiosulfate is most useful. These fixing agents may be used in an amount of from 0.1 mol/liter up to a dissolvable extent, but generally of 0.5 to 3 mol/liter.

The fixer bath and bleach-fix bath may contain a single of or two or more kinds of pH buffers such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, acetic acid, sodium acetate and ammonium hydroxide; may also contain a brightening agent, defoaming agent or surfactant: and may further contain additives including a preservatives such as hydroxylamine, hydrazine or a hydrogensulfite addition product of an aldehyde compound, an organic chelating agent such as aminopolycarboxylic acid, a stabilizer such as nitro-alcohol or a nitrate, and an organic solvent such as methanol, dimethylsulfoamide or dimethylsulfoxide.

The invention can conspicuously exhibit its improving effect when the light-sensitive material is processed in a stabilizer bath following the fixer bath or bleach-fix bath.

The replenishing amount of a replenisher to the stabilizer bath is preferably 1 to 80 times, and more preferably 2 to 60 times the carry-in amount per m^2 of a color light-sensitive material for camera use from the preceding bath. In the invention, the concentration of the carried-in components (bleach-fix or fixer solution) in the final stabilizer bath is preferably 1/500 or less, and more preferably 1/1000 or less. Further, from the standpoint of antipollution and preservability of the stabilizer solution, the stabilizer bath should be constituted so as to make the concentration preferably 1/500 to 1/100000, and more preferably 1/2000 to 1/50000.

The stabilizer bath consists of a plurality of baths, preferably not less than two baths and not more than six baths, more preferably two or three baths, and most preferably two baths. And it is preferable for the effect

of the invention as well as for antipollution to constitute the baths to be of a couter-current system, in which the solution is supplied to the final bath and overflown into the preceding bath.

The carry-in amount depends on the type of a light-sensitive material used, the transport speed, transport system and the system of squeezing the surface of the light-sensitive material of an automatic processor used, but in the case of a color light-sensitive material, usually color roll film, for camera use, the carry-in amount is normally 50 to 150ml/m^2, while in the case of a light-sensitive material for making color prints, the carry-in amount is 15 to 100ml/m^2. The effective replenishing amount to make up for the loss of the stabilizer bath due to the carry-in amount is in the range of 50ml/m^2 to 4.0 liters/m^2, and the more effective replenishing amount is 75ml to 900ml/m^2.

The light-sensitive material is processed in the stabilizer bath at a temperature of preferably 15° to 60°C, and more preferably 20° to 45°C.

The stabilizer bath may contain a chelating agent. Chelating agents are detailed in the prior patent application specification, pp.73-82, filed by us, the inventor.

The stabilizer bath of the invention is used at a pH of preferably 4.0 to 9.0, more preferably 4.5 to 8.5, and most preferably 5.0 to 8.5 for the effect of the invention as well as for improving the preservability of the resulting image.

Any of those generally known alkali or acid agents may be used as a pH control agent for the stabilizer bath of the invention.

To the stabilizer bath of the invention may be added an organic acid salt such as a salt of citric acid, acetic acid, succinic acid, oxalic acid or maleic acid; a pH control agent such as phosphoric acid, boric acid, hydrochloric acid or sulfuric acid; a surfactant; anticeptic; and a metallic salt such as a salt of Bi, Mg, Zn, Ni, Al, Sn, Ti or Zr. These compounds may be added in any combination of appropriate amounts to an extent necessary to maintain pH of the stabilizer bath of the invention and neither to affect the preservability of the resulting image nor to cause precipitation.

Useful examples of the fungicide used in the stabilizer bath of the invention include hydroxybenzoate compounds, phenol compounds, thiazole compounds, pyridine compounds, guanidine compounds, carbamate compounds, morpholine compounds, quaternary phosphonium compounds, ammonium compounds, urea compounds, isooxazole compounds, propanolamine compounds, sulfamide compounds, amino acid compounds, active halogen-releasing compounds and benzotriazole compounds. These fungicides are detailed in the previously mentioned prior patent application specification pp. 84-90, filed by us, the inventor.

In the invention, silver recovery from the stabilizer, fixer and bleach-fix baths may be performed in accordance with various methods such as the electrolysis method described in French Patent No. 2,299,667, the precipitation method described in JP O.P.I. No. 73037/1977 and West German Patent No. 2,331,220, the ion-exchange method described in JP O.P.I. No. 17114/1976 and West German Patent No. 2,548,237, and the metal substitution method described in British Patent No. 1,353,805. In the silver recovery, after recovering silver by any one of the above methods from the water-soluble silver salt contained in the overflow of the above baths, the residual liquids may be either disposed as waste liquids or used as a replenisher or processing solution after adding a regenerant thereto. It is especially preferable to recover silver from a mixture of the stabilizer, fixer and bleach-fix solutions.

The silver recovery can also be made by subjecting the stabilizer solution to an ion-exchange resin contact treatment, the electrodialysis treatment described in Japanese Patent Application No. 96352/1984 or the reverse osmosis treatment described in Japanese Patent Application No. 96532/1984.

The use of in advance demineralized water for the stabilizer solution of the invention is suitable for improving the fungicidality and preservability of the stabilizer solution and the preservability of the resulting image. The demineralization treatment may be conducted by any means as long as the wash water after the treatment has a permittivity of not more than 50μa/cm and contains not more than 5ppm of Ca and Mg ions, but it is preferable that the demineralization treatment be performed by single or combined use of an ion-exchange resin and a reverse osmotic membrane. The ion-exchange resin and the reverse osmotic membrane are described in detail in Research Disclosure 87-1984, but it is preferable to use a strong acid H-type cation-exchange resin and a strong basic OH-type anion-exchange resin.

In the invention, the stabilizer bath is required to have a salt concentration of preferably 1000 ppm or less, and more preferably 800 ppm or less to increase the washing effect as well as to improve the white background and fungicidality.

The processing time in the stabilizer bath of the invention is preferably not longer than 2 minutes, and more preferably not longer than 1 minute and 30 seconds.

In the invention, a hexamethylenetetramine compound, a N-methylol compound or a triazine compound is preferably used in the stabilizer bath in order to improve the resulting dye image's stabilization, particularly to prevent yellow stain. Especially, the hexamethylenetetramine compound is most useful.

The hexamethylenetetramine in the invention includes hexamethylenetetramine and its derivatives. Examples of the hexamethylene derivatives include the hexamethylenetetramine's halogen adducts, inorganic acid adducts, metallic salt adducts, phenol derivativ adducts, alkylsulfonic acid adducts, arylsulfonic acid adducts, alkyl sulfate adducts, alkylcarboxylic acid adducts, arylcarboxylic acid adducts and alkylhalide adducts.

Examples of the hexamethylenetetramine and its derivatives of the invention include the compounds exemplified in Beilsteins Handbuch der Organischen Chemie, 2nd edition revised and enlarged, vol.26, pp.200-212. Of these compounds those soluble in water are preferred for the invention, and more preferred are the compounds (1) to (25) described in Japanese Patent Application No. 36571/1989, pp.96-101.

The following are the preferred examples of the processing steps of the invention:

(1) A: Color dev. — Bleach — Fix — Stabilize
B: Color dev. — Bleach — Fix — Stabilize

(2) A: Color dev. — Bleach — Bleach-fix — Stabilize
B: Color dev. — Bleach — Fix — Stabilize

(3) A: Color dev. — Bleach — Wash — Fix — Wash — Stabilize
B: Color dev. — Bleach — Fix — Wash

(4) A: Color dev. — Bleach — Fix — Stabilize
B: Color dev. — Bleach-fix — Stabilize

(5) A: Color dev. — Bleach — Bleach-fix — Stabilize
B: Color dev. — Bleach-fix — Stabilize

(6) A: Color dev. — Bleach-fix — Stabilize
B: Color dev. — Bleach-fix — Stabilize

In the above processing steps, the 'Stabilize' may consist of either a single stabilizing step or two different stabilizing steps, and the arrow → means the stream of overflow, showing that the overflow from B is utilized as a replenisher to A. The A and B are different processing lines for different light-sensitive materials. In the invention, preferably A represents a color negative film processing line, while B is a color paper processing line. In the processing method of the invention, at least one, preferably two, and more preferably all of the processing solutions except the color developer solution used in each of the lines A and B are preferably the same for realizing compact replenisher baths therefor.

In the invention, to highly activate the bleaching solution, if desired, the air or oxygen may be blown into or an appropriate oxydation agent such as hydrogen peroxide, a bromate or persulfate may be added to the bleaching bath or its replenisher storage tank.

In practicing the invention, silver recovery from the fixer bath or bleach-fix bath may be conducted in accordance with known methods, such as the electrolysis method described in French Patent No. 2,299,667, the flocculation method described in JP O.P.I. No. 73037/1977 and West German Patent No. 2,331,220, the ion-exchange method described in JP O.P.I. No. 17114/1976 and West German Patent No. 2,548,237, and the metal substitution method described in British Patent No. 1,353,805.

Making the silver recovery directly from the baths is preferable for further improving the processing rapidity, but silver may be recovered from the overflown waste liquid and recycled.

Particularly, the processing rapidity as well as the effect of the invention can be more improved by bringing the anion-exchange resin described in International Patent Publication WO-89/06381 into contact with the fixer or bleach-fix solution.

The effect of the invention can be further improved when the replenishing amount of replenishers to the

fixer bath or bleach-fix bath of the invention is not more than 800 ml, particularly 20 to 700ml, and more particularly 50 to 600ml per m^2 of the color negative film. In the case of color photographic paper, the same improved effect can be obtained when the replenishing amount is not more than 500ml, particularly 5 to 300ml and more particularly 10 to 200ml per m^2 of the paper.

The' silver halide grain of the emulsion used in the invention may be of either a regular crystal or a twin crystal, having an arbitrary (1.0.0) face / (1.1.1) face proportion. The silver halide grain may be of either a homogeneous crystal structure or a core/shell-type heterogeneous crystal structure. The grain may be of either a type of forming a latent image mainly on its surface or a type of forming a latent image mainly inside. Further, the tabular silver halide grain described in JP O.P.I. No. 113934/1983 and Japanese Patent Application No. 170070/1984 may also be used.

The above silver halide grain may be prepared in accordance with an acid, neutral or ammoniacal process, or may also be prepared in the manner that seed grains are first prepared by the acid process and then grown fast into a given size by the ammonical process. Where the silver halide grain is grown, it is preferable to pour sequentially, simultaneously silver ions and halide ions in amounts corresponding to the growing rate of the silver halide grain into the reaction vessel with pH and pAg controlled as described in JP O.P.I. No. 48521/1979. The thus obtained silver halide grains are called the silver halide emulsion in the present invention.

The silver halide color photographic light-sensitive material having silver halide grains substantially not containing silver iodide in the invention is, for example, a color photographic paper. The light-sensitive material has a silver halide emulsion layer containing silver halide grains having preferably at least 80 mol%, more preferably not less than 90 mol% and most preferably not less than 95 mol% silver chloride content from the viewpoint of the adaptability to rapid processing. The silver halide color photographic light-sensitive material having a silver iodide content of 0.5 mol% or more is a light-sensitive material for camera use such as color negative film or color reversal film. Of these films the color negative film, having emulsion layers containing a silver iodide content of 1.0 mol% or more, preferably 2.0 mol% to 20 mol%, is the preferred embodiment of the invention.

The silver halide emulsion of the invention may be chemically sensitized in the usual manner; i.e., by a sulfur sensitization process using a sulfur compound or active gelatin, a selenium sensitization process using a selenium compound, a reduction sensitization process using a reductive substance, or a noble-metal sensitization process using a gold compound or other noble metal compound, which may be used alone or in combination.

The silver halide emulsion of the invention may be spectrally sensitized to desired wavelength regions by using appropriate sensitizing dyes known to those skilled in the art. These sensitizing dyes may be used alone or in combination. Together with these sensitizing dyes there may also be incorporated into the emulsion a supersensitizer that is a dye in itself having no spectral sensitization effect or a compound substantially not absorbing visible rays but capable of enhancing the sensitization effect of sensitizing dyes.

To the silver halide emulsion of the invention may be added a compound known as an antifoggant or stabilizer to those skilled in the art during and/or at the time of completion of and/or after completion of the chemical ripening for the purpose of preventing fog and/or maintaining the photographic characteristics of the light-sensitive material stable in the course of its manufacture, storage or photographic processing.

As the binder or protective colloid for the silver halide emulsion of the invention there may be used hydrophilic colloid materials such as gelatin, gelatin derivatives, graft polymers of gelatin with other high-molecular materials, proteins, sugar derivatives, cellulose derivatives, and synthetic hydrophilic homo- or copolymers.

The photographicemulsion layers and other hydrophilic colloid layers of the light-sensitive material which uses the silver halide emulsion of the invention may be hardened by the single or combined use of hardeners capable of cross-linking the binder molecules to increase the layer strength. The hardener should be sufficiently added to the light-sensitive material so as not to necessitate its addition to processing baths, but is allowed to be added to the baths.

A plasticizer may be added to the light-sensitive material having the silver halide emulsion of the invention for the purpose of increasing the plasticity of the silver halide emulsion layers and/or other hydrophilic colloid layers thereof.

A water-insoluble or less-soluble synthetic polymer dispersion (latex) may be incorporated into the emulsion layers and other hydrophilic colloid layers of the light-sensitive material containing the silver halide emulsion of the invention for improving the dimentional stability thereof.

The emulsion layer of the light-sensitive material of the invention may contain a dye-forming coupler which, in a color developer solution, is capable of reacting with the oxidation product of an aromatic primary amine developing agent, such as p-phenylenediamine derivative or aminophenol derivative, to form a dye. In general, selection of an appropriate dye-forming coupler for each individual emulsion is made so as to absorb the spectral light to which the emulsion is sensitive; a yellow dye-forming coupler is used for the blue-sensitive emulsion

layer, a magenta dye-forming coupler for the green-sensitive emulsion layer and a cyan dye-forming coupler for the red-sensitive emulsion layer. However, there are cases where different coupler/emulsion combinations from the above may be used according to purposes.

