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(54) Method of processing silver halide color photographic light sensitive materials.

(57) A method of processing a silver halide color photographic light-sensitive material is disclosed. The material comprises a support and provided thereon, a silver halide emulsion layer containing silver halide grains having an average silver chloride content of not less than 80 mol%. The method comprises the step of imagewise exposing the material, and developing the exposed material with a color developing solution, wherein the color developing solution contains 4×10^{-2} to 3.0×10^{-1} mol per liter of chloride, 1.0×10^{-2} to 2.0×10^{-2} mol per liter of a color developing agent, and 5.0 to 100 g per liter of a compound represented by the following Formula 1,
Formula 1

$$R\text{-}SO_3X$$

wherein R represents an alkyl group having 1 to 8 of carbon atoms or a phenyl group, provided that R may be a polymer having a repetition unit in which an ethylenically unsaturated bond is open, and X represents a hydrogen atom, a sodium atom, potassium atom, a lithium atom or an ammonium group.

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FIELD OF THE INVENTION

This invention relates to a method of processing a silver halide color photographic light sensitive material and particularly to silver halide color photographic light sensitive materials which can rapidly be processed even in a series of continuous processes without producing any stain in the unexposed areas of the light sensitive materials and can display an excellent processing stability.

BACKGROUND OF THE INVENTION

Generally, when a color image is to be obtained by processing an imagewise exposed light sensitive material, a desilvering step for desilvering a produced metal silver and then a washing or stabilizing step are to be carried out after completing a color developing step.

In recent years, light sensitive materials have been processed in a running treatment through an automatic processor installed each at most photofinishing laboratories. For such a processing treatment of light sensitive materials as mentioned above, it has been demanded to finish up and return them to the customers within the very day when the photofinishing orders have been received, as a part of the customer services, so that further developments of the rapid processing techniques have been demanded so far. In addition to the above, the photofinishers have most recently been required to return every finished product to the customers within several hours after receiving the photofinishing orders, so that still further developments of the rapid processing techniques have been getting required more than ever.

Under such a background as mentioned above, Eastman Kodak Company proposes a technique of rapidly processing color papers, that is so-called Process RA-4 comprising three processing steps, namely, a 45-second color developing step, a 45-second fixing and bleaching step and a 90-second stabilizing step so as to process a color paper within 3 minutes at a processing temperature of 35°C.

When judging the conventional techniques of rapidly processing light sensitive materials, they may be roughly classified into the following three categories;

(1) A technique by which a light sensitive material is improved;

(2) Another technique in which a physical means is used in a developing step; and

(3) A further technique by which the composition of a processing solution is improved when it is used in a developing step.

The techniques falling within the above classification (1) include, for example, (i) the techniques each by which a silver halide composition is improved, (e.g., a technique of making a silver halide finely grained, such as disclosed in Japanese Patent Publication Open to Public Inspection - hereinafter abbreviated to as JP OPI Publication- No. 51-77223/1976 and the other techniques each of making a silver halide to have a low silver iodide content, such as disclosed in JP OPI Publication No. 58-18142/1983 and JP Examined Publication No. 56-18939/1981); (ii) the techniques each in which an additive is used, (e.g., the techniques each in which 1-aryl-3-pyrazolidone having a specific structure is added to a light sensitive material, such as disclosed in JP OPI Publication No. 56-64339/1981 and the other techniques each in which 1-aryl pyrazolidone is added to a light sensitive material, such as disclosed in JP OPI Publication Nos. 57-144547/1982, 58-50534/1983, 58-50535/1983 and 58-50536/1983); (iii) the techniques each in which a rapidly reactive coupler is used, (e.g., the techniques each in which a rapidly reactive yellow coupler is used, such as disclosed in JP Examined Publication No. 51-10783/1976 and JP OPI Publication Nos. 50-123342/1975 and 51-102636/1976); (iv) the techniques each for making a photographic component layer thinner, (e.g., the techniques each for making a photographic component layer thinner, such as JP OPI Publication No. 62-65040/1987).

The techniques falling within the above classification (2) include, for example, the techniques each for stirring a processing solution, (e.g., the techniques each for stirring a processing solution, such as disclosed in JP OPI Publication No. 62-180369/1987).

The techniques falling within the above classification (3) include, for example, the known techniques such as (i) a technique in which a development accelerator is used; (ii) another technique for making a concentration of a color developing agent higher; and (iii) a further technique for making a concentration of halide ions including particularly bromide ions lower.

Out of the above-given rapidly processing techniques, the following techniques can display particularly excellent rapid processing functions; namely, the techniques such as those disclosed in JP OPI Publication Nos. 58-95345/1983, 60-19140/1985 and 58-95736/1983 each in which a light sensitive material having a high silver chloride content is used, that is retated to the above-mentioned techniques of classification (1).

However, the above-mentioned techniques have not been satisfactory for the users who have been requesting a further rapid processability. As seeing in the fast-food market of the food industry where a waiting time has been demanded to be shortened, a further rapid processing operations have also been requested in the photographic industry.

On the other hand, environment issues have been closed up recently. In the photographic industry, therefore, many products capable of saving a replenishment and reducing a waste solution have been put on the market from many photographic companies, for the purpose of abating pollution loads.

When trying to make a replenishment lower in addition to the improvements of rapidly processing operations, there has raised a serious problem that a maximum density is varied when carrying out a continuously processing operation and the market values of the products deteriorate. This problem is particularly serious in the case of a color developer. It was also found that another problem to produce yellow stains was further raised.

SUMMARY OF THE INVENTION

It is, accordingly, an object of the invention to provide a method of processing a silver halide color photographic light sensitive material wherein a rapid processing can be performed even in a series of continuous processing operations, a stain can be prevented from producing in every unexposed are, an excellent processing stability can be displayed and a long-term continuous processing can be performed.

From the results obtained by the present inventors in studying every aspect described above, they have discovered that the above-mentioned object of the invention can be achieved in a method of processing a silver halide color photographic light sensitive material comprising a support and provided thereon, a silver halide emulsion layer containing silver halide grains having an average silver chloride content of not less than 80 mol%, comprising the step of;

imagewise exposing the material, and

developing the exposed material with a color developing solution,

wherein said color developing solution contains 4×10^{-2} to 3.0×10^{-1} mol per liter of chloride, 1.0×10^{-2} to 2.0×10^{-2} mol per liter of a color developing agent, and 5.0 to 100 g per liter of a compound represented by the following Formula 1.

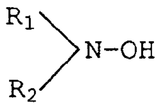
Formula 1

$$R\text{-}SO_3X$$

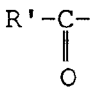
wherein R represents an alkyl group having 1 to 8 carbon atoms or a phenyl group, provided that R may be a polymer having a repetition unit in which an ethylenically unsaturated bond is open, and X represents a hydrogen atom, a sodium atom, potassium atom, a lithium atom or an ammonium group.

In the above-mentioned method, it was discovered that the above-mentioned object can further effectively be achieved when the above-mentioned silver halide color photographic light sensitive material contains a silver coating weight of not more than 0.75 g/m^2 or a compound represented by the following Formula (2).

Formula (2)



wherein R_1 and R_2 represent each a hydrogen atom, an alkyl group, an aryl group,



$$R'-\underset{\underset{O}{\|}}{C}-$$

in which R′ represents an alkoxy group, an alkyl group or an aryl group or R_1 and R_2 may combine to form a ring, provided that R_1 and R_2 are not a hydrogen atom simultaneously.

DETAILED DESCRIPTION OF THE INVENTION

When the Cl^- concentration of a color developer is not less than 4×10^{-2} mols per liter in the case where a light sensitive material containing an emulsion having a highly silver chloride content is used and low replenishment to the developer is carried out, it was found that the aforementioned problems are raised remarkably. From the results of the investigations, it was also found that the problems can be improved by processing the light sensitive material with a processing solution containing a color developing agent in an amount of not less than 1.0x10^{-2} mols per liter, however, on the other hand, the other new problems are raised, that is, a problem that the color developing agent is substantially low in solubility so that it can hardly be dissolved unless it is heated upto a high temperature or it is deposited at a low temperature, and another problem that the developing agent is deposited in the course of trying a running experiment. The present inventors have discovered that the solubility and deposition of the color developing agent can be improved so that the stable characteristics can be displayed, when making a compound represented by Formula (1) present in a processing solution so as to solve the problems, and the inventors have achieved the objects of the invention. It was also unexpectedly proved to be effective for improving the tar production in the color developer.

The following processing steps may be included in the preferable processing steps carried out in the method in which a processing solution of the invention is applied;

(1) Color developing → bleach-fixing → stabilizing;
(2) Color developing → bleaching → fixing → stabilizing;
(3) Color developing → bleaching → bleach-fixing → stabilizing;
(4) Color developing → bleach-fixing → fixing → stabilizing;
(5) Color developing → bleach-fixing → bleach-fixing → stabilizing; and
(6) Color developing → bleaching → bleach-fixing → fixing → stabilizing

Among the above-given processing steps, the steps (1), (2) and (3) are preferably applied.

The color developing solutions applicable to the invention are each to contain a compound represented by Formula (1).

In Formula (1), the alkyl groups having 1 to 8 carbon atoms, which are represented by R, include for example, a methyl group, a carboxymethyl group, a phenylmethyl group, an ethyl group, a hydroxyethyl group, a sulfonylethyl group, a propyl group, a butyl group, a heptyl group and an octyl group. These groups may be straight-chained or branched and may also include those each having a substituent. Such substituents include, for example, a halogen atom (such as a chlorine atom and a bromine atom), an aryl group (such as a phenyl group), a hydroxyl group, an amino group, a nitro group, a carboxylic acid group (including the salts thereof) and a sulfonic acid group (including the salts thereof).

The phenyl groups represented by R include those each having a substituent. Such substituents include, for example, a halogen atom (such as a chlorine atom and a bromine atom), an alkyl group (including, preferably, an alkyl group having 1 to 4 carbon atoms, such as a methyl group, an ethyl group, a propyl group and a butyl group), a hydroxyl group, an amino group, a nitro group, a carboxylic acid group (including the salts thereof) and a sulfonic acid group (including the salts thereof). The substituents on the phenyl groups may be a single substituent or 2 to 5 substituents. In the case of 2 to 5 substituents, these substituents may be the same as or the different from each other.

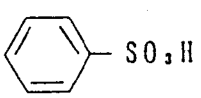
Further, R may represent an ethylenically-unsaturated group or a polymer having the repetition unit of these ethylenically-unsaturated groups.

R represents, desirably, a phenyl group and, preferably, a phenyl group having a substituent. The preferable substituents thereto include, for example, an alkyl group having 1 to 4 carbon atoms, a hydroxyl group, a carboxylic acid group (including the salts thereof) and a sulfinic acid group (including the salts thereof).

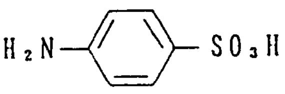
The typical examples of the sulfonic acid derivatives of the invention, which are applicable to the invention and represented by the Formula (1), will be given below. It is to be understood that the invention shall not be limited thereto.

