

⑫

**EUROPEAN PATENT APPLICATION**

⑰ Application number: 88301886.3

⑸ Int. Cl.4: **G03C 7/42** , **G03C 7/30**

⑱ Date of filing: 03.03.88

⑳ Priority: **04.03.87 JP 49469/87**  
**17.04.87 JP 94594/87**

㉓ Date of publication of application:  
**21.09.88 Bulletin 88/38**

㉔ Designated Contracting States:  
**DE FR GB IT NL**

㉑ Applicant: **KONICA CORPORATION**  
**No. 26-2, Nishi-Shinjuku 1-chome**  
**Shinjuku-ku**  
**Tokyo 106(JP)**

㉒ Inventor: **Ishikawa, Masao**  
**c/o Konica Corporation 1 Sakura-machi**  
**Hino-shi Tokyo(JP)**  
Inventor: **Hagiwara, Moeko**  
**c/o Konica Corporation 1 Sakura-machi**  
**Hino-shi Tokyo(JP)**  
Inventor: **Koboshi, Shigeharu**  
**c/o Konica Corporation 1 Sakura-machi**  
**Hino-shi Tokyo(JP)**  
Inventor: **Takabayashi, Naoki**  
**c/o Konica Corporation 1 Sakura-machi**  
**Hino-shi Tokyo(JP)**

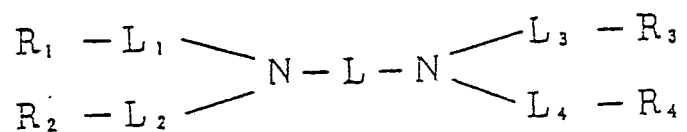
㉕ Representative: **Ellis-Jones, Patrick George**  
**Armine et al**  
**J.A. KEMP & CO. 14 South Square Gray's Inn**  
**London WC1R 5EU(GB)**

㉖ **Method for processing lightsensitive silver halide color photographic material improved in color restoration.**

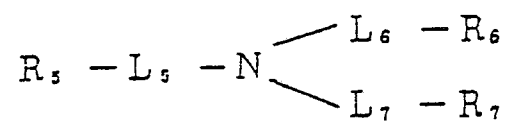
㉗ Disclosed is a method for processing a light-sensitive silver halide color photographic material, which comprises subjecting an exposed light-sensitive silver halide color photographic material to color developing processing and then applying at least desilverization processing, characterized in that the processing bath to be used in said desilverization processing contains a ferric complex of at least one compound selected from the compounds represented by the formula (I) and the formula (II) shown below, and after said desilverization processing, processing with an alkali bath having a pH of 8.0 or more and containing a buffering agent is performed,

**EP 0 283 174 A2**

Formula (I)



Formula (II)



wherein L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub>, L<sub>5</sub>, L<sub>6</sub>, L<sub>7</sub> and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> are as defined in the specification.

Disclosed is also a processing solution for light-sensitive silver halide color photographic material, which is an alkali processing solution to be used after an exposed light-sensitive silver halide color photographic material is subjected to color developing processing and desilverization processing by use of a ferric complex of at least one compound selected from the compounds represented by the formula (I) and the formula (II) shown above.

Method for processing light-sensitive silver halide color photographic material improved in color restoration badness and processing solution suitable therefor

BACKGROUND OF THE INVENTION

5 This invention relates to a method for processing a light-sensitive silver halide color photographic material and a processing solution to be used for the method, more particularly to a method for light-sensitive silver halide color photographic material which can be applied for a light-sensitive silver halide color photographic material of high sensitivity, high silver content to improve color restoration badness by suppressing the leuco formation of cyan dye, and a processing solution to be used for said processing method.

10 Generally speaking, the basic steps of processing of a color light-sensitive material are color developing step and desilverization step. In color developing step, exposed silver halide is reduced with a color developing agent to generate silver, and the color developing agent oxidized reacts with a color forming agent (coupler) to give a dye image. In the subsequent desilverization, through the action of an oxidizing agent (generally called bleaching agent), the silver generated in the color developing step is oxidized, and thereafter dissolved with a complexing agent of silver ions generally called fixing agent. By passing through  
15 the desilverization step, only a dye image can be completed on the color light-sensitive material.

The desilverization step as mentioned above may include the case in which it is carried out in two baths of a bleaching bath containing a bleaching agent and a fixing bath containing a fixing agent, the case in which it is carried out in a bleach-fixing bath containing the bleaching agent and the fixing agent co-present  
20 therein, and further the case in which those baths are combined.

In practical developing processing, in addition to the above basic steps, for maintaining photographic, physical quality of the image, or for improving storability of the image, various auxiliary steps are included. For example, there may be included film hardening bath, stopping bath, image stabilizing bath, water washing bath, etc.

25 As the bleaching agent in general, red prussiate, bichromate, ferric chloride, ferric complex of aminopolycarboxylic acid, ferric complex of aminopolyphosphonic acid, persulfate, etc. have been known.

However, red prussiate, bichromate involve the problem in environmental pollution concerning cyan compounds, hexavalent chromium, and their uses require special treating installations. Also, in ferric chloride, there are various obstacles in practical application such as the problems of formation of iron  
30 hydroxide or generation of stain in the subsequent water washing step. As for persulfate, its bleaching action is very weak, thus involving the drawback of requiring a remarkably long bleaching time. With regard to this point, there is also proposed a method to enhance the bleaching action by using in combination a bleaching accelerator, but persulfate itself is subject to regulation of a dangerous material under Fire Law, whereby various precautions are required in storage. Thus, various drawbacks are involved, which make  
35 practical application of persulfate difficult.