It is preferable for the coupler to have in the molecules thereof a group, called ballasting group, having not less than 8 carbon atoms capable of making the coupler nondiffusible. The dye-forming coupler may be either a 4-equivalent coupler that requires 4 moles of silver ions to be reduced for forming one mole of a dye or a 2-equivalent coupler that requires 2 moles of silver ions to be reduced for forming one mole of a dye. The dye-forming coupler may contain a compound which, as a result of effecting a coupling reaction with the oxidation product of a developing agent, releases photographically useful fragments such as a development accelerator, bleaching accelerator, developing agent, silver halide solvent, toning agent, hardener, fogging agent, antifoggant, chemical sensitizer, spectral sensitizer and desensitizer. These dye-forming couplers may be used in combination with colored couplers for color correction and DIR couplers capable of releasing development inhibitors in the course of development to improve the sharpness and graininess of the resulting image. In this instance, the DIR coupler is desirable to form a similar coler to the color of the dye formed from the dye-forming coupler contained in the same emulsion layer, but is allowed to be one to form a different color in the case where the color impurity formed thereby is not conspicuous. In lieu of or together with the DIR coupler there may be used a DIR compound capable of effecting a coupling reaction with the oxidation product of a color developing agent to form a colorless compound and at the same time to release a development inhibitor.

The DIR coupler and DIR compound used in the invention include those having an inhibitor directly combined to its coupling position and those having an inhibitor so combined through a divalent group to its coupling position as to release an inhibitor as a result of the intramolecular nucleophilic reaction or intramolecular electron-transfer reaction inside the group that has split off by the coupling reaction, which are called timing couplers and timing DIR compounds. Also, as for the inhibitor, those diffusible and nondiffusible after splitting off may be used either alone or in combination. In combination with the dye-forming coupler there may also be used a colorless coupler that effects a coupling reaction with the oxidation product of an aromatic primary amine developing agent but forms no dye.

As the yellow dye-forming coupler there may be suitably used known acylacetanilide couplers. Preferred among these couplers are benzoylacetanilide couplers and pivaloylacetanilide couplers. Particular examples of the yellow coupler usable in the invention are those described in British Patent No. 1,077,874, Japanese Patent Examined Publication No. 40757/1970, JP O.P.I. Nos. 1031/1972, 26133/1972, 94432/1973, 87650/1975, 3631/1976, 115219/1977, 99433/1979, 133329/1979 and 30127/1981, and U.S. Patent Nos. 2,875,057, 3,253,924, 3,265,506, 3,408,194, 3,551,155, 3,551,156, 3,664,841, 3,725,072, 3,730,722, 3,891,445, 3,900,483, 3,929,484, 3,933,500, 3,973,968, 3,990,896, 4,012,256, 4,022,620, 4,029,508, 4,057,432, 4,106,942, 4,133,958, 4,269,936, 4,286,053, 4,304,845, 4,314,023, 4,336,327, 4,356,258, 4,386,155 and 4,401,752.

Useful as the magenta dye-forming coupler are known 5-pyrazolone couplers, pyrazolobenzimidazole couplers, pyrazolotriazole couplers and closed-chain acylacetonitrile couplers. Examples of the magenta coupler usable in the invention are those described in Japanese Patent Application Nos. 164882/1983, 167326/1983, 206321/1983, 214863/1983, 217339/1983 and 24653/1984, Japanese Patent Examined Publication Nos. 6031/1965, 6035/1965, 40757/1970, 27411/1972 and 37854/1974, JP O.P.I. Nos. 13041/1975, 26541/1976, 37646/1976, 105820/1976, 42121/1977, 123129/1978, 125835/1978, 129035/1978, 48540/1979, 29236/1981, 75648/1981, 17950/1982, 35858/1982, 146251/1982 and 99437/1984, British Patent No. 1,252,418, and U.S. Patent Nos. 2,600,788, 3,005,712, 3,062,653, 3,127,265, 3,214,437, 3,253,924, 3,311,476, 3,419,391, 3,519,429, 3,558,319, 3,582,322, 3,615,506, 3,658,544, 3,705,896, 3,725,067, 3,758,309, 3,823,156, 3,834,908, 3,891,445, 3,907,571, 3,926,631, 3,928,044, 3,935,015, 3,960,571, 4,076,533, 4,133,686, 4,237,217, 4,241,168, 4,264,723, 4,031,235 and 4,310,623.

Useful as the cyan dye-forming coupler are known naphthol couplers and phenol couplers. Examples of the cyan dye-forming coupler usable in the invention are those described in British Patent Nos. 1,038,331 and 1,543,040, Japanese Patent Examined Publication No. 36894/1973, JP O.P.I. Nos. 59838/1973, 137137/1975, 146828/1976, 105226/1978, 115230/1979, 29235/1981, 104333/1981, 126833/1981, 133650/1982, 155538/1982, 204545/1982, 118643/1983, 31953/1984, 31954/1984, 59656/1984, 124341/1984 and 166956/1984, and U.S. Patent Nos. 2,369,929, 2,423,730, 2,434,272, 2,474,293, 2,698,794, 2,772,162, 2,801,171, 2,895,826, 3,253,924, 3,311,476, 3,458,315, 3,476,563, 3,591,383, 3,737,316, 3,758,308, 3,767,411, 3,790,384, 3,880,661, 3,926,634, 4,004,929, 4,009,035, 4,012,258, 4,052,212, 4,124,396, 4,134,766, 4,138,258, 4,146,396, 4,149,886, 4,178,183, 4,205,990, 4,254,212, 4,264,722, 4,288,532, 4,296,199, 4,296,200, 4,299,914, 4,333,999, 4,334,011, 4,386,155, 4,401,752 and 4,427,767.

As the colored coupler there may be used those described in British Patent Nos. 937,621, 1,035,959 and 1,255,111, JP O.P.I. Nos. 22028/1973 and 42121/1977, Japanese Patent Examined Publication Nos.

22335/1963, 2016/1969 and 15754/1969, and U.S. Patent Nos. 2,449,966, 2,521,908, 2,543,691, 2,801,171, 2,983,608, 3,005,712, 3,034,892, 3,061,432, 3,419,391, 3,476,560, 3,476,563, 3,481,741, 3,519,429, 3,583,971, 3,622,328, 3,684,514, 4,004,929, 4,070,191, 4,138,258, 4,138,264, 4,163,670, 4,292,400 and 4,639,248.

Useful as the DIR coupler are the compounds described in British Patent No. 953,454, U.S. Patent Nos. 3,227,554, 3,615,506, 3,617,291, 3,701,783, 3,933,500, 4,095,984, 4,149,886, 4,286,054 and 4,359,521, and JP O.P.I. Nos. 90932/1977, 116029/1981 and 151944/1982, and the timing DIR couplers described in U.S. Patent Nos. 4,248,962 and 4,409,323, and JP O.P.I. Nos. 154234/1982, 162949/1983, 205150/1983, 195643/1984, 206834/1984, 206836/1984, 210440/1984 and 7429/1985.

Useful as the DIR compounds are those described in U.S. Patent Nos. 3,632,345, 3,928,041, 3,938,996, 3,958,993, 3,961,959, 4,046,574, 4,052,213, 4,171,223 and 4,186,012, and JP O.P.I. Nos. 65433/1977, 130327/1977 and 128335/1982.

Incorporation of a hydrophobic compound such as the dyeforming coupler, which need not be adsorbed to the surface of silver halide grains, into the hydrophilic colloid layer may be carried out by a solid dispersion process, latex dispersion process or oil-in-water-type emulsion dispersion process, which may be arbitrarily selected according to the chemical structure of the hydrophobic compound such as the coupler used. In the case of the oil-in-water-type emulsion dispersion process, generally the hydrophobic compound is dissolved in a high-boiling organic solvent having a boiling point of 150°C or higher, if necessary, in combination with a low-boiling water-soluble organic solvent, and the solution is then emulsifiedly dispersed in a water-soluble binder such as gelatin in combination with a surfactant by use of a dispersing means such as a stirrer, homogenizer, colloid mill, flow-jet mixer or ultrasonic disperser, and the obtained dispersion is added to the objective hydrophilic colloid layer. At the time of dispersion, the low-boiling solvent may be removed.

As the high-boiling solvent having a boiling point of 150°C of higher there may be used phenol derivatives, phthalates, phosphates, citrates, benzoates, alkylamides, fatty acid esters or trimesic acid esters, which do not react with the oxidation product of a developing agent.

As a dispersing aid for use in the mechanical or ultrasonic dispersion of the low-boiling and/or high-boiling solvent solution of the hydrophobic compound into water there may be used anionic surfactants, nonionic surfactants or cationic surfactants.

An anti-color-fog agent may be used in order to prevent possible color contamination, sharpness deterioration and roughened graininess attributable to the transfer of the oxidation product of a color developing agent or of an electron transfer agent between the emulsion layers (layers having the same color-sensitivity or different color sensitivity) of the color photographic light-sensitive material of the invention.

The anti-color-fog agent may be added either to the emulsion layer or to an intermediate layer provided between the emulsion layer and another emulsion layer adjacent thereto.

To the color light-sensitive material having the silver halide emulsion layer of the invention may be applied an image stabilizer in order to prevent possible deterioration of the resulting dye image.

The hydrophilic colloid layers such as the protective layer and intermediate layers of the light-sensitive material of the invention may contain a ultraviolet absorbent in order to prevent possible electrostatic marks caused by the discharge of static electricity generated by friction of the light-sensitive material or to prevent possible deterioration of the resulting image due to UV light.

The color light-sensitive material having the silver halide emulsion layer may be provided with auxiliary layers such as filter layers, antihalation layer and/or antiirradiation layer. These layers and/or the emulsion layer may contain a dye that is dissolved out from the color light-sensitive material or bleached out in the course of development.

A matting agent may be added to the silver halide emulsion layer and/or other hydrophilic colloid layers of the light-sensitive material having the silver halide emulsion of the invention in order to reduce the surface gloss thereof for improving retouchability as well as for inter-light-sensitive-material adhesion prevention.

A lubricant may be added in order to reduce possible friction of the light-sensitive material containing the silver halide emulsion of the invention.

An antistatic agent may be added to the light-sensitive material containing the silver halide emulsion of the invention for static electricity prevention.

The antistatic agent may be used either in an antistatic layer on the non-emulsion side of the support and/or in the protective layer alone on the emulsion layer-coated side of the support.

Various surfactants may be used in the photographic emulsion layer and/or other hydrophilic colloid layers of the light-sensitive material containing the silver halide emulsion of the invention for the purpose of its coatability improvement, static charge prevention, slidability improvement, emulsion dispersion, adhesion prevention, and improvement of photographic characteristics such as development acceleration, contrast and sensitivity.

Materials for the support, on which are coated the emulsion layers and other layers of the light-sensitive

material containing the silver halide emulsion of the invention, include elastic reflective supports such as baryta-coated paper, α-olefin polymer-laminated paper and synthetic paper, semi-synthetic or synthetic films such as cellulose acetate film, nitrocellulose film, polystyrene film, polyvinyl chloride film, polyethylene terephthalate film, polycarbonate film and polyamide film, and stiff materials such as glass, metals and ceramics.

On the above support, after its surface is subjected to corona discharge treatment, ultraviolet radiation treatment or flame treatment, the silver halide light-sensitive material layers of the invention are coated directly or through one or two subbing layers for improving the support surface's adhesion property, antistatic characteristics, dimensional stability, wear resistance, hardness, antihalation characteristic, friction characteristic and/or other characteristics.

In coating the silver halide emulsion of the invention, a viscosity increasing agent may be used for improving its coatability. The coating may be conducted by an extrusion coating process or curtain coating process capable of simultaneously coating two or more different layers.

EXAMPLES

In all the following examples of the invention, the adding amounts of silver halide and colloidal silver are indicated in silver equivalents, those of sensitizing dyes are in moles per mole of silver, and those of other components are in grams per m^2 unless otherwise stated.

Example 1

On a triacetyl cellulose film support were formed in order from the support side the following layers, whereby a color negative film Sample 1 was prepared.

Layer 1: Antihalation layer HC

Black colloidal silver	0.15
UV absorbent UV-1	0.20
Colored cyan coupler CC-1	0.02
High-boiling solvent Oil-1	0.20
'' Oil-2	0.20
Gelatin	1.6

Layer 2:Intermediate layer IL-1

Gelatin	1.3

Layer 3: Low-speed red-sensitive emulsion layer R-L

Silver iodobromide emulsion Em-1	0.4
'' Em-2	0.3
Sensitizing dye S-1	3.2×10^{-4}

'' S-2	3.2×10^{-4}
'' S-3	0.2×10^{-4}
Cyan coupler C-1	0.50
'' C-2	0.13
Colored cyan coupler CC-1	0.07
DIR compound D-1	0.006
'' D-2	0.01
High-boiling solvent Oil-1	0.55
Additive SC-1	0.003
Gelatin	1.0

Layer 4: High-speed red-sensitive emulsion layer R-H

Silver iodobromide emulsion Em-3	0.9
Sensitizing dye S-1	1.7×10^{-4}
'' S-2	1.6×10^{-4}
'' S-3	0.1×10^{-4}
Cyan coupler C-2	0.23
Colored cyan coupler CC-1	0.03
DIR compound D-2	0.02
High-boiling solvent Oil-1	0.25
Additive SC-1	0.003
Gelatin	1.0

Layer 5: Intermediate layer IL-2

Gelatin	0.8

Layer 6: Low-speed green-sensitive emulsion layer G-L

Silver iodobromide emulsion Em-1	0.6

''	Em-2	0.2
Sensitizing dye	S-4	6.7×10^{-4}
''	S-5	0.8×10^{-4}
Magenta coupler	M-1	0.17
''	M-2	0.43
Colored magenta coupler	CM-1	0.10
DIR compound	D-3	0.02
High-boiling solvent	Oil-2	0.70
Additive	SC-1	0.003
Gelatin		1.0

Layer 7: High-speed green-sensitive emulsion layer G-H

Silver iodobromide emulsion	Em-3	0.9
Sensitizing dye	S-6	1.1×10^{-4}
''	S-7	2.0×10^{-4}
''	S-8	0.3×10^{-4}
Magenta coupler	M-1	0.03
''	M-2	0.13
Colored magenta coupler	CM-1	0.04
DIR compound	D-3	0.004
High-boiling solvent	Oil-2	0.35
Additive	SC-1	0.003
Gelatin		1.0

Layer 8: Yellow filter layer YC

Yellow colloidal silver		0.1
Additive	HS-1	0.07

Additive HS-2	0.07
Additive SC-2	0.12
High-boiling solvent Oil-2	0.15
Gelatin	1.0

Layer 9: Low-speed blue-sensitive emulsion layer B-L

Silver iodobromide emulsion Em-1	0.25
'' Em-2	0.25
Sensitizing dye S-9	5.8×10^{-4}
Yellow coupler Y-1	0.60
'' Y-2	0.32
DIR compound D-1	0.003
'' D-2	0.006
High-boiling solvent Oil-2	0.18
Additive SC-1	0.004
Gelatin	1.3

Layer 10: High-speed blue-sensitive emulsion layer B-H

Silver iodobromide emulsion Em-4	0.5
Sensitizing dye S-10	3.0×10^{-4}
'' S-11	1.2×10^{-4}
Yellow coupler Y-1	0.18
'' Y-2	0.10
High-boiling solvent Oil-2	0.05
Additive SC-1	0.002
Gelatin	1.0

Layer 11: First protective layer PRO-1

Silver iodobromide emulsion Em-5	0.3
UV absorbent UV-1	0.07
'' UV-2	0.1
Additive HS-1	0.2
Additive HS-2	0.1
High-boiling solvent Oil-1	0.07
'' Oil-3	0.07
Gelatin	0.8

Layer 12: Second protective layer PRO-2

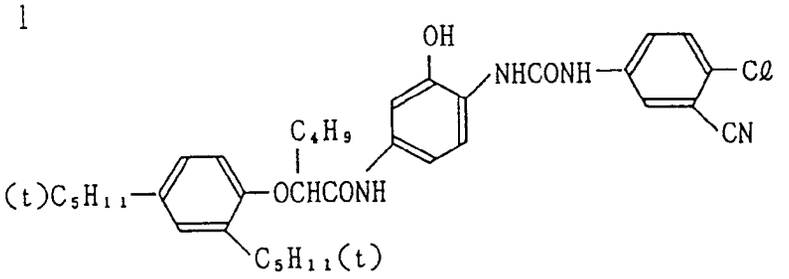
Alkali-soluble matting agent (average particle size: 2μm)	0.13
Polymethyl methacrylate (average particle size: 3μm)	0.02
Lubricant WAX-1	0.04
Charge control agent SU-1	0.004
'' SU-2	0.02
Gelatin	0.5

In addition to the above components, to each of the above layers were added appropriate amounts of a coating aid SU-4, a dispersion aid SU-3, hardeners H-1 and H-2, a stabilizer ST-1, a preservative DI-1, antifoggants AF-1 and AF-2 and dyes AI-1 and AI-2.

