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54 **Method for processing light-sensitive silver halide color photographic material.**

57 There is disclosed a method for processing a light-sensitive silver halide color photographic material comprising subjecting to imagewise exposure a light-sensitive silver halide color photographic material having a total dried film thickness of the light-sensitive silver halide emulsion layer and the non-light-sensitive layer on one surface of a support of 10 μm or more, then processing the exposed material with a color forming developer containing substantially no benzyl alcohol, thereafter processing the material with a processing solution having fixing ability and subsequently processing the material with a stabilizing solution substituting for water washing having a surface tension of 8 to 50 dyne/cm and containing substantially no aldehyde compound, followed by drying.

Description

Method for processing light-sensitive silver halide color photographic material

BACKGROUND OF THE INVENTION

This invention relates to a method for processing of a light-sensitive silver halide color photographic material (hereinafter called light-sensitive material) in which water washing processing step is omitted, more particularly to a processing method without water washing of a light-sensitive material in which stain generation at an unexposed portion by continuous processing is prevented.

Generally speaking, light-sensitive materials, after imagewise exposure, are processed according to the processing steps such as color developing, bleaching, fixing, stabilizing, bleach-fixing, water washing, etc. And, in such processing steps, the increased cost for water washing due to exhaustion of water resources, and rise in price of crude oils are becoming a serious problem increasingly in recent years.

For this reason, as the method for omitting the water washing processing step or reducing extremely the amount of washing water, there have been proposed the multi-stage countercurrent stabilizing processing technique as disclosed in Japanese Provisional Patent Publication No. 8543/1982 and the processing technique with a stabilizing solution substituting for water washing containing a bismuth complex as disclosed in Japanese Provisional Patent Publication No. 134636/1983.

However, in the processing with a stabilizing solution substituting for water washing, when continuous processing is continued for such a long term that the total amount of the supplementing solution relative to the stabilizing tank solution becomes 6 to 7-fold or more of the stabilizing tank volume, it has been found by the present inventors that color contamination is generated in the processed light-sensitive material to become conspicuous as stain. Above all, color contamination, namely stain is conspicuous at an unexposed portion and, particularly in color paper, there is the problem that even a slight contamination may become a vital defect because the unexposed portion is white ground.

Also, it has been found that generation of such a stain worsens storage durability particularly under irradiation of light when the dye image is stored.

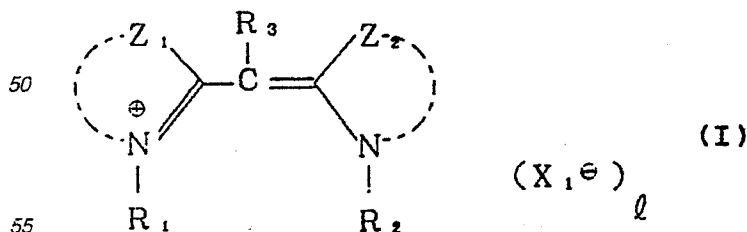
SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a method for processing in which contamination at the unexposed portion of a light-sensitive material generated in the case of continuous processing by use of a stabilizing solution substituting for water washing is prevented.

Another object of the present invention is to provide a method for processing in which deterioration of storage stability, particularly deterioration of light fading characteristic of the dye image when continuously processed by use of a stabilizing solution substituting for water washing is prevented.

The present inventors have studied intensively and consequently found that the object of the present invention can be accomplished by a method for processing a light-sensitive silver halide color photographic material, which comprises subjecting a light-sensitive silver halide color photographic material having a total dried film thickness of the light-sensitive silver halide emulsion layer and the non-light-sensitive layer on one surface of a support of 10 μm or more to imagewise exposure, then processing the exposed material with a color forming developing solution containing substantially no benzyl alcohol, thereafter processing the material with a processing solution having fixing ability and subsequently processing the material with a stabilizing solution substituting for water washing having a surface tension of 8 to 50 dyne/cm and containing substantially no aldehyde compound, followed by drying.

The present inventors have also found that the effect of the present invention is more marked when the light-sensitive material contains a sensitizing dye represented by the formula (I) shown below as a preferable embodiment of the present invention.



wherein each of Z₁ and Z₂ represents a group of atoms necessary for formation of benzoxazole nucleus, naphthoxazole nucleus, benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus, naphtoselenazole nucleus, benzoimidazole nucleus, naphthoimidazole nucleus, pyridine nucleus or quinoline nucleus, each of R₁ and R₂ represents an alkyl group, an alkenyl group or an aryl group, R₃ represents a hydrogen atom, a methyl group or an ethyl group and X₁[⊖] represents an anion and *l* represents 0 or 1.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the water washing processing step after developing, bleaching and fixing processing of the prior art, all of the emulsion compositions and processing solution compositions (including color developing agent, benzyl alcohol, bleaching agent, thiosulfate, etc.) or their reaction materials, oxidized materials, etc., are washed away from within the light-sensitive material and the surface of the light-sensitive material with a large amount of washing water. Accordingly, in the processing with a stabilizing solution substituting for water washing which has eliminated water washing processing, all of these components are dissolved out in the stabilizing solution to be accumulated therein. Particularly, when the amount of the stabilizing solution substituting for water washing supplemented is small, the accumulated concentration of the above materials to be washed will be increased. Further, the stabilizing solution substituting for water washing will be stored over a long term due to lowering in the rate of renewal thereof, and the stabilizing solution substituting for water washing is considerably colored due to the coloring components of the above substances in the stabilizing solution substituting for water washing. Accordingly, it may be estimated that these coloring components are adsorbed onto the light-sensitive material in the stabilizing solution substituting for water washing, or washing-out from the light-sensitive material is inhibited, whereby the unexposed portion of the light-sensitive material becomes stained.

Benzyl alcohol has been used for a long time in a color developing solution generally as a developing accelerator. Also, it is well known in the art that formalin which is an aldehyde compound has been used in the final stabilizing solution for the purpose of image stability in the final step of conventional color processing steps.

However, it is surprising that the above problem inherent in the stabilizing solution substituting for water washing can be solved by carrying out a combination of processings in which a light-sensitive material with a dried film thickness of 10 μm or more is subjected to color developing with a color developing solution containing substantially no benzyl alcohol, then processing the material with a processing solution having a fixing ability and further processing the material with a stabilizing solution substituting for water washing having a surface tension of 8 to 50 dyne/cm and containing substantially no aldehyde compound. Further, it has been found that the present invention is very effective for light-sensitive material containing a sensitizing dye represented by the above formula (I).

In the present invention, processing with a processing solution having fixing ability after color developing refers to the step by use of a fixing bath or a bleach-fixing bath for the purpose of fixing of the light-sensitive material after processing with a conventional color developing solution. That is, the present invention has solved the problem with the stabilizing solution substituting for water washing after a processing in a bleaching bath - fixing bath or a bleach-fixing bath after color developing. The present invention is particularly effective for the latter, namely processing in a bleach-fixing bath.

In the present invention, the color developing solution containing substantially no benzyl alcohol refers to a color developing solution containing benzyl alcohol in such an amount that the color developing solution has substantially no developing accelerating effect. More specifically, the color developing solution containing benzyl alcohol in an amount of 1 ml or less per liter of the color developing solution, and more preferably it contains no benzyl alcohol.

In the present invention, when processing is conducted with a processing solution having fixing ability and subsequently processing is conducted with a stabilizing solution substituting for water washing without substantial water washing, it indicates processing directly with a stabilizing solution substituting for water washing next to a fixing bath or a bleach-fixing bath, and this processing step is entirely different from the step known in the art in which water washing processing and processing with a stabilizing solution are performed after a fixing bath or a bleach-fixing bath.

Thus, in the present invention, processing with a stabilizing solution substituting for water washing refers to a processing for stabilizing processing in which stabilizing processing is performed without substantial water washing processing, or without using flowing water immediately after processing with a processing solution having fixing ability. That is, while a large amount of water is required for conventional water washing using flowing water which is led into a processing machine from outward thereof, in the present invention, since the stabilizing solution substituting for water washing may be a stabilizing solution or water pooled in a processing machine, its amount is extremely small. Further, the processing solution used for said stabilizing processing is called the stabilizing solution substituting for water washing, and the processing tank is called a stabilizing bath or a stabilizing tank.

In the present invention, the effect of the present invention is great when the stabilizing tank consists of 1 to 5 tanks, particularly preferably 1 to 3 tanks. That is, with the same amount of supplementing solution, the effect of the present invention becomes weaker as the number of the tanks is increased, because concentrations of contaminating components in the final stabilizing tank becomes lower.

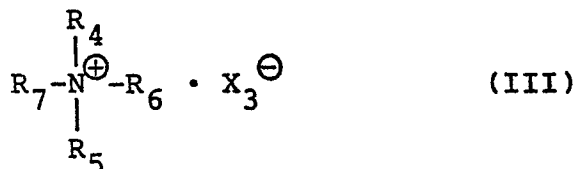
The surface tension of the stabilizing solution substituting for water washing to be used in the processing of the present invention is measured according to the general measuring method as described in "Analysis and Test Method of Surfactants" (written by Fumio Kitahara, Shigeo Hayano and Ichiro Hara, published by Kodansha K.K., March 1, 1982), etc., and, in the present invention, the surface tension is the value measured according to the conventional general measuring method at 20 °C.

The stabilizing solution of the present invention may be used any compound which can give a surface tension of 8 to 50 dyne/cm (20 °C), but it is particularly preferable to use at least one compound selected from

the compounds of the following formula (II), formula (III) and water-soluble organic siloxane type compounds with respect to the effect for the object of the present invention.

A-O-(B)_m-X₂ (II)

In the above formula, A is a monovalent organic group, for example, an alkyl group having 6 to 20, preferably 6 to 12 carbon atoms such as hexyl, heptyl, octyl, nonyl, decyl, undecyl or dodecyl. Alternatively, it may be an aryl group substituted with an alkyl group having 3 to 20 carbon atoms, and the substituent may be preferably an alkyl group having 3 to 12 carbon atoms such as propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl or dodecyl. The aryl group may be phenyl, tolyl, xylyl, biphenyl or naphthyl, preferably phenyl or tolyl. The position at which the alkyl group is bonded to the aryl group may be either ortho-, meta- or para-position. B represents ethylene oxide or propylene oxide, and *m* represents an integer of 4 to 50. X₂ represents a hydrogen atom, SO₃Y or PO₃Y₂, and Y represents a hydrogen atom, an alkali metal (Na, K or Li, etc.) or ammonium ion.