In contrast, ferric complex of aminopolycarboxylic acid (typically ferric complex of ethylenediaminetetraacetic acid) has little problem in environmental pollution possessed by the above bleaching agents, and also no problem in storage, and therefore it is the bleaching agent practically applied most broadly at present time.

40 However, the bleaching power of ferric complex of aminopolycarboxylic acid cannot be necessarily said to be sufficient, and in the processing solution by use of this as the bleaching agent, although the desired object can be accomplished in the case of bleaching or bleach-fixing processing of a low sensitivity light-sensitive silver halide material composed mainly of silver chlorobromide emulsion, in the case of processing  
45 of a light-sensitive color photographic material of high sensitivity composed mainly of silver chlorobromiodide or silver iodobromide emulsion, particularly, a color reversal light-sensitive material for photographing, a color negative light-sensitive material for photographing by use of high silver content emulsion, there have been involved the drawbacks such that desilverization badness occurred, that color restoration badness frequently occurred, and that a long time is required for bleaching.

For example, in the case of bleaching processing of a color negative light-sensitive material for  
50 photographing with the use of a ferric complex of an aminopolycarboxylic acid, at least 4 minutes or longer of bleaching time are required, and also for desilverization subsequent to the bleaching processing, processing with a fixing solution of at least 3 minutes or longer is required. If the bleaching time is attempted to be shortened, there are involved the problems of generation of desilverization badness and color restoration badness as mentioned above, and therefore the bleaching time was elongated. Accord-

ingly, it has been desired to shorten the time required for desilverization time requiring such long time.

As the method for enhancing desilverization performance by shortening the bleaching time, there have been known the method in which pH of the bleaching solution is lowered, the method in which the concentration of the bleaching agent is increased, further the methods in which bleaching accelerators as represented by mercapto compounds as disclosed in U.S. Patent No. 3,893,858, Japanese Unexamined Patent Publications Nos. 95631/1978 and 141623/1978, compounds having disulfide bond as disclosed in Japanese Unexamined Patent Publication No. 95630/1978, thiazolidine derivatives as disclosed in Japanese Patent Publication No. 9854/1978, isothiourea derivatives disclosed in Japanese Unexamined Patent Publication No. 94927/1978 are added in the bleaching solution or previous bath. However, the method of lowering pH of the bleaching solution has the drawback that color restoration badness is liable to occur, although bleaching speed may be improved. Also, in the case of increasing the concentration of the bleaching agent, the same drawback as mentioned above is liable to occur, because it cannot be added in large amount due to the problem of precipitation of iron complex. Also, the method of adding a bleaching accelerator involves the drawback that it is liable to form a difficultly soluble silver complex with silver, and further that it is poorly soluble, and even if used, color restoration is not sufficient.

Accordingly, as described above, it has been required to take a long time for bleaching.

As the method for expediting the desilverization step, it has been known to perform processing with a bleach-fixing solution containing a ferric complex of an aminopolycarboxylic acid and a thiosulfate which is the fixing agent in one bath as disclosed in West German Patent No. 866,605.

However, in the above bleach-fixing solution, because the oxidation power of the ferric complex of aminopolycarboxylic acid is originally weak and moreover the sulfite which is the co-existing preservative and the thiosulfate which is the fixing agent are reducing agents, they serve to further weaken the oxidation power of the ferric complex of aminopolycarboxylic acid, consequently having the drawbacks of not only lowering desilverization performance, but also readily changing the cyan dye formed in color developing to leuco dye, and also being poor in the ability of developing leuco dye, whereby vital defect of color restoration badness in color reproduction is caused.

The above phenomenon will appear more conspicuously with lapse of time when the light-sensitive material is processed continuously over a long term.

The present inventors have investigated variously on the above problems, and consequently found that the above coloration restoration badness is a problem generated commonly when a ferric complex of an aminopolycarboxylic acid and a ferric complex of an aminopolyphosphonic acid are used as the bleaching agent in the bleaching solution or the bleach-fixing solution in the desilverization step, which problem becomes particularly great as the result of the action of the ferric complex of aminopolycarboxylic acid or aminopolyphosphonic acid as the oxidizing agent, whereby ferrous complex (complex ions) of aminopolycarboxylic acid or aminophosphonic acid formed by reduction of itself is accumulated in the processing solution or the light-sensitive material.

Also, accumulation of the above ferrous complex ions depends on pH of the bleaching solution or bleach-fixing solution, and it has been found that formation of ferrous complex ions will occur more readily as the pH is higher. Further, it has been found that formation of ferrous complex ions, in addition to the phenomenon caused by decomposition of the ferric complex of aminopolycarboxylic acid or aminopolyphosphonic acid, when using a bleach-fixing solution, also occurs by reduction of the ferric complex ions with the sulfite contained as the preservative in the bleach-fixing solution, or alternatively the ferric complex itself is reduced by oxidizing silver by processing of a light-sensitive material of high silver content to become ferrous complex ions, whereby ferrous complex ions exist at high concentration in the coating of the light-sensitive photographic material during processing to covert cyan dye to leuco dye.

Color restoration badness due to such leuco formation of cyan dye has been particularly marked in a light-sensitive color photographic material of high sensitivity, high silver content type with a thickness of 13  $\mu\text{m}$  or more.

When the above ferrous complex ions are accumulated at high concentration in the bleaching solution or the bleach-fixing solution, the ferric complex ions in the coating of the light-sensitive photographic material formed in the bleaching reaction is remarkably inhibited in diffusion outside of the coating, whereby it may be considered that formation of leuco dye is increased to make greater the color restoration badness.

Generally speaking, for activating the above ferrous complex ions of aminopolycarboxylic acid or aminophosphonic acid to ferric complex ions by oxidation, the method called aeration which performs oxidation by blowing air into the processing solution has been well known in the art.