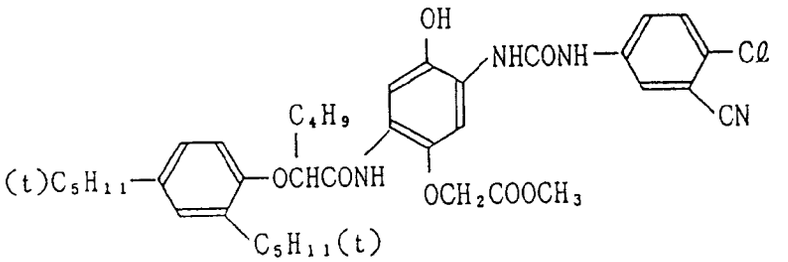
The emulsions used in the above sample are octahedral, inside high-iodide content-type monodisperse grain emulsions having the following silver iodide contents and grain sizes.

Em-I: average AgI content: 7.5 mol%, grain size: 0.55μm
Em-2: average AgI content: 2.5 mol%, grain size: 0.36μm
Em-3: average AgI content: 8.0 mol%, grain size: 0.84μm
Em-4: average AgI content: 8.5 mol%, grain size: 1.02μm
Em-5: average AgI content: 2.0 mol%, grain size: 0.08μm

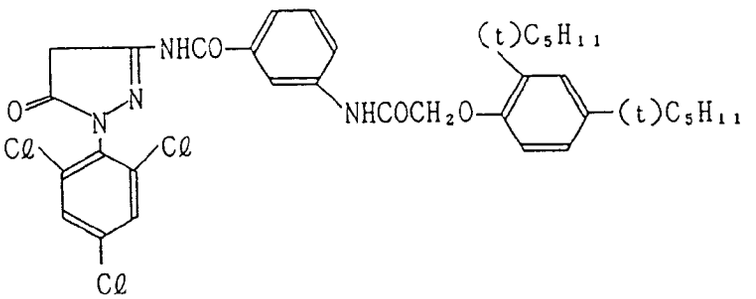
C - 1



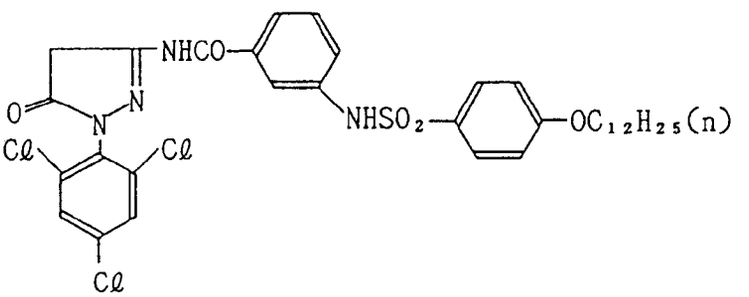
C - 2



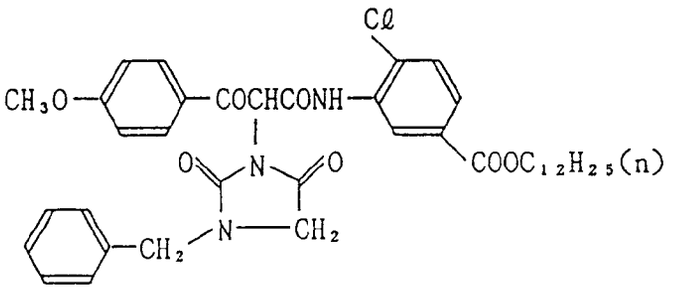
M - 1



M - 2



Y − 1



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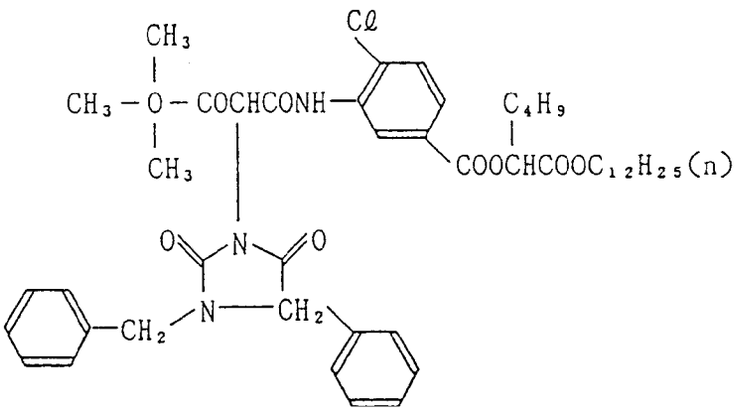
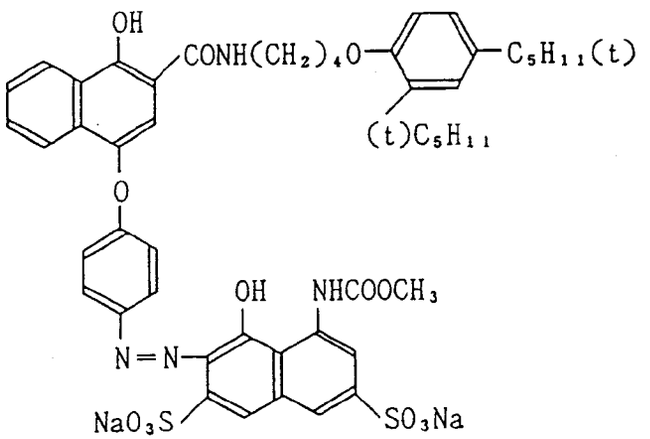
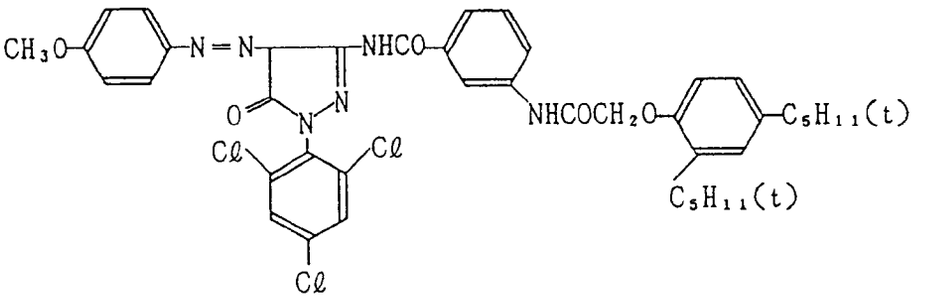


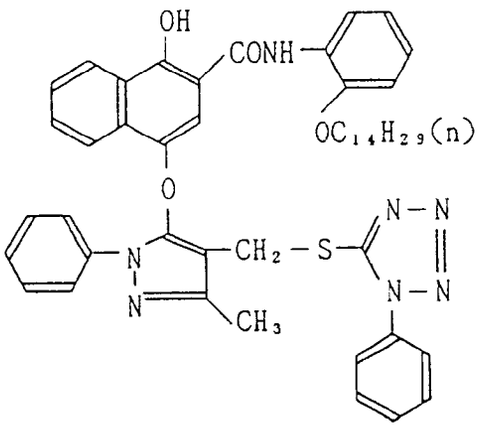
C C − 1



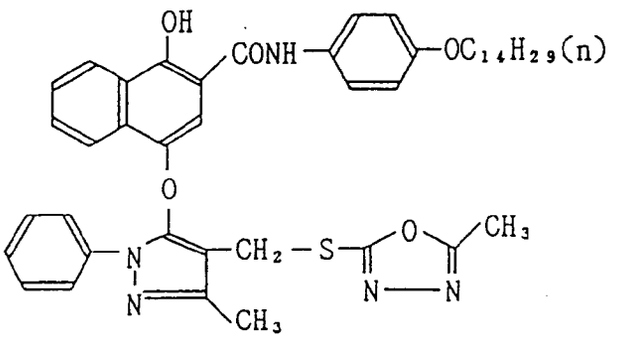
C M - 1



D - 1



D - 2



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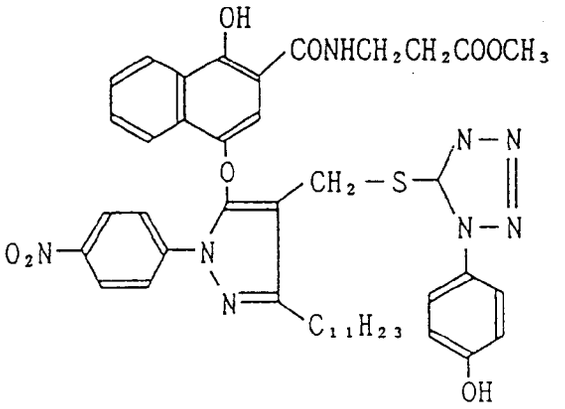
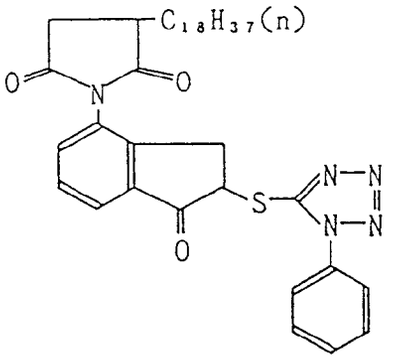
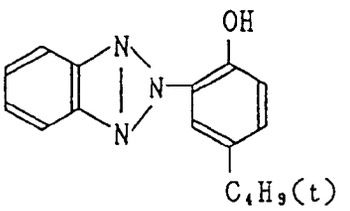


D − 4



U V − 1



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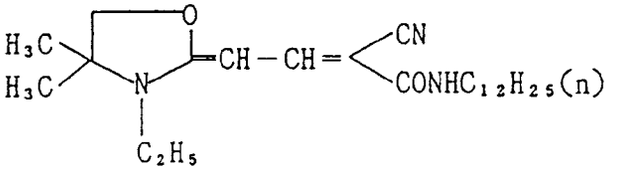
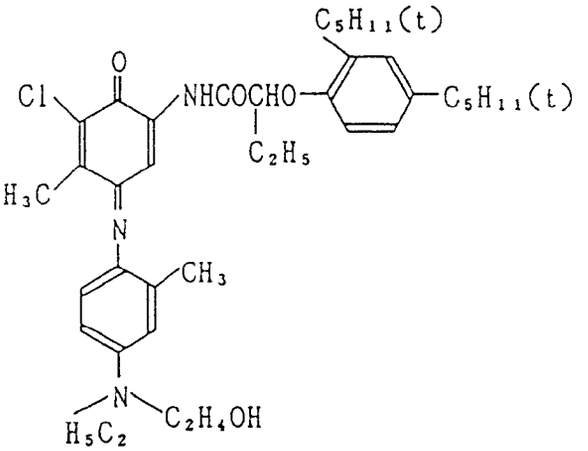
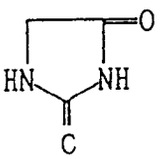


F − 1



H S − 1



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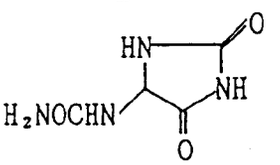

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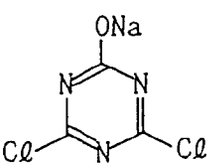
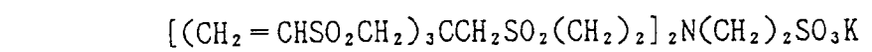
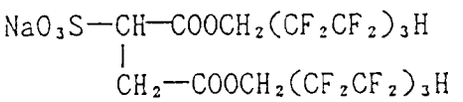


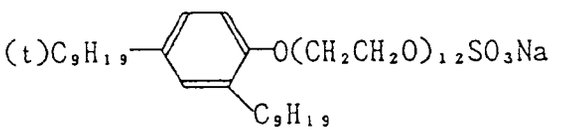
H — 2



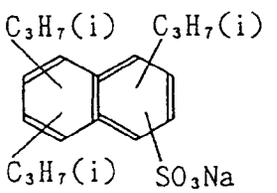
Su — 1



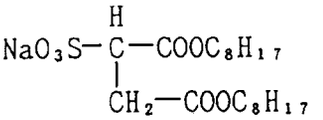
Su — 2



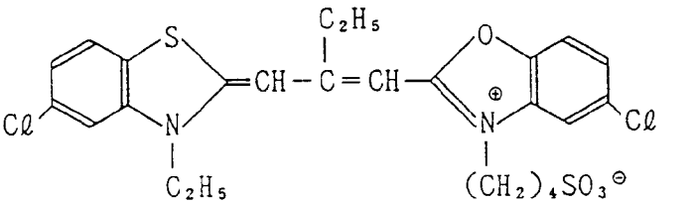
Su — 3 (Alkanol XC)