Exemplified compounds

(I − 1)



(I − 2)



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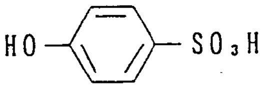

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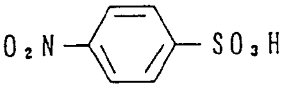

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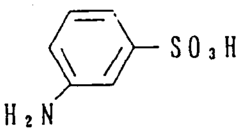

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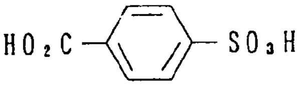

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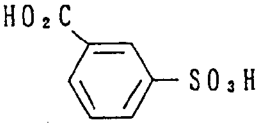

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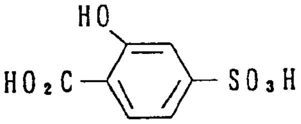
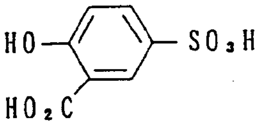
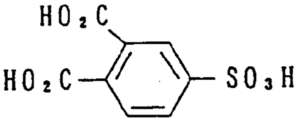


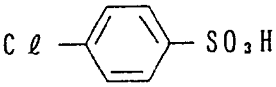
(I－9)



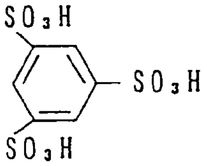
(I－10)



(I－11)



(I－12)



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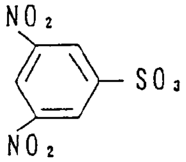

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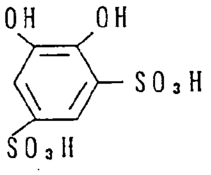

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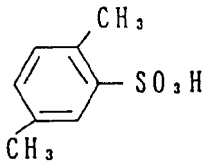

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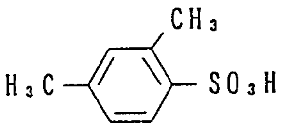

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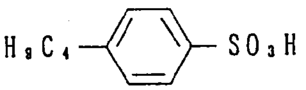
(I-18)



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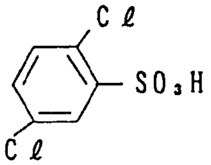

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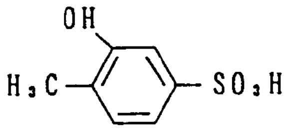

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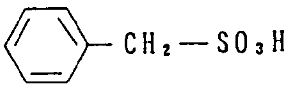
(I-22)



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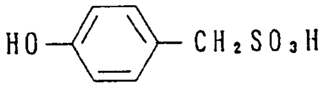

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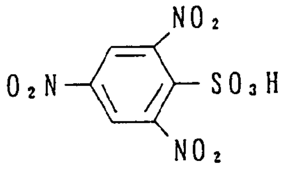

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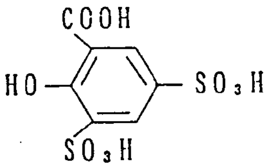

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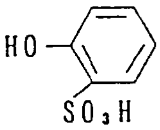

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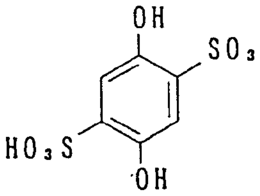

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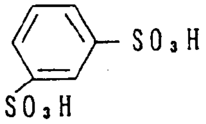

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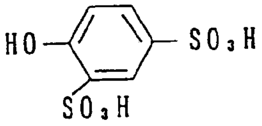

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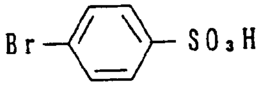

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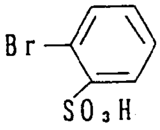

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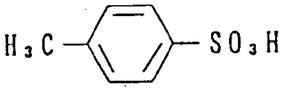

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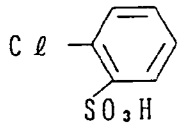


(I－34)

H_3CSO_3H

(I－35)

$H_2C(SO_3H)_2$

(I－36)

$C_6H_{13}SO_3H$

(I－37)

$C_7H_{15}SO_3H$

(I－38)

$C_8H_{17}SO_3H$

(I－39)

$C_3H_7SO_3H$

(I－40)

$C_4H_9SO_3H$

(I－41)

$C_5H_{11}SO_3H$

(I－42)

$HO_3S—C_2H_4—SO_3H$

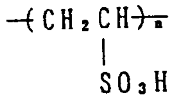
(I－43)

$HO—C_2H_4—SO_3H$

(I－44)

$HO_2CCH_2SO_3H$

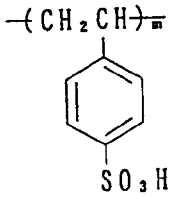
(I－45)



$$-\!\!\left(CH_2\underset{\displaystyle SO_3H}{\underset{|}{C}}H\right)_{\!n}\!-$$

n＝3～300

(I－46)



m＝3～300

In the above-given typically exemplified compounds, each of the compounds having a sulfonic acid group or a carboxylic acid group includes, as the matter of course, the compounds such as the sodium salts, potassium salts and lithium salts of the respective compounds, because they are to be used in a color developer that is an alkaline solution.

Some parts of the above-mentioned sulfonic acid derivatives of the invention are disclosed in British Patent Nos. 669,505 and 837,491, and JP OPI Publication Nos. 51-147322/1976 and 51-80229/1976 and they may readily be available by any person skilled in the art.

The sulfonic acid derivatives of the invention may be used independently or in combination. They may be used in an amount within the range of, desirably, 5.0 g to 100 g and, preferably, 10 g to 80 g per liter of a color developer to be used.

In particular, they may be used preferably in an amount within the range of 20 g to 70 g. In the invention, to be more concrete, the effects of the invention can hardly be displayed when making use of the sulfonic acid derivatives represented by Formula (1) in an amount not more than 5.0 g per liter of a color developer to be used and, when making use thereof in an amount not less than 10 g/liter and, preferably, not less than 20 g/liter, a color developing agent contained in a color developing replenisher and a color developer can be so remarkably maintained as to be a high concentration, so that the characteristics of a subject light sensitive material can be stabilized and, in particular, the effects of the invention can also remarkably be displayed in a color developer having a substantially high chloride concentration.

Now, the processing solutions applicable to the invention will be detailed below.

In the invention, a color developing solutions applicable to a developing step include, preferably, an alkaline solution principally comprising an aromatic primary amine type color developing agent. As for this type of color developing agents, a paraphenylenediamine type compound is preferably used. The examples thereof include, typically, 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-(β-hydroxyethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(β-methoxyethyl) aniline and the sulfates, hydrochlorides, phosphates or p-toluenesulfonates thereof. Among the above-given diamines, the salts thereof are generally stable more than the diamines themselves. It is, therefore, preferred to use them in the forms of the salts thereof. Among the salts thereof, a p-toluenesulfonate is rather useful from the viewpoint of making a color developing agent highly concentrated. Among the above-mentioned color developing agents, the following compounds may preferably be used;

(1) 3-methyl-4-amino-N-ethyl-N-(β-hydroxyethyl)aniline and

(2) 3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline

There may be some instances where both of the above-given compounds may be used in combination so as to meet the purposes of the application.

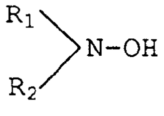
In the invention, the color developing agents may be commonly used in an amount within the range of 1×10^{-2} to 2×10^{-2} mol per liter of a color developer to be used. When the color developing agents are used in a color developing replenisher, they may be used in an amount within the range of 1.5×10^{-2} to 2.0×10^{-1} mol/liter and, preferably, 2.0×10^{-2} to 1.0×10^{-1} mol/liter.

In the invention, the preservatives applicable to a color developing solutions include, for example, a sulfite. Such sulfites include, for example, sodium sulfite, sodium hydrogensulfite, potassium sulfite and potassium hydrogensulfite. The sulfites may be used in an amount of not more than 1.0×10^{-2} mol/liter, desirably not more than 5.0×10^{-3} mol/liter and, preferably 0 from the viewpoint of a rapidity.

The other preservatives than the above-mentioned sulfites, which may preferably be applicable thereto, include, for example, an organic preservatives such as hydroxylamine, the hydroxylamine derivatives disclosed in JP OPI Publication Nos. 63-146043/1988, 63-32547/1988, 63-146042/1988, 63-146041/1988, 63-146040/1988, 63-135938/1988 and 63-118748/1988, the hydroxamic acids, a hydrazine, a hydrazide, a phenol, an α-hydroxyketone, an α-aminoketone, a sugar, a monoamine, a diamine, a quaternary ammonium salt, a nitroxyradical, an alcohol, an oxime, a diamide compound and a condensed ring type amine disclosed in JP OPI Publication Nos. 64-62639/1989 and 1-226862/1989.

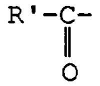
Among the preservatives given above, the effects of the invention including, particularly, the staining prevention effect can excellently be displayed when making use of a compound represented by the following Formula 2 or B and a dialkyl hydrazine in a color developing solution.

Formula 2



$$R_1(R_2)N-OH$$

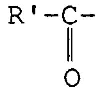
wherein R_1 and R_2 represent each a hydrogen atom, an alkyl group, an aryl group or



$$R'-\underset{\underset{O}{\|}}{C}-$$

in which R′ represents an alkoxy group, an alkyl group or an aryl group; provided, R_1 and R_2 shall not represent hydrogen atoms at the same time and both of R_1 and R_2 may form a ring.

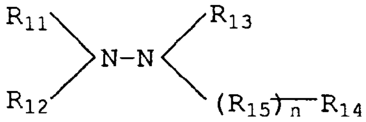
In Formula 2, R_1 and R_2 represent each an alkyl group, an aryl group,



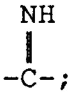
$$R'-\underset{\underset{O}{\|}}{C}-$$

or a hydrogen atom, provided, both of R_1 and R_2 shall not represent hydrogen atoms at the same time. The alkyl groups represented respectively by R_1 and R_2 may be the same with or the different from each other and, among the alkyl groups, those having 1 to 3 carbon atoms are preferred. R′ represents an alkoxy group, an alkyl group or an aryl group. The alkyl groups and the aryl groups each represented by R_1, R_2 and R′ include those having a substituent. R_1 and R_2 are allowed to couple to each other so as to form a ring including, for example, a heterocyclic ring such as those of piperidine, pyridine, triazine or morpholine.

Formula B



wherein R_{11}, R_{12} and R_{13} represent each a hydrogen atom, a substituted or non-substituted alkyl, aryl or heterocyclic group and R_{14} represents a hydroxy group, a hydroxyamino group or a substituted or unsubstituted alkyl, aryl, heterocyclic, alkoxy, aryloxy, carbamoyl or amino group. The heterocyclic group has a 5 or 6 membered ring and is comprised of each of C, H, O, N and S atoms and a halogen atom, and they may be saturated or unsaturated; R_{15} represents a divalent group selected from the group consisting of -CO-, $-SO_2-$ and



$$-\overset{\overset{NH}{\|}}{C}-;$$

and n is an integer of 0 or 1, provided, in the case of n=0, R_{14} represents a group selected from the group consisting of an alkyl group, an aryl group and a heterocyclic group, and R_{13} and R_{14} are allowed to form a heterocyclic ring in association with each other.

Some typical examples of the hydroxylamine type compounds represented by the foregoing Formula 2 are given in U.S. Patent Nos. 3,287,125, 3,293,034 and 3,287,124. The particularly preferable compounds thereof include, for example, diethyl hydroxylamine, N-hydroxymorpholine and dimethoxyethyl hydroxylamine each typically exemplified in JP Application No. 2-172374/1990, pp.51-53.

In the foregoing Formula B, R_{11}, R_{12} and R_{13} represent each desirably a hydrogen atom or an alkyl group having 1 to 10 carbon atoms and R_{11} and R_{12} preferably represent each a hydrogen atom.

In the Formula B, R_{14} represents desirably an alkyl, aryl, carbamoyl or amino group and particularly an alkyl or a substituted alkyl group. The preferable substituents for the alkyl groups include, for example, a carboxyl group, a sulfo group, a nitro group, an amino group and a phosphono group.

The typical examples of the compounds represented by Formula B include the compounds given in JP Application No. 2-172374/1990, pp.55~59.

The compounds represented by Formula 2 or B are commonly used in the forms of a free amine, a hydrochloride, a sulfate, a p-toluenesulfonate, an oxalate, a phosphate or an acetate.

In a color developing solutions, the compounds represented by Formula 2 or B are to have a concentration within the range of commonly 0.4 to 100 g/liter, preferably 1.0 to 60 g/liter and more preferably 2 to 30 g/liter.

The compounds represented by Formula 2 or B may be used together with any conventional hydroxylamines and a variety of organic preservatives in combination. It is, however, preferred not to use any hydroxylamine, from the viewpoint of the developability.

The compounds represented by Formula 2 or B may be used independently or in combination.

From the viewpoint of displaying the effects of the invention, it is preferred to contain a triazinyl stilbene type fluorescent whitening agent in the color developing solutions of the invention. Among these triazinyl stilbene type fluorescent whitening agent, those given in JP Application No. 2-172374/1990, pp.65-67, in particular, may preferably be used.

The triazinyl stilbene type fluorescent whitening agent preferably applicable to the invention can be synthesized in an ordinary process such as the process described in, for example, The Chemical Products Industry Association, 'Fluorescent Whitening Agents', issued in Aug. 1976, p.8.

Among the exemplified compounds represented by Formula (E) disclosed in the foregoing JP Application No. 2-172374/1990, those preferably applicable to the invention include, for example, the compounds E-4, E-24, E-34, E-35, E-36, E-37 and E-41.

The triazinyl stilbene type fluorescent whitening agent may be used in an amount within the range of, preferably, 2 to 10 g/liter of a color developing solution to be used and, more preferably, 0.4 to 5 g/liter thereof.

In addition to the above, to the color developing solution applicable to the invention can be added methyl cellosolve, methanol, acetone, dimethyl formamide, β-cyclodextrin and, the compounds described in JP Examined Publication Nos. 47-33378/1972 and 44-9509/1969, if required, so as to serve as an organic solvent for increasing the solubility of a developing agent to be used.