However, this method also oxidizes the sulfite which is a preservative, and therefore, although there is no danger when renewal ratio of the solution is relatively higher with relatively greater amount of processed

amount as in the case of processing of color paper, etc., oxidation of the solution will proceed too far in the case of relatively smaller processing amount as in color nega, whereby the sulfite which is a preservative is oxidized and the thiosulfate decomposed to precipitate sulfur (sulfide) to form a precipitate, thus involving a danger of causing a vital inconvenience.

5 Therefore, it has been strongly demanded to have a method which does not cause color restoration badness even if there may exist ferrous complex ions to some extent.

Also, it has been known that the above coloration badness can be improved by enhancing the pH of the bleaching solution or bleach-fixing solution, but as described in U.S. Patent No. 3,773,510, when pH of the bleaching solution or bleach-fixing solution is increased, not only the bleaching power is contrariwise  
10 weakened, but also ammoniums of ammonium thiosulfate and ferric ammonium salt will be readily volatilized, whereby the odor generated will cause contamination of the environment. Thus, it is impossible to realize increase of pH of the bleaching solution or bleach-fixing solution for improvement of color restoration badness.

Also, in U.S. Patent No. 3,189,452, there is disclosed the method in which a red prussiate bleaching  
15 solution is used after bleaching, fixing to return the leuco dye to cyan dye by oxidation. However, use of red prussiate involves the problem in environmental pollution as mentioned above, and therefore there is involved the drawback that extremely difficult operation for recovery of red prussiate is accompanied for practical application.

Therefore, it has been strongly demanded to provide a processing method which will not cause color  
20 restoration badness even if ferrous complex ions may be accumulated when a long term running is performed.

#### SUMMARY OF THE INVENTION

25

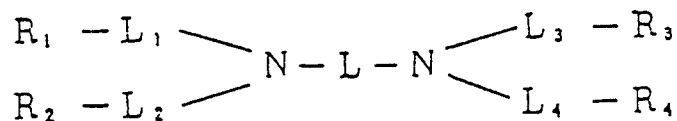
Accordingly, a first object of the present invention is to provide a method for processing a light-sensitive silver halide color photographic material by which leuco formation of cyan dye will occur with difficulty even in processing of a light-sensitive color photoraphic material, particularly a light-sensitive silver halide color photographic material having a high film thickness of the high sensitivity high silver amount type and a  
30 processing solution to be used for said processing method. A second object of the present invention is to provide a method for developing a dye which can be practiced easily without problem in environmental pollution.

The above objects of the present invention were found to be accomplished by a method for processing a light-sensitive silver halide color photographic material, which comprises subjecting an exposed light-  
35 sensitive silver halide color photographic material to color developing processing and then applying at least desilverization processing, characterized in that the processing bath to be used in said desilverization processing contains a ferric complex of at least one compound selected from the compounds represented by the formula (I) and the formula (II) shown below, and after said desilverization processing, processing with an alkali bath having a pH of 8.0 or more and containing a buffering agent is performed,

40

Formula (I)

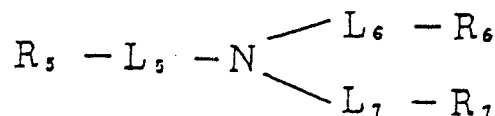
45



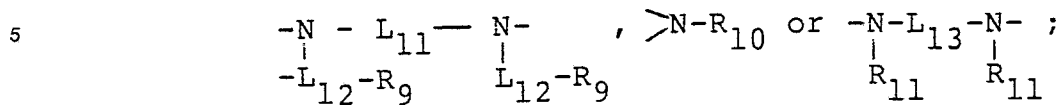
50

Formula (II)

55



wherein L represents an alkylene group, a cycloalkylene group, a phenylene group,  $-L_2-O-L_3-O-L_2-$  or  $-L_3-Z-L_3-$ ; where Z represents  $\geq N-L_{10}-R_8$ ,



10 L<sub>1</sub> to L<sub>13</sub> each represent an alkylene group; R<sub>1</sub> to R<sub>11</sub>, each represent a hydrogen atom, a hydroxyl group, a carboxylic acid group (including its salt) or a phosphonic acid group (including its salt); with proviso that at least two of R<sub>1</sub> to R<sub>4</sub> are carboxylic acid groups (including salts thereof) or phosphonic acid groups (including salts thereof), and at least one of R<sub>5</sub> to R<sub>7</sub> is a carboxylic acid group (including its salt) or a phosphonic acid group (including its salt),

15 or by using a processing solution for a light-sensitive silver halide color photographic material, which is an alkali processing solution to be used after an exposed light-sensitive silver halide color photographic material is subjected to color developing processing and desilverization processing by use of a ferric complex of at least one compound selected from the compounds represented by the formula (I) and the formula (II) shown above, said alkali processing solution having a pH of 8.0 or more and containing a buffering agent.

20 As further preferred embodiments, the above objects can be accomplished further efficiently by (1) containing a chelating agent with a chelate stability constant with iron ions (logKMA) of 6 or more in the above alkali bath, (2) containing  $1 \times 10^{-3}$  mol or more of ferric complex of an aminopolycarboxylic acid per 1 liter of the bath in the above alkali bath, (3) containing an oxidizing agent in the above alkali bath.

25

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

30 In the present invention, after desilverization processing by use of a ferric complex of at least one compound selected from the compounds represented by the formula (I) and the formula (II) (hereinafter called ferric complex of the compound of the present invention) as the bleaching agent, by processing with an alkali bath with pH of 8.0 or higher, the ferrous complex ions of the compound of the present invention formed and accumulated by adsorption in the gelatin coating of the light-sensitive silver halide color photographic material are desorbed, diffused quickly out of the above gelatin coating to make the atmosphere alkaline, whereby developing of cyan dye is remarkably accelerated to improve color restoration badness.