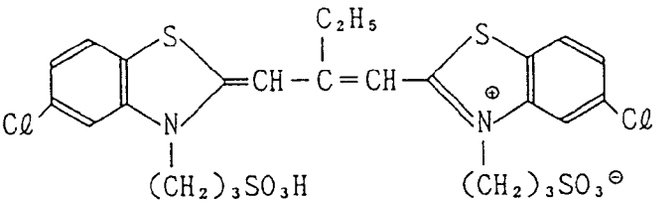
S u − 4



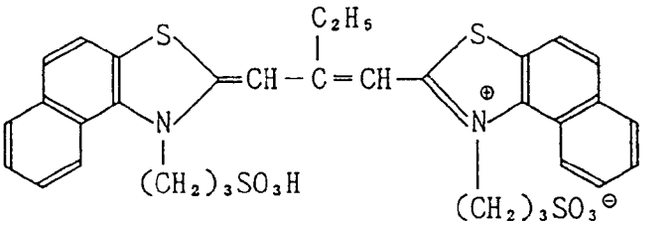
S − 1



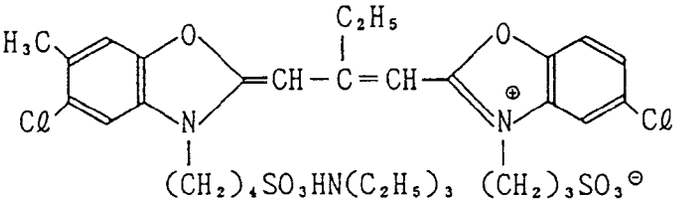
S − 2



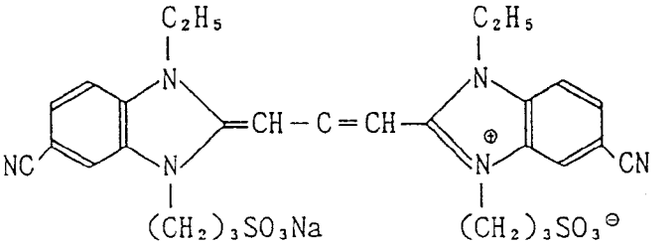
S − 3



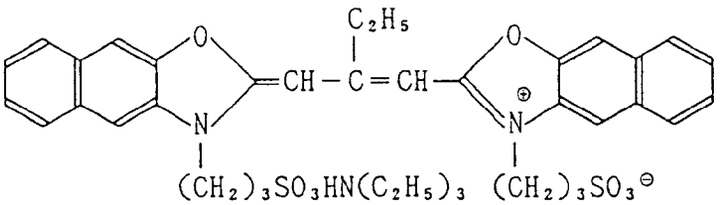
S – 4



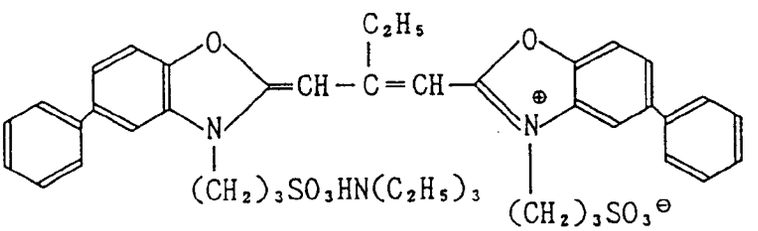
S – 5



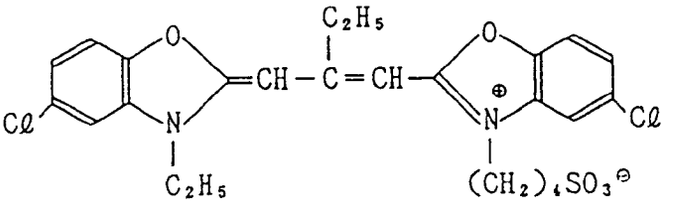
S – 6



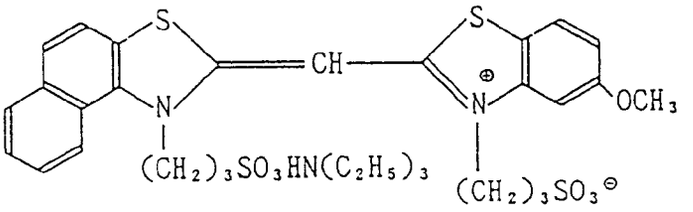
S – 7



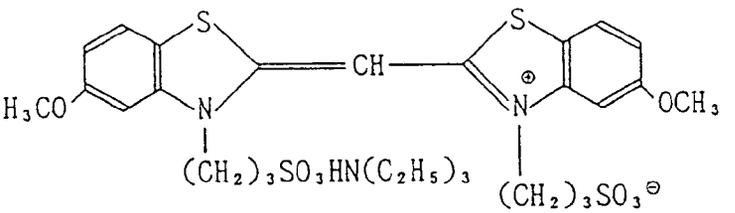
S - 8



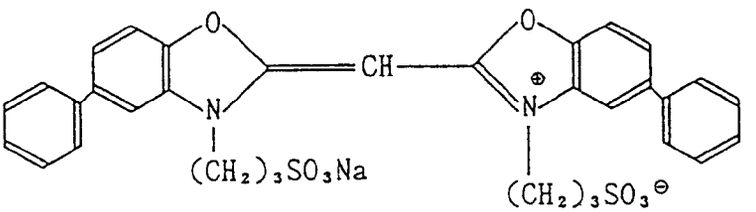
S - 9



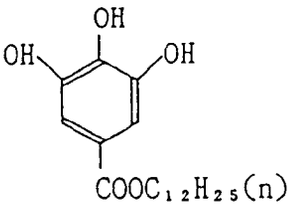
S - 10



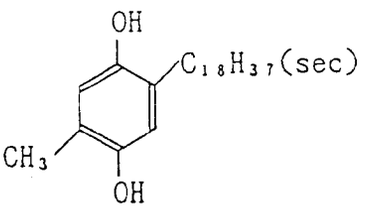
S - 11

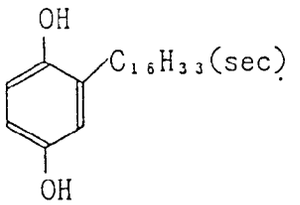


Sc-1



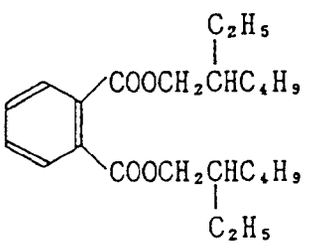
Sc-2



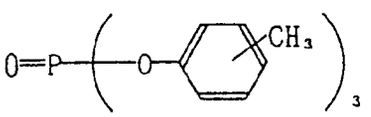


Mixture (2:3)

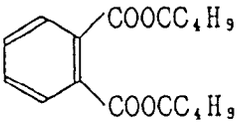
Oil-1



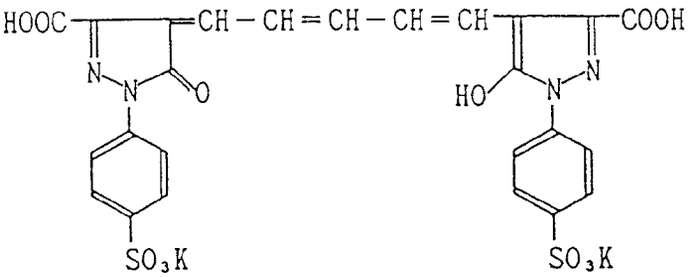
Oil-2



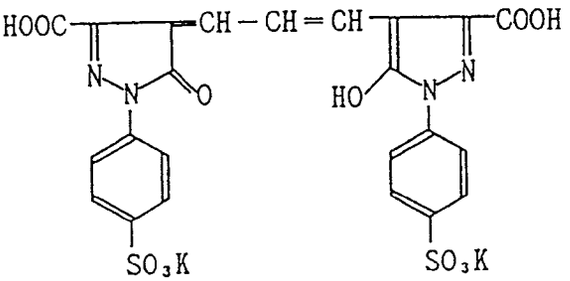
Oil-3



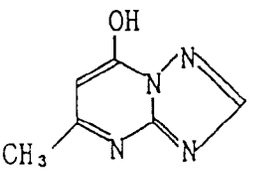
AI-1



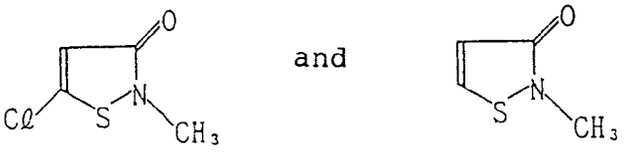
AI-2



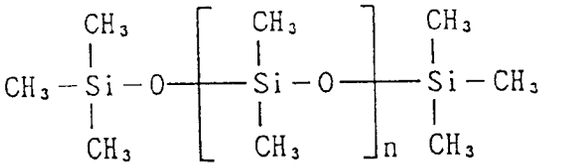
ST-1



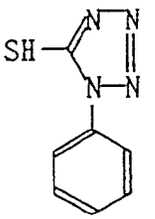
D I - 1



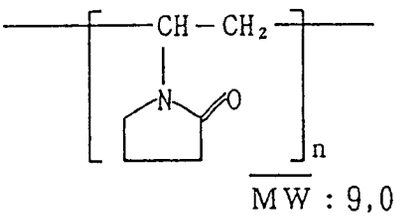
W A X - 1



A F - 1



A F - 2



Next, a color photographic paper Sample 2 was prepared as follows:

A paper support one side of which is laminated with polyethylene and the other side of which is laminated with polyethylene containing titanium oxide was used, and the following layers were coated on the titanium oxide-containing polyethylene-laminated side, whereby a multilayer silver halide color photographic paper was prepared. The coating liquids were prepared as follows:

Twenty-six point seven grams of yellow coupler Y-3, 10.0g of dye image stabilizer ST-2, 6.67g of dye image stabilizer ST-3 and 0.67g of additive HQ-1 were dissolved in 6.67g of a high-boiling solvent DNP with 60ml of ethyl acetate, and this solution was emulsifiedly dispersed by means of a ultrasonic homogenizer in 220ml of

a 10% gelatin solution containing 7ml of 20% surfactant SU-5, whereby a yellow coupler dispersion was prepared. This dispersion was mixed with a blue-sensitive silver halide emulsion containing 10g of silver, prepared underthe following conditions, whereby a coating liquid for Layer 1 was prepared.

Coating liquids for Layers 2 to 7 also were prepared in similar manner to the above coating liquid.

Hardener H-3 was added to Layers 2 and 4, and hardener H-1 to Layer 7. Surfactants SU-6 and SU-1 were added as coating aids to adjust the surface tension of each coating liquid.

Layer	Component	Amount(g/m²)
Layer 7 (Protective layer)	Gelatin	0.40
Layer 6 (UV absorbing layer	Gelatin	0.40
	UV absorbent UV-3	0.10
	UV absorbent UV-4	0.04
	UV absorbent UV-5	0.16
	Antistain agent HQ-1	0.01
	DNP	0.20
	PVP	0.03
	Antiirradiation dye AI-4	0.02
Layer 5 (Red-sensitive layer)	Gelatin	1.30
	Red-sensitive AgBrCl emulsion Em-R	0.21
	Cyan coupler C-3	0.17
	Cyan coupler C-4	0.25
	Dye image stabilizer ST-2	0.20
	Antistain agent HQ-1	0.01
	HBS-1	0.20
	DOP	0.20
Layer 4 (UV absorbing layer)	Gelatin	0.94
	UV absorbent UV-3	0.28
	UV absorbent UV-4	0.09
	UV absorbent UV-5	0.38
	Antistain agent HQ-1	0.03
	DNP	0.40

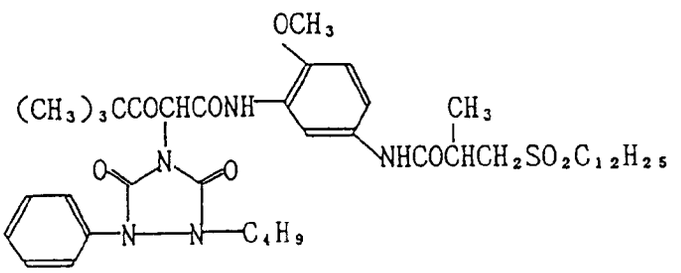
(Continued)

(Continued)

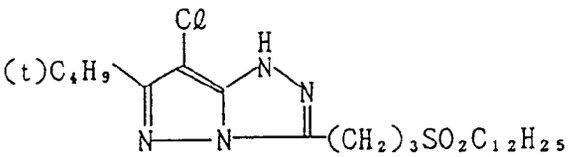
Layer	Component	Amount(g/m²)
Layer 3 (Green-sensitive layer)	Gelatin	1.40
	Green-sensitive AgBrCl emulsion Em-G	0.17
	Magenta coupler M-3	0.35
	Dye image stabilizer ST-4	0.15
	Dye image stabilizer ST-5	0.15
	Dye image stabilizer ST-6	0.15
	DNP	0.20
	Antiirradiation dye AI-3	0.01
Layer 2 (Intermediate layer)	Gelatin	1.20
	Antistain agent	0.12
	DIDP	0.15
Layer 1 (Blue-sensitive layer	Gelatin	1.20
	Blue-sensitive AgBrCl emulsion Em-B	0.26
	Yellow coupler Y-3	0.80
	Dye image stabilizer ST-2	0.30
	Dye image stabilizer ST-3	0.20
	Antistain agent HQ-1	0.02
	Antiirradiation dye AI-5	0.01
	DNP	0.20
Support	Polyethylene-laminated paper	

The added amount of each silver halide emulsion is in silver equivalent.