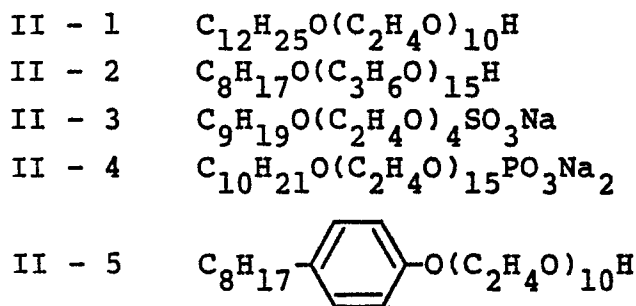


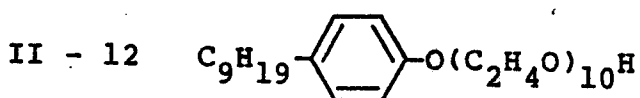
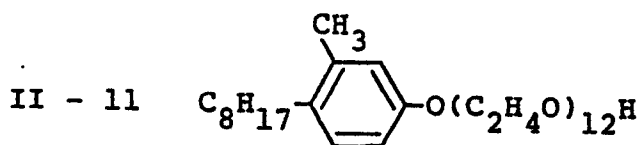
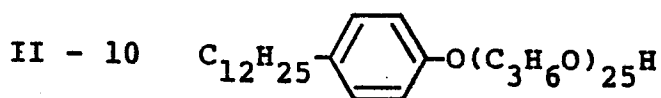
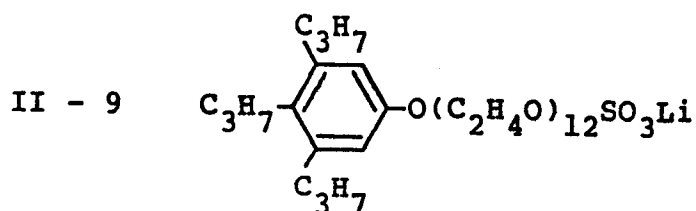
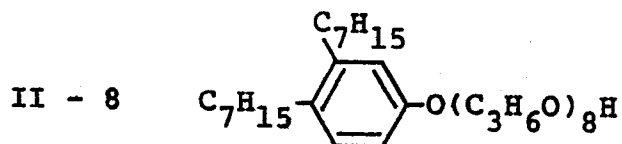
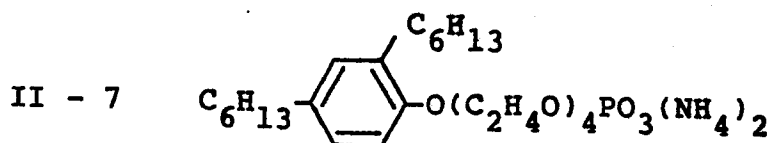
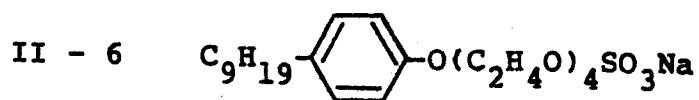
In the above formula, each of R₄, R₅, R₆ and R₇ represents a hydrogen atom, an alkyl group or a phenyl group, and the total carbon atoms of R₄, R₅, R₆ and R₇ is 3 to 50. X₃ represents an anion such as a halogen atom, a hydroxyl group, a sulfate group, a carbonate group, a nitrate group, an acetate group, a p-toluenesulfonate group, etc.

The water-soluble organic siloxane type compound of the present invention means water-soluble organic siloxane type compounds in general as described in, for example, Japanese Provisional Patent Publication No. 18333/1972, Japanese Patent Publication No. 51172/1980, Japanese Patent Publication No. 37538/1976, Japanese Provisional Patent Publication No. 62128/1974 and U.S. Patent No. 3,545,970, etc.

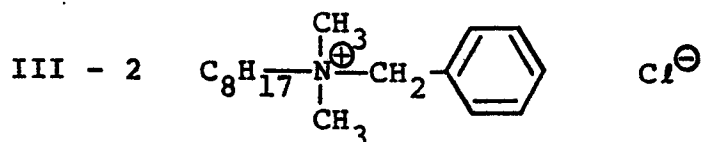
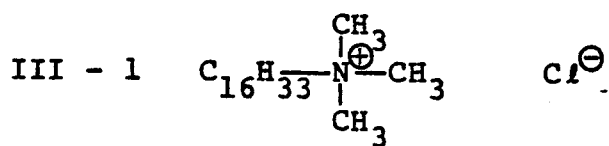
In the following, typical examples of the compounds represented by the formulae (II), (III) and water-soluble organic siloxane type compounds are set forth, but the compounds according to the present invention are not limited thereto.

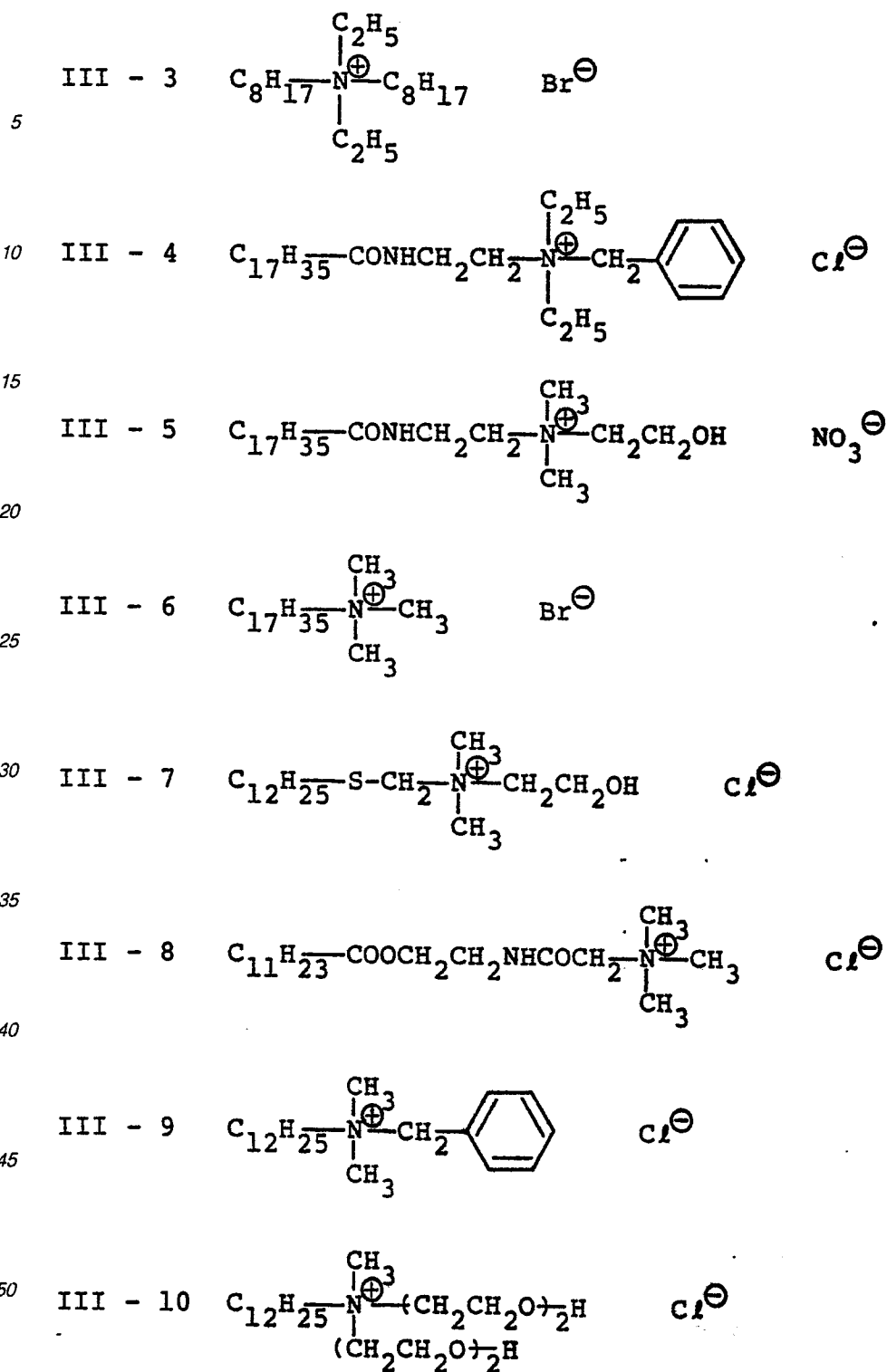
Examples of compounds represented by the formula (II)



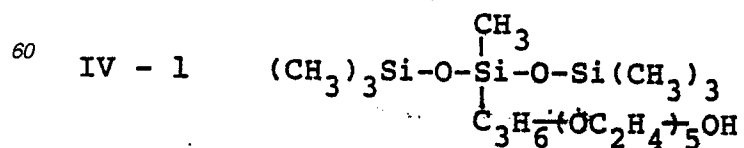


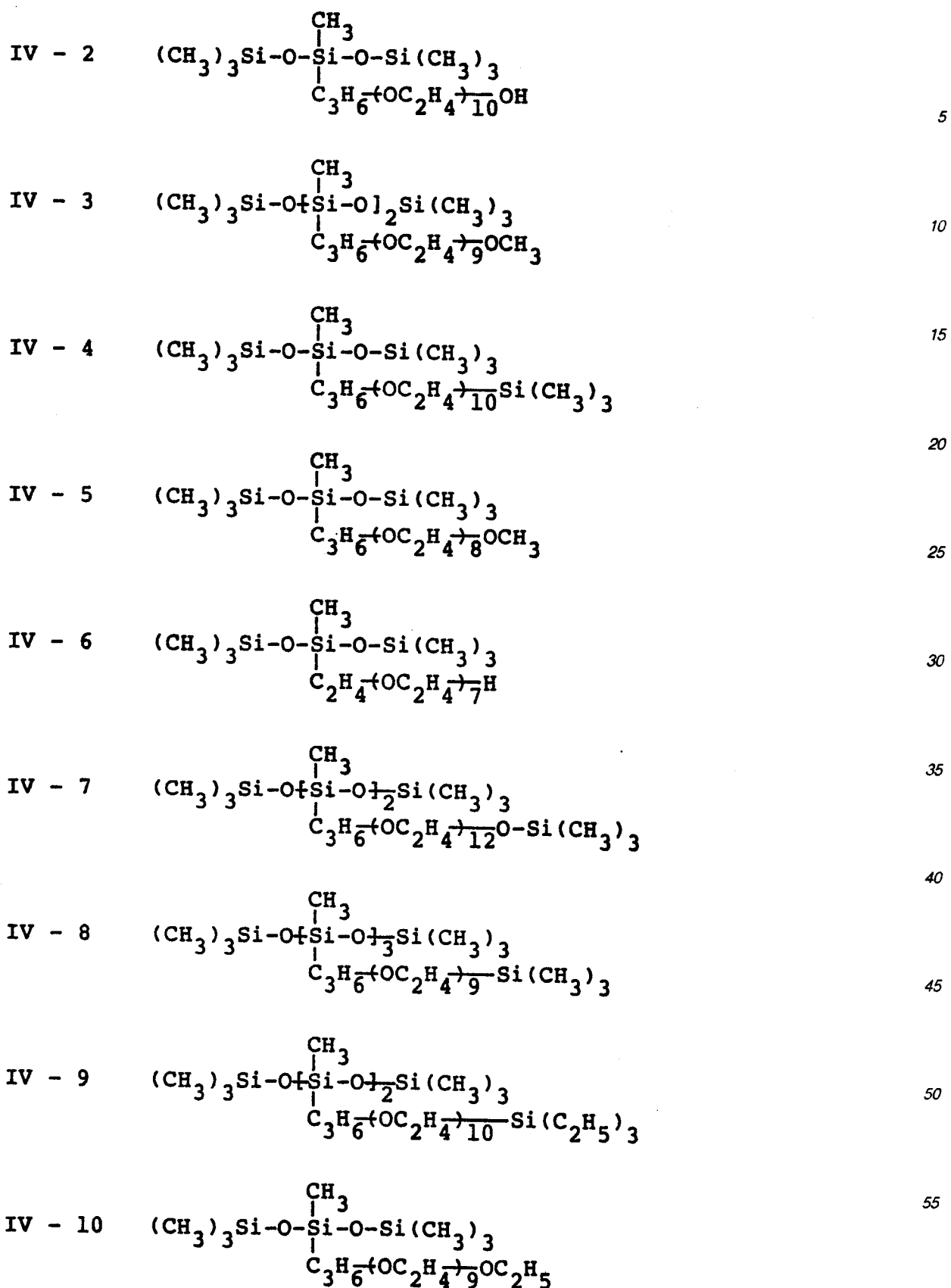
Examples of compounds represented by the formula (III)