It is also allowed to use an auxiliary developing agent together with a developing agent. The known auxiliary developing agents include, for example, an N-methyl-p-aminophenol sulfate, phenidone, N,N-diethyl-p-aminophenol hydrochloride and an N,N,N',N'-tetramethyl-p-phenylenediamine hydrochloride. These auxiliary developing agents may be added in an amount within the range of, commonly, 0.01 to 1.0 g/liter.

Besides the above, it is further allowed to use a variety of additives such as a staining inhibitor, a sludging inhibitor and an interlayer effect accelerator.

In the invention, a color developing solution is to have a concentration of chlorides (such as potassium chloride, sodium chloride and ammonium chloride) is to be not less than $4x10^{-2}$ mol/liter and preferably within the range of $6.0x10^{-2}$ mol/liter to $3.0x10^{-1}$ mol/liter of the color developing solution. When the concentration thereof is less than $4.0x10^{-2}$ mol/liter, the effects of the invention can hardly be displayed satisfactorily and, when exceeding $3.0x10^{-1}$ mol/liter, the concentration is libely to be lowered even if making a color developing agent highly concentrated.

The suspending agents applicable to the invention include, for example, a variety of metal chelate-forming compounds such as an aminopolycarboxylic acid, e.g., ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, hydroxyethyliminodiacetic acid and cyclohexanediaminetetraacetic acid; an aminopolyphosphonic acid, e.g., ethylenediaminetetramethylenephosphonic acid and nitrilotrimethylenephosphonic acid; and an alkylidenediphosphonic acid typified by 1-hydroxyethylidene-1,1-diphosfonic acid.

The above-given chelating agents may be added in an amount within the range of 0.1 to 20 g/liter of a color developing solution to be used and preferably 0.2 to 8 g/liter thereof.

It is further preferable that the color developing solutions of the invention are to contain each of anionic, cationic, amphoteric and nonionic surfactants therein and, in particular, the compounds represented by Formula I given in JP Application No. 2-38072/1990 are useful for enhancing the effects of the invention.

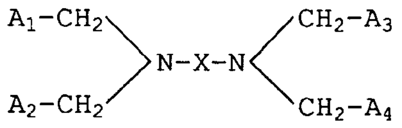
In the invention, the above-mentioned color developing solutions may be used within any desired range of pH values. However, from the viewpoint of a rapid processing efficiency, they may be used at a pH within the range of, preferably, pH9.5 to 13.0 and, more preferably, pH9.8 to 12.0. They may also be used at a processing temperature of not lower than 36.0°C, preferably, within the range of 38.0 to 43.0°C, and more preferably, 38.5 to 41°C. They may further be used for a processing time of not longer than 90 seconds and within the range of, preferably, not shorter than 3 seconds to not longer than 45 seconds and, more preferably, not shorter than 5 seconds to not longer than 35 seconds.

For embodying the invention, it is allowed to use an organic inhibitor such as a nitrogen-containing heterocyclic compound, a mercapto group-containing compound, an aromatic compound, an onium compound and a compound having an iodine atom in the substituent thereof.

The color developing solutions relating to the invention may be replenished in an amount of, ordinarily, not more than 160 ml per m^2 of a light sensitive material to be processed and within the range of, preferably, 20 ml to 120 ml, more desirably, 30 ml to 100 ml and, more preferably, 35 ml to 90 ml

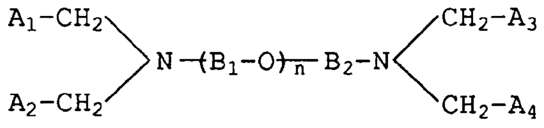
In the invention, it is desired to process a light sensitive material with a processing solution having a bleaching function, after completing a color development. As for the bleaching agents applicable to a bleaching solution or a bleach-fixing solution, the ferric organic acid complex salts represented by the following Formula C or D may preferably be used for embodying the invention.

Formula C



wherein A_1 through A_4 may be the same as or the different from each other and represent each $-CH_2OH$, $-COOM$ or $-PO_3M_1M_2$ in which M, M_1 and M_2 represent each a hydrogen atom, an alkali metal or ammonium; and X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms.

Formula D



wherein A_1 through A_4 are each synonymous with those defined in the above-given Formula C; n is an integer of 1 to 8; and B_1 and B_2 may be the same as or the different from each other and represent each a substituted or unsubstituted alkylene group having 2 to 5 carbon atoms.

The ferric organic acid complex salts represented by Formula C or D are detailed in JP OPI Publication Nos. 1-206340/10989 and 1-206342/1989 and JP Application Nos. 2-240400/1990 and 2-240401/1990. Among the complex salts, ferric 3-diaminopropane tetraacetate complex and ferric glycoletherdiamine tetraacetate complex may particularly be preferable.

In other words, when making use of the above-mentioned ferric organic acid complex salts; a bleach-fog is seriously produced particularly in a mixing step. However, when embodying the invention, such a bleach-fog as mentioned above can effectively be prevented and the effects of the invention can also remarkably be displayed.

In the invention, it is also allowed to make a combination use of the complex salts of iron (III) aminopolycarboxylic acid such as ethylenediamine tetraacetic acid, diethylenetriamine pentaacetic acid, cyclohexanediamine tetraacetic acid and methylimino diacetic acid, besides the above-mentioned ferric organic acid complex salts. These complex salts may be used in various combinations as detailed in Research Disclosure No. 24023, April, 1984.

From the viewpoint of more excellently displaying the effects of the invention, however, it is preferable to use a bleaching solution substantially comprising of only the ferric complex salts of the compounds represented by the foregoing Formula C or D. The expression, 'substantially', herein means that these ferric complex salts are contained in a proportion of at least not less than 70% (in terms of mols) in the whole ferric complex salts. This proportion is to be, preferably, not less than 80%, more preferably, not less than 90% and, preferably, not less than 95%.

The ferric complex salts of the compounds represented by the foregoing Formula C or D are to be used in an amount of at least 0.10 mol per liter of a bleaching solution to be used and within the range of, desirably, 0.15 mol to 0.6 mol and, preferably, 0.18 mol to 0.5 mol. When they are to be used in a bleach-fixing solution, they are to be used in an amount within the range of 0.03 mol to 0.3 mol per liter of the bleach-fixing solution to be used and, preferably, 0.05 mol to 0.25 mol per liter.

The processing solutions having a bleaching function, which are relative to the invention, are allowed to contain the compounds represented by Formulas I through IX given in JP Application No. 2-41549/1990, imidazole and the derivatives thereof. When this is the case, not only a bleaching acceleration effect but also a silver-sludge improvement can be displayed besides the above-mentioned effects.

The above-mentioned bleaching accelerators may be used independently or in combination. They can display the excellent effects as described above, when they are generally added in an amount within the range of about 0.01 to 100 g per liter of a bleaching solution to be used. However, when the amount thereof added is too small, the bleaching acceleration effect is not so much displayed and when it is unnecessarily too much, a precipitation is produced sometimes to stain a silver halide color photographic light sensitive material to be processed. It is, therefore, recommendable to add then in an amount within the range of, preferably, 0.05 to 50 g per liter of a processing solution having a bleaching function to be used and, more preferably, 0.05 to 15 g/liter.

In the case of adding a bleaching accelerator, it may be added to be solved as it is. However, it is general to add it upon dissolving it in advance in water, an alkaline solution or an organic acid. If required, it is also allowed to add it upon dissolving it with an organic solvent such as methanol, ethanol and acetone.

The above-mentioned bleaching solution are used at a pH within the range of, desirably, pH2.0 to 5.5 and, preferably, not lower than pH3.0 to not higher than pH5.0. When the pH of a bleaching solution is not lower than 5.5, there may be some instances where a bleach-fog may not satisfactorily be prevented or when the pH thereof is not higher than 2, the photographic characteristics may sometimes be affected, though the bleach-fog may be prevented. The processing temperature is to be kept within the range of, preferably, 20°C to 50°C and, more preferably, 25°C to 45°C.

The above-mentioned bleaching solutions are usually used upon adding a halide such as ammonium bromide. These bleaching solutions are also allowed to contain pH-buffers comprising a variety of salts including, for example, boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide, independently or in combination. Further, a variety of fluorescent whitening agents, defoamers, surfactants or antimolds may also be contained therein.

In the above-mentioned bleaching solutions, an ammonium ion content is to be not more than 50 mol% of the whole cation, preferably, not more than 20 mol% thereof and, more preferably, not more than 10 mol% thereof. When this is the case, any bleach-fog can be prevented.

The above-mentioned bleaching solutions may be replenished in an amount within the range of, 20 ml to 400 ml per m^2 of a silver halide color photographic light sensitive material to be processed, preferably, 30 ml to 350 ml, more preferably, 40 ml to 300 ml and, most preferably, 50 ml to 250 ml.

In the courses of processing steps, it is preferable that the above-described bleaching solutions are to be used immediately after completing a color development.

From the viewpoint of making a rapid processing in the invention, it is preferable that a subject light sensitive material is to be processed with a bleaching solution and successively processed with a fixing solution or a bleach-fixing solution.

The above-mentioned fixing solutions and the bleach-fixing solutions are inevitable to contain the so-called fixing agents therein.

The fixing agents include, for example, a compound capable of forming the complex salts of an aqueous solution upon making a reaction with a silver halide. Such compounds mentioned above include, for example, a thiosulfate such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate; a thiocyanate such as potassium thiocyanate, sodium thiocyanate and ammonium thiocyanate; thiourea; and thioether. Among them, a thiosulfate and a thiocyanate are preferably used and a thiocyanate is more preferably used. For embodying the invention, it is preferred to contain ammonium ions in a fixing solution or a bleach-fixing solution in an amount of not more than 50 mol% of the whole cation as in the aforementioned bleaching solution and, preferably, not more than 20 mol%. In this embodiment of the invention, a stain-prevention effect may be displayed though the effects may be displayed a little.

The fixing solutions and the bleach-fixing solutions are also allowed to contain, besides the above-mentioned fixing agents, pH buffers comprising a variety of the salts including, for example, sulfites such as ammonium sulfite, potassium sulfite, ammonium bisulfite, potassium by sulfite, sodium bisulfite, ammonium metabisulfite, potassium metabisulfite and sodium metabisulfite, and various salts of boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide, independently or in combination.

It is further desirable to contain a large amount of an alkali halide or an ammonium halide including, for example, a re-halogenizing agent such as potassium bromide, sodium bromide, sodium chloride and ammonium bromide. It is further allowed to suitably add, for example, a pH buffer such as a borate, an oxalate, an acetate, a carbonate and a phosphate, and the compounds generally known as the additives for fixing solutions and bleach-fixing solutions, such as an alkylamine and a polyethylene oxide.

The above-mentioned fixing agents are to be added in an amount of not less than 0.1 mols per liter of a processing solution to be used and within the range of, desirably, 0.3 mols to 4 mols, more desirably, 0.5 mols to 3.0 mols and, preferably, 0.6 mols to 2.0 mols per liter thereof.

In the invention, it is allowed, if required, to blow the air or oxygen into a processing bath and a processing replenisher reservoir tank or a suitable oxidizer such as hydrogen peroxide, a bromate and a persulfate may further be added so as to enhance the activity of a bleaching solution or a bleach-fixing solution.

In the invention, a silver recovery can be carried out of a fixing solution or a bleach-fixing solution in any known methods. For example, it is effective for the silver recoveries to utilize the electrolysing method (refer to French Patent No. 2,299,667), the precipitation methods (refer to JP OPI Publication No. 52-73037/1977 and German Patent No. 2,331,220), the ion-exchange methods (refer to JP OPI Publication No. 51-17114/1976 and German Patent No. 2,548,237) and the transmetallation method (refer to British Patent No 1,353,805).

It is preferred to recover silver, in particular, from a tank solution in an in-line system, because a rapid processing aptitude can be made more excellent. On the other hand, it is also allowed to recover silver from an overflow waste solution so as to reuse the recovered silver.

In the invention, a fixing solution or a bleach-fixing solution may be replenished in an amount of, not more than 800 ml per m^2 of a subject light sensitive material, preferably, within the range of 20 ml to 650 ml per m^2 thereof and, more preferably, within the range of 30 ml to 400 ml per m^2 thereof. In the latter case, the excellent results can be enjoyed.

When a fixing solution or a bleach-fixing solution contains an iodide (such as ammonium iodide, potassium iodide, sodium iodide and lithium iodide) in an amount within the range of 0.1 g/liter to 10 g/liter, the effects of the invention can be promoted.

In particular, when adding them in an amount within the range of 0.3 g/liter to 5 g/liter, preferably, 0.5 g/liter to 3 g/liter and, most preferably, 0.8 g/liter to 2 g/liter, the excellent results can be enjoyed.