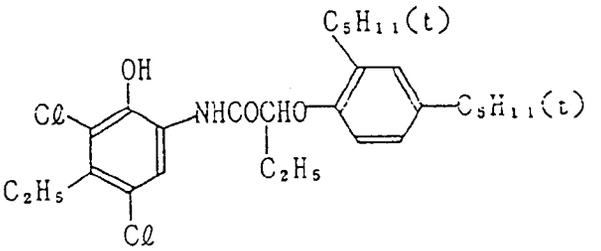
Y — 3



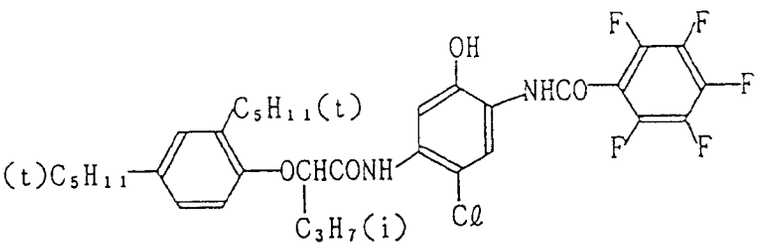
M — 3



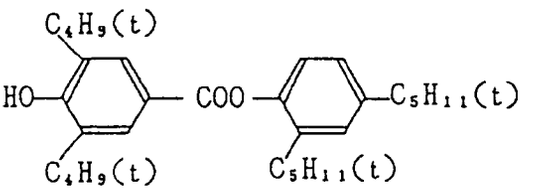
C — 3



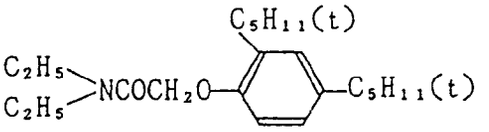
C — 4



S T — 2



S T — 3



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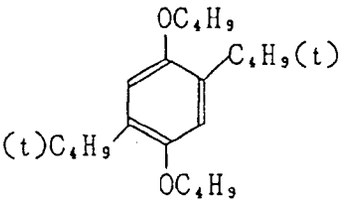
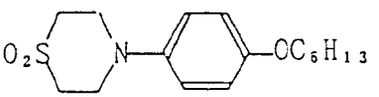
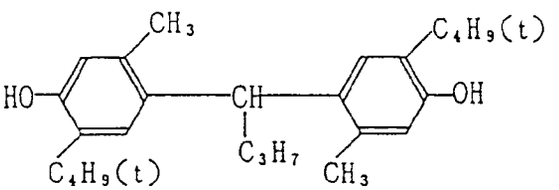


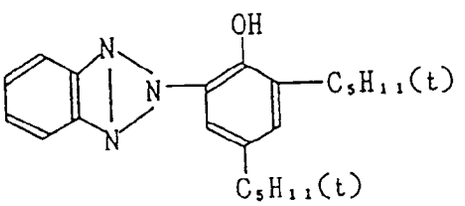
S T — 5



S T — 6



U V — 3



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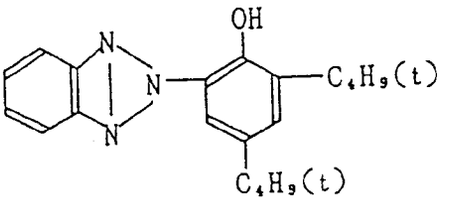
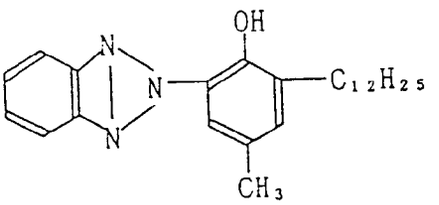
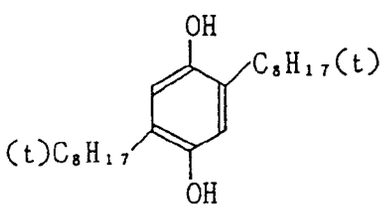


U V — 5



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

H Q — 1



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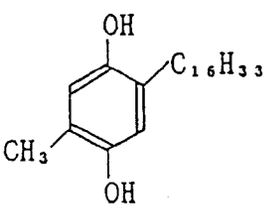
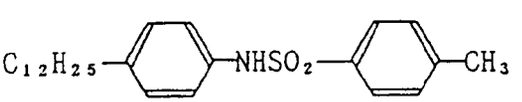
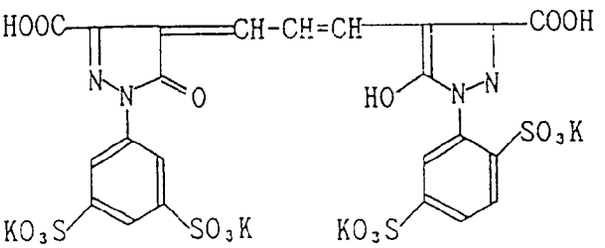


H B S — 1



A I - 3



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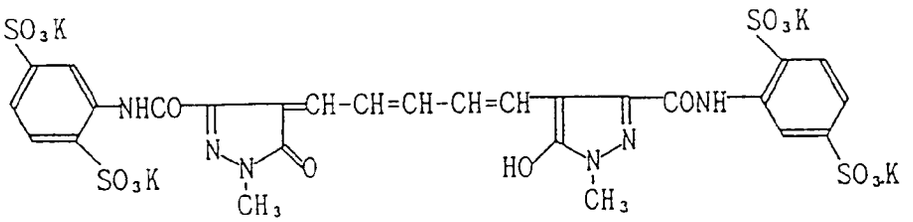

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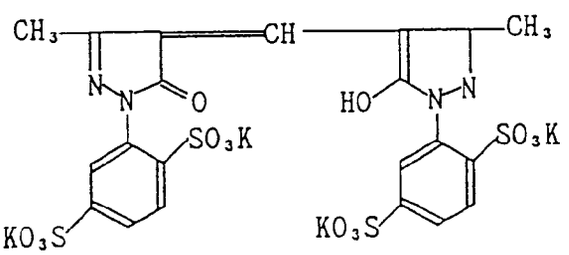
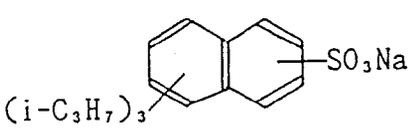
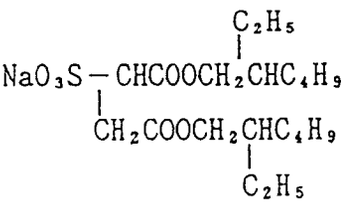


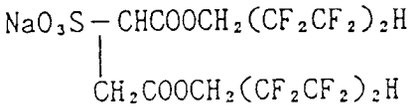
S U - 5



S U - 6

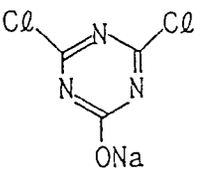


SU-1



H-3

H-1



Preparation of blue-sensitive silver halide emulsion

To 1000ml of a 2% aqueous gelatin solution maintained at 40°C were added the following Solutions A and B simultaneously in 30 minutes with pAg and pH controlled at 6.5 ane 3.0, respectively, and further Solutions C and D simultaneously in 180 minutes with pAg and pH controlled at 7.3 and 5.5, respectively.

The above pAg control was conducted according to the method described in JP O.P.I. No. 45437/1984, while the pH control was made with use of sulfuric acid or a sodium hydroxide solution.

Solution A:	
Sodium chloride	3.42g
Potassium bromide	0.03g
Water to make	200 ml
Solution B:	
Silver nitrate	10 g
Water to make	200 ml
Solution C:	
Sodium chloride	102.7 g
Potassium bromide	1.0 g
Water to make	600 ml
Solution D:	
Silver nitrate	300 g
Water to make	600 ml

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

The above emulsion EMP-1, with use of the following compounds, was chemically ripened at 50°C for 90 minutes to thereby obtain a blue-sensitive silver halide emulsion Em-B.

Sodium thiosulfate	0.8mg/mol AgX
Chloroauric acid	0.5mg/mol AgX
Stabilizer STAB-1	$6x10^{-4}$ mol/mol AgX
Sensitizing dye	$4x10^{-4}$ mol/mol AgX
Sensitizing dye BS-2	$1x10^{-4}$ mol/mol AgX

Preparation of Green-sensitive silver halide emulsion

A monodisperse cubic emulsion EMP-2, having an average grain size of 0.43μm, a variation coefficient ($\sigma/\bar{r}$) of 0.08 and a silver chloride content of 99.5 mol%, was prepared in the same manner as in EMP-1 except that the adding time of Solutions A and B and that of Solutions C and D were changed.

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

Sodium thiosulfate	1.5mg/mol AgX
Chloroauric acid	1.0mg/mol AgX

Stabilizer STAB-1	$6x10^{-4}$ mol/mol AgX
Sensitizing dye GS-1	$4x10^{-4}$ mol/mol AgX

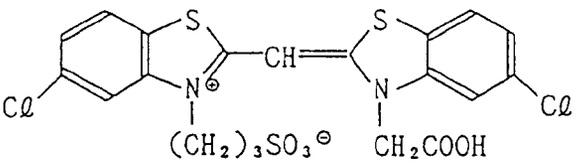
Preparation of Red-sensitive silver halide emulsion

A monodisperse cubic emulsion EMP-3, having an average grain size of 0.50μm, a variation coefficient ($\sigma/\bar{r}$) of 0.08 and a silver chloride content of 99.5 mol%, was prepared in the same manner as in EMP-1 except that the adding time of Solutions A and B and that of Solutions C and D were changed..

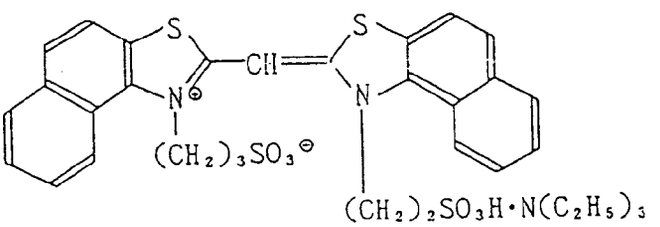
The emulsion EMP, with use of the following compounds, was chemically ripened at 60°C for 90 minutes, whereby a red-sensitive silver halide emulsion Em-R was obtained.

Sodium thiosulfate	1.8mg/mol AgX
Chloroauric acid	2.0mg/mol AgX
Stabilizer STAB-1	$6x10^{-4}$ mol/mol AgX
Sensitizing dye RS-1	$1.0x10^{-4}$ mol/mol AgX

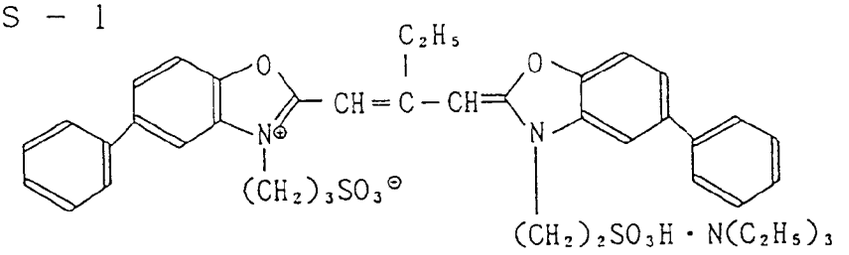
B S − 1



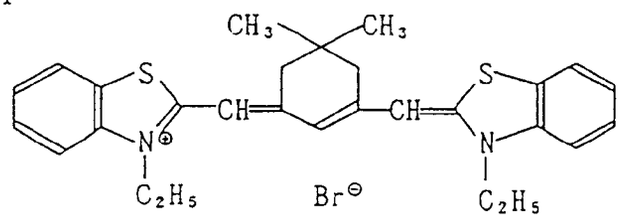
B S − 2



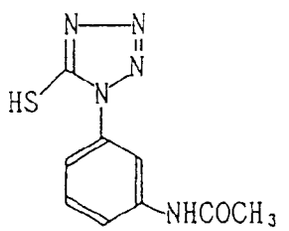
G S − 1



R S − 1



S T A B − 1



Sample 1, prepared above, was exposed through an optical wedge to a white light, and then processed as follows:

Processing A	Time	Temp.	Replenishing amt.
Color developing	3 min. 15 sec.	38°C	536 ml
Bleaching	45 sec.	38°C	134 ml
Fixing	1 min. 30 sec.	38°C	536 ml
Stabilizing	90 sec.	38°C	536 ml
Drying	1 min.	40 - 70°C	--

The above replenishing amount is a value per m^2 of the light-sensitive material. The stabilizing process was performed in a three-bath cascade system.

The composition of the color developer solution used is as follows:

Potassium carbonate	30 g
Sodium hydrogencarbonate	2.5 g
Potassium sulfite	3.0 g
Sodium bromide	1.3 g
Potassium iodide	1.2mg
Hydroxylamine sulfate	2.5 g
Sodium chloride	0.6 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxylethyl)-aniline sulfate	4.5 g
Diethylenetriaminepentaacetic acid	3.0 g
Potassium hydroxide	1.2 g

Water to make 1 liter. Adjust pH to 10.06 with potassium hydroxide or a 20% sulfuric acid solution.

The composition of the color developer replenisher used is as follows:

Potassium carbonate	35 g
Sodium hydrogencarbonate	3 g
Potassium sulfite	5 g
Sodium bromide	0.4 g
Hydroxylamine sulfate	3.1 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxylethyl)-aniline sulfate	5.8 g
Potassium hydroxide	2 g

Water to make 1 liter. Adjust pH to 10.12 with potassium hydroxide or a 20% sulfuric acid solution.

The composition of the bleaching bath used is as follows:

Ferric-ammonium 1,3-propylenediamine-tetraacetate	150 g
Disodium ethylenediaminetetraacetate	2 g
Ammonium bromide	178 g
Glacial acetic acid	50 ml

Water to make 1 liter. Adjust pH to 4.5 with ammonia water or glacial acetic acid.

The composition of the bleaching bath replenisher used is as follows:

Ferric-ammonium 1,3-propylenediamine-tetraacetate	180 g
Disodium ethylenediaminetetraacetate	2 g
Ammonium bromide	178 g
Glacial acetic acid	50 ml

Water to make 1 liter. Adjust pH to 3.5 with ammonia water or glacial acetic acid.

The composition of the fixer bath and the replenisher thereof used is as follows:

Ammonium thiosulfate	180 g
Ammonium thiocyanate	120 g
Anhydrous sodium sulfite	15 g
Sodium metabisulfite	3 g
Disodium ethylenediaminetetraacetate	0.8 g

Water to make 1 liter. Adjust pH to 6.5 with acetic acid or ammonia water.

The composition of the solution common to the stabilizer bath and the replenisher therefor is as follows:

Formaldehyde (37% solution)	0.5 ml
5-Chloro-2-methyl-4-isothiazoline-3-one	0.05g
Triton x-100, produced by Rohm & Haas	1 ml
Sodium formaldehyde-bisulfite adduct	2 g
Hexamethylenetetramine	0.3 g

Water to make 1 liter. Adjust pH to 8.7 with ammonia water or a 50% sulfuric acid solution.