35 In the present invention, the desilverization processing applied after the color developing step can be any step, provided that the ferric complex of the compound of the present invention is used as the bleaching agent, but a preferable representative desilverization step by application of the present invention is as exemplified below.

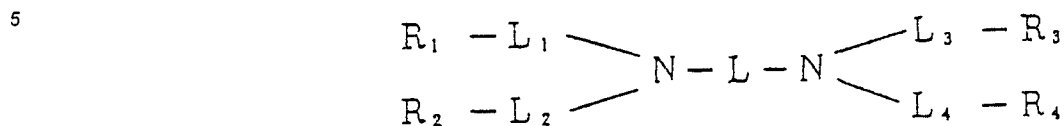
- 40 [1] Bleaching - fixing  
 [2] Bleach-fixing  
 [3] Bleaching - bleach-fixing  
 [4] Bleaching - bleach-fixing - fixing  
 45 [5] Bleach-fixing - bleaching - fixing  
 [6] Fixing - bleaching - bleach-fixing

In the above desilverization step, in the bleaching and bleach-fixing processing bath, namely the processing solution having bleaching ability, the ferric complex of the compound of the present invention is used as the bleaching agent.

50 The compound of the present invention is at least one compound selected from the compounds represented by the formula (I) and the formula (II) shown below:

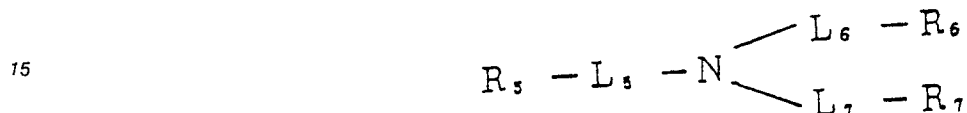
55

## Formula (I)



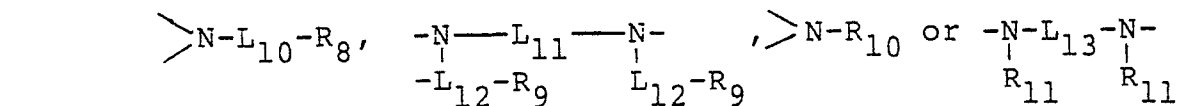
10

## Formula (II)



20

wherein L represents an alkylene group, a cycloalkylene group, a phenylene group,  $-L_8-O-L_8-O-L_8-$  or  $-L_8-Z-L_8-$ ; where Z represents



30

L<sub>1</sub> to L<sub>13</sub> each represent an alkylene group; R<sub>1</sub> to R<sub>11</sub>, each represent a hydrogen atom, a hydroxyl group, a carboxylic acid group (including its salt) or a phosphonic acid group (including its salt); with proviso that at least two of R<sub>1</sub> to R<sub>4</sub> are carboxylic acid groups (including salts thereof) or phosphonic acid groups (including salts thereof), and at least one of R<sub>5</sub> to R<sub>7</sub> is a carboxylic acid group (including its salt) or a phosphonic acid group (including its salt).

The ferric complex of the compound of the present invention to be used in the processing solution having bleaching ability of the present invention is a complex of ferric ions (Fe<sup>3+</sup>) with a compound of the present invention.

35

In the following, representative specific examples of the compound of the present invention are shown.

- A-1 Ethylenediaminetetraacetic acid  
 A-2 Disodium ethylenediaminetetraacetate  
 A-3 Diammonium ethylenediaminetetraacetate  
 A-4 Tetra(trimethylammonium) ethylenediaminetetraacetate  
 A-5 Tetrapotassium ethylenediaminetetraacetate  
 A-6 Tetrasodium ethylenediaminetetraacetate  
 A-7 Trisodium ethylenediaminetetraacetate  
 A-8 Ammonium diethylenetriaminepentaacetate  
 A-9 Pentasodium diethylenetriaminepentaacetate  
 A-10 Ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate  
 A-11 Trisodium ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate  
 A-12 Triammonium ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate  
 A-13 Ammonium propylenediaminetetraacetate  
 A-14 Disodium propylenediaminetetraacetate  
 A-15 Nitrilotriacetic acid  
 A-16 Sodium nitrilotriacetate  
 A-17 Cyclohexanediaminetetraacetic acid  
 A-18 Disodium cyclohexanediaminetetraacetate  
 A-19 Iminodiacetic acid  
 A-20 Dihydroxyethylglycine  
 A-21 Ethyl ether diaminetetraacetic acid  
 A-22 Glycol ether diaminetetraacetic acid  
 A-23 Ethylenediaminetetrapropionic acid

55

- A-24 Ammonium 1,2-diaminopropanetetraacetate  
 A-25 Sodium 1,2-diaminopropanetetraacetate  
 A-26 Ammonium hydroxyiminodiacetate  
 A-27 Sodium hydroxyiminodiacetate  
 5 A-28 Triethylenetetraminehexaacetic acid  
 A-29 1,3-Diaminopropane-2-ol-tetraacetic acid  
 A-30 Phenylenediaminetetraacetic acid  
 A-31 Nitrilotripropionic acid  
 A-32 Ethylenediaminetetramethylenephosphonic acid  
 10 A-33 Diethylenetriaminepentamethylenephosphonic acid  
 A-34 Cyclohexanediaminetetramethylenephosphonic acid  
 A-35 Nitrilotrimethylenephosphonic acid  
 A-36 Iminodimethylenephosphonic acid

Among these compounds, aminopolycarboxylic acids are preferred, particularly preferably A-1 to A-3,  
 15 A-8, A-13, A-14, A-17 to A-19, A-22, A-24 to A-27.