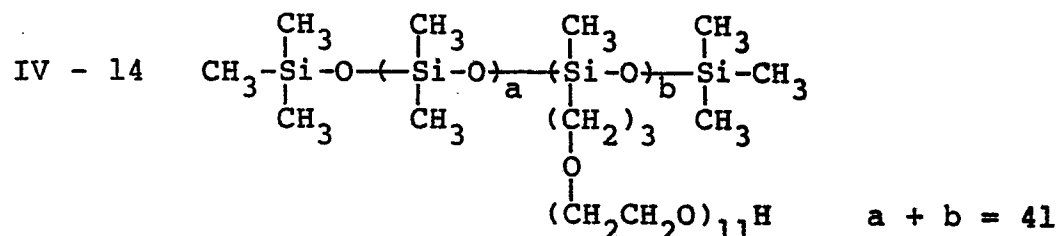
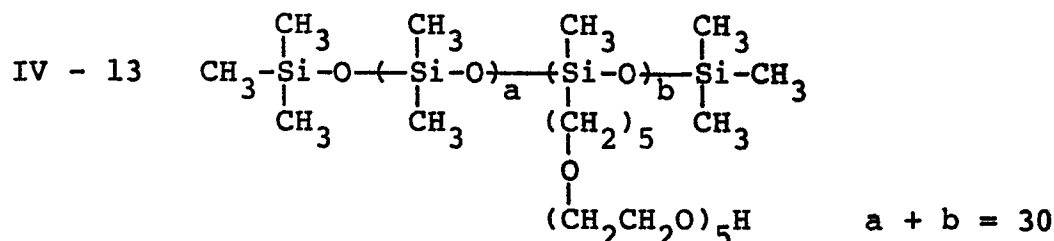
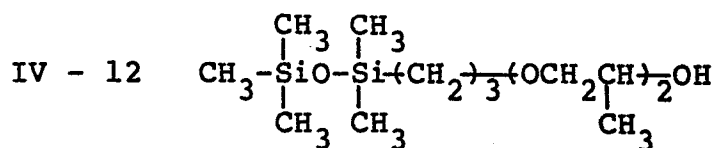
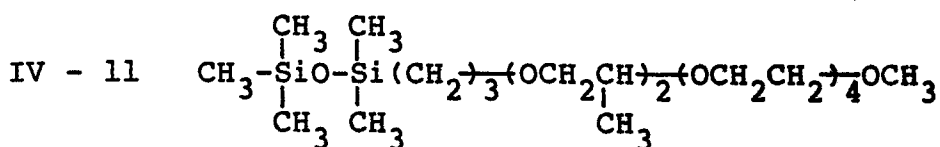
55 Water-soluble organic siloxane type compounds



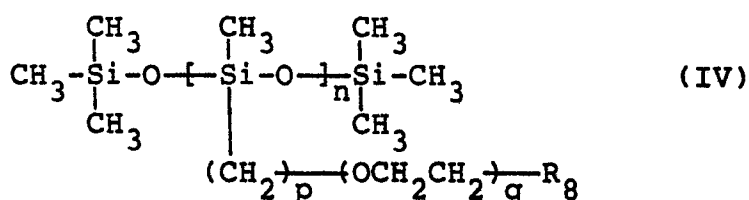


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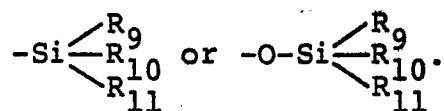
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Of the above water-soluble organic siloxane type compounds, the compounds represented by the formula (IV) shown below can be more preferably be used, since they can exhibit well the effect of the object of the present invention.



In the above formula, R_8 represents a hydrogen atom, a hydroxy group, a lower alkyl group, an alkoxy group,



Each of R_9 , R_{10} and R_{11} represents a lower alkyl group (preferably an alkyl group having 1 to 3 carbon atoms such as methyl, ethyl, propyl, etc.), and the above R_9 , R_{10} and R_{11} may be either the same or different. n represents an integer of 1 to 4, and each of p and q represents an integer of 1 to 15.

In the present invention, of the compounds capable of giving a surface tension of 8 to 50 dyne/cm to the second stabilizing solution, those capable of giving a surface tension of 15 to 40 dyne/cm are particularly preferred in aspect of the effect for the present invention.

These compounds represented by the above formulae (II), (III) and water-soluble organic siloxane type compounds may be used either individually or as a combination. Further, their amounts added may be within the range of from 0.01 to 20 g per 1 l of the stabilizing solution to exhibit good effect.

In the present invention, the stabilizing solution substituting for water washing containing substantially no

aldehyde compound refers to a stabilizing solution substituting for water washing with a concentration of 0.1 g/l or less of the aldehyde which has been added at a concentration of 1.5 to 2.0 g/l for the purpose of improvement of storability of the dye image into the final stabilizing solution in the processing step accompanying water washing of the prior art. A concentration of about 0.02 g/l comes within the region containing substantially no aldehyde, but it is particularly preferred to contain no aldehyde at all.

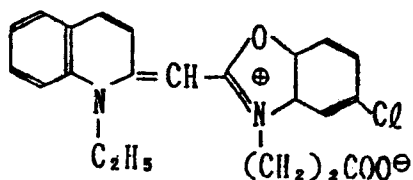
As the aldehyde to be used in the stabilizing bath in the processing step of the prior art, formaldehyde has been exclusively used, and other examples of aldehyde may include glutaraldehyde, chloral, mucochloric acid, formaldehyde sodium bisulfite, glutaraldehyde sodium bisulfite, etc., and they will not only deteriorate storability of the dye image but also gives troubles such as precipitation formation or others in the stabilizing solution substituting for water washing of the present invention.

In the sensitizing dye represented by the above formula (I) to be used in the present invention, the nucleus represented by Z₁ and Z₂ may be substituted, and examples of the substituent may include halogen atoms, (e.g. chlorine), alkyl groups (e.g. methyl, ethyl), alkoxy groups (e.g. methoxy, ethoxy), alkoxycarbonyl groups (e.g. methoxycarbonyl, ethoxycarbonyl), aryl groups (e.g. phenyl), cyano group, etc.

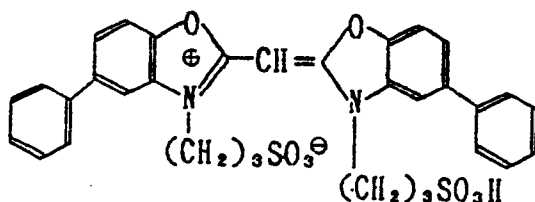
The alkyl group and the alkenyl group represented by R₁ and R₂ may preferably have 5 or less carbon atoms, and R₁ and R₂ may preferably be alkyl groups.

Specific compounds of the sensitizing dyes represented by the formula [I] are shown below, but these are not limitative of the present invention.

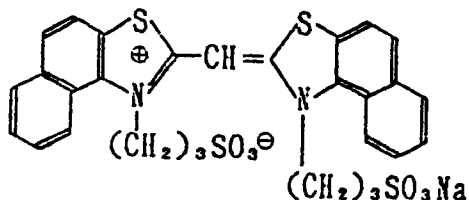
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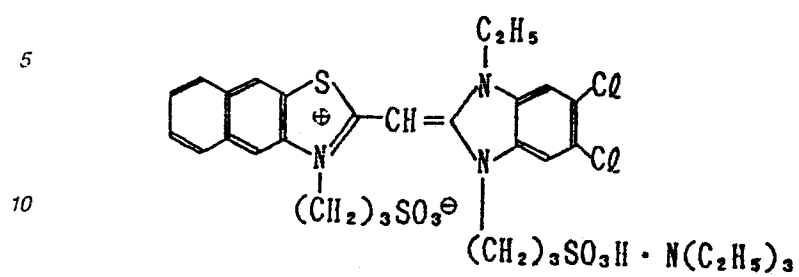
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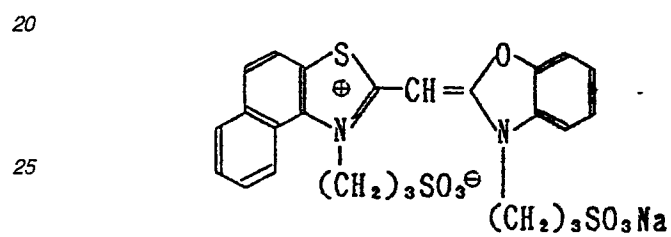


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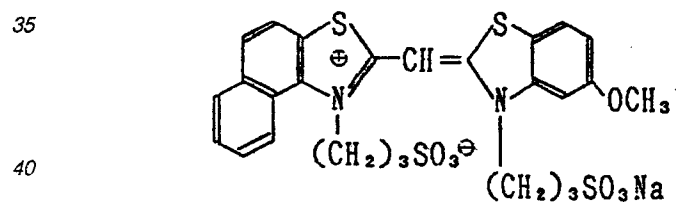
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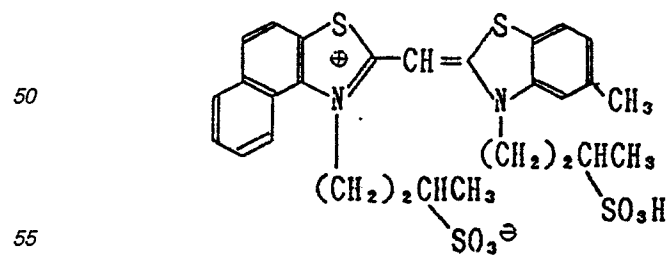