Sample 2, the color paper prepared above, was exposed and then processed as follows:

Processing B	Time	Temp.	Replenishing amt.
Color developing	20 seconds	38°C	61 ml
Bleaching	20 seconds	35°C	20 ml
Fixing	20 seconds	35°C	61 ml
Stabilizing	40 seconds	35°C	101 ml
Drying	30 seconds	60 - 80°C	--

The above replenishing amount is a value per m^2 of the light-sensitive material.

Color developer

Diethylene glycol	15 g
Potassium bromide	0.01g
Potassium chloride	2.3 g
Potassium sulfite (50% solution)	0.5 ml
Color developing agent, 3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate	6.0 g
Diethylhydroxylamine (85%)	5.0 g
Hydrazinodiacetic acid	3.0 g
Triethanolamine	10.0 g
Potassium carbonate	30 g
Sodium ethylenediaminetatraacetate	2.0g
Brightening agent, Keicol PK-Conc, produced by Nippon Soda Co.	2.0 g

Water to make 1 liter. Adjust pH to 10.15 with potassium hydroxide or sulfuric acid.

Color developer replenisher

Diethylene glycol	17 g
Potassium chloride	3.0 g
Potassium sulfite (50% solution)	1.5 ml
Color developing agent, 3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate	8.8 g
Diethylhydroxylamine (85%)	7.0 g
Triethanolamine	10.0 g
Hydrazinodiacetic acid	5.0 g
Potassium carbonate	30 g
Sodium ethylenediaminetetraacetate	2.0 g
Brightening agent, Keicol PK-Conc, produced by Nippon Soda Co.	2.5 g

Water to make 1 liter. Adjust pH to 10.40 with potassium hydroxide or sulfuric acid.

Bleaching bath

Ferric-ammonium 1,3-propylenediamine-tetraacetate	150 g
Disodium ethylenediaminetatraacetate	2 g
Ammonium bromide	178 g
Glacial acetic acid	50 ml

Water to make 1 liter. Adjust pH to 4.5 with ammonia water or glacial acetic acid.

Bleaching bath replenisher

Ferric-ammonium 1,3-propylenediamine-tetraacetate	180 g
Disodium ethylenediaminetetraacetate	2 g
Ammonium bromide	178 g
Glacial acetic acid	50 ml

Water to make 1 liter. Adjust pH to 3.5 with ammonia water or glacial acetic acid.

Fixer bath, fixer replenisher

Ammonium thiosulfate	180 g
Ammonium thiocyanate	120 g
Anhydrous sodium bisulfite	15 g
Sodium metabisulfite	3 g
Disodium ethylenediaminetetraacetate	0.8 g

Water to make 1 liter. Adjust pH to 6.5 with acetic acie or ammonia water.

Stabilizer bath, stabilizer replenisher

Sodium o-phenylphenol	0.3 g
5-Chloro-2-methyl-4-isothiazoline-3-one	0.02g
2-Methyl-4-isothiazoline-3-one	0.01g
Cinopal SFP, produced by Ciba Geigy	0.3 g
Trisodium nitrilotriacetate	1.5 g

Water to make 1 liter. Adjust pH to 7.5 with ammonia water or a 50% sulfuric acid solution.

Experiment 1:

Processing A (for color negative film)

Color developing - bleaching - fixing - stabilizing

Processing B (for color photographic paper) Color developing - bleaching - fixing - stabilizing

The respective steps of the above processings A and B are replenished with the corresponding replenishers.

The overflow from the fixer bath of Processing B is all used as a replenisher to Processing A to thereby perform running processings. That is, the running processings were conducted through piping arranged so as to have all the overflow from the color photographic paper fixer bath flow to (replenish) the color negative film fixer bath. The running processings were continuously carried out until the total flow amount of the fixer replenisher came up to twice the capacity of the fixer bath for color negative film.

Regarding the relation between the processing number of color photographic papers and that of color negative films, the running processings were made so as to process 24 sheets of 8.2cmx11.7cm-size color paper, while processing one roll of 135-sized color negative film for 24 exposures.

Experiment 2:

Running processings were performed in similar manner to Experiment 1 except that pipe arrangement was made so as to allow no overflow from the fixer bath for color photographic paper into the fixer bath for color negative film.

Experiment 3:

Running processings were conducted in similar manner to Experiment 1 except that pipe arrangement was made so as to allow the overflow from the fixer bath for color negative film into the fixer bath for color photographic paper.

Experiment 4:

Running processings were carried out in similar manner to Experiment 1 except that the color photographic paper as Sample 3 prepared according to the following method was used and Processing B was changed as follows:

Sample 3

A paper support one side of which was laminated with polyethylene and the other side of which was laminated with polyethylene-containing titanium oxide was used to coat the following layers on the titanium oxide-containing polyethylene side, whereby a multilayer silver halide light-sensitive material was prepared. The coating liquids used were prepared as follows:

Coating liquid for Layer 1

Twenty-six point five grams of yellow coupler Y-4, 10.0g of dye image stabilizer ST-2 and 0.46g of additive HQ-1 were dissolved in 10g of a high-boiling organic solvent DNP with 60 ml of ethyl acetate, and this solution was emulsifiedly dispersed by means of a ultrasonic homogenizer in 220 ml of a 10 % aqueous gelatin solution containing 7ml of 20% surfactant SU-6, whereby a yellow coupler dispersion was prepared. This dispersion was mixed with a blue-sensitive silver halide emulsion, containing 10g of silver, prepared under the following conditions, whereby a coating liquid for Layer 1 was prepared. Coating liquids for Layers 2 to 7 also were prepared in similar manner to the above coating liquid for Layer 1.

Layer	Component	Adding amt. (g/m^2)
Layer 1 (Blue-sensitive layer)	Gelating	1.4
	Blue-sensitive AgBrCl emulsion (in silver equivalent)	0.3
	Yellow coupler Y-4	0.8
	Dye image stabilizer ST-2	0.3
	Additive HQ-3	0.015
	DNP	0.3
Layer 2 (Intermediate layer)	Gelatin	1.0
	Additive HQ-3	0.02
	Additive HQ-4	0.06
	DIDP	0.13
Layer 3 (Green-sensitive layer)	Gelatin	1.3
	Green-sensitive AgBrCl emulsion (in silver equivalent)	0.28
	Magenta coupler M-4	0.35
	Dye image stabilizer ST-3	0.1
	Dye image stabilizer ST-4	0.2
	Dye image stabilizer ST-8	0.015
	Additive HQ-3	0.01
	DIDP	0.28
	Antiirradiation dye AI-6	4.0×10^{-3}
Layer 4 (UV absorbing layer)	Gelatin	1.1
	UV absorbent UV-3	0.18
	UV absorbent UV-4	0.52

(Continued)-

(Continued)

	Additive HQ-3	0.04
	DNP	0.45
	Antiirradiation dye AI-7	0.015
	Catechol derivative CA-1	7.0×10^{-3}
Layer 5 (Red-sensitive layer)	Gelatin	1.4
	Red-sensitive AgBrCl emulsion (in silver equivalent)	0.23
	Cyan coupler C-5	0.13
	Cyan coupler C-4	0.26
	Dye image stabilizer ST-2	0.20
	Additive HQ-3	5.5×10^{-3}
	DOP	0.20
Layer 6 (UV absorbing layer)	Gelatin	0.50
	UV absorbent UV-3	0.07
	UV absorbent UV-4	0.23
	Additive HQ-3	0.016
	DNP	0.2
	Antiirradiation dye AI-7	2×10^{-2}
	Catechol derivative CA-1	3.0×10^{-3}
Layer 7 (Protective layer)	Gelatin	1.0
	Silicon dioxide	3.0×10^{-3}

The above respective color-sensitive emulsions were prepared as follows:

Blue-sensitive silver chlorobromide emulsion

A silver chlorobromide emulsion having an average grain size of 0.7μm and a silver bromide content of 90 mol% was optimally sensitized at 57°C with use of sodium thiosulfate and sensitizing dye BS-1, and stabilizer Z-1 was added thereto.

Green-sensitive silver chlorobromide emulsion

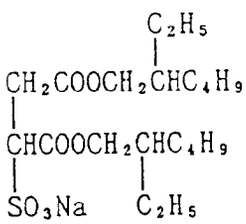
A silver chlorobromide emulsion having an average grain size of 0.5μm and a silver bromide content of 70 mol% was optimally sensitized at 59°C with use of sodium thiosulfate and sensitizing dye GS-1, and stabilizer Z-1 was added thereto.

Red-sensitive silver chlorobromide emulsion

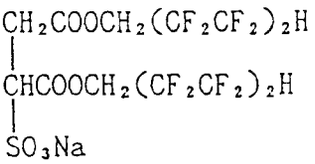
A silver chlorobromide emulsion having an average grain size of 0.4μm and a silver bromide content of 60 mol% was optimally sensitized at 60°C with use of sodium thiosulfate, sensitizing dye RS-2 and a phenol resin, and stabilizer Z-1 was added thereto.

In addition, to each of the above emulsions were added coating aids SU-1 and SU-6, and hardeners H-1 and H-3.

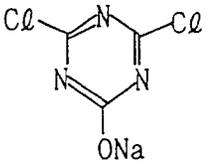
SU-6



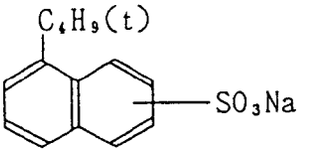
SU-1



H — 1

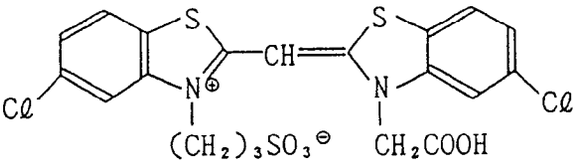


S U — 7

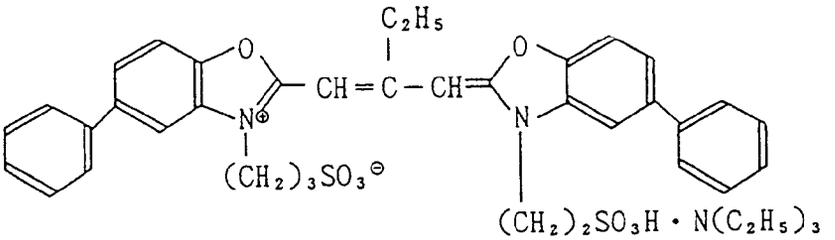


H — 3 $C(CH_2SO_2CH=CH_2)_4$

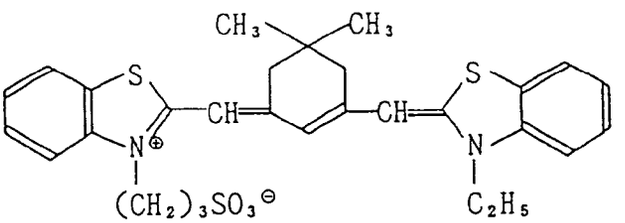
B S — 1



G S — 1



R S — 2



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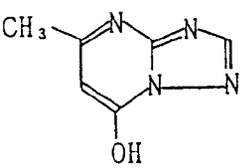

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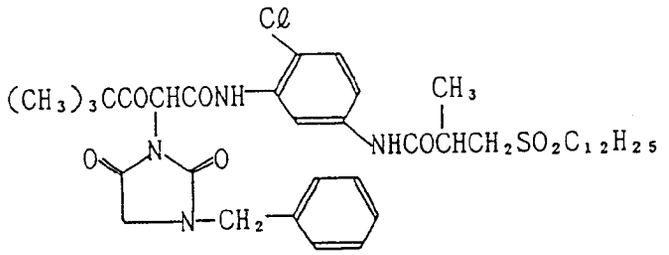
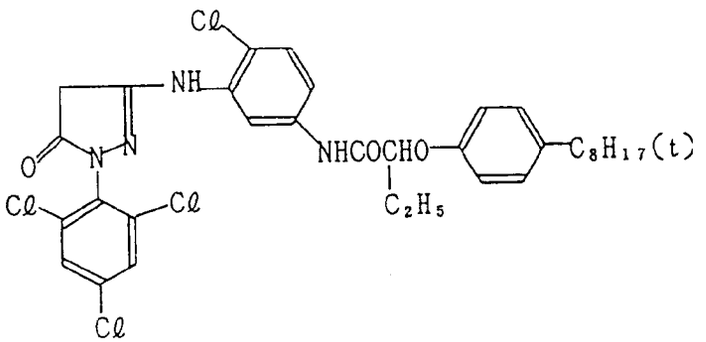
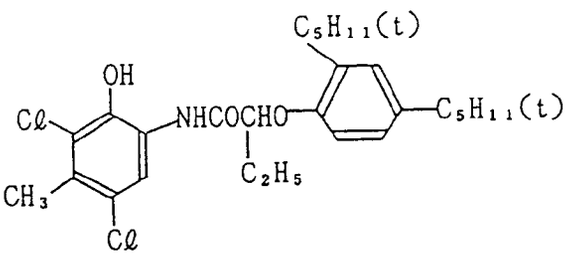


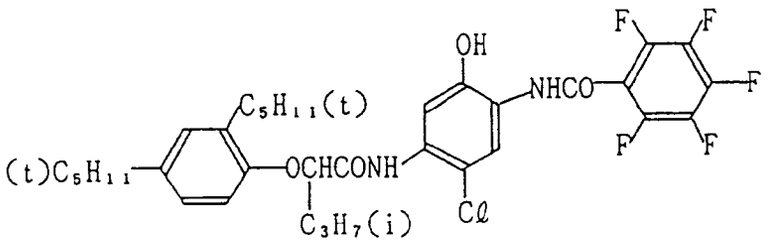
M — 4



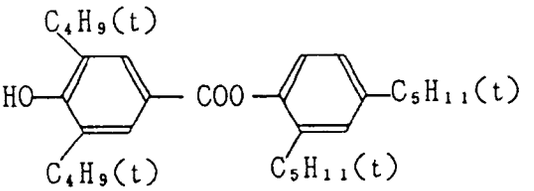
C — 5



C — 4



S T — 2



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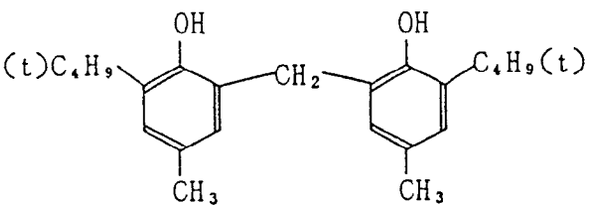