The compounds represented by Formula [FA] or [FB] given in JP Application No. 2-41549/1990 are preferably used in a fixing solution or a bleach-fixing solution, for the purpose of freeing ammonia.

A sulfite adduct is preferably used in a fixing solution or a bleach-fixing solution. Such sulfite adducts preferably applicable thereto include, for example, those having Formulas (A-1) through (A-11) given in JP Application No. 2-41549/1990.

Such a sulfite adduct is used in an amount within the range of, desirably, 0.1 g to 80 g/liter of a processing solution to be used and, preferably, 0.5 to 40 g/liter thereof.

The total processing time of a bleaching solution and a processing solution (i.e., a fixing solution or a bleach-fixing solution) having a fixing function is not longer than 3 minutes 45 seconds and within the range of, preferably, 40 seconds to 3 minutes and, more preferably, 60 seconds to 2 minutes 40 seconds.

Any desired bleaching time may freely be selected out of the above-mentioned range of the total processing time, however, it is to be within the range of, preferably, 10 seconds to 70 seconds and, more preferably, 20 seconds to 55 seconds. Any desired processing time of the processing solutions each having a fixing function may freely be selected, however, it is to be preferably not longer than 3 minutes 10 seconds and within the range of, more preferably, 10 seconds to 2 minutes 40 seconds.

In the preferable embodiments of the invention, the cross-over time between a color developing solution tank and a bleaching solution tank is to be desirably not longer than 10 seconds and, preferably, not longer than 7 seconds, from the viewpoint of preventing a bleach-fog production.

In the invention, it is preferred to forcibly stir a bleaching solution, a fixing solution and a bleach-fixing solution.

The expression, '--- to forcibly stir ---', does not mean herein that a solution is dispersed and moved in an ordinary manner, but means that a stirring means is so provided as to forcibly stir a solution.

The forcibly stirring means include, for example, the following means;

1. A high-pressure spraying method or a spray-stirring method;
2. An air-bubbling method;
3. A supersonic oscillation method; and
4. A vibration method.

The above-given methods are typically described in JP Application No. 2-41549/1990.

Now, the stabilizing solutions applicable to the invention will be detailed. The stabilizing solutions applicable to the invention can be applied to a stabilizing solution to be used in a stabilizing step that is the final processing step applicable to a silver halide color photographic light sensitive material. The stabilizing solutions mentioned above can also be applied to the cases where a silver halide color photographic light sensitive material is processed with a processing solution having a fixing function such as a fixing solution or a bleach-fixing solution and is then stabilized in a stabilizing step without substantially washing it.

The stabilizing solution may be replenished in an amount, preferably, 1 to 80 times as much as an amount carried therein from the precedent bath in terms of a unit area of a subject color light sensitive material. In the invention, however, the stabilization processing tank is preferably so constructed that the concentration of the component of the precedent bath (i.e., a bleach-fixing solution or a fixing solution), which are carried into the stabilizing solution bath, is to be not more than 1/100 and is to be within the range of 1/100 to 1/100000 and preferably 1/200 to 1/50000 as dense as the whole concentration of the stabilizing solution in the stabilizing tank, from the viewpoints of maintaining a low pollution and a preservability.

The above-mentioned stabilizing tank may be comprised of a plurality of tanks and it is preferable for the invention that the plural tanks consist of not less than 2 to not more than 6 tanks.

In the invention, when the tanks consist of not less than 2 tanks, it is particularly preferable to constitute the tank system to be a counter-current system (that is a system in which a solution is supplied to a back-bath so that an overflow can be flowed from the fore-bath.), from the viewpoint of the improvements of low pollution and image preservation.

The amounts of a solution to be carried into the following bath may be varied according to the kinds of light sensitive materials, the transport rates and transport systems of an automatic processor used and the systems for squeezing the surfaces of light sensitive materials. In the case of color light sensitive materials, the amount to be carried thereinto are ordinarily within the range of 50 ml/m^2 to 150 ml^2. The amounts of a solution to be replenished relative to the above-mentioned amounts to be carried in, which may remarkably be able to display the effects of the invention, are to be within the range of 50 ml/m^2 to 4.0 liters/m^2 and, preferably, 100 ml/m^2 to 1500 ml/m^2.

When processing a light sensitive material with a stabilizing solution, the processing temperature thereof is to be within the range of 15 to 60°C and, preferably, 20 to 45°C.

The stabilizing solutions applicable to the invention are each preferable to contain a chelating agent represented by the formulas [CH-I] through [CH-III] given in JP Application No. 2-41549/1990.

The chelating agents preferably applicable to the above-mentioned stabilizing solutions may be used in an amount within the range of, 0.01 to 100 g, preferably, 0.05 to 50 g and, more preferably, 0.1 to 20 g.

The pH values of the above-mentioned stabilizing solutions are to be within the range of, desirably, pH4.0 to 9.0 and, preferably, pH5.5 to 9.0, for the purpose of improving the image preservability.

The pH controllers applicable to the stabilizing solutions include any one of the generally known alkalizers and acidifiers.

The stabilizing solutions may be added with organic acid (such as citric acid, acetic acid, succinic acid, oxalic acid and benzoic acid), pH controllers (such as a phosphate, a borate, a hydrochloride and a sulfate), a surfactant, an antiseptic and metal salts such as those of Bi, Mg, Zn, Ni, Al, Sn, Ti and Zr. These compounds may be added thereinto in any amount, provided, the amount thereof can be necessary to keep the pH of the stabilizing solution used. The compounds may be used in any combination, provided, any color photographic image preservation stability and any precipitation preventability cannot be spoiled. For displaying the above-mentioned effects, it is also preferred to make Ca ions and Mg ions are to be not more than 5 ppm in a stabilizing solution.

The antimolds preferably applicable to the stabilizing solutions applicable to the invention include, for example, a hydroxy benzoate compound, a phenol type compound, a thiazole type compound, a piridine type compound, a guanidine type compound, a carbamate type compound, a morpholine type compound, a quaternary phosphonium type compound, an ammonium type compounds, a urea type compound, an isooxazole type compound, a propanol amine type compound, a sulfamide type compound, an amino acid type compound and a benztriazole type compound.

Among them, a phenol type compound, a thiazole type compound and a benztriazole type compound may further preferably be used, from the viewpoint of a solution preservability.

These further preferable compounds include, typically, 1,2-benzisothiazoline-3-one, 2-methyl-4-isothiazoline-3-one, 2-octyl-4-isothiazoline-3-one, 5-chloro-2-methyl-4-isothiazoline-3-one, sodium 0-phenylphenol and benztriazole. The amounts of these antimolds to be added into a stabilizing solution are within the range of, desirably, 0.001 g to 20 g per liter of the stabilizing solution to be used and, preferably, 0.005 g to 10 g per liter thereof.

The stabilizing solutions may be added in combination with the compounds given in JP Application Nos. 2-234776/1990 and 2-234780/1990, including, for example, formalin, hexamethylene tetramine, a triazine type compound, an N-methylol compound (such as dimethylol urea, trimethylol urea, dimethylol guanidine, N-hydroxymethyl hydroxyethyl amine and trimethylol melamine) and aliphatic aldehyde. It is, however, preferable to make formalin to be substantially zero from the viewpoint of pollution prevention and that is a preferable embodiment from the viewpoint of solution preservability.

It is preferable that the stabilizing solutions each applicable to the invention contain a surfactant represented by Formulas [I] and [III], triethanol amine and polyvinyl pyrrolidones.

The above-mentioned surfactants and a water-soluble organic siloxane type compound are to be added in an amount within the range of 0.01 to 20 g per liter of a stabilizing solution to be used. When this is the case, an excellent result can be displayed.

When the above-mentioned surfactants and the compounds are added in an amount not more than 0.01 g, stains becomes loud on the surfaces of a light sensitive material being treated. When they are added in an amount of not less than 20 g, a large amount of the organic siloxane type compound adhere to and stain the surfaces of a light sensitive material.

The above-mentioned water-soluble organic siloxane type compounds mean each common water-soluble organic siloxane type compounds such as those given in JP OPI Publication No. 47-18333/1972, JP Examined Publication Nos. 55-51172/1980 and 51-37538/1976, JP OPI Publication No. 49-62128/1974 and U.S. Patent No. 3,545,970, respectively.

The above-mentioned water-soluble organic siloxane type compounds may readily be available from UCC (standing for Union Carbide Corp.) and Shin-Etsu Chemical Industrial Co., Ltd.

Now, the light sensitive materials applicable to the processing methods of the invention will be detailed below.

The color light sensitive materials applicable to the invention comprise each silver halide grains principally containing silver chloride in a proportion of at least not less than 80 mol%, preferably, not less than 90 mol%, more preferably, not less than 95 mol% and, most preferably not less than 99 mol%. Besides the silver chloride, these silver halide emulsions principally comprising the above-mentioned silver halide grains are also allowed to contain silver bromide so as to serve as a composition of the silver halides thereof. When this is the case, the silver bromide proportion thereof is to be not more than 20 mol%, preferably not more than 10 mol% and more preferably not more than 3 mol%. When silver iodide is made present therein, the proportions thereof is to be preferably not more than 1 mol%, more preferably not more than 0.5 mol% and most preferably zero. The above-mentioned silver halide grains principally comprising silver chloride having a proportion of not less than 80 mol% may be applied to at least one of silver halide emulsion layers and, preferably, to all of the silver halide emulsion layers.

The crystals of the above-mentioned silver halide grains may be any one of regular crystals, twinned crystals and others and, therefore, the crystals having any crystal ratios of [1,0,0] faces to [1,1,1] faces may be used. The crystal configurations of the above-mentioned silver halide grains may be uniform from the inside to the outside thereof or may be a grain-layer structure having the inside thereof heterogeneous from the outside thereof (i.e., a core-shell type crystal structure). Also, these silver halides may be of a type of forming a latent image mainly on the surfaces of the grains or another type of forming a latent image inside the grains. Further, tabular-shaped silver halide grains may be used, (For the details, refer to JP OPI Publication No. 58-113934/1983 and JP Application No. 53-170070/1978). Still further, silver halides given in JP OPI Publication Nos. 64-26837/1989, 64-26838/1989 and 64-77047/1989 can be used.It is further allowed to use the silver halide grains prepared in any one of an acidic method, a neutral method and an ammoniacal method.

They may also be prepared in a method that seed grains are prepared in an acidic method and are then grown up in an ammoniacal method having a fast grain-growth rate so that the grains are grown up to a specific grain-size. When growing silver halide grains, it is preferred that the pH and pAg of a reaction chamber are controlled and then silver ions and halide ions are put thereinto in such an amount so as to meet the growth rate of the silver halide grains as disclosed in JP OPI Publication No. 54-48521/1979.

In a light sensitive material to be processed in the invention, the silver halide emulsion layers thereof are each to contain color couplers. These color couplers produce each a non-diffusible dye upon making reaction with the oxidized products of a color developing agent. Advantageously, the color couplers are incorporated into a light sensitive layer or a layer adjacent thereto, in the non-diffusible state.

In the above-described manner, a red-light sensitive layer can contain, for example, a non-diffusible color coupler capable of producing the color image of cyan-colored portions and, generally, a phenol or α-naphthol type coupler. A green-light sensitive layer can contain, for example, at least one non-diffusible color coupler capable of producing the color image of magenta-colored portions and, generally, a 5-pyrazolone type coupler and pyrazolotriazole. A blue-light sensitive layer can contain, for example, at least one non-diffusible color coupler capable of producing the color image of the yellow-colored portions and, generally, a color coupler having an open-chained ketomethylene group. Such a color coupler as mentioned above may be any one of 6-, 4- or 2-equivalent couplers.

In the invention, 2-equivalent couplers, in particular, are preferably used.

The couplers suitably applicable to the invention are disclosed in, for example, the following publications: Nitteilungln aus den Forschungslaboratorien der Agfa, Leverkusen/Munchen, Vol.III, p.111, 1961, W. Pelz, 'Farbkuppler'; K. Venkataraman, 'The Chemistry of Synthetic Dyes', Vol.4, pp.341-387, Academic Press; 'The Theory of the Photographic Process', 4th Ed., pp.353-362; and Research Disclosure No. 17643, Section VII.