The ferric complex of the compound of the present invention to be used in the present invention may be used in the form of a complex, or a ferric ion complex may be formed in a solution by use of a ferric salt, for example, ferric sulfate, ferric chloride, ferric nitrate, ferric ammonium sulfate, ferric phosphate, etc. together with the compound of the present invention. When used in the form of a complex, one kind of  
 20 complex may be used, or two or more kinds of complexes may be used. On the other hand, when a complex is formed in a solution by use of a ferric salt and the compound of the present invention, one or two or more kinds of the ferric salt may be used. Further, one or two or more kinds of the compound of the present invention may be also used. In either case, the compounds of the present invention may be used in an excess more than forming a ferric ion complex.

Also, in the solution having bleaching ability containing the above ferric ion complex, metal ion complex  
 25 of metals other than iron such as cobalt, copper, nickel, etc. may be contained.

In the solution having bleaching ability of the present invention, the above ferric complex of the compound of the present invention may be preferably in the range from 0.05 to 2 mol, more preferably from 0.1 to 1.0 mol, particularly preferably from 0.2 to 0.6 mol, per 1 liter of the solution having bleaching ability.

In the desilverization step of the present invention, when employing a bleaching solution, the bleaching  
 30 solution can contain, in addition to the ferric complex of the compound of the present invention as the above bleaching agent, any of known additives which can be used in conventional bleaching solution, including buffering agents comprising various salts of boric acid, borax, metaboric acid, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate,  
 35 acetic acid, sodium acetate, ammonium hydroxide, etc., halide compounds such as potassium bromide, hydrochloric acid, hydrobromic acid, lithium bromide, sodium bromide, ammonium bromide, potassium iodide, sodium iodide, ammonium iodide, etc.

The pH of the bleaching solution of the present invention may be preferably in the range from 4.0 to 8.0, more preferably from 5.0 to 6.5.

When a bleach-fixing solution is used in the desilverization step of the present invention, in the bleach-  
 40 fixing solution, in addition to the compounds which can be added in the above bleaching solution, there may be employed a compound capable of forming a water-soluble complex through the reaction with a silver halide as used in conventional fixing processing as the silver halide fixing agent, for example, thiosulfate such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate and thiocyanate such as  
 45 potassium thiocyanate, sodium thiocyanate, ammonium thiocyanate, thiourea, thioether, highly concentrated bromide, iodide, etc. These fixing agents can be used in amounts within the range which can be solved of 5 g/liter or more, preferably 50 g/liter or more, more preferably 70 g/liter or more.

Further, various optical brighteners, defoaming agents, surfactants or antifungal agents can be also  
 50 contained. It is also possible to incorporate appropriately preservatives such as hydroxylamine, hydrazine, sulfite, metabisulfite, bisulfite adduct of aldehyde or ketone compound, etc.; organic chelating agents such as acetylacetone, phosphonocarboxylic acid, polyphosphoric acid, organic phosphonic acid, oxycarboxylic acid, polycarboxylic acid, dicarboxylic acid and aminopolycarboxylic acid, etc. or stabilizers such as nitro alcohol, nitrate, etc.; solubilizing agents such as alkanolamine, etc.; stain preventives such as organic amine, etc.; other additives; or organic solvents such as methanol, dimethylformamide, dimethyl sulfoxide, etc.

The pH of the bleach-fixing solution of the present invention may be preferably in the range from 3.0 to 9.8, more preferably from 5.6 to 8.5, particularly preferably from 6.0 to 8.3.

When a fixing solution is used in the desilverization step of the present invention, the fixing solution contains a fixing agent such as thiosulfate, thiocyanate, etc. as mentioned above for bleach-fixing solution



as the silver halide fixing agent.

Also, as the preservative for the fixing agent, preservatives such as hydroxylamine, hydrazine, sulfite, metabisulfite, bisulfite adducts of aldehyde or ketone compounds, etc., further known additives conventionally used in fixing solution such as various pH buffering agents as mentioned for bleaching solution, halide compounds, etc. can be contained.

The pH of the fixing solution may be preferably in the range from 5.0 to 8.5, more preferably from 6.0 to 8.0.

In the above desilverization processing step, a part or all of the bleaching bath overflow solution used which flow out from the bleaching bath as the result of addition of bleaching replenishing solution into the bleaching bath, and a part or all of the fixing bath overflow solution used which flow out from the fixing bath as the result of addition of fixing replenishing solution into the fixing bath, respectively can be introduced into the bleach-fixing bath. In that case, overflow solutions from the both bleaching and fixing baths can be reutilized effectively, without giving bad influence on desilverization performance, and also reduction in the total amount of replenishing solution is possible. Thus, it is a preferred embodiment.

In the present invention, the light-sensitive silver halide color photographic material subjected to the above desilverization processing is processed in an alkali bath having pH of 8.0 or higher and containing a buffering agent. Here, during processing in an alkali bath, processing in an alkali bath may be practiced continuously after the desilverization processing, as a matter of course, and also before the alkali bath processing, water washing, rinsing, and further the water washing substitutive stabilization which extremely reduces the amount of washing water, etc. may be applied. In view of the cost, etc., it is preferable to perform the alkali bath processing continuously after the desilverization processing.

The above alkali bath can be operated by maintaining its pH value at 8.0 or more, specifically pH 8.0 to 14.0, preferably 8.0 to 12.0, more preferably 8.5 to 12.0, most preferably 9.0 to 11.5

In the following, the alkali processing solution having pH of 8.0 or higher and containing a buffering agent of the present invention (hereinafter called merely alkali bath of the present invention) is to be described.