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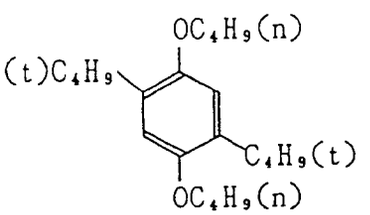

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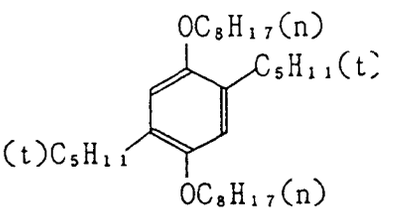
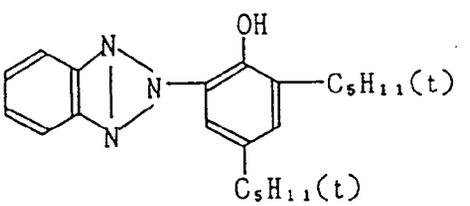
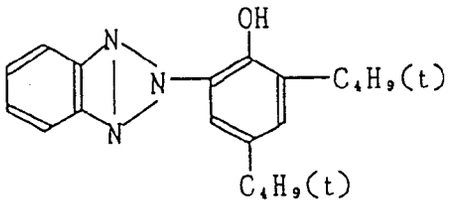


U V — 3

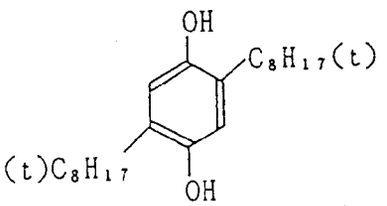


U V — 4

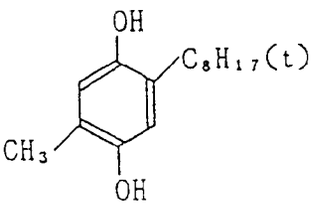


DOP Dioctyl phthalate
DNP Dinonyl phthalate
DIDP Diisodecyl phthalate

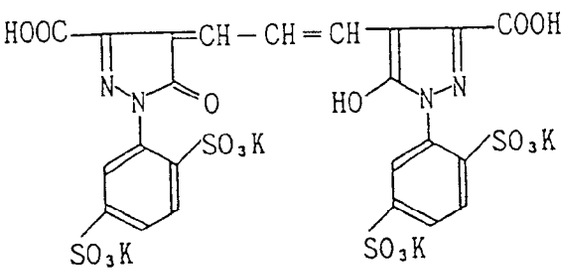
H Q — 1



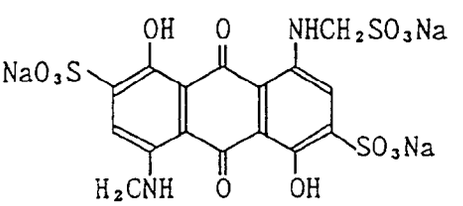
H Q — 3



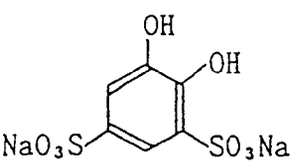
A I — 6



A I — 7



C A — 1



Color developer

Benzyl alcohol	15 ml
Ethylene glycol	15 ml
Potassium sulfite	2.0 g
Potassium bromide	0.7 g
Sodium chloride	0.2 g
Potassium carbonate	30.0 g
Hydroxylamine sulfate	3.0 g
Polyphosphoric acid (TPPS)	2.5 g
3-Methyl-4-amino-N-ethyl-N-(β-methane-sulfonamidoethyl)-aniline sulfate	5.5 g
Brightening agent, 4,4'-diaminostilbensulfonic acid derivative	1.0 g
Potassium hydroxide	2.0 g
Water to make 1 liter.	

Color developer replenisher

Benzyl alcohol	20 ml
Ethylene glycol	20 ml
Potassium sulfite	3.0 g
Potassium carbonate	30.0 g
Hydroxylamine sulfate	4.0 g
Polyphosphoric acid (TPPS)	3.0 g
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfon-amidoethyl)-aniline sulfate	7.0 g
Brightening agent, 4,4'-diaminostilbenesulfonic acid derivative	1.5 g
Potassium hydroxide	3.0 g

Water to make 1 liter.

Processing temperature: 33°C

Processing time: 3 minutes and 30 seconds

Replenishing amount: 227 ml

A flow diagram of the respective solutions is shown in Fig.1.

The total amount of the residual silver in the unexposed area of the processed color negative film and both at the start and at the end (after two rounds) of the running processing and the presence of sediment on the periphery of the fixer bath at the end of the processing were measured. The results are shown in Table 1.

Table 1

Experiment No.		Residual silver (mg/m^2)	Sediment
Experiment 1 (Inv.)	At start	0	
	At end	0.2	a
Experiment 2 (Comp.)	At start	0	
	At end	1.2	d
Experiment 3 (Comp.)	At start	0	
	At end	1.3	c
Experiment 4 (Inv.)	At start	0	
	At end	0.5	b

Note: a ... No sediment appears on the squeeze roller.
b ... Little sediment appears.
c ... Sediment appears.
d ... Sediment conspicuously appears.
e ... Much sediment badly appears.

(The same shall apply hereinafter)

As is apparent from Table 1, the use of the processing method of the invention makes it possible to lessen the amount of residual silver and to restrain the generation of sediment on the periphery of the fixing bath.

Example 2

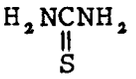
Experiment 5:

An experiment, the same as Experiment 2 of Example 1, was performed as a comparative experiment.

Experiment 6:

An experiment was performed in the same manner as in Experiment 5 except that the following Compound A-1 was added to the fixer bath in an amount of 0.1 mol/liter.

A-1



Experiment 7:

An experiment was performed in the same manner as in Experiment 1 of Example 1 except that Compound A-1 was added to the fixer bath in an amount of 0.1 mol/liter.

Experiment 8:

An experiment was conducted in the same manner as in Experiment 1 of Example 1.
The results are shown in Table 2.

Table 2

Experiment No.	Fixing accelerator	Residual silver (mg/dm^2)		Sediment
5 (Comp.)	--	At start	0	
		At end	1.2	c
6 (Comp.)	A-1	At start	0	
		At end	0.2	d
7 (Inv.)	A-1	At start	0	
		At end	0.1	b
8 (Inv.)	--	At start	0	
		At end	0.2	a

As is apparent from Table 2, the processing method of the invention shows a fixing ability the same as or more than in the case where the fixing accelerator is used and keeps the periphery of the fixer bath free of sediment.

Example 3

A similar experiment was conducted, using the following Processing A' in place of the color negative film processing used in Example 1.

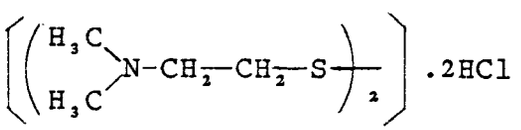
Processing A'	Time	Temp.	Rep.amt.	Bath capacity
Color developing	3 min.15 sec.	38°C	760 ml	10 liters
Bleaching	1 min.	38°C	610 ml	4 liters
Bleach-fix	3 min.15 sec.	38°C	920 ml	10 liters
Stabilizing	1 min.	38°C	920 ml	10 liters
Drying	1 min.	55°C	--	--

The above stabilizing was performed in a three-bath cascade system. The color developer and stabilizer bath are the same as those used in Example 1.

The bleaching bath and bleach-fix bath used above are as follows:

Bleaching bath, bleaching bath replenisher

Ferric-ammonium ethylenediaminetetraacetate dihydrate	120.0 g
Disodium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	120.0 g
Ammonium nitrate	20.0 g
Bleaching accelerator	0.005 mol



.2HCl

Ammonia water (27%)	15.0 ml

Water to make 1 liter. pH=6.3

Bleach-fix bath, bleach-fix bath replenisher

Ferric-ammonium ethylenediaminetetraacetate dihydrate	50.0 g
Ammonium bromide	20.0 g
Disodium ethylenediaminetetraacetate	5.0 g
Sodium sulfite	12.0 g
Ammonium thiosulfate solution (20%)	240.0 ml
Ammonia water (27%)	6.0 ml

Water to make 1 liter. pH=6.5

Water to make 1 liter. pH=6.5

Processing A′ (for color negative film) Color developing - Bleaching - Bleach-fix - Stabilizing

Processing B (for color photographic paper) Color developing - Bleaching - Fixing - Stabilizing

A flow diagram of the processing solutions is shown in Fig.2.

Experiment 9:

The respective processing baths of the above processing lines are replenished with the corresponding replenishers. The overflow from Processing B was further used as the replenisher to Processing A′. That is, the running processings were made through piping arranged so as to have the overflow from the color photographic paper fixer bath flow to (replenish) the bleach-fix bath for color negative film. The running processings were continously performed until the flow-in amount of the fixer replenisher solution came up to twice (2 rounds) the bleach-fix bath capacity.

The running processings were made in the same color photographic paper/color negative paper-processing quantity proportion as in Example 1.

Experiment 10:

Running processings were made in like manner except that pipe arrangement was made so as to allow no overflow from the color photographic paper fixer bath into the color negative film bleach-fix bath.

Experiment 11:

To the bleach-fix bath for color negative film was added Compound A-1 in an amount of 0.1 mol/liter, and running processings were performed with use of the same pipe arrangement as in Experiment 10.

The results are shown in Table 3.

Table 3

Experiment No.		Residual silver (mg/dm²)	Sediment	Total amt of waste liquid
9 (Inv.)	At start	0		
	At end	0.3	a	89
10 (Comp.)	At start	0		
	At end	1.5	c	100
11 (Comp.)	At start	0		
	At end	0.2	d	100

Note: The total amount of waste liquid is shown in a relative value to the amount of Experiment 10.

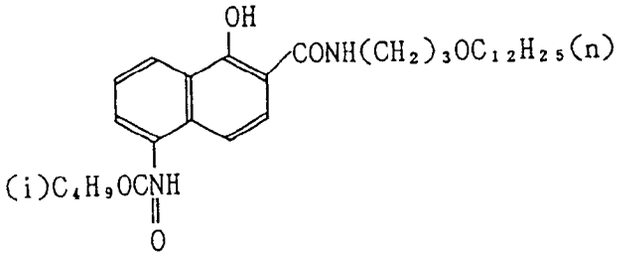
As is apparent from Table 3, the processing method of the invention shows excellent fixing characteristics in running processing, well keeps the periphery of the bath free of sediment, and discharges less waste liquid.

Example 4

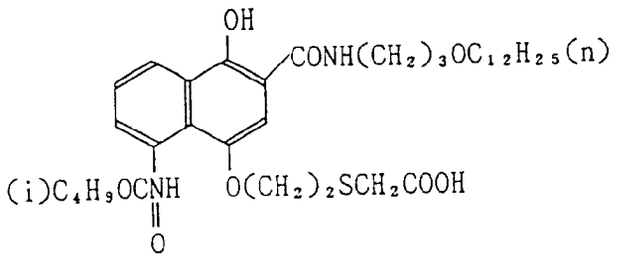
Experiments were carried out in the same manner as those of Example 1 except that the cyan couplers

C-1 and C-2. magenta couplers M-1 and M-2, and yellow coupler Y-1 used in the color negative film Sample 1 of Example 1 were replaced by C-6, C-7, M-5, M-6 and Y-5, respectively, and the cyan couplers C-3 and C-4, magenta coupler M-3 and Yellow coupler Y-3 of the color photographic paper Sample 2 were replaced by the following C-8, C-9. M-7 and Y-6, respectively. Consequently, similar results to the preceding examples were obtained.