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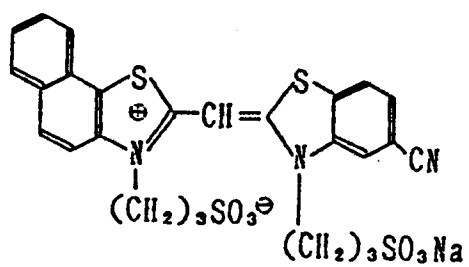
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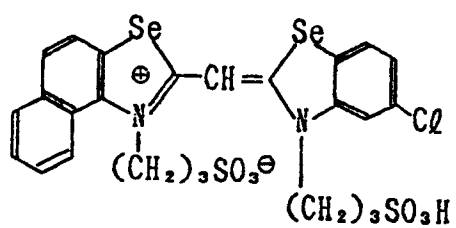
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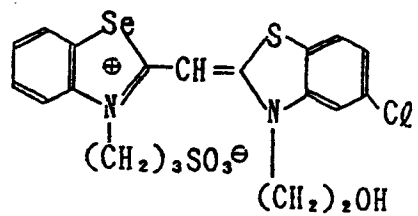
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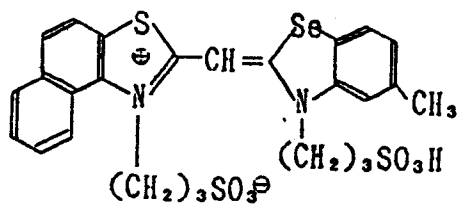
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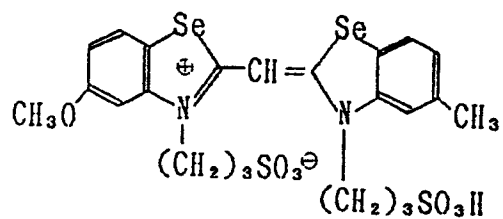
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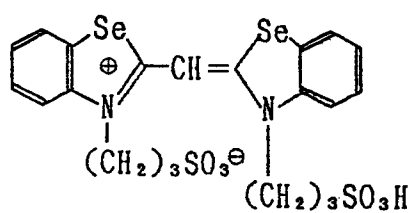


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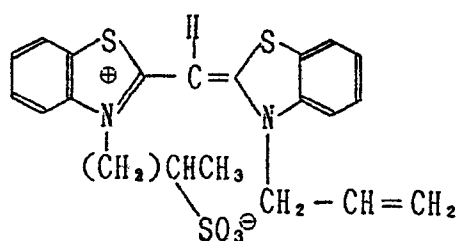


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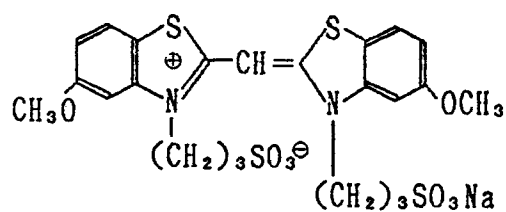
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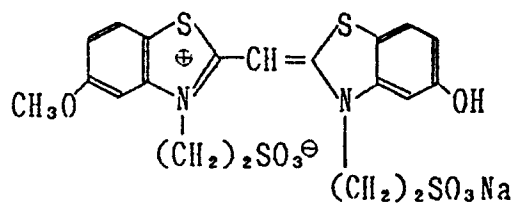
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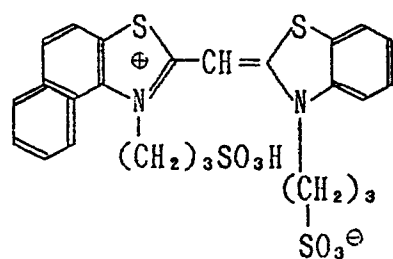
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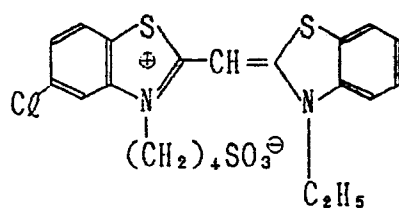
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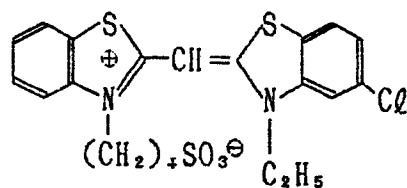
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[I - 22]



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65 The amount of the sensitizing dye represented by the above formula (I) added in the emulsion may be appropriately within the range of from 2×10^{-6} to 1×10^{-3} mole, preferably from 5×10^{-6} to 5×10^{-4} mole per

mole of silver halide.

Most of the above sensitizing dyes are sensitizing dyes having spectral sensitizing ability at the wave-length region which is called green-sensitive or blue-sensitive in light-sensitive materials, and the light-sensitive material to be used in the present invention should desirably be spectrally sensitized with the above sensitizing dye within the limit afforded by spectral sensitizing ability, and it is preferred that at least the sensitizing dye in the sum of green-sensitive emulsion and blue-sensitive emulsion may comprise for the greater part (50 mole % or more) the above sensitizing dye.

It is preferable to incorporate a mildewproofing agent in the stabilizing solution substituting for water washing of the present invention. Examples of mildewproofing agents preferably used are salicylic acid, sorbic acid, dehydroacetic acid, hydroxy benzoic acid type compounds, alkylphenol type compounds, thiazole type compounds, pyridine type compounds, guanidine type compounds, carbamate type compounds, morpholine type compounds, quaternary phosphonium type compounds, ammonium type compounds, urea type compounds, isoxazole type compounds, propanolamine type compounds, sulfamide derivatives and amino acid type compounds.

Examples of the above hydroxybenzoic acid type compounds include hydroxybenzoic acid and ester compounds of hydroxybenzoic acid such as methyl ester, ethyl ester, propyl ester, butyl ester, etc., preferably n-butyl ester, isobutyl ester and propyl ester of hydroxybenzoic acid, more preferably a mixture of the aforesaid three kinds of hydroxybenzoic acid esters.

The alkylphenol type compounds are compounds in which the alkyl group has, as the substituent, an alkyl group having 1 to 6 carbon atoms, preferably orthophenylphenol and ortho-cyclohexylphenol.

The thiazole type compound is a compound having nitrogen atom and sulfur atom in a five-membered ring, including preferably 1,2-benzisothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, 2-octyl-4-isothiazolin-3-one, 5-chloro-2-methyl-4-isothiazolin-3-one, 2-(4-thiazolyl)-benzimidazole.

Specific examples of the pyridine compounds may include 2,6-dimethylpyridine, 2,4,6-trimethylpyridine, sodium-2-pyridinethiol-l-oxide, etc., preferably sodium-2-pyridinethiol-l-oxide.

The guanidine type compounds may be specifically cyclohexidine, polyhexamethylenebiguanidine hydrochloride, dodecylguanidine hydrochloride, etc., preferably dodecylguanidine and salts thereof.

The carbamate type compounds may be exemplified by methyl-l-(butylcarbamoyl)-2-benzimidazolecarbamate, methylimidazolecarbamate, etc.

Typical examples of the morpholine type compounds are 4-(2-nitrobutyl)morpholine, 4-(3-nitrobutyl)morpholine, etc.

The quaternary phosphonium type compounds may include tetraalkylphosphonium salt, tetraalkoxyphosphonium salt, etc., preferably tetraalkylphosphonium salt, more preferably tributyl•tetradecylphosphonium chloride and triphenyl•nitrophenylphosphonium chloride.

Specific examples of the quaternary ammonium compounds include benzalconium salt, benzetonium salt, tetraalkylammonium salt, alkylpyridinium salt, etc., more specifically dodecyldimethylbenzylammonium chloride, dodecyldimethylammonium chloride, laurylpyridinium chloride, etc.

Urea type compounds may be exemplified by N-(3,4-dichlorophenyl)-N'-(4-chlorophenyl)urea, N-(3-trifluoromethyl-4-chlorophenyl)-N'-(4-chlorophenyl)urea, etc.

A typical example of the isoxazole type compound is 3-hydroxy-5-methyl-isoxazole, etc.

The propanolamine type compounds may include n-propanols and isopropanols, specifically DL-2-benzylamino-l-propanol, 3-diethylamino-l-propanol, 2-dimethylamino-2-methyl-l-propanol, 3-amino-l-propanol, isopropanolamine, diisopropanolamine, N,N-dimethylisopropanolamine, etc.

Specific examples of the sulfamide derivatives may include fluorinated sulfamide, 4-chloro-3,5-dinitrobenzenesulfamide, sulfanylamide, acetosulfamide, sulfapyridine, sulfaguanidine, sulfathiazole, sulfadiadine, sulfameladine, sulfamethadine, sulfaisooxazole, homosulfamide, sulfisomidine, sulfaguanidine, sulfametizole, sulfapyrazine, phthalisulfathiazole, succinylsulfathiazole, etc.

A typical example of the amino acid type compound is N-lauryl-β-alanine.

Of the above mildewproofing agents, the compounds preferably used in the present invention are pyridine type compounds, guanidine type compounds and quaternary ammonium type compounds.

The amount of the antifungal agent added in the stabilizing solution substituting for water washing may be within the range of from 0.002 g to 50 g, preferably from 0.005 to 10 g, per 1 ℓ of the stabilizing solution substituting for water washing.

The pH of the stabilizing solution substituting for water washing in the present invention, in order to accomplish more effectively the present invention, may preferably be within the range of from 3.0 to 10.0, more preferably from 5.0 to 9.5, particularly preferably from 6.0 to 9.0. As the pH adjustor which can be contained in the stabilizing solution substituting for water washing of the present invention, there may be employed any of the alkali agents or acid agents generally known in the art.

The present invention can exhibit great effect when the amount of the stabilizing solution substituting for water washing supplemented into the stabilizing bath is small, and it is preferred that said supplemented amount should be within the range of from 1 to 50-fold of the amount brought in from the previous bath per unit area of the light-sensitive material to be processed, and the effect of the present invention is particularly marked when said amount is within the range of from 2 to 20-fold.

The processing temperature for the stabilizing processing may be 15 °C to 60 °C, preferably be 20 °C to 45 °C. The processing time may preferably as short as possible from the standpoint of rapid processing, but

generally 20 seconds to 10 minutes, most preferably 1 minute to 3 minutes. In the case of the stabilizing processing by use of a plural number of tanks, it is preferred that the processing time should be shorter for earlier stage tanks and longer for later stage tanks. Particularly, it is desirable that processing should be successively performed in a processing time increased by 20% to 50 % as compared with that in the tank of the preceding stage.

The method for feeding the stabilizing solution substituting for water washing in the stabilizing processing step according to the present invention, when a multi-tank countercurrent system is used, may be preferably to feed the solution to the later bath and permitted to overflow from the earlier bath. Of course, it is possible to perform processing in a single tank. As the method for adding the above compounds, they can be added according to any desired addition method. For example, they can be added into the stabilizing solution as a concentrated solution. Alternatively, the above compounds and other additives may be added to the stabilizing solution substituting for water washing to be fed into the stabilizing tank and this is used as the feed solution for the stabilizing supplementing solution substituting for water washing.

The bleaching solution or bleach-fixing solution to be used in the present invention should preferably contain an organic acid ferric complex salt as the bleaching agent.

As the organic acid for forming the organic acid ferric complex salt may include those as set forth below.