From the viewpoint of displaying the effects of the invention, it is preferred to use, in particular, the following couplers in the invention; namely, the magenta couplers having the formula [M-1] such as those disclosed in JP OPI Publication No. 63-106655/1988, p.28, among which, the typically exemplified magenta couplers include No.1 through No.77 given in JP OPI Publication No. 63-106655/1988, pp.29-34; the cyan couplers having the formula [C-I] or [C-II] given in ibid., p.34, among which, the typically exemplified cyan couplers include (C′-1) through (C′-82) and (C″-1) through (C″-36) given in ibid., pp.37-42; the high-speed yellow couplers given in ibid., p.20, among which, the typically exemplified cyan couplers include (Y′-1) through (Y′-39) given in ibid., pp.21-26.

When applying a nitrogen-containing heterocyclic mercapto compound into a light sensitive material, not only the effects of the invention can excellently be displayed, but also the other effects can be displayed so as to remarkably diminish any bad influences on the photographic characteristics of the light sensitive material when a bleaching solution or a bleach-fixing solution is mixed into a color developing solution. This embodiment can therefore be included in the preferred embodiments of the invention.

The typical examples of the above-mentioned nitrogen-containing mercapto compounds include, for example, (I′-1) through (I′-87) given in JP OPI Publication No. 63-106655/1988, pp.42-45.

The above-mentioned silver halide emulsions may be prepared in any ordinary preparation process (including, for example, a single or double influent preparation process in which the materials of the emulsion are flowed in at a constant or accelerating rate.). Among these preparation processes, the double influent preparation process is preferable to be carried out with controlling the pAg of the emulsion materials. For the details thereof, refer to Research Disclosure No. 17643, Sections I and II.

Such an emulsion as mentioned above can be chemically sensitized. They may be chemically sensitized with a sulfur-containing compounds including, particularly, an allylisocyanate, an allylthiourea or a thiosulfate. A reducing agents can also serve as a chemical sensitizer. These reducing agents include, for example, the silver compounds disclosed in Belgian Patent Nos. 493,464 and 568,687 and the polyamines or aminomethylsulfinic acid derivatives, such as diethylene triamine disclosed in Belgian Patent No. 547,323. The suitable sensitizers further include, for example, the noble metals such as gold, platinum, palladium, iridium, ruthenium and rhodium and the compounds thereof. The chemical sensitization methods are disclosed in, for example, R. Kosiovsky's treatise appeared in Z. Wiss. Photo., 46, pp.65-72, 1951; and, for further details, refer to Research Disclosure No. 17643. Section III.

The emulsions can be optically sensitized in the generally known sensitizing methods in which the ordinary polymethine dyes such as a neutrocyanine, a basic or acidic carbocyanine, a rhodacyanine and a hemicyanine, a styryl dye, an oxonol and the like. For the details, refer to F.M. Hamer, 'The Cyanine Dyes and Related Compounds', 1964, Ullmanns Enzyklpadie der Technischen Chemie, 4th Ed., Vol.18, PP. 431- the next page; and to Research Disclosure No. 17643, Section IV.

The emulsions may be applied thereto with any commonly usable antifoggants and stabilizers. Among them, azaindene is a particularly suitable stabilizer and, among them, desirably, tetra- and penta-azaindenes and, preferably, those substituted with a hydroxyl or amino group can be applied thereto. This type of the compounds are given in, for example, Birr's treatise disclosed in Z. Wiss. Photo., 47, 1952, pp.2-58 and the above-given Research Disclosure No. 17643, Section IV, respectively.

The components of a light sensitive material can be contained in the light sensitive material in any commonly known methods. For the details, refer to U.S. Patent Nos. 2,322,027, 2,533,514, 3,689,271, 3,764,336 and 3,765,897, for example. The components of a light sensitive material such as a coupler and a UV absorbent may be contained in the form of an electrically charged latex; For the details, refer to German Patent DT-OS No. 2,541,274 and European Patent Application No. 14,921, for example. The components thereof can also be fixed in the form of the polymers in the subject light sensitive material; For the details, refer to German Patent DT-OS No. 2,044,992 and U.S. Patent Nos. 3,370,952 and 4,080,211, for example.

In the invention, a silver halide color photographic light sensitive material is to have a silver coating weight of, preferably, not more than 0.75 g per m^2 of the light sensitive material and, more preferably, within the range of 0.2 to 0.7 g per m^2 thereof.

As for the supports of the above-mentioned light sensitive materials, any ordinary types of supports can be used. In the case of a color paper, for example, a reflective support such as a paper support may be used for and they may be coated thereon with a polyolefin including, particularly, polyethylene and polypropylene. For the details thereof, refer to the foregoing Research Disclosure No. 17643, Sections V and VI.

The above-mentioned light sensitive materials may be applied to any kinds of light sensitive materials including, for example, those comprising a color paper, a color negative film, a color positive film, a color reversal slide film, a color reversal cinematographic film, a color reversal TV film and a color reversal paper.

Now, the invention will be more detailed with reference to some examples of the invention. It is, however, to be understood that the invention shall not be limited thereto.

EXAMPLE-1

A multilayered silver halide color photographic light sensitive material (1) was prepared by coating the layers having the following compositions onto a paper support laminated thereon with polyethylene on one side of the paper support and laminated with polyethylene containing titanium oxide on the 1st layer of the other side of the paper support The coating solutions applied thereonto were each prepared in the following manner.

The 1st layer coating solution

Yellow coupler (Y-1) of 25.0 g, dye-image stabilizers (ST-1) of 10.0 g and (ST-2) of 6.67 g, and additive (HQ-1) of 0.53 were each added into high boiling organic solvent (DNP) of 6.3 g and ethyl acetate of 60 ml so as to be dissolved together. The resulting solution was added into an aqueous 10% gelatin solution of 220 ml containing 7 ml of a 20% surfactant (SU-1) solution, and so dispersed as to be emulsified by making use of a supersonic homogenizer, so that a yellow coupler dispersion solution could be prepared. The resulting dispersion was mixed with a blue-sensitive silver halide emulsion (containing 10 g of silver) prepared under the following conditions, so that the 1st layer coating solution could be prepared.

The coating solutions each for the 2nd layer through the 7th layer could be prepared in the same manner as in the 1st layer coating solution.

As for the layer hardeners, (H-1) was added into the 2nd and 4th layers and, (H-2), into the 7th layer, respectively. As for the coating aids, surfactants (SU-2) and (SU-3) were each added so as to control the surface tension of each of the coating solutions.

Table 1

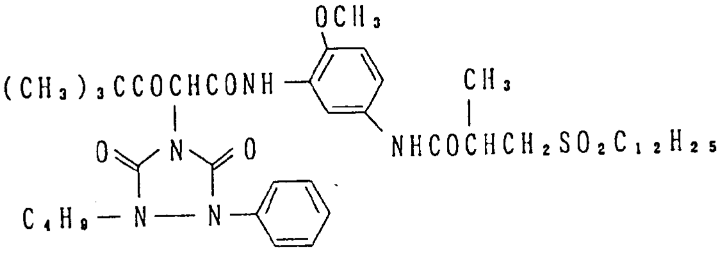
Layer	Composition	Amount added (g/m^2)
7th layer (Protective layer)	Gelatin	0.9
	Antimold (F-1)	0.002
6th layer (UV absorbing layer)	Gelatin	0.35
	UV absorbent (UV-1)	0.10
	UV absorbent (UV-2)	0.04
	UV absorbent (UV-3)	0.16
	Anti-staining agent (HQ-1)	0.01
	DNP	0.2
	PVP	0.03
	Anti-irradiation dye (AI-2)	0.02
5th layer (Red-sensitive layer)	Gelatin	1.20
	Red-sensitive silver chlorobromide emulsion (Em-R), in terms of silver content	0.21
	Cyan coupler (C-1)	0.19
	Cyan coupler (C-2)	0.23
	Dye-image stabilizer (ST-1)	0.20
	Anti-staining agent (HQ-1)	0.01
	HBS-1	0.20
	DOP	0.25
4th layer (UV absorbing layer)	Gelatin	1.0
	UV absorbent (UV-1)	0.28
	UV absorbent (UV-2)	0.09
	UV absorbent (UV-3)	0.38
	Anti-staining agent (HQ-1)	0.03
	DNP	0.35

(To be continued)

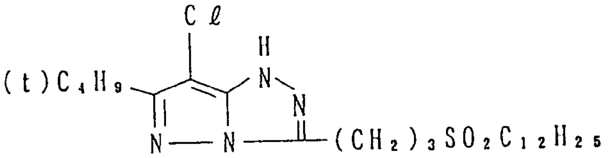
Table 1 (continued)

Layer	Composition	Amount added (g/m^2)
3rd layer	Gelatin	1.30
(Green-sensitive layer)	Green-sensitive silver chlorobromide emulsion (Em-G), in terms of silver content	0.17
	Magenta coupler (M-1)	0.19
	Magenta coupler (M-2)	0.20
	Dye-image stabilizer (ST-3)	0.15
	Dye-image stabilizer (ST-4)	0.20
	Dye-image stabilizer (ST-5)	0.15
	DNP	0.20
	Anti-irradiation dye (AI-1)	0.01
2nd layer	Gelatin	1.20
(Interlayer)	Anti-staining agent (HQ-2)	0.12
	DIDP	0.15
	Antimold (F-1)	0.002
1st layer	Gelatin	1.20
(Blue-sensitive layer)	Blue-sensitive silver chlorobromide emulsion (Em-B), in terms of silver content	0.26
	Yellow coupler (Y-1)	0.80
	Dye-image stabilizer (ST-1)	0.30
	Dye-image stabilizer (ST-2)	0.20
	Anti-staining agent (HQ-1)	0.02
	Anti-irradiation dye (AI-3)	0.01
	DNP	0.19
Support	Polyethylene-laminated paper	

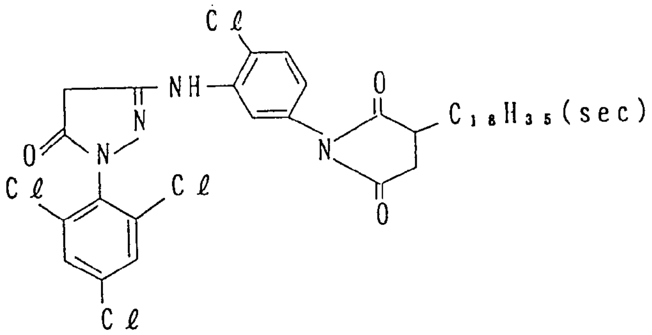
Y − 1



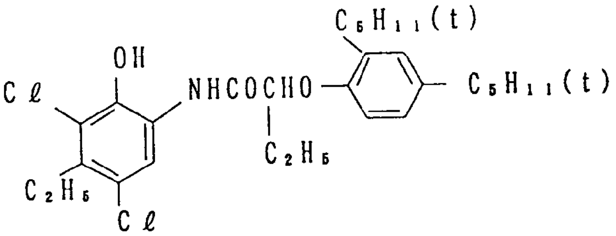
M − 1



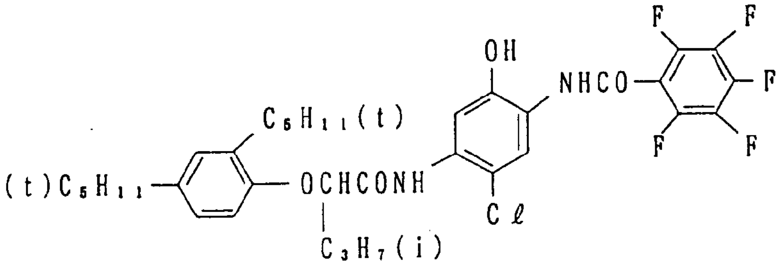
M − 2



C − 1

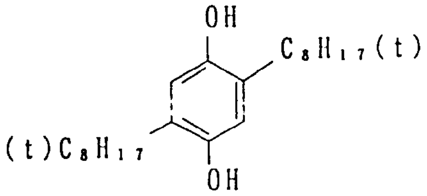


C－2

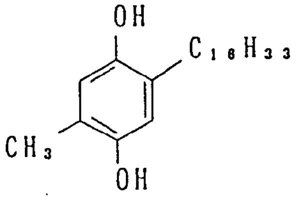


DOP	dioctylphthalate	DNP	dinonylphthalate
DIDP	diisodecylphthalate	PVP	polyvinylpyrrolidone