As the buffering agent to be used in the alkali bath of the present invention, any compound having stable buffering action in an aqueous solution of pH 8.0 or higher may be employed. Specific examples may include inorganic salts such as sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, ammonium carbonate, ammonium bicarbonate, boric acid, borax, sodium metaborate, sodium phosphate, potassium phosphate, sodium primary phosphate, etc.; amines such as ethanolamine, ethylenediamine, methylamine, trimethylamine, propylamine, etc.; amino acids such as hydroxyproline, leucine, glycine, alanine, aspartic acid,  $\gamma$ -aminobutylic acid, etc.; various organic compounds such as sulfosalicylic acid, piperazine, guanidine, etc., and these can be used either alone or in combination.

As the buffering agent to be used in the present invention, in view of the cost, the color restoration badness improvement effect of the present invention, the pH maintenance effect during continuous use over a long term and further bad influence on other photographic performances, sodium carbonate, potassium carbonate, potassium bicarbonate, boric acid, borax, sodium metaborate, sodium phosphate, potassium phosphate, sodium primary phosphate, sulfosalicylic acid, etc. may be preferably used. Although the buffering agent may serve as an alkali agent, an alkali agent such as sodium hydroxide and potassium hydroxide may be added separately.

The amount of the above buffering agent used in the alkali bath of the present invention may differ greatly depending on the pH of the alkali bath, the kind of the buffering agent employed, and if it is used in too much amount, staining may be generated on the processed light-sensitive material, or if it is too small, the problem such as small buffering effect, etc. may ensue. Thus, although it may be determined depending on the alkali bath conditions, as a measure, an amount ranging from 0.2 to 50 g per one liter of the alkali bath, more preferably 0.5 to 30 g may be employed.

The alkali bath processing in the present invention can be done without problem by use of one or multiple tanks, but preferably 1 to 2 tanks may be employed.

Also, the alkali bath of the present invention may be used similarly as the manner in which other processing baths for photography are used, specifically with sufficient supply of a replenishing solution, but it is preferable to make the amount replenished minimum in view of environmental pollution, etc.

The amount of the processing solution carried over from the preceding bath into the alkali bath may differ depending on the kind of the light-sensitive material, the conveying speed and conveying system of the automatic developing machine, the squeezing system of the light-sensitive material surface, etc., but in the present invention, the amount carried over may be preferably 25 ml/m<sup>2</sup> to 150 ml/m<sup>2</sup> with the unit area of the light-sensitive material processed as the standard, and the replenished amount at which the effect of the present invention is more marked for the amount carried over may be in the range from 50 ml/m<sup>2</sup> to 3.0

liter/m<sup>2</sup>, with the replenished amount with particularly remarkable effect being in the range from 100 ml/m<sup>2</sup> to 950 ml/m<sup>2</sup>.

In the above alkali bath of the present invention, a chelating agent with a chelate stability constant with iron ions (logKMA) of 6 or more can be incorporated, whereby the effect of the present invention, specifically improvement of the color restoration badness can be effectively accomplished. Also, it has the effect of preventing effectively formation of hydroxides of soluble iron salts carried over into the alkali bath.

Here, the chelate stability constant means the constant generally known by L.G. Sill, en. A.E. Martell, "Stability Constants of Metal-ion Complexes", The Chemical Society, London (1964), S. Chaberek, A.E. Martell, "Organic Sequestering Agents", Wiley (1959), etc.

In the present invention, chelating agents with chelate stability constant for iron ions of 6 or more, there may be included organic carboxylic acid chelating agents, organic aminopolycarboxylic acids, organic phosphoric acid chelating agents, inorganic phosphoric acid chelating agents, polyhydroxy compounds, etc. The above iron ions mean both of ferric ions (Fe<sup>3+</sup>) and ferrous ions (Fe<sup>2+</sup>).

In the present invention, specific compound examples having chelate stability constant with iron ions of 6 or more may include the following compounds, which are not limitative of the present invention. That is, there are ethylenediamine diorthohydroxyphenylacetic acid, diaminopropanetetraacetic acid, nitrilotriacetic acid, hydroxyethylethylenediaminetriacetic acid, dihydroxyethylglycine, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, iminodiacetic acid, diethylenetriaminepentaacetic acid, hydroxyethyliminodiacetic acid, diaminopropanolteraacetic acid, transcyclohexanediaminetetraacetic acid, ethylenediaminetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediaminetetrakis-methylenephosphonic acid, nitrilotrimethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, 1,1-diphosphonoethane-2-carboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxy-1-phosphonopropane-1,2,3-tricarboxylic acid, catechol-3,5-disulfonic acid, sodium pyrophosphate, sodium tetrapolyphosphate, sodium hexametaphosphate, of which particularly preferred are diaminopropanetetraacetic acid, diethylenetriaminepentaacetic acid, hydroxyethyliminodiacetic acid, diaminopropanolteraacetic acid, ethylenediaminetetraacetic acid and salts thereof.

The amount of the above chelating agent used in the present invention may be in the range from 0.01 to 50 g, preferably from 0.05 to 20 g, to give good results.

In the present invention, it is extremely preferable in improving the color restoration badness to incorporate a complex of the above chelating agent with iron ions, namely iron complex, in the alkali bath. Particularly preferable compounds may include ferric sodium ethylenediaminetetraacetate, ferric sodium diethylenetriaminepentaacetate, ferric sodium propylenediaminetetraacetate, ferric sodium 1,2-diaminopropanetetraacetate, etc., and it may be added in an amount of 0.5 to 30 g, particularly preferably 2 to 15 g, per liter of the alkali bath.