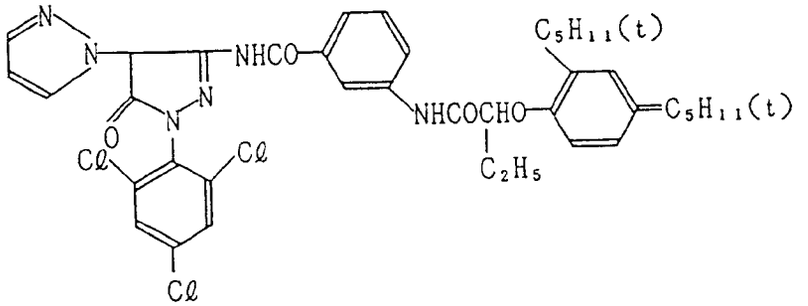
C - 6



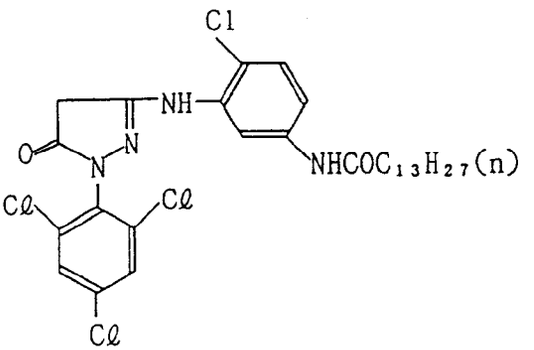
C - 7



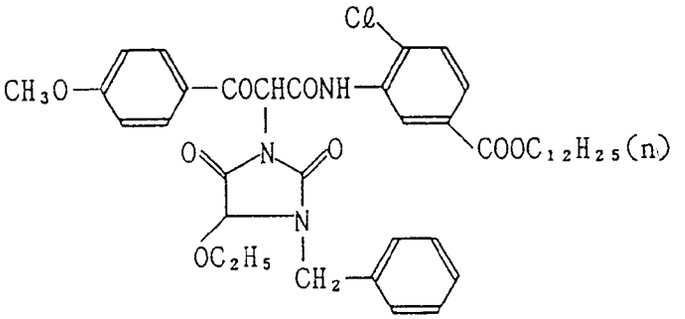
M - 5



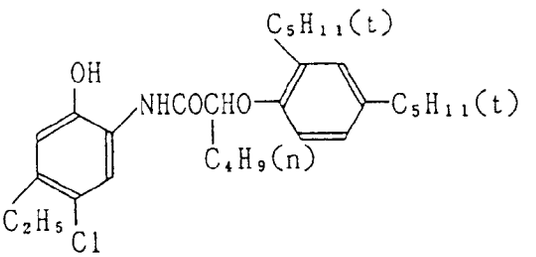
M - 6



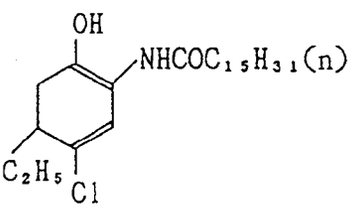
Y - 5



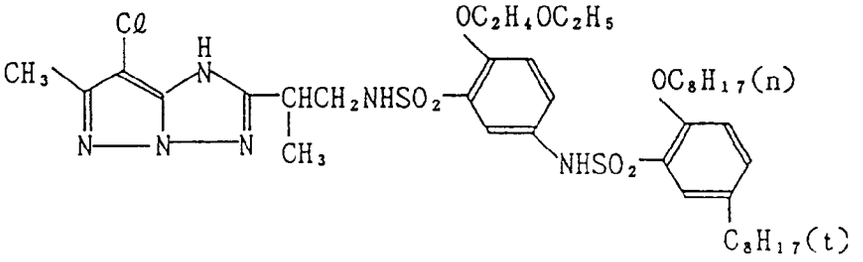
C - 8



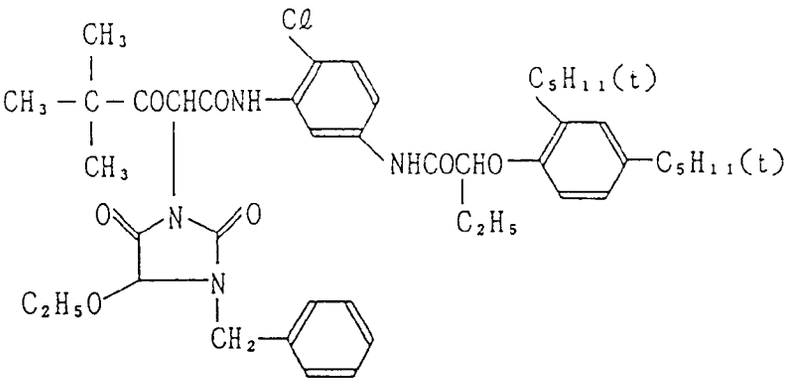
C - 9



M − 7



Y − 6



Example 5

Running processings were conducted in the same manner as in Example 1 except that the replenishing amount of the replenisher to the fixer bath of Processing A used in Experiment 1 (Exp. Nos.13 - 17) and Experiment 2 of Example 1 (Exp. Nos.18 - 20) was changed, and the amount of the residual silver of the processed color negative film and the presence of sediment on the periphery of the fixer bath at the end of the processings were examined. The results are shown in Table 4.

Table 4

Experiment No.	Replenishing amt.(ml/m²)	Residual silver (mg/dm²)	Sediment
13 (Inv.)	600	0.1	a
14 (Inv.)	400	0.2	a
15 (Inv.)	200	0.2	b
16 (Inv.)	100	0.5	b
17 (Inv.)	50	0.7	b
18 (Comp.)	600	1.2	c
19 (Comp.)	400	1.4	c
20 (Comp.)	200	1.4	d
21 (Comp.)	100	1.7	d
22 (Comp.)	50	2.0	e

As is apparent from Table 4, the flow-in of the overflow from the fixer bath (Nos.13 - 17) makes it possible to provide better photographic characteristics with a less replenishing amount than in the conventional processing method.

Claims

1. A method for processing a silver halide color photographic light-sensitive material (A) comprising a support having thereon a silver halide emulsion layer containing silver halide grains having a silver iodide content of not less than 0.5 mol%, said method comprising:
developing said photographic material with a color developer;
bleaching said photographic material with a bleaching solution; and
fixing said photographic material with a fixing solution (FA);
wherein the fixing solution (FA) is replenished by a fixing solution (FB) that has processed a silver halide photographic material (B) comprising a support having thereon a silver halide emulsion layer containing silver halide grains substantially not containing silver iodide.

2. A method according to claim 1, wherein said solutions (FA) and (FB) each are a fixer or a bleach-fixer.

3. A method according to claim 1 or 2, wherein said solutions (FA) and (FB) each contain a fixing agent in an amount of not less than 0.1 mol/liter.

4. A method according to any one of the preceding claims, wherein said photographic material (B) has been developed with a color developer; bleached with a bleaching solution; and fixed with the fixing solution (FB).

5. A method according to any one of the preceding claims, wherein said photographic materials (A) and (B) each are further processed with a stabilizer following the fixing.

6. A method according to claim 5, wherein at least one of the bleaching solution, the fixing solution and the stabilizer has an identical composition for processing each of the photographic materials (A) and (B).

7. A method according to any one of the preceding claims, wherein said silver halide emulsion layer in said photographic material (A) contains silver halide grains having a silver iodide content of from 2.0 to 20 mol%.

8. A method according to any one of the preceding claims, wherein said photographic material (A) is a color negative film.

9. A method according to any one of the preceding claims, wherein said silver halide emulsion layer in said photographic material (B) contains silver halide grains having a silver chloride content of at least 80 mol%.

10. A method according to claim 9, wherein said silver halide grains are silver chlorobromide or silver chloride.

11. A method according to any one of the preceding claims, wherein the amount of solution replenished to the solution (FA) is from 50 to 600 m(per m^2 of the color negative film.

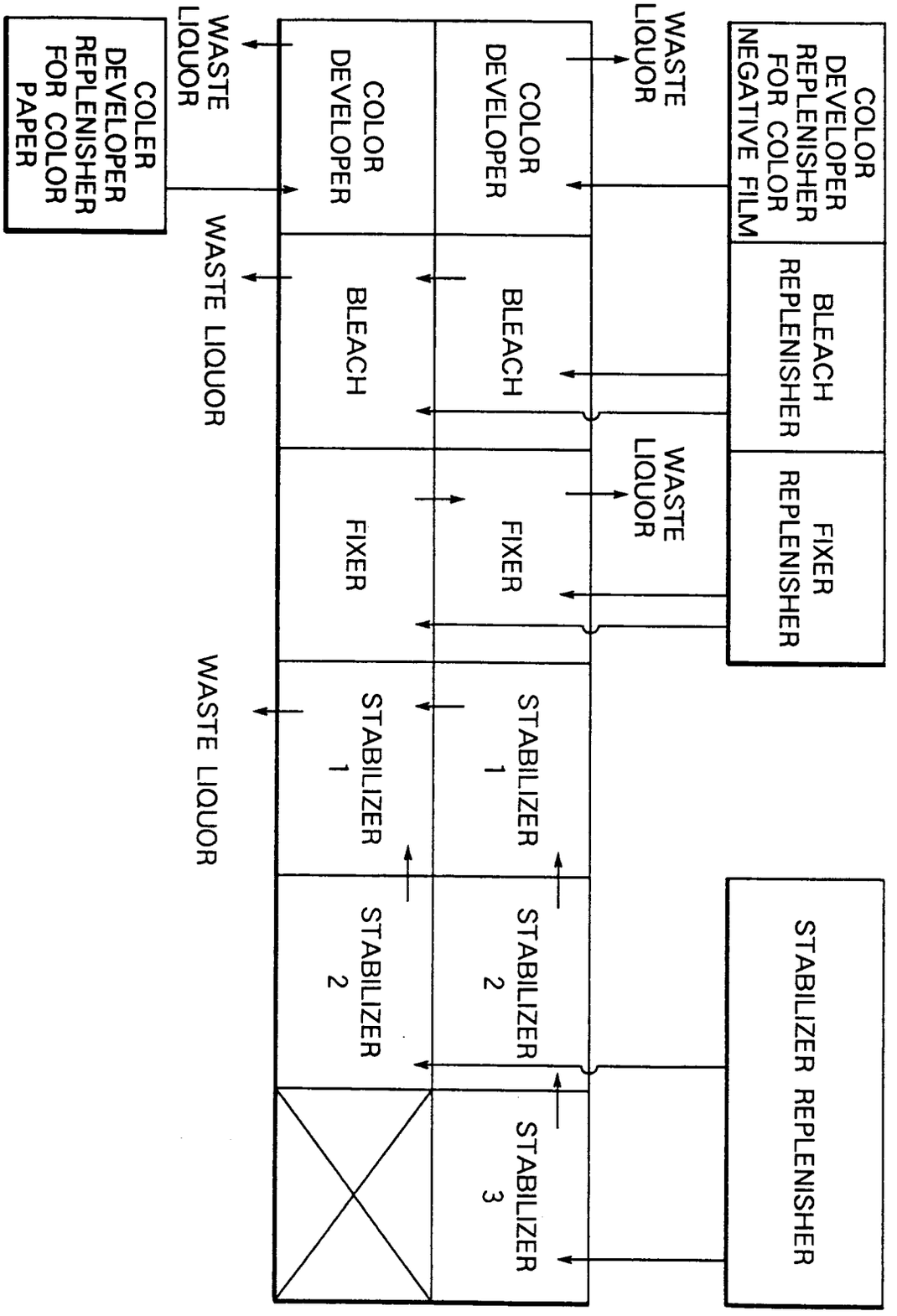

COLOR DEVELOPER REPLENISHER FOR COLOR NEGATIVE FILM
BLEACH REPLENISHER
FIXER REPLENISHER
STABILIZER REPLENISHER
PROCESS A
PROCESS B
WASTE LIQUOR
COLOR DEVELOPER
BLEACH
FIXER
STABILIZER 1
STABILIZER 2
STABILIZER 3
WASTE LIQUOR
COLER DEVELOPER REPLENISHER FOR COLOR PAPER
WASTE LIQUOR
WASTE LIQUOR

FIG. 1

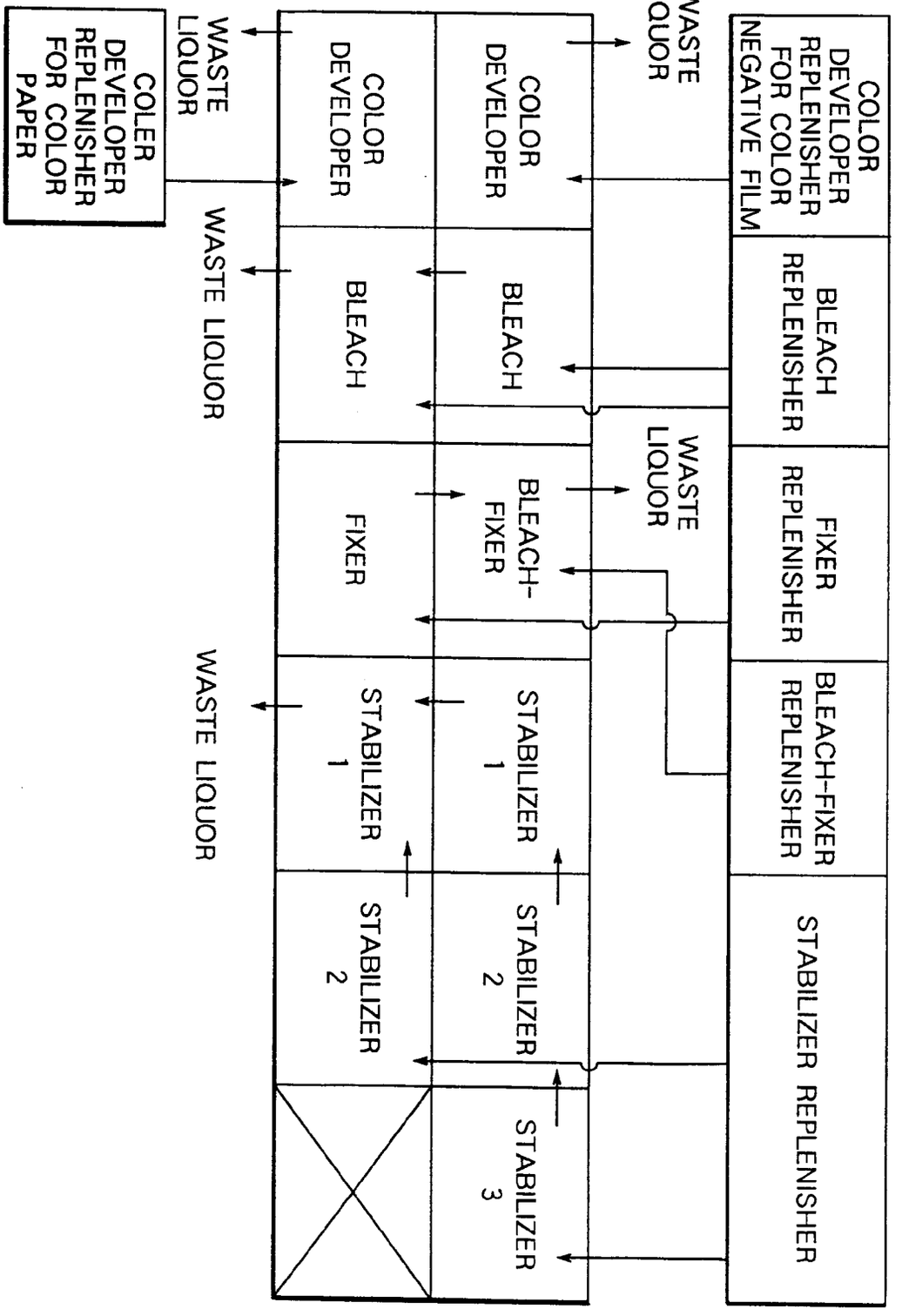

COLOR DEVELOPER REPLENISHER FOR COLOR NEGATIVE FILM
BLEACH REPLENISHER
FIXER REPLENISHER
BLEACH-FIXER REPLENISHER
STABILIZER REPLENISHER
WASTE LIQUOR
WASTE LIQUOR
PROCESS A'
COLOR DEVELOPER
BLEACH
BLEACH-FIXER
STABILIZER 1
STABILIZER 2
STABILIZER 3
PROCESS B
COLOR DEVELOPER
BLEACH
FIXER
STABILIZER 1
STABILIZER 2
WASTE LIQUOR
WASTE LIQUOR
WASTE LIQUOR
COLER DEVELOPER REPLENISHER FOR COLOR PAPER

FIG. 2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 5690

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 147 148 (KONISHIROKU PHOTO-INDUSTRY CO. LTD.) * page 9, line 5 - line 14 *	1-11	G03C7/44 G03C7/30 G03C7/407
P,Y	EP-A-0 399 434 (FUJI PHOTO FILM CO. LTD.) * abstract * * page 3, line 56 - page 4, line 7 *	1-11	
Y	EP-A-0 330 442 (EASTMAN KODAK COMPANY) * abstract *	1-11	
P,X	US-A-5 001 506 (T.NAKAMURA) * column 4, line 29 - line 39 * * column 5, line 28 - line 34 *	1-11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 OCTOBER 1991	BOLGER W.

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

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