EQ－1

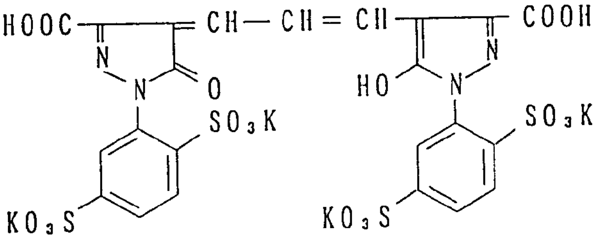


HQ－2

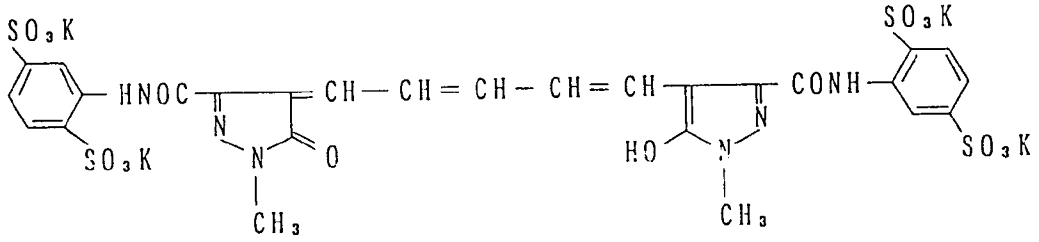


HBS－1

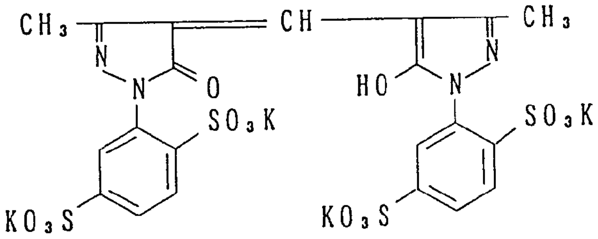
AI－1



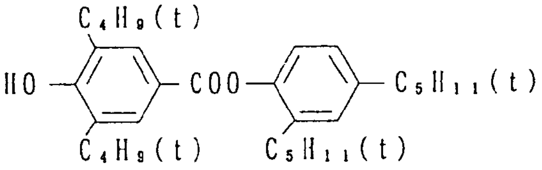
AI－2



AI－3



ST－1



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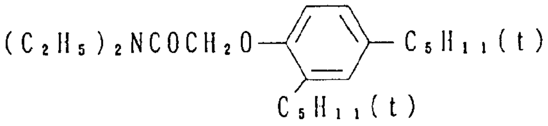

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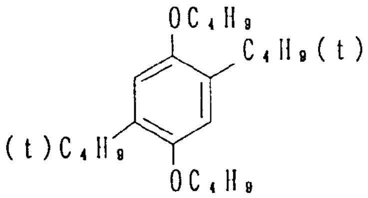
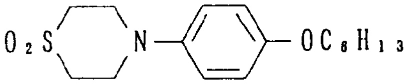
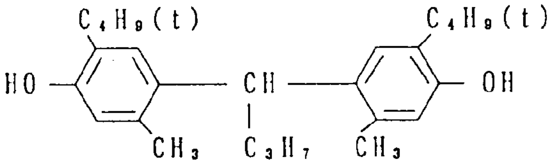


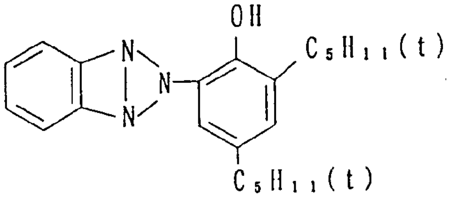
ST－4



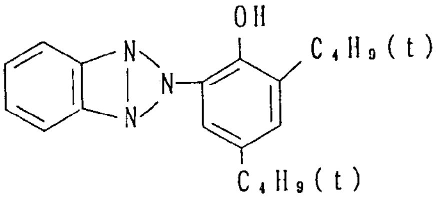
ST－5



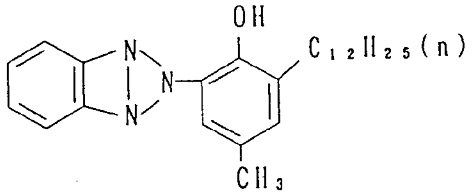
UV－1



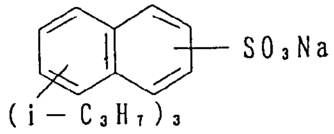
UV－2



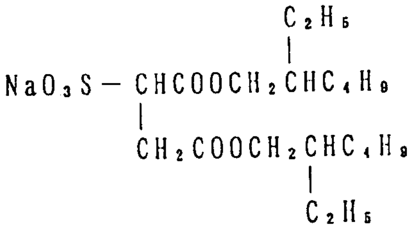
UV－3



SU－1

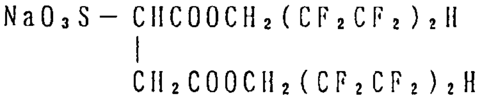


SU－2



$$NaO_3S-\underset{\displaystyle CH_2COOCH_2\underset{\displaystyle C_2H_5}{CH}C_4H_9}{CHCOOCH_2\overset{\displaystyle C_2H_5}{CH}C_4H_9}$$

SU－3

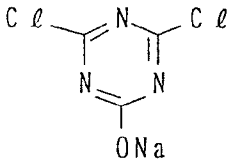


$$NaO_3S-\underset{\displaystyle CH_2COOCH_2(CF_2CF_2)_2H}{CHCOOCH_2(CF_2CF_2)_2H}$$

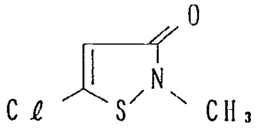
H－1

$C(CH_2SO_2CH=CH_2)_4$

H－2



F－1



[Preparation of Blue-Sensitive Silver Halide Emulsion]

The following solutions (A) and (B) were each added, at the same time and by taking 30 minutes, into 1000 ml of an aqueous 2% gelatin solution kept at 40°C while controlling the pAg and pH to be 6.5 and 3.0, respectively, and then the following solutions (C) and (D) were each added, at the same time and by taking 180 minutes, thereinto while controlling the pAg and pH to be 7.3 and 5.5, respectively.

In the above-mentioned courses of the addition, the pAg controls were made by the method described in JP OPI Publication No. 59-45437/1984 and the pH controls were made by making use of an aqueous sulfuric acid or sodium hydroxide solution

Solution (A)

Sodium chloride	3.42 g
Potassium bromide	0.3 g
Add water to make	200 ml

Solution (B)

Silver nitrate	10 g
Add water to make	200 ml

Solution (C)

Sodium chloride	102.7 g
Potassium bromide	1.0 g
Add water to make	600 ml

Solution (D)

Silver nitrate	300 g
Add water to make	600 ml

After completing the addition, desalting treatment was carried out by making use of an aqueous solution of 5% Demol N (manufactured by Kao-Atlas Corp.) and an aqueous 20% magnesium sulfate solution. After that, the resulting desalted solution was mixed with an aqueous gelatin solution, so that a monodisperse type cubic emulsion EMP-1 having an average grain size of 0.85 μm, a variation coefficient (σ/r) of 0.07 and silver chloride content of 99.5% was prepared.

The resulting emulsion EMP-1 was subjected to a chemical sensitization by making use of the following compounds by taking 90 minutes, so that blue-sensitive silver halide emulsion (Em-B) could be prepared.

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

[Preparation of Green-Sensitive Silver Halide Emulsion]

A monodisperse type cubic emulsion EMP-2 was so prepared as to have an average grain size of 0.43 μm, a variation coefficient (σ/r) of 0.08 and silver chloride content of 99.5% in the same manner as in EMP-1, except that the time for adding solutions (A) and (B) and the time for adding solutions (C) and (D) were changed.

The resulting EMP-2 was subjected to a chemical sensitization by making use of the following compounds at 55°C by taking 120 minutes, so that green-sensitive silver halide emulsion (Em-G) was prepared.

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

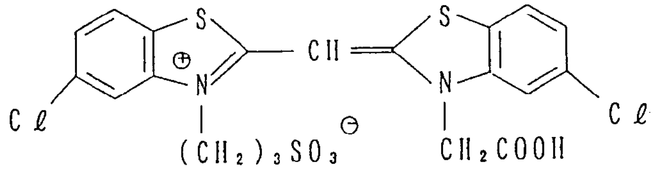
[Preparation of Red-Sensitive Silver Halide Emulsion]

A monodisperse type cubic emulsion EMP-3 was so prepared as to have an average grain size of 0.50 µm, a variation coefficient (σ/r) of 0.08 and a silver chloride content of 99.5% in the same manner as in EMP-1, except that the time for adding solutions (A) and (B) and the time for adding solutions (C) and (D) were changed.

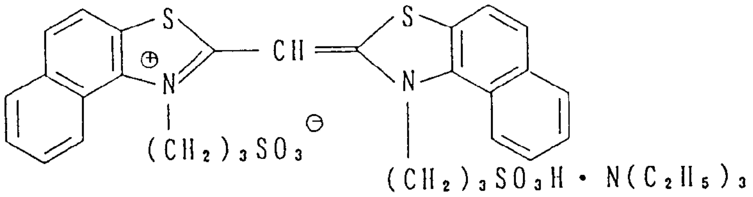
The resulting EMP-3 was subjected to a chemical sensitization by making use of the following compounds at 60°C by taking 90 minutes, so that red-sensitive silver halide emulsion (Em-R) was prepared.

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

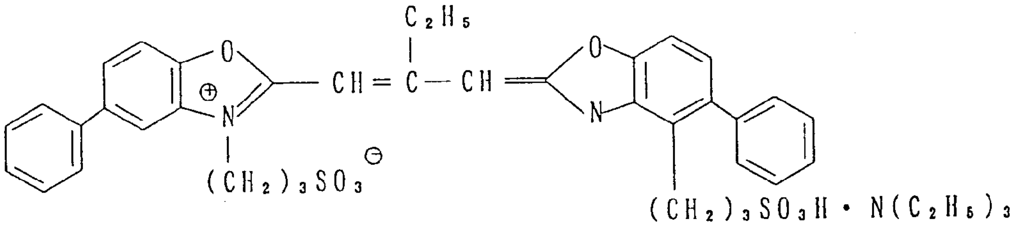
BS－1



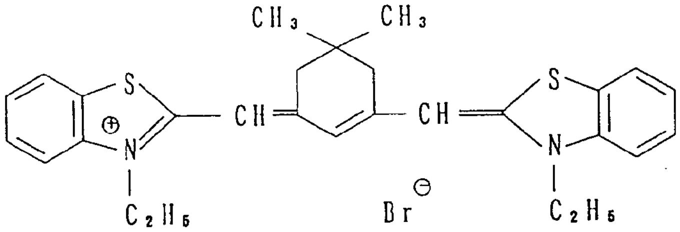
BS－2



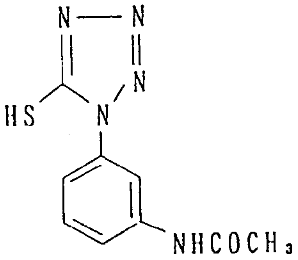
GS－1



RS-1



STAB-1



The resulting color paper samples had the silver chloride contents of 99.5%. Each of the experimental color paper was prepared by changing the above-mentioned silver chloride content as shown in the following Table 4 and they were tested. Each of the above prepared color paper was subject to the conventional wedgewise exposure and was processed according to the Processing step (1) as shown in Table 3 below.

Table 3

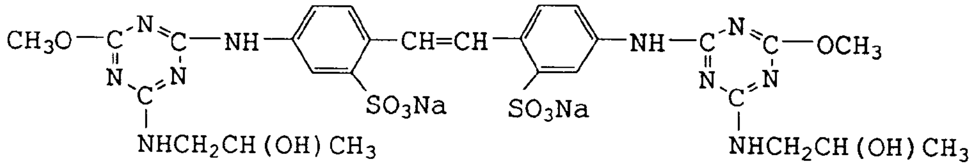
Processing step (1)	Processing temperature	Processing time	Amount replenished (ml/m^2)
(1) Color developing	39°C	25 sec.	81
(2) Bleaching	39°C	25 sec.	51
(3) Fixing	39°C	25 sec.	51
(4) Stabilizing*	30°C	20 sec for 1st tank 20 sec.for 2nd tank	250
(5) Drying	60 to 80°C	20 sec.	—

* The 1st and 2nd stabilizing tanks were each constructed in a counter-current system and the replenishing solution was supplied into the 2nd tank.