- (1) Diethylenetriaminepentaacetic acid (MW = 393.27)
- (2) Diethylenetriaminepentamethylenephosphonic acid (MW = 573.12)
- (3) Cyclohexanediaminetetraacetic acid (MW = 364.35)
- (4) Cyclohexanediaminetetramethylenephosphonic acid (MW = 488.0)
- (5) Triethylenetetraminehexaacetic acid (MW = 494.45)
- (6) Triethylenetetraminehexamethylenephosphonic acid (MW = 710.72)
- (7) Glycoletherdiaminetetraacetic acid (MW = 380.35)
- (8) Glycoletherdiamine etramethylenephosphonic acid (MW = 524.23)
- (9) 1,2-diaminopropanetetraacetic acid (MW = 306.27)
- (10) 1,2-diaminopropanetetramethylenephosphonic acid (MW = 450.15)
- (11) 1,3-diaminopropane-2-ol-tetraacetic acid (MW = 322.27)
- (12) 1,3-diaminopropane-2-ol-tetramethylenephosphonic acid (MW = 466.15)
- (13) Ethylenediaminediortho-hydroxyphenylacetic acid (MW = 360.37)
- (14) Ethylenediaminediortho-hydroxyphenylmethylenephosphonic acid (MW = 432.31)
- (15) Ethylenediaminetetramethylenephosphonic acid (MW = 436.13)
- (16) Ethylenediaminetetraacetic acid (MW = 292.25)
- (17) Nitrilotriacetic acid (MW = 191.14)
- (18) Nitrilotrimethylenephosphonic acid (MW = 299.05)
- (19) Iminodiacetic acid (MW = 133.10)
- (20) Iminodimethylenephosphonic acid (MW = 205.04)
- (21) Methyliminodiacetic acid (MW = 147.13)
- (22) Methyliminodimethylenephosphonic acid (MW = 219.07)
- (23) Hydroxyethyliminodiacetic acid (MW = 177.16)
- (24) Hydroxyethyliminodimethylenephosphonic acid (MW = 249.10)
- (25) Ethylenediaminetetrapropionic acid (MW = 348.35)
- (26) Hydroxyethylglycidine (MW = 163.17)
- (27) Nitrilotripropionic acid (MW = 233.22)
- (28) Ethylenediaminediacetic acid (MW = 176.17)
- (29) Ethylenediaminedipropionic acid (MW = 277.15)

The organic acid ferric complex salt is not limited to these, and any desired one species selected from these can be used or a combination of two or more species can be used, if desired.

Of the organic acids for forming the organic acid ferric complex salt to be used in the present invention, particularly preferable ones include the following.

- (1) Diethylenetriaminepentaacetic acid (MW = 393.27)
- (3) Cyclohexanediaminetetraacetic acid (MW = 364.35)
- (5) Triethylenetetraminehexaacetic acid (MW = 494.45)
- (7) Glycoletherdiaminetetraacetic acid (MW = 380.35)
- (9) 1,2-diaminopropanetetraacetic acid (MW = 306.27)
- (11) 1,3-diaminopropane-2-ol-tetraacetic acid (MW = 322.27)
- (19) Iminodiacetic acid (MW = 133.10)
- (21) Methyliminodiacetic acid (MW = 147.13)
- (23) Hydroxyethyliminodiacetic acid (MW = 177.16)
- (28) Ethylenediaminediacetic acid (MW = 176.17)

The organic acid ferric complex salt to be used in the present invention may be used in the form of a free acid (hydroacid salt), an alkali metal salt such as sodium salt, potassium salt, lithium salt, etc., or an ammonium salt, or a water-soluble amine salt such as triethanol amine, etc., preferably potassium salt, sodium salt and ammonium salt.

These bleaching agents are used in amounts of 5 to 450 g/l, more preferably 20 to 250 g/l. For a bleach-fixing solution, a solution having a composition containing a silver halide fixing agent other than the

above bleaching agent and also containing a sulfite as the preservative, if desired, is applied. It is also possible to use a bleach-fixing solution such as a bleach-fixing solution comprising a composition in which a small amount of a halide such as ammonium bromide other than the organic acid iron (III) complex salt bleaching agent and the above silver halide fixing agent, or a bleach-fixing solution comprising a composition in which a halide such as ammonium bromide is conversely added in a large amount, or further a special bleach-fixing solution comprising a composition in which the organic acid iron (III) complex salt bleaching agent is combined with a large amount of a halide such as ammonium bromide or the like. As the above halide, other than the ammonium bromide, hydrochloric acid, hydrobromic acid, lithium bromide, sodium bromide, potassium bromide, sodium iodide, potassium iodide, ammonium iodide, etc., may be also used.

As the silver halide fixing agent contained in the fixing solution or bleach-fixing solution, there may be employed compounds capable of forming water-soluble complex salts by reaction with silver halide as used in the conventional fixing processing, including typically thiosulfates such as potassium thiosulfate, sodium thiosulfate, ammonium thiosulfate, etc., thiocyanates such as potassium thiocyanate, sodium thiocyanate, ammonium thiocyanate, etc., thiourea, thioether, etc. These fixing agents may be used in an amount of 5 g/l or more within the range which can be dissolved, but generally within the range of from 70 to 250 g/l.

The bleach-fixing solution can contain various kinds of pH buffering agents such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate, ammonium hydroxide, etc., either alone or as a combination of two or more kinds. Further, various kinds of fluorescent brighteners, defoaming agents or surfactants may be contained. Also, organic chelating agents such as hydroxylamine, hydrazine, aminopolycarboxylic acid, etc., stabilizers such as nitroalcohol, nitrate, etc., or organic solvents such as methanol, dimethylsulfoamide, dimethyl sulfoxide, etc., may be contained appropriately.

In the bleach-fixing solution to be used in the present invention, various bleaching accelerators can be added as disclosed in Japanese Provisional Patent Publication No. 280/1971, Japanese Patent Publications No. 8506/1970 and No. 556/1971, Belgian Patent No. 770,910, Japanese Patent Publications No. 8836/1970 and No. 9854/1978, Japanese Provisional Patent Publications No. 71634/1979 and No. 42349/1974, etc.

The bleach-fixing solution is used at pH of 4.0 or higher, generally from pH 5.0 to pH 9.5, desirably from pH 6.0 to pH 8.5, most preferably at pH 6.5 to pH 8.5. The processing temperature is 80 °C or lower and lower by 3 °C or more, preferably 5 °C or more than the processing solution temperature in the color developing tank, desirably 55 °C or lower while suppressing evaporation, etc.

The light-sensitive material to be used in the method of the present invention comprises silver halide emulsion layers and non-light-sensitive layers (non-emulsion layers) coated on a support. As the silver halide emulsion, any silver halide such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver chloroiodide, silver iodobromide, silver chloroiodobromide, etc. In these emulsion layers and non-light-sensitive layers, all couplers and additives known in the field of photography can be contained. For example, there may be contained appropriately yellow dye forming couplers, magenta dye forming couplers, cyan dye forming couplers, stabilizers, sensitizing dyes, gold compounds, high boiling point organic solvents, antifoggants, dye image fading preventives, color staining preventives, fluorescent brighteners, antistatic agents, film hardeners, surfactants, plasticizers, wetting agents and UV-ray absorbers, etc.

The light-sensitive material to be used in the method of the present invention can be prepared by providing by coating the respective constituent layers of emulsion layers and non-light-sensitive layers containing various additives for photography as mentioned above, if necessary, on a support applied with corona discharging treatment, flame treatment or UV-ray irradiation treatment, or alternatively through intermediary subbing layer or intermediate layer on the support. The support advantageously used may be, for example, baryta paper, polyethylene coated paper, polypropylene synthetic paper, glass plate, cellulose acetate, cellulose nitrate or polyester film such as polyethylene terephthalate, etc., polyamide film, polycarbonate film, polystyrene film, etc.

Most of the above silver halide emulsion layers and non-light-sensitive layers are generally in the form of hydrophilic colloid layers containing a hydrophilic binder. As the hydrophilic binder, gelatin or gelatin derivatives such as acylated gelatin, guanidylated gelatin, phenylcarbamylation gelatin, phthalated gelatin, cyanoethanolated gelatin, esterified gelatin, etc., may be preferably used.

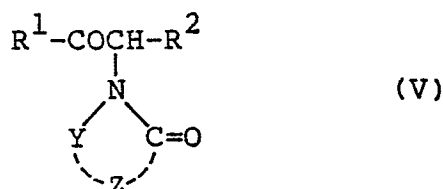
As the film hardening agent for hardening the hydrophilic colloid layer, it is possible to use, for example, chromium salts (chromium alum, chromium acetate, etc.) aldehydes (formaldehyde, glyoxal, glutaraldehyde, etc.), N-methylol compounds (dimethylolurea, methyloldimethylhydantoin, etc.), dioxane derivatives (2,3-dihydroxydioxane), etc., active vinyl compounds (1,3,5-triacryloyl-hexahydro-s-triazine, 1,3-vinylsulfonyl-2-propanol, etc.), active halide compounds (2,4-dichloro-6-hydroxy-s-triazine, etc.), mucohalogenic acids (mucochloric acid, mucophenoxychloric acid, etc.) and the like, either alone or in a combination.

Also, the present invention is particularly effective in the case of the so-called oil protect type in which a dispersion of a coupler contained in a high boiling point organic solvent is contained. The effect of the present invention is great when using, as such a high boiling point organic solvent, organic acid amides, carbamates, esters, ketones, urea derivatives, etc., particularly phthalic acid esters such as dimethyl phthalate, diethyl phthalate, dipropyl phthalate, dibutyl phthalate, di-n-octyl phthalate, diisooctyl phthalate, diamyl phthalate, dinonyl phthalate, diisodecyl phthalate or the like; phosphoric acid esters such as tricresyl phosphate, triphenyl phosphate, tri-(2-ethylhexyl)phosphate, trinonyl phosphate or the like; sebacic acid esters such as dioctyl sebacate, di-(2-ethylhexyl)sebacate, diisodecyl sebacate or the like; glycerine esters such as glycerol

tripropionate, glycerol tributylate or the like; or otherwise adipic acid esters, glutaric acid esters, succinic acid esters, maleic acid esters, fumaric acid esters, citric acid esters, phenol derivatives such as di-tert-amylphenol, n-octylphenol, etc.

The layer constitution of the light-sensitive material to be used in the present invention can be a constitution known in color negative film, color paper and reversal color film. For example, it can include an embodiment having a blue-sensitive silver halide emulsion layer containing a yellow dye forming coupler, a green-sensitive silver halide emulsion layer containing a magenta dye forming coupler and a red-sensitive silver halide emulsion layer containing a cyan dye forming coupler on one surface of a support (these respective color-sensitive layers may consist of one layer or two or more layers).

In the light-sensitive material to be used in the present invention, it is preferable to use a yellow coupler represented by the following formula (V).



In the above formula, R¹ represents an alkyl group, an alkenyl group, an aryl group or a heterocyclic group each of which may have a substituent, R² represents a cyano group or an N-phenylcarbamy group which may have a substituent, Y represents -CO-, -SO₂-, a nitrogen atom, an oxygen atom, a sulfur atom, a carbon atom having no oxygen atom bonded with a double bond, and Z represents a group of non-metallic atoms necessary for completion of a 4- to 6-membered nitrogen containing heterocyclic nucleus.

In the present invention, specific examples of the yellow coupler represented by the above formula (V) which can be effectively used may include those as described in Japanese Provisional Patent Publications No. 85426/1978, No. 102636/1976 and No. 2613/1972.

Specific examples are shown below, but these are not limitative of the present invention.