In the present invention, by permitting the overflow solution of the above solution having bleaching ability to flow into the alkali solution and have the ferric complex of an aminopolycarboxylic acid exist at a concentration of  $1 \times 10^{-3}$  mol or higher per one liter of the alkali bath, further color restoration badness can be well prevented.

Also, by incorporating an oxidizing agent in the alkali bath, for example, hydrogen peroxide, sodium percarbonate, sodium perborate, potassium persulfate, ammonium persulfate, sodium perchlorate, sodium hypochlorite, potassium hydrobromide, ammonium hydrobromide, sodium hydrobromide, etc., further color restoration badness can be well prevented. The amount of the oxidizing agent may be preferably 0.01 g to 30 g/liter.

In the processing method of the present invention, the above alkali bath processing may be the final step, or further water washing processing or processing with stabilizing processing substantially without use of washing water may be practiced.

In the present invention, as the processing after the alkali bath, stabilizing processing substantially without use of washing water of the latter is preferred.

The components in the stabilizing solution may comprise basically only water, but various compounds can be also added, and the compounds preferably used in the present invention may include formalin, surfactants, ammonium salts, chelating agent and metal salts.

In the above alkali bath or stabilizing solution of the present invention, an antifungal agent may be used, if necessary. Useful antifungal agents may include hydroxybenzoic acid compounds, phenol compounds, thiazole compounds, pyridine compounds, guanidine compounds, carbamate compounds, morpholine compounds, quaternary phosphonium compounds, quaternary ammonium compounds, urea compounds, isooxazole compounds, propanolamine compounds, sulfamide derivatives, amino acid compounds, triazine compounds and benzotriazole compounds.

In the processing method of the present invention, in addition to the steps of color developing,

desilverization processing and the alkali bath processing according to the present invention, there may be also added various auxiliary steps such as film hardening, neutralization, monochromatic developing, reversal, the step of washing with small amount of water, etc., if necessary.

The light-sensitive silver halide color photographic material to be applied for the processing method of the present invention is not basically limited in its kind, but particularly effectively used in the present invention are high sensitivity photographic light-sensitive materials having silver halide grains containing 0.5 mol% or more, preferably 3 to 10 mol% of silver iodide in at least one layer of the silver halide emulsion layers. Also, it is a light-sensitive material in which the sum of the dried film thicknesses of the all photographic constituent layers on the side having the silver halide emulsion layer on the support should be preferably 13  $\mu\text{m}$  or more preferably 15  $\mu\text{m}$  to 28  $\mu\text{m}$ , more preferably 17  $\mu\text{m}$  to 24  $\mu\text{m}$ , and further a high silver content light-sensitive material in which the amount of the coated silver on the support may be 20 mg/100  $\text{cm}^2$  or more, preferably 30 mg/100  $\text{cm}^2$  to 80 mg/100  $\text{cm}^2$ , more preferably 40 mg/100  $\text{cm}^2$  to 70 mg/100  $\text{cm}^2$ .

The silver halide emulsion of the light-sensitive silver halide color photographic material applicable for the present invention can be chemically sensitized in conventional manner, and optically sensitized to a desired wavelength region by use of a sensitizing dye.

In the silver halide emulsion, antifoggant, stabilizer, etc. can be added. As the binder for said emulsion, gelatin may be advantageously used.

The emulsion or other hydrophilic colloid layers can be subjected to film hardening, and also plasticizers, dispersions of water-insoluble or difficultly soluble synthetic polymers (latex) can be incorporated therein.

In the emulsion layer of the light-sensitive material for color photography, a coupler is used.

Further, there can be used colored couplers having the effect of color correction, competitive couplers, and compounds releasing useful fragments for photography such as developing accelerator, bleaching accelerator, developer, silver halide solvent, color controller, film hardening agent, foggant, antifoggant, chemical sensitizer, spectral sensitizer and desensitizer through coupling with the oxidized product of a developing agent.

In the light-sensitive material, auxiliary layers such as filter layer, halation preventive layer, irradiation preventive layer, etc. can be provided. In these layers and/or the emulsion layers, a dye flowed out from the light-sensitive material or bleached during developing processing may be also contained.

In the light-sensitive material, matting agent, lubricant, image stabilizer, surfactant, color antifoggant, developing accelerator, developing retarder or bleaching accelerator can be added.

As the support, papers laminated with polyethylene, etc., polyethyleneterephthalate film, baryta paper, cellulose triacetate, etc. can be used.

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

#### Example - 1

Simulating the layer constitution employed for high sensitivity light-sensitive silver halide color photographic material in this field of art, while interposing various auxiliary layers, black colloidal silver halation preventive layer, red-sensitive silver halide emulsion layer, green-sensitive silver halide emulsion layer and blue-sensitive silver halide emulsion layer were arranged from the support side, and a mono-dispersed high sensitivity silver halide emulsion layer was arranged at the outermost side of said blue-sensitive silver halide emulsion layer. The amount of silver coated was 60 mg/100  $\text{cm}^2$ , and the dried film thickness was made 25  $\mu\text{m}$ .

Layer 1...0.8 g of black colloidal silver obtained by reducing silver nitrate with the use of hydroquinone as the reducing agent exhibiting high absorption at a wavelength of 400 to 700 nm was dispersed in 3 g of gelatin to prepare a dispersion and a halation preventive layer was provided by coating.

Layer 2...intermediate layer comprising gelatin.