(Color developing tank solution)

Diethylene glycol	10 g
Potassium bromide	0.03 g
Potassium chloride	Added to have the Cl^- concentration shown in Table 4
Potassium sulfite, (in an aqueous 50% solution)	0.5 ml
Color developing agent	See Table 4
Compound represented by Formula (1)	See Table 4
Diethyl hydroxylamine	5 g
Triethanolamine	10 g
Potassium carbonate	30 g
Diethylenetriamine pentaacetate	2 g
Fluorescent whitening agent, (Compound E-34 represented below)	2 g
Add water to make	1 liter
Adjust pH with potassium hydroxide or sulfuric acid to be	pH 10.15

E-34



(Color developing replenishing solution)

Diethylene glycol	17 g
Potassium sulfite (in an aqueous 50% solution)	1.0 ml
Color developing agent	See Table 4
Compound represented by Formula (1)	See Table 4
Diethyl hydroxylamine	7 g
Triethanolamine	10 g
Potassium carbonate	40 g
Diethylenetriamine pentaacetate	2 g
Fluorescent whitening agent, (Exemplified compound E-34)	2.5 g
Add water to make	1 liter
Adjust pH with potassium hydroxide or sulfuric acid to be	pH 11.0

(Bleaching tank solution)

Ferric ammonium 1,3-diaminopropane-tetraacetate	0.35 mol
Ethylenediaminetetraacetic acid	2 g
Ammonium bromide	125 g
Glacial acetic acid	50 ml
Aqueous ammonia (in a 25% solution)	38 ml
Add water to make	1 liter
Adjust pH with aqueous ammonia or glacial acetic acid suitably to be	pH 4.5

(Bleaching replenishing solution)

Ferric ammonium 1,3-diaminopropane-tetraacetate	0.42 g
Ethylenediaminetetraacetic acid	2 g
Ammonium bromide	178 g
Glacial acetic acid	50 ml
Aqueous ammonia (in a 25% solution)	23 ml
Add water to make	1 liter
Adjust pH with aqueous ammonia or glacial acetic acid suitably to be	pH 3.2

(Fixing tank solution and Fixing replenishing solution)

Ammonium thiosulfate	250 g
Sodium metabisulfite	20 g
Ethylenediamine tetraacetic acid	0.8 g
Add water to make	1 liter
Adjust pH with acetic acid and an aqueous ammonia to be	pH 6.5

(Stabilizing tank solution and stabilizing replenishing solution)

Orthophenyl phenol	0.15 g
$ZnSO_4 \cdot 7H_2O$	0.2 g
Bismuth chloride	0.5 g

Ammonium sulfite (in an aqueous 40% solution)	5.0 ml
1-hydroxyethylidene-1,1-diphosphonic acid, (in a 60% solution)	3.8 g
Ethylenediaminetetraacetic acid	2.0 g
Fluorescent whitening agent, (Cinopal SFP, manufactured by Ciba Geigy AG)	2.0 g
Adjust pH with aqueous ammonia or an aqueous 50% sulfuric acid solution to be	pH 7.8
Add water to make	1 liter

The running treatment was carried out by filling up the above-given color developing tank solution in an automatic processor and, at the same time, a bleaching tank solution, a fixing tank solution and a stabilizing tank solution were filled up therein and then, the above-mentioned color paper samples were each processed while replenishing the above-mentioned color developing replenishing solution, bleaching replenishing solution, fixing replenishing solution and stabilizing replenishing solution each through the metering pumps.

Immediately after completing the running treatment, the magenta density (i.e., the magenta reflection density) in the unexposed areas and the yellow dye density (i.e., the yellow reflection density) in the exposed areas (i.e., the maximum density areas) in the wedgewise exposed and processed color paper samples were each measured. In succession, a further running treatments were continuously carried out until the total amount of the developing solution replenished could be 3 times as much as the amount of the developing tank solution. When completing the above-mentioned treatment, the wedgewise exposed color paper samples were each processed and then the resulting yellow dye densities thereof (i.e., the reflection densities thereof) in the exposed areas (having the maximum density) were measured, so that the density differences from those obtained in the precedent treatment were obtained and evaluated. Further, the behavior of the precipitation (i.e., the crystal deposition) of the solution produced when completing the running treatment and the tar produced in the developing tank were observed upon allowing the developing tank solution completed the running treatment to stand at room temperature for 10 days.

The results thereof are shown in Table 5 given below.

Table 4

	Experiment No.	AgCl content of light sensitive material, (mol%)	Cl^- concentration of color developer, (mol%)	Color developing agent*3		Compound of the invention having Formula (1), (g/l)
				Color developer, (mol/l)	Color developer replenisher, (mol/l)	
Comparison	1-1	60	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Comparison	2	70	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	3	80	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	4	90	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	5	95	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	6	99	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	7	99.5	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	8	100	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Comparison	9	99.5	3.0×10^{-2}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Comparison	10	99.5	3.5×10^{-2}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	11	99.5	4.0×10^{-2}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	12	99.5	6.0×10^{-2}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	13	99.5	8.0×10^{-2}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	14	99.5	2.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	15	99.5	2.5×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(I-32) 20
Comparison	16	99.5	1.0×10^{-1}	0.5×10^{-2}	0.75×10^{-2}	(I-32) 20
Comparison	17	99.5	1.0×10^{-1}	0.75×10^{-2}	1.25×10^{-2}	(I-32) 20
Invention	18	99.5	1.0×10^{-1}	1.0×10^{-2}	1.50×10^{-2}	(I-32) 20
Invention	19	99.5	1.0×10^{-1}	1.25×10^{-2}	2.0×10^{-2}	(I-32) 20
Invention	20	99.5	1.0×10^{-1}	1.60×10^{-2}	3.0×10^{-2}	(I-32) 20
Invention	21	99.5	1.0×10^{-1}	1.80×10^{-2}	4.0×10^{-2}	(I-32) 20
Invention	22	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	(I-32) 3.0
Invention	23	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	(I-32) 5.0
Invention	24	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	(I-32) 10
Invention	25	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	(I-32) 20
Invention	26	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	(I-32) 30
Invention	27	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	(I-32) 50
Invention	28	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	(I-32) 80
Invention	29	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	(I-32) 85
Invention	30	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	(I-32) 100
Invention	31	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	(I-32) 105
Comparison	32	99.5	1.0×10^{-1}	1.30×10^{-2}	2.70×10^{-2}	- -

Table 5

	Experiment No.	Magenta density in unexposed areas	Yellow density in exposed areas	Yellow density difference in wedgewise exposed areas processed continuously	Precipitation produced after completing the running treatment *1	Tar produced after allowing to stand for 210 days at room temperature *2
Comparison	1-1	0.01	1.96	0.16	○	○
Comparison	2	0.01	2.03	0.15	○	○
Invention	3	0.01	2.20	0.03	**○**	**○**
Invention	4	0.01	2.20	0.02	**○**	**○**
Invention	5	0.01	2.20	0.02	**○**	**○**
Invention	6	0.01	2.20	0.01	**○**	**○**
Invention	7	0.01	2.20	0.01	**○**	**○**
Invention	8	0.01	2.20	0.00	**○**	**○**
Comparison	9	0.05	2.20	0.00	**○**	○
Comparison	10	0.05	2.20	0.00	**○**	○
Invention	11	0.03	2.20	0.01	**○**	**○**
Invention	12	0.03	2.20	0.01	**○**	**○**
Invention	13	0.01	2.20	0.01	**○**	**○**
Invention	14	0.01	2.20	0.01	**○**	**○**
Invention	15	0.01	2.04	0.02	**○**	**○**
Comparison	16	0.01	1.83	0.03	**○**	**○**
Comparison	17	0.01	1.89	0.03	**○**	**○**
Invention	18	0.01	2.18	0.01	**○**	**○**
Invention	19	0.01	2.20	0.01	**○**	**○**
Invention	20	0.01	2.20	0.01	**○**	**○**
Invention	21	0.02	2.20	0.01	**○**	○
Invention	22	0.01	2.20	0.01	○ - △	○
Invention	23	0.01	2.20	0.01	○ - △	○
Invention	24	0.01	2.20	0.01	**○**	**○**
Invention	25	0.01	2.20	0.01	**○**	**○**
Invention	26	0.01	2.20	0.01	**○**	**○**
Invention	27	0.01	2.20	0.01	**○**	**○**
Invention	28	0.01	2.20	0.01	**○**	**○**
Invention	29	0.01	2.20	0.01	○	**○**
Invention	30	0.01	2.20	0.01	○	**○**
Invention	31	0.01	2.20	0.02	○ - △	**○**
Comparison	32	0.01	1.72	0.30	××	××

Evaluation procedures

*1: Precipitation produced after completing the running treatment
◎ : Nothing produced at all.
○ : The least amount produced, but not problematic.
△ : A slight amount produced to be problematic for products
× : Produced apparently to be problematic for products
××: Produced a lot

*2: Tar produced after allowing to stand at 30°C for 10 days
◎ : Nothing produced at all
○ : The least amount produced, but not problematic.
△ : A slight amount produced to be problematic.
× : Produced apparently to be problematic for products.
××: Produced a lot.

*3: Color developing agent
3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamido-ethyl)aniline

From the Table 5, it was proved that, when a silver halide color photographic light sensitive material comprising a silver halide emulsion having an average silver chloride content of not less than 80 mol% is processed with a color developing solution having a Cl^- concentration of not less than $4x10^{-2}$ mols per liter, a color developing agent in an amount of not less than $1.0x10^{-2}$ mols per liter and containing compound I-32 represented by the foregoing Formula (1), a rapid processing treatment can be performed and any stains can also be prevented so that a processing stability can excellently be displayed.

EXAMPLE 2

The light sensitive materials each prepared in Example 1 were subjected to the running process by making use of the color developing solution used in Example 1 and the following processing solutions in accordance with the following processing steps (2).

Processing steps (2)	Temperature	Processing time	Amount replenished
(1) Color developing	39°C	25 sec.	40 ml/m^2
(2) Bleach-fixing	39°C	30 sec.	51 ml/m^2
(3) Stabilizing*	30°C	25 sec for 1st tank 25 sec for 2nd tank	120 ml/m^2
(4) Drying	60-80°C	30 sec.	

* The stabilizing tanks for the 1st and 2nd tanks were constructed in the counter-current system and the replenishing solution was replenished into the tank for the 2nd tank.

[Bleach-fixing tank solution and the replenishing solution thereof]

Ferric ammonium ethylenediaminetetraacetate	53.0 g
Ethylenediamine tetraacetic acid	3.0 g
Ammonium thiosulfate, (in a 70% solution)	123.0 g
Ammonium sulfite, (in a 40% solution)	51.0 g
Adjust pH with aqueous ammonia or glacial acetic acid to be	pH 5.4
Add water to make in total	1 liter

[Stabilizing tank solution and the replenishing solution thereof]

Orthophenyl phenol	0.1 g
Ubitex (manufactured by Ciba Geigy AG)	1.0 g
$ZnSO_4 \cdot 7H_2O$	0.1 g
Ammonium sulfite, (in a 40% solution)	5.0 ml
1-hydroxyethylidene-1,1-diphosphonic acid, (in a 60% solution)	3.0 g
Ethylenediamine tetraacetic acid	1.5 g
Adjust pH with aqueous ammonia or sulfuric acid to be	pH 7.8
Add water to make	1 liter

The running process was carried out by filling up the above-given processing solutions into an automatic processor and, at the same time, while processing the foregoing color paper samples and replenishing every 3 minutes the above-mentioned color developing replenishing solution, bleach-fixing replenishing solution and stabilizing replenishing solution each through a quantitative pump.

The running process was carried out by replenishing the color developing replenishing solution into the color developing tank solution until the total amount of the color developing replenishing solution was 3 times as much as the capacity of the color developing tank solution.

The evaluation was made in quite the same manner as in Example 1. The results thereof were proved to be quite the same behavior as in Example 1 and the invention was able to display the effects thereof even when a series of a bleach-fixing step through a stabilizing step were carried out after completing a color developing step.

EXAMPLE 3

By making use of Sample 1, which was so prepared in Example 1 as to have an average silver chloride content of 99.5 mol%, as the base, and the silver coating weights were changed as shown in the following Table 6, so that color paper samples 2-1 through 2-4 each for experimental use was prepared. The resulting samples were each processed in the same processing steps (1) as in Example 1. As for the processing solutions, those used in Experiments No. 1 through No. 7 of Example 1 were used.

Table 6

Light sensitive material sample	Silver coating weight
1	0.64 g/m^2
2-1	0.90 g/m^2
2-2	0.80 g/m^2
2-3	0.75 g/m^2
2-4	0.50 g/m^2

The experiments and the evaluation thereof were each carried out in quite the same manner as in Example 1, and the results thereof are collectively shown in the following Table 7.