- Y - 1 α-(4-carboxyphenoxy)-α-pivalyl-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide
- Y - 2 α-pivalyl-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)-butyramido]acetanilide
- Y - 3 α-(4-carboxyphenoxy)-α-pivalyl-2-chloro-5-[α-(3-pentadecylphenoxy)butyramido]acetanilide
- Y - 4 α-(1-benzyl-2,4-dioxo-3-imidazolidinyl)-α-pivalyl-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide
- Y - 5 α-[4-(1-benzyl-2-phenyl-3,5-dioxo-1,2,4-triazolidinyl)]-α-pivalyl-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide
- Y - 6 α-[4-(4-benzyloxyphenylsulfonyl)phenoxy]-α-pivalyl-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide
- Y - 7 α-pivalyl-α-(4,5-dichloro-3(2H)-pyridazo-2-yl)-2-chloro-5-[(hexadecyloxy)carbonyl]methoxycarbonyl]acetanilide
- Y - 8 α-pivalyl-α-[4-(p-chlorophenyl)-5-oxo-Δ²-tetrazolin-1-yl]-2-chloro-5-[α-dodecyloxy)carbonyl]ethoxycarbonyl]acetanilide
- Y - 9 α-(2,4-dioxo-5,5-dimethyloxazolidin-3-yl)-α-pivalyl-2-chloro-5-[α-2,4-di-t-amylphenoxy)butyramido]acetanilide
- Y - 10 α-pivalyl-α-[4-(1-methyl-2-phenyl-3,5-dioxo-1,2,4-triazolidinyl)]-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide
- Y - 11 α-pivalyl-α-[4-(p-ethylphenyl)-5-oxo-Δ²-tetrazolin-1-yl]-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide
- Y - 12 α-(4-nitrophenoxy)-α-pivalyl-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide

These yellow couplers can be synthesized according to the synthetic methods in general as described in West German OLS's No. 20 57 941 and No. 21 63 812, Japanese Provisional Patent Publications No. 26133/1972, No. 29432/1973, No. 65231/1975, No. 3631/1976, No. 50734/1976, No. 102636/1976, No. 66834/1973, No. 66835/1973, No. 94432/1973, No. 1229/1974, No. 10739/1974 and Japanese Patent Publication No. 25733/1976.

In the light-sensitive material to be used in the present invention, the effect of the present invention can be exhibited when the total dried film thickness of the light-sensitive silver halide emulsion layers on one surface of a support is 10 μm or more, and the effect of the present invention is particularly remarkable when it is preferably 30 μm or less, particularly within the range of from 15 to 25 μm. If the total dried film thickness is less than 10 μm, the improved effect against staining of the present invention becomes small.

For color developing in the present invention, aromatic primary amine color forming agents are used and various known compounds widely used in color photographic process are included in said developing agent. These developing agents are inclusive of aminophenol type and p-phenylenediamine type derivatives. These compounds are used generally in the form of a salt such as hydrochloride or sulfate, since it is more stable than in the form of a free state. These compounds are used generally at a concentration of about 0.1 g to about 30 g per l of the color developing solution, preferably at a concentration of about 1 g to about 1.5 g per l of color developing solution.

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

Particularly useful aromatic primary amine type color developing agents are N,N'-dialkyl-p-phenylenediamine type compounds of which the alkyl group and phenyl group may be substituted with any desired substituent. Among them, examples of particularly useful compounds may include N,N'-diethyl-p-phenylenediamine hydrochloride, N-methyl-p-phenylenediamine hydrochloride, N,N-dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-(N-ethyl-N-dodecylamino)-toluene, N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate, N-ethyl-N-β-hydroxyethylaminoaniline, 4-amino-3-methyl-N,N'-diethylaniline, 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluenesulfonate, etc.

In the present invention, the color developing solution containing substantially no benzyl alcohol contains substantially no benzyl alcohol, namely at a concentration of 1 ml/l or lower, which is contained at a concentration of 10 to 20 ml/l in a conventional color developing solution. Of course, a concentration of about 0.5 ml/l comes within the region containing substantially no benzyl alcohol, but it is particularly preferred to contain no benzyl alcohol at all.

In the color developing solution, in addition to the above aromatic primary amine type color developing agent, various components generally added in color developing solution, for example, alkali agents such as sodium hydroxide, sodium carbonate, potassium carbonate, etc., alkali metal thiocyanates, alkali metal halides, water softeners and thickeners, etc., can be contained as desired. The pH value of the color developing solution using the aromatic primary amine type color developing agent as the color developing agent may be usually 7 or higher, most generally about 10 to about 13.

The soluble silver complex salt contained in the stabilizing solution substituting for water washing and the bleach-fixing solution to be used in the processing method of the present invention may be subjected to silver recovery according to the known method. For example, it is possible to utilize the electrolytic method (disclosed in French Patent No. 2,299,667), the precipitation method (disclosed in Japanese Provisional Patent Publication No. 73037/1977 and West German Patent No. 23 31 220), the ion exchange method (disclosed in Japanese Provisional Patent Publication No. 17114/1976 and West German Patent No. 25 48 237) and the metal substitution method (disclosed in U.K. Patent No. 1,353,805).

The processing method of the present invention can be advantageously applied for processing of color negative film, reversal color film, color negative paper, color positive paper and reversal color paper.

Also, the processing steps for which the present invention can be applied particularly effectively include the following (1) and (2).

- (1) Color developing - bleach-fixing - stabilizing processing substituting for water washing
- (2) Color developing - bleaching - fixing - stabilizing processing substituting for water washing.

EXAMPLES

The present invention is described in more detail by referring to the following Examples, by which the embodiments of the present invention are not limited at all.

Example 1

Experiments were carried out with the use of the color paper, the processing solutions and the processing steps as described below.

[Color paper]

On a polyethylene coated paper support, the respective layers shown below were coated successively from the support side to prepare a light-sensitive material.

The polyethylene coated paper used was prepared by forming a coated layer of a composition comprising a mixture of 200 parts by weight of a polyethylene having an average molecular weight of 100,000 and a density of 0.95 and 20 parts by weight of a polyethylene having an average molecular weight of 2,000 and a density of 0.80 added with 6.8 % by weight of an anatase type titanium oxide according to the extrusion coating method to a thickness of 0.035 mm onto the surface of a pure paper with a weight of 170 g/m² and providing a coated layer with a thickness of 0.040 mm only of a polyethylene on the back surface. After application of pre-treatment by corona discharging on the polyethylene coated surface on the support surface, the respective layers were coated successively.

First layer:

This is a blue-sensitive silver halide emulsion layer comprising a silver chlorobromide emulsion containing 80 mole % of silver bromide, and said emulsion contains 450 g of gelatin per mole of silver halide, is sensitized with 2.5×10^{-3} mole of a sensitizing dye of the present invention (exemplary compound I - 12) per mole of silver halide (isopropyl alcohol is used as the solvent), contains 200 mg/m² of 2,5-di-t-butyl hydroquinone dispersed by dissolving in dibutylphthalate and 2×10^{-3} mole per mole of silver halide of Y - 5 as the yellow coupler, and is coated to a silver quantity of 500 mg/m².

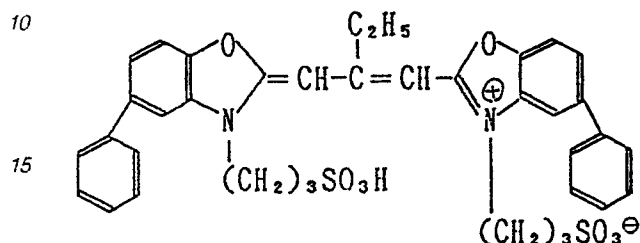
Second layer:

This is a gelatin layer containing 300 mg/m² of di-t-octylhydroquinone dispersed by dissolving in dibutylphthalate and 200 mg/m² of a mixture of 2-(2'-hydroxy-3',5'-di-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-5'-t-

butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole and 2-(2'-hydroxy-3',5'-di-t-butylphenyl)-5-chloro-benzotriazole as UV-absorber and is coated to a gelatin content of 2000 mg/m².

5 Third layer:

This is a green-sensitive silver halide emulsion layer comprising a silver chlorobromide emulsion containing 85 mole % of silver bromide, and said emulsion contains 450 g of gelatin per mole of silver halide, is sensitized with 2.5×10^{-3} mole of a sensitizing dye having the following structure:



20 per mole of silver halide, contains 150 mg/m² of 2,5-di-t-butylhydroquinone dispersed by dissolving in a solvent comprising a mixture of 2 : 1 of dibutylphthalate and tricresyl phosphate and 1.5×10^{-1} mole of 1-(2,4,6-trichlorophenyl)-3-(2-chloro-5-octadecenylsuccinimidoanilino)-5-pyrazolone per mole of silver halide as the magenta coupler, and is coated to a silver quantity of 400 mg/m². Also, as the antioxidant, 0.3 mole of 2,2,4-trimethyl-6-lauryloxy-7-t-octylchroman per mole of the coupler.

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Fourth layer:

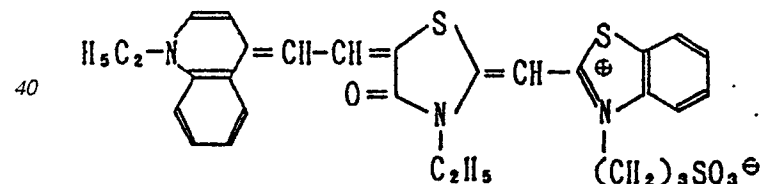
This is a gelatin layer containing 30 mg/m² of di-t-octylhydroquinone dispersed by dissolving in dioctyl phthalate and 500 mg/m² of a mixture (2 : 1.5 : 1.5 : 2) of 2-(2'-hydroxy-3',5'-di-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-5'-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole and 2-(2'-hydroxy-3',5'-t-butylphenyl)-5-chlorobenzotriazole as the UV-ray absorber, and is coated to a gelatin quantity of 2000 mg/m².

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Fifth layer:

This is a red-sensitive silver halide emulsion layer comprising a silver chlorobromide emulsion containing 85 mole % of silver bromide, and said emulsion contains 500 g of gelatin per mole of silver halide, is sensitized with 2.5×10^{-3} mole of a sensitizing dye having the following structure:

35



45 per mole of silver halide, contains 55 mg/m² of 2,5-di-t-butylhydroquinone dispersed by dissolving in dibutyl phthalate and 3.5×10^{-1} mole of 2,4-dichloro-3-methyl-6-[γ-(2,4-diamylphenoxy)butyramido]phenol per mole of silver halide as the cyan coupler, and is coated to a silver quantity of 400 mg/m².

Sixth layer:

50 This is a gelatin layer and is coated to a gelatin quantity of 1000 mg/m².

The silver halide emulsions used for the respective light-sensitive emulsion layers (the first, third and fifth layers) were prepared according to the method as described in Japanese Patent Publication No. 7772/1971, and each of them was chemically sensitized with sodium thiosulfate pentahydrates and incorporated with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene as the stabilizer, bis(vinylsulfonylmethyl)ether as the film hardener and saponin as the coating aid.

55

The film thickness after coating and drying as described above was measured to be 17 μm.

The color paper prepared according to the above method was exposed to light and then the experiments were conducted with the use of the following processing steps and processing solutions.

60 Standard processing steps

- [1] Color developing 38 °C 3 min. 30 sec.
- [2] Bleaching fixing 33 °C 1 min. 30 sec.
- [3] Stabilizing processing 25 °C - 35 °C 3 min.
- [4] Drying 75 °C - 100 °C about 2 min.

65

Processing solution compositions

< Color developing tank solution >

Benzyl alcohol 15 ml	
Potassium sulfite 2.0 g	5
Potassium bromide 1.3 g	
Sodium chloride 0.2 g	
Potassium carbonate 30.0 g	
3-Methyl-4-amino-N-ethyl-N-(β -methanesulfonamidoethyl)aniline sulfate 5.5 g	
Fluorescent brightener (4,4'-diaminostyrene type) 1.0 g	10
Hydroxylamine sulfate 3.0 g	
1-Hydroxyethylidene-1,1-diphosphonic acid 0.4 g	
Hydroxyethyliminodiacetic acid 5.0 g	
Magnesium chloride hexahydrates 0.7 g	
1,2-Dihydroxybenzene-3,5-disulfonic acid-disodium salt 0.2 g	15
(made up to 1 liter with addition of water, and adjusted to pH 10.20 with potassium hydroxide or sulfuric acid).	

< Color developing supplementing solution >

Benzyl alcohol 20.0 ml	20
Potassium sulfite 3.0 g	
Potassium carbonate 30.0 g	
Hydroxylamine sulfate 4.0 g	
3-Methyl-4-amino-N-ethyl-N-(β -methanesulfonamidoethyl)aniline sulfate 7.5 g	
Fluorescent brightener 2.5 g	25
1-Hydroxyethylidene-1,1-diphosphonic acid 0.5 g	
Hydroxyethyliminodiacetic acid 5.0 g	
Magnesium chloride hexahydrates 0.8 g	
1,2-dihydroxybenzene-3,5-disulfonic acid disodium salt 0.3 g	
(made up to 1 liter with addition of water, and adjusted to pH 10.70 with potassium hydroxide).	30

< Bleach-fixing tank solution >

Ferric methyliminodiacetate 60 g	
Methyliminodiacetic acid 3 g	
Ammonium thiosulfate (70 % solution) 100 ml	35
Ammonium sulfite (40 % solution) 27.5 ml	
(made up to 1 liter with addition of water, and adjusted to pH 7.1 with potassium carbonate or glacial acetic acid).	

< Bleach-fixing supplementing solution A >

Ferric methyliminodiacetate 260 g	40
Potassium carbonate 420 g	
(made up to the total amount of 1 liter with addition of water; this solution has a pH of 6.7 ± 0.1).	

< Bleach-fixing supplementing solution B >

Ammonium thiosulfate (70 % solution) 500 ml	45
Ammonium sulfite (40 % solution) 250 ml	
Methyliminodiacetic acid 17 g	
Glacial acetic acid 85 ml	
(made up to the total amount of 1 liter with addition of water; this solution has a pH of 5.3 ± 0.1).	

< Stabilizing tank solution substituting for water washing and supplementing solution >

5-Chloro-2-methyl-4-isothiazolin-3-one 0.02 g	
2-Methyl-4-isothiazolin-3-one 0.02 g	
Ethylene glycol 1.0 g	55
2-Octyl-4-isothiazolin-3-one 0.01 g	
Aqueous ammonia (25 % aqueous ammonium hydroxide solution) 2.5 g	
(made up to 1 liter with addition of water, and adjusted to pH 7.0 with sulfuric acid).	

Experiment C (control experiment by washing with running water)

An automatic developing machine was filled with the above color developing tank solution, bleach-fixing tank solution and the stabilizing tank with tap water and continuous processing was performed by processing color paper while supplementing the color developing supplementing solution and the bleach-fixing supplementing solutions A and B as described above through quantitating cups at intervals of 3 minutes. The amounts supplemented were, per 1 m ² of color paper, 190 ml for the color developing tank, and each 50 ml of	60
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the bleach-fixing supplementing solutions A and B for the bleach-fixing tank, and 20 ℓ of tap water were flowed to the stabilizing processing bath per 1 m².

Experiment I to Experiment 9

5 By use of the above color paper, processing was performed in the same manner as the above Experiment C by using the above color developing tank solution and the color developing supplementing solution as such or a formulation in which only benzyl alcohol was removed from the above color developing solution formulation for the color developing solution as shown in Table I, and by using a formulation in which the compound as indicated in Table I was added for the stabilizing solution substituting for water washing (Experiments I to 9).
10 The supplementing amount of the stabilizing supplementing solution substituting for water washing into the stabilizing tank solution was made 250 mℓ per 1 m² of color paper.

The stabilizing processing tank in the automatic developing machine was made a stabilizing tank consisting of the first tank to the third tank in the direction of the flow of the light-sensitive material, and a multitank countercurrent system was employed in which supplementing was conducted from the final tank, the overflow from the final tank was permitted to flow into the tank in the preceding stage, and further the overflow from this
15 stage was permitted to flow into the tank in the stage preceding thereto.

Experiments 10 and 11

In the above light-sensitive material, a light-sensitive material was prepared in entirely the same manner except for removing the sensitizing dye (exemplary compound I - 12) added in the first layer, by use of this light-sensitive material, processing as shown in Table I was conducted similarly as Experiments I to 9.
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Also, for a stabilizing solution substituting for water washing having added the compound in Table I in the above stabilizing solution formulation substituting for water washing, surface tension was measured in a conventional manner to obtain the result as shown in Table I.
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Table 1

Experiment No.	Presence of sensitizing dye	Presence of benzyl alcohol	Stabilizing solution substituting for water washing		
			Compound No.	Amount (g/l)	Surface tension (dyne/cm)
C (Control)	Do	Do	Washing with running water	-	-
1 (Comparative)	Do	Do	-	-	70
2 (Comparative)	Do	Do	II - 5	0.5	36
3 (Comparative)	Do	None	-	-	70
4 (Comparative)	Do	None	II - 5	0.5	37
5 (This invention)	Do	None	Compound A*	3.0	36
6 (This invention)	Do	None	II - 5	0.5	44
7 (This invention)	Do	None	II - 6	1.0	45
8 (This invention)	Do	None	III - 3	0.3	29
9 (This invention)	Do	None	III - 8	0.5	23
10 (Comparative)	None	Do	IV - 4	0.5	70
11 (This invention)	None	None	-	-	23

* Compound A: Formaldehyde bisulfite adduct

The white grounds of the unexposed portions of the samples obtained by processing in Experiment C to Experiment II were observed with eyes. Further, the spectral reflective densities at 440 nm of the white grounds of the unexposed portions were measured by means of a color analyzer (produced by Hitachi Ltd.).

Also, for the portion color formed in yellow of the samples obtained by processing, light resistance test by a xenon arc lamp was performed for 300 hours, and the densities of the dye images before and after the light resistance test were measured with the blue light of an optical densitometer (PDA - 65, produced by Konishiroku Photo Industry Co.) to determine the fading percentage. These results are shown in Table 2.

Table 2

Experiment No.	Visual observation of white ground (note 1)	Spectral reflective density (440 nm)	Fading percentage of yellow dye (%)
C (Control)	○	0.101	25
1 (Comparative)	x	0.132	34
2 (Comparative)	x	0.130	34
3 (Comparative)	x	0.130	33
4 (Comparative)	x	0.134	37
5 (This invention)	⊙	0.098	22
6 (This invention)	○	0.104	27
7 (This invention)	○	0.105	28
8 (This invention)	⊙	0.095	21
9 (This invention)	⊙	0.094	19
10 (Comparative)	x	0.115	30
11 (This invention)	⊙	0.093	19

Note 1) X: white ground tinted with gray and yellow as compared with water washing processing.

○: white ground similar to that by water washing processing.

⊙: white ground appears more white as compared with that by water washing processing.

From Table 2, it can be seen that, in the case of the processing methods of Comparative examples No. 1 to No. 4, stain is deteriorated with bad white ground of unexposed portion by visual observation and higher spectral reflective density value as compared with running water washing (Experiment C). Also, the same is the case in color fading. In contrast, in No. 5 to No. 9 of the present invention, it can be appreciated that the white ground of unexposed portion as well as light fading percentage of yellow dye are very preferable, exhibiting values similar to those in running water washing. Also, it can be seen that the effect of the present invention is higher in No. 5, No. 8 and No. 9 which exhibit small surface tension of the stabilizing solution substituting for water washing.

Further, from No. 1, No. 9, No. 10 and No. 11, it can be understood that the present invention is particularly effective when the light-sensitive materials contain a sensitizing dye represented by the formula (I).

Example 2

In the light-sensitive material of Example 1, the sixth layer was coated after coating of the first layer to prepare a light-sensitive material in which none of the second layer to the fifth layer were provided. Similarly, light-sensitive materials were prepared by varying the amount of the first layer coated to 2-fold, 3-fold, 4-fold,

5-fold and 6-fold. These dried film thicknesses were found to be 7.1 μm , 12.8 μm , 18.4 μm , 24.2 μm , 29.9 μm and 35.7 μm , respectively.

These light-sensitive materials were subjected to processing with the use of the processing solutions after continuous processing of Experiment I and Experiment 9.

For the respective samples after processing, the respective grounds were measured by visual observation and spectral reflective density (440 nm) similarly as in Example I. The results are shown in Table 3.

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Table 3

Processing conditions	Coated amount of first layer	1-fold	2-fold	3-fold	4-fold	5-fold	6-fold
	Dried film thickness (μm)	7.1	12.8	18.4	24.2	29.9	35.7
Experiment 1 (Comparative): Color developing solution (containing benzyl alcohol), Stabilizing solution substituting for water washing (surface tension 70 dyne/cm)	Visual observation of white ground (note 2)	⊙	x	x	x	x	x
	Spectral reflective density of white ground (440 nm)	0.103	0.127	0.138	0.142	0.144	0.148
Experiment 9 (This invention): Color developing solution (containing no benzyl alcohol), Stabilizing solution (Exemplary compound IV - 4, surface tension 23 dyne/cm)	Visual observation of white ground (note 2)	⊙	⊙	⊙	⊙	○	x
	Spectral reflective density of white ground (440 nm)	0.90	0.94	0.97	0.101	0.107	0.125

note 2) sic note 1 in Table 2.

As is apparent from Table 3, the present invention is effective when the light-sensitive material has a dried film thickness of 10 μm or more, particularly effective in the range from about 10 μm to 30 μm , most preferably in

the range from about 15 μm to 25 μm .

Example 3

On a triacetate film base, a halation preventive layer and a gelatin layer were provided, and a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a filter layer containing yellow colloidal silver and a blue-sensitive silver halide emulsion layer were coated thereon to a total silver quantity of 70 mg/100 cm^2 .