Table 7

Experiment No.	Light sensitive material sample No. (Silver coating weight)	Cl^- concentration of color developer (mol/l)	Developing agent		Compound of the invention having Formula (1)	Magenta density in unexposed areas	Yellow density in exposed areas	Yellow density difference in wedgewise exposed areas processed continuously	Precipitation produced after running processed	Tar production after aging for 10 days at room temperature
			Color developer (mol/l)	Developing replenisher (mol/l)						
3-1	1 (0.64g/m^2)	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	0.01	2.20	0.01	◎	◎
3-2	2-1 (0.90g/m^2)	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	0.02	2.20	0.03	◎	◎
3-3	2-2 (0.76g/m^2)	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	0.01	2.20	0.03	◎	◎
3-4	2-3 (0.75g/m^2)	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	0.01	2.20	0.01	◎	◎
3-5	2-4 (0.50g/m^2)	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	0.00	2.20	0.01	◎	◎

It was proved from the above-given Table 7 that, when the silver coating weight of every light sensitive material sample was not more than 0.75 g/m^2, the effects of the invention could was displayed excellently.

EXAMPLE 4

By making use of the color paper samples prepared in Example 1, the wedgewise exposures were made according to the ordinary method and the running process were then carried out according to the same processing steps (1) as in Example 1. After that, the experiments and evaluation were made in the same way as in Example 1. The results thereof are shown in the following Table 8. The processing solutions applied to the experiments were as follows.

[Color developing tank solution]

Diethylene glycol	15 g
Potassium bromide	0.03 g
Potassium chloride	Added to have [Cl^-] shown in Table 8
Potassium sulfite (in a 50% solution)	0.5 ml
Color developing agent	See Table 8
Triethanolamine	10 g
Potassium carbonate	30 g
Diethyleneamine pentaacetic acid	2 g
Fluorescent whitening agent, (Exemplified compound E-34)	2 g
Compound having Formula (2) or (B)	See Table 8
Compound having Formula (1)	See Table 8
Add water to make in total of	1 liter
Adjust pH with potassium hydroxide or sulfuric acid to be	pH 10.15

[Color developing replenishing solution]

Diethylene glycol	17 g
Potassium sulfite (in a 50% solution)	1.0 ml
Color developing agent	See Table 8
Compound having Formula (1)	See Table 8
Preservative	See Table 8
Triethanolamine	10 g
Potassium carbonate	40 g
Diethylenetriamine pentaacetic acid	2 g
Fluorescent whitening agent, (Compound E-34)	2.5 g
Add water to make in total of	1 liter
Adjust pH with potassium hydroxide or sulfuric acid to be	pH 12.0

[Bleaching tank solution and the replenishing solution thereof], [fixing tank solution and the replenishing solution thereof] and [stabilizing tank solution and the replenishing solution thereof] used therein were each the same as in Example 1.

Table 8

Experiment No.	Cl^- concentration of color developer (mol/l)	Color developing agent		Compound of the invention having Formula (1)	*4 Formula (2)	Magenta density in unexposed areas	Yellow density in exposed areas	Yellow density difference in wedgewise exposed areas processed continuously	Precipitation produced after completing a running process
		Color developer (mol/l)	Developing replenisher (mol/l)						
4-1	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	DEHA 5g	0.0	2.20	0.01	◎
4-2	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	NHM ☆	0.02	2.20	0.02	◎
4-3	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	DMHA ☆	0.01	2.25	0.01	◎
4-4	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	HDA ☆	0.01	2.25	0.01	◎
4-5	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	Unadded -	0.05	2.10	0.06	○
4-6	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	DEHA 1g	0.03	2.23	0.01	○
4-7	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	DEHA 2g	0.01	2.20	0.01	◎ - ○
4-8	1.0×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	DEHA 10g	0.01	2.20	0.01	◎

☆ The same mol numbers were added as in DEHA.

It was proved that the compounds having Formulas (2) and (B) can display the effects of the invention excellently and, particularly, they can preferably display the effects of the invention when they were used in an amount of not less than 2 g.

*4: DEHA = Diethylhydroxylamine
DMHA = Dimethoxyethyl hydroxyamine
HDA = Hydrazinodiacetic acid
NHM = N-hydroxymorpholine

It was proved that the effects of the invention could further excellently be displayed when adding the compounds represented by Formula (2) or (B) and, particularly, it was preferred to add then in an amount not less than 2 g.

EXAMPLE 5

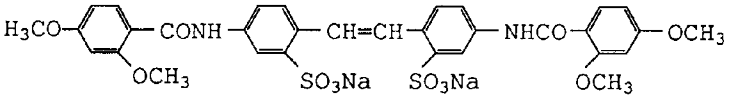
By making use of the color paper samples prepared in Example 1, the wedgewise exposures were made in the ordinary method and then the running processes were carried out in accordance with the processing steps (1) for Example 1. After that, the experiments and evaluation were made in the same manners as in Example 1. The results thereof are shown in the following Table 9. The processing solutions applied to the experiments were the same processing solutions used in Experiment No. 1-13 of Example 1, except that the fluorescent whitening agent (i.e., Compound E-34) was changed to those shown in Table 9.

Table 9

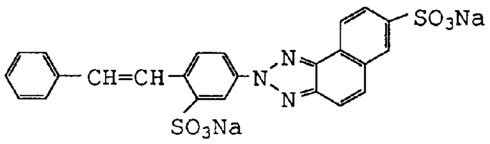
Experiment No.	Cl^- concentration of color developer (mol/1)	Color developing agent		Compound of the invention having Formula (1)	Fluorescent whitening agent (g) *5		Magenta density in unexposed areas	Yellow density in exposed areas	Yellow density difference in wedgewise exposed areas processed continuously	Precipitation produced after completing a running process	Tar produced after aging for 10 days at room temperature
		Color developer (mol/1)	Developing replenisher (mol/1)								
5-1	0.8×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	E-34	2g	0.01	2.20	0.01	◎	◎
5-2	0.8×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	E-4	☆	0.01	2.20	0.01	○	◎
5-3	0.8×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	E-34	☆	0.01	2.20	0.01	◎	○
5-4	0.8×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	E-35	☆	0.01	2.20	0.01	◎	○
5-5	0.8×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	E-36	☆	0.01	2.20	0.01	○	◎
5-6	0.8×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	E-37	☆	0.01	2.20	0.01	○	○
5-7	0.8×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	E-41	☆	0.01	2.20	0.01	◎	◎
5-8	0.8×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	F-2	☆	0.02	2.20	0.01	○ - △	○ - △
5-9	0.8×10^{-1}	1.3×10^{-2}	2.70×10^{-2}	(1-32) 20g/ℓ	F-3	☆	0.02	2.20	0.01	○ - △	○ - △

☆ The same mol numbers as 2g of E-34 were added.

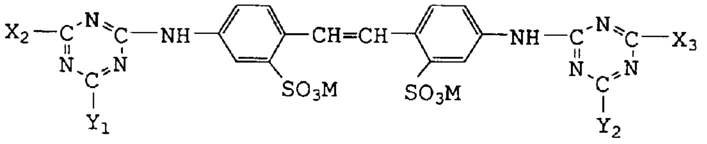
*5 (F-2)

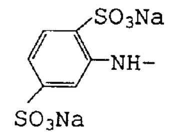
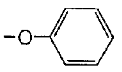
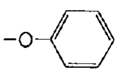
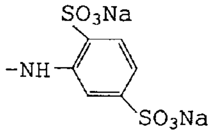
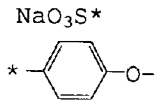
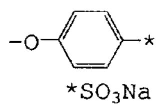
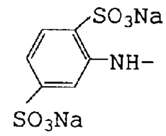
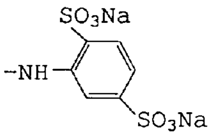


(F-3)



Formula E



Compound No.	M	X_2	Y_1	Y_2	X_3
E-4	Na	$(HOC_2H_4)_2N-$	$-OCH_3$	$-OCH_3$	$-NHC_2H_4SO_3Na$
E-35	Na				
E-36	Na		$-N(C_2H_4OH)_2$	$-N(C_2H_4OH)_2$	
E-37	Na		$-N(C_2H_5)_2$	$-N(C_2H_5)_2$	
E-41	Na	CH_3O-	$-NHC_2H_4SO_3Na$	$-NHC_2H_4SO_3Na$	$-OCH_3$

It was proved from the results shown in Table 9 that the effects of the invention could further excellently be displayed when making combination use of the compounds (i.e., fluorescent whitening agents) having the foregoing Formula [E] in a color developing solution applicable to the process of the invention

EXAMPLE 6

When each of the same evaluation was made as in Example 5, except that the compound I-32 of the invention applied to Example 5 was replaced by I-2, I-21, I-20 or I-37, it was proved that almost the same results of the behavior as in I-32 could be obtained, but the precipitation and the tar each produced after completing the running process were somewhat deteriorated

Claims

1. A method of processing a silver halide color photographic light-sensitive material comprising a support and provided thereon, a silver halide emulsion layer containing silver halide grains having an average silver chloride content of not less than 80 mol%, comprising the step of;
imagewise exposing the material, and
developing the exposed material with a color developing solution,
wherein said color developing solution contains 4×10^{-2} to 3.0×10^{-1} mol per liter of chloride, 1.0×10^{-2}

to 2.0×10^{-2} mol per liter of a color developing agent, and 5.0 to 100 g per liter of a compound represented by the following Formula 1
Formula 1

$$R\text{-}SO_3X$$

wherein R represents an alkyl group having 1 to 8 of carbon atoms or a phenyl group, provided that R may be a polymer having a repetition unit in which an ethylenically unsaturated bond is open, and X represents a hydrogen atom, a sodium atom, potassium atom, a lithium atom or an ammonium group.

2. The material of claim 1, wherein said silver halide grains have an average silver halide chloride content of 95 mol%.

3. The material of claim 1, wherein said silver halide grains have an average silver halide chloride content of 99 mol%.

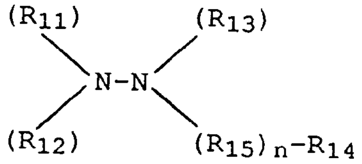
4. The material of claim 1, wherein said silver halide emulsion layer contains not more than 0.75g/m^2 of silver.

5. The material of claim 1, wherein said R represents a phenyl group or a phenyl group having an alkyl group of 1 to 4 carbon numbers, a hydroxyl group, a carboxyl group or a salt thereof, or a sulfonic acid group or a salt thereof as a substituent.

6. The material of claim 1, wherein said color developing solution further contains 0.4 to 100 g per liter of a compound represented by the following Formula 2 or B,
Formula 2

$$(R_1)(R_2)NOH$$

wherein R_1 and R_2 each represent a hydrogen atom, an alkyl group, an aryl group, or R′-CO- wherein R′ represents an alkoxy group, an alkyl group or aryl group, provided that R_1 and R_2 are not a hydrogen atom simultaneously and R_1 and R_2 may combine together with each other to form a ring,
Formula B



wherein R_{11}, R_{12}, and R_{13} each represent a hydrogen atom, an alkyl group, an aryl group or a heterocyclic ring, R_{14} represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic ring, an alkoxy group, an aryloxy group, a carbamoyl group or an amino group, provided that R_{13} and R_{14} may combine together with each other to form a ring, R_{15} represents -CO-, -SO$_2$- or -C(=NH)-, and n is an integer of 0 or 1.

7. The method of claim 6, wherein R_{11}, R_{12}, and R_{13} in said Formula B each represent a hydrogen atom, or an alkyl group having 1 to 10 carbon atoms.

8. The method of claim 6, wherein R_{11} and R_{12} in said Formula B each represent a hydrogen atom.

9. The method of claim 1, wherein said developing step is carried out in 3 to 45 seconds at a temperature of 38.0 to 43.0 °C using the color developing solution having pH of 9.5 to 13.0.

10. The method of claim 9, wherein said developing step is carried out in 5 to 35 seconds at a temperature of 38.5 to 41.0 °C using the color developing solution having pH of 9.8 to 12.0.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 1406

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-0 366 954 (FUJI PHOTO FILM CO) * claims *	1-10	G 03 C 7/407
Y	DE-A-2 901 468 (KONISHIROKU PHOTO INDUSTRY CO LTD) * claims; page 19, compound B-1 *	1-10	
A	EP-A-0 330 035 (AGFA-GEVAERT) * whole document *	1,2,6-10	
A,D	US-A-2 618 558 (P. VITTUM et al.) * whole document *	1,5	
A	RESEARCH DISCLOSURE no. 287, March 1988, page 128, Emsworth, Hampshire, GB; ANON.: "The Use of Hydrolysed Polymers of Maleic Anhydride in Photographic Colour Developers for Rapid Development and Colour Developers of Reduced Benzyl Alcohol Content" * whole paper *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	EP-A-0 312 984 (FUJI PHOTO FILM CO) * claims; page 3, lines 27-30 *	2-8	G 03 C
A	US-A-4 859 567 (E. OKUTSU et al.) * whole document *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	20-05-1992	STOCK H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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