The above emulsion layers comprise a silver iodobromide containing about 4.5 mole % of silver iodide and, in this case, Y - 12 was employed as the yellow coupler in the blue-sensitive silver halide emulsion layer: 1-(2,4,6-trichlorophenyl)-3-[[α -(2,4-di-t-amylophenoxy)acetamido]benzamido]-3-pyrazolone and 1-(2,4,6-trichlorophenyl)-3-[[α -(2,4-di-t-amylophenoxy)acetamido]benzamido]-4-(4-methoxyphenylazo)-5-pyrazolone were employed as the magenta coupler in the green-sensitive silver halide emulsion layer; 1-hydroxy-N-[α -(2,4-t-amylophenoxy)butyl]-2-naphthoamide was employed as the cyan coupler in the red-sensitive silver halide emulsion layer; and the additives of sensitizing dye, film hardener and extender were added in the respective emulsion layers. However, in the blue-sensitive silver halide emulsion layer, the exemplary compound (I - 16) was used as the sensitizing dye.

The color negative film thus obtained was found to have a dried film thickness of 23 μm .

Experiment 12

The above light-sensitive material was applied with exposure in a conventional manner and then experiment was conducted with the use of the following processing steps and processing solutions.

Processing step	Processing temperature ($^{\circ}\text{C}$)	Processing time
1 Color developing	37.8	3 min. 15 sec.
2 Bleach-fixing	37.8	6 min. 30 sec.
3 Water washing	30 to 40	3 min. 15 sec.
4 Stabilizing	30 to 34	1 min. 37 sec.
5 Drying		

<Color developing tank solution>

Potassium carbonate 30 g
Sodium sulfite 2.0 g
Hydroxylamine sulfate 2.2 g
Potassium bromide 1.2 g
Diethylenetriaminepentaacetic acid 2.0 g
Sodium hydroxide 3.4 g
N-ethyl-N- β -hydroxyethyl-3-methyl-4-aminoaniline sulfate 4.6 g
(made up to 1 liter with addition of water and adjusted to pH 10.06 with potassium hydroxide).

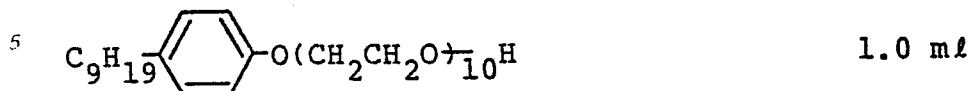
<Color developing supplementing solution>

Potassium carbonate 30 g
Sodium sulfite 2.0 g
Hydroxylamine sulfate 2.2 g
Potassium bromide 1.2 g
Diethylenetriaminepentaacetic acid 2.0 g
Sodium hydroxide 3.4 g
N-ethyl-N- β -hydroxyethyl-3-methyl-4-aminoaniline sulfate 4.6 g
(made up to 1 liter with addition of water and adjusted to pH 10.35 with potassium hydroxide).

<Bleach-fixing tank solution and supplementing solution>

Diethylenetriaminepentaacetic acid ferric complex salt 0.31 mole
Nitrilotriacetic acid 5.0 g
Ammonium sulfite 15 g
Ammonium thiosulfate 150 g
(made up to 1 liter with addition of water and adjusted to pH 7.0 with aqueous ammonia (28 % solution)).

< Stabilizing tank solution and supplementing solution >
 Formalin (35 % aqueous solution) 7.0 ml



10 (made up to 1 liter with addition of water).

An automatic developing machine was filled with the above color developing tank solution, the bleach-fixing tank solution, the washing water and the stabilizing tank solution, and continuous processing was performed by processing the color negative film while supplementing the above color developing supplementing solution, the bleach-fixing supplementing solution and the stabilizing supplementing solution through quantitating cup at the intervals of 3 minutes. The amounts supplemented were, per 1 m² of the color negative film, 1475 ml for the color developing tank, 926 ml for the bleach-fixing tank and 926 ml of the stabilizing supplementing solution for the stabilizing processing tank, respectively.

The amount of the washing water in the washing step was 30 l/m².

20 Experiment I3 to Experiment I6

By use of the above color negative film, Experiments were conducted with the use of the following steps and processing solutions.

Processing step	Processing temperature (°C)	Processing time
1 Color developing	37.8	3 min. 15 sec.
2 Bleach-fixing	37.8	6 min. 30 sec.
3 Stabilizing substituting for water washing	30 to 34	4 min. 52 sec.
4 Drying		

35 In the stabilizing step substituting for water washing, a multi-tank countercurrent system was used, in which the stabilizing tank consisted of the first tank to the third tank in the direction of the flow of the light-sensitive material, and supplement was performed from the final tank, with the overflow from the final tank being flowed into the tank in the preceding stage and further the overflow from this stage being flowed into the tank in the stage preceding thereto.

40 Both of the color developing solution and the bleach-fixing solution were the same as in Experiment I2, and the stabilizing solution substituting for water washing employed was prepared by adding the compound as indicated in Table 4 to the formulation shown below, and continuous processing was performed similarly as in Experiment I2 (Experiments I3 to I6).

45 The amount supplemented of the stabilizing solution substituting for water washing was the same as the stabilizing solution in Experiment I2.

< Stabilizing tank solution substituting for water washing and supplementing solution >

Dodecylguanidine hydrochloride 0.1 g

50 Ethylene glycol 1.0 g

(made up to 1 liter with water, and adjusted to pH 7.0 with sulfuric acid or potassium hydroxide).

The surface tensions of the stabilizing solution and the stabilizing solution substituting for water washing employed in the Experiments were measured in a conventional manner and the results are shown in Table 4.

55 Also, for the yellow image portions of the samples obtained in the respective experiments, light resistance test with a xenon arc lamp was conducted for 200 hours, and the density of before and after light resistance test were measured with the blue light of an optical densitometer (PDA - 65, produced by Konishiroku Photo Industry Co., Ltd.) to determine fading percentage. These results are shown in Table 4.

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Table 4

Experiment No.	Compound added to stabilizing solution substituting for water washing	Amount added (g/l)	Surface tension (dyne/cm)	Fading percentage of yellow dye (%)
12 (Comparative)	Water washing - stabilizing	-	24	29
13 (Comparative)	-	-	70	42
14 (Comparative)	Formalin Exemplary comp. IV - 4	6 ml 0.5	24	43
15 (This invention)	Exemplary compound II - 5	1.0	35	27
16 (This invention)	Exemplary compound IV - 4	0.5	23	24

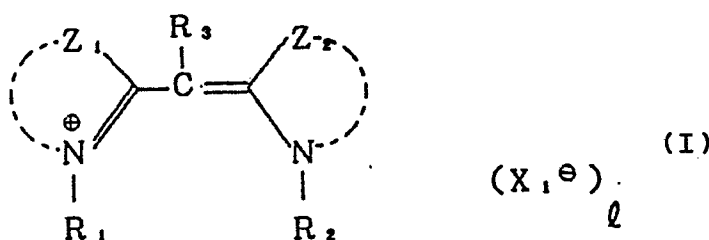
From Table 4, it can be seen that water washing-stabilizing processing (containing formalin) generally practiced at present as in the Experiment 12 can be replaced with stabilizing processing substituting for water

washing after bleach-fixing by practicing the present invention, whereby elimination of water washing is rendered possible.

Claims

1. A method for processing a light-sensitive silver halide color photographic material, which comprises subjecting to imagewise exposure a light-sensitive silver halide color photographic material having a total dried film thickness of the light-sensitive silver halide emulsion layer and the non-light-sensitive layer on one surface of a support of 10 μm or more, then processing the exposed material with a color forming developer containing substantially no benzyl alcohol, thereafter processing the material with a processing solution having fixing ability and subsequently processing the material with a stabilizing solution substituting for water washing having a surface tension of 8 to 50 dyne/cm and containing substantially no aldehyde compound, followed by drying.

2. A method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein said light-sensitive silver halide color photographic material contains a sensitizing dye represented by the following formula (I):



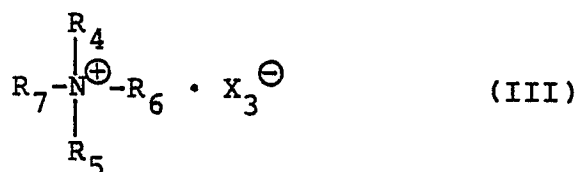
wherein each of Z_1 and Z_2 represents a group of atoms necessary for formation of benzoxazole nucleus, naphthoxazole nucleus, benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus, naphthoselenazole nucleus, benzoimidazole nucleus, naphthoimidazole nucleus, pyridine nucleus or quinoline nucleus, each of R_1 and R_2 represents an alkyl group, an alkenyl group or an aryl group, R_3 represents a hydrogen atom, a methyl group or an ethyl group and X_1^\ominus represents an anion and ℓ represents 0 or 1.

3. A method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein a stabilizing tank containing said stabilizing solution consists of 1 to 5 tanks.

4. A method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein said stabilizing solution substituting for water washing has a surface tension of 15 to 40 dyne/cm.

5. A method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein said stabilizing solution substituting for water washing contains at least one compound selected from the compounds represented by the following formulae (II) and (III), and water-soluble organic siloxane type compounds:

A-O-(B) m -X $_2$ (II) wherein A is a monovalent organic group of an alkyl group having 6 to 20 and an aryl group substituted with an alkyl group having 3 to 20 carbon atoms; B represents ethylene oxide or propylene oxide; m represents an integer of 4 to 50; and X $_2$ represents a hydrogen atom, SO $_3$ Y or PO $_3$ Y $_2$ where Y represents a hydrogen atom, an alkali metal or ammonium ion,



wherein each of R_4 , R_5 , R_6 and R_7 represents a hydrogen atom, an alkyl group or a phenyl group, and the total carbon atoms of R_4 , R_5 , R_6 and R_7 is 3 to 50; X_3 represents an anion of a halogen atom, a hydroxyl group, a sulfate group, a carbonate group, a nitrate group, an acetate group or a p-toluenesulfonate group.

6. A method for processing a light-sensitive silver halide color photographic material according to Claim 5, wherein an amount of said compounds is within the range of from 0.01 to 20 g per 1 ℓ of the stabilizing solution.

7. A method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein said color developing solution contains 0.1 mL/ ℓ or less of benzyl alcohol.

8. A method for processing a light-sensitive silver halide color photographic material according to Claim 7, wherein said color developing solution contains no benzyl alcohol.

9. A method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein said stabilizing solution substituting for water washing contains 0.1 g/l or less of an aldehyde compound.

10. A method for processing a light-sensitive silver halide color photographic material according to Claim 9, wherein said stabilizing solution substituting for water washing contains no aldehyde at all.

11. A method for processing a light-sensitive silver halide color photographic material according to Claim 2, wherein an amount of the sensitizing dye represented by the formula (I) added in the emulsion is within the range of from 2×10^{-6} to 1×10^{-3} mole per mole of the silver halide.

12. A method for processing a light-sensitive silver halide color photographic material according to Claim 11, wherein an amount of the sensitizing dye represented by the formula (I) added in the emulsion is within the range of from 5×10^{-6} to 5×10^{-4} mole per mole of the silver halide.

13. A method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein the amount of the stabilizing solution substituting for water washing supplemented into a stabilizing bath is within the range of from 1 to 50-fold of an amount brought in from a previous bath per unit area of the light-sensitive material to be processed.

14. A method for processing a light-sensitive silver halide color photographic material according to Claim 13, wherein said amount is within the range of from 2 to 20-fold.

15. A method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein a processing is successively performed in a processing time increased by 20 % to 50 % as compared with that in a tank of a preceding stage.

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