Layer 3...low sensitivity red-sensitive silver halide emulsion layer containing 1.5 g of a low sensitivity red-sensitive silver iodobromide emulsion (AgI; 7 mol%), 1.6 g of gelatin and 0.4 g of tricresyl phosphate hereinafter called TCP) containing 0.80 g of 1-hydroxy-4-( $\beta$ -methoxyethylaminocarbonyl-methoxy)-N-[ $\delta$ -2,4-di-t-amylphenoxy]butyl]-2-naphthoamide (hereinafter called cyan coupler (C-1)) and 0.028 g of 1-hydroxy-4-[4-(1-hydroxy-8-acetamido-3,6-disulfo-2-naphthyl-azo)phenoxy]-N-[ $\delta$ -(2,4-di-amylphenoxy)butyl]-2-naphthoamide disodium (hereinafter called colored cyan coupler (CC-1)) dissolved therein.

Layer 4...high sensitivity red-sensitive silver halide emulsion layer containing 1.1 g of a high sensitivity red-sensitive silver iodobromide emulsion (Agl; 6 mol%), 1.2 g of gelatin and 0.15 g of TCP containing 0.23 g of cyan coupler (C-1) and 0.020 g of colored cyan coupler (CC-1) dissolved therein.

Layer 5...intermediate layer containing 0.04 g of dibutyl phthalate (hereinafter called DBP) containing 0.07 g of 2,5-di-t-octylhydroquinone (hereinafter called staining preventive (HQ-1) and 1.2 g of gelatin.

Layer 6...low sensitivity green-sensitive silver halide emulsion layer containing 1.6 g of a low sensitivity green-sensitive silver iodobromide emulsion (Agl; 12 mol%), 1.7 g of gelatin and 0.3 g of TCP containing three kinds of couplers of 0.30 g of 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-t-amyphenox-yacetamido)benzeneamido]-5-pyrazolone (hereinafter called magenta coupler (M-1)), 0.20 g of 4,4-methylenebis-11-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-t-amyphenox-yacetamido)benzenamido]-5-pyrazolone (hereinafter called magenta coupler (M-2)) and 0.066 g of 1-(2,4,6-trichlorophenyl)-4-(1-naphthylazo)-3-(2-chloro-5-octadecenylsuccinimidoanilino)-5-pyrazolone (hereinafter called colored magenta coupler (CM-1)) dissolved therein.

Layer 7...high sensitivity green-sensitive silver halide emulsion layer containing 1.5 g of a high sensitivity green-sensitive silver iodobromide emulsion (Agl; 10 mol%), 1.9 g of gelatin and 0.12 g of TCP containing 0.093 g of magenta coupler (M-1), 0.094 g of magenta coupler (M-2) and 0.049 g of colored magenta coupler (CM-1) dissolved therein.

Layer 8...yellow filter layer containing 0.2 g of yellow colloidal silver, 0.11 g of DBP containing 0.2 g of stain preventive (HQ-1) dissolved therein and 2.1 g of gelatin.

Layer 9...low sensitivity blue-sensitive silver halide emulsion containing 0.95 g of a low sensitivity blue-sensitive silver iodobromide emulsion (Agl; 7 mol%), 1.9 g of gelatin and 0.93 g of DBP containing 1.84 g of  $\alpha$ -[4-(1-benzyl-2-phenyl-3,5-dioxo-1,2,4-triazolidinyl)]- $\alpha$ -pivaloyl-2-chloro-5-[ $\gamma$ -(2,4-di-t-amyphenox-y)butaneamido]acetanilide (hereinafter called yellow coupler (Y-1)) dissolved therein.

Layer 10...high sensitivity blue-sensitive silver halide emulsion layer containing 1.2 g of a high sensitivity mono-dispersed blue-sensitive silver iodobromide emulsion (Agl; 6 mol%), 2.0 g of gelatin and 0.23 g of DBP containing 0.46 g of yellow coupler (Y-1) dissolved therein.

Layer 11...the second protective layer comprising gelatin.

Layer 12...the first protective layer containing 2.3 g of gelatin.

This sample was cut into pieces, and by use of the piece to which wedge exposure was given in a conventional manner, processing was performed by use of a processing device for piece according to the following steps (hereinafter called hand developing processing).

<u>Processing step</u>	<u>Processing temp. (°C)</u>	<u>Number of tanks</u>	<u>Processing time</u>
1. Color developing	37.8	1	3 min. 15 sec.
2. Bleach-fixing (pH of bleach-fixing solution was made as shown below in Table 1)	37.8	1	3 min. 30 sec.
3. Alkali bath (pH of alkali bath was made as shown below in Table 1)	30 - 34	2	3 min. 30 sec.
4. Stabilizing	30 - 34	1	2 min. 10 sec.
5. Drying			

For the color developing solution, the bleach-fixing solution, the alkali bath solution and the stabilizing solution, those shown below were used.

[Color developing solution] Potassium carbonate 30 g  
 Sodium hydrogen carbonate 2.5 g  
 Potassium sulfite 5.0 g  
 Sodium bromide 1.2 g  
 5 Potassium iodide 2 mg  
 Hydroxylamine sulfate 2.5 g  
 Sodium chloride 0.6 g  
 Sodium diethylenetriaminepentaacetate 2.0 g  
 N-ethyl-N- $\beta$ -hydroxyethyl-3-methyl-4-aminoaniline sulfate 4.5 g  
 10 Potassium hydroxide 1.2 g  
 (made up to one liter with addition of water, and adjusted to pH 10.06 with sodium hydroxide or 20% sulfuic acid)

15 [Bleach-fixing solution] Ammonium ethylenediaminetetraacetate 2.0 g  
 Ferric diammonium ethylenediaminetetraacetate (complex of exemplary compound No. A-3) 150 g  
 70% Aqueous ammonium thiosulfate 250 ml  
 Ammonium sulfite 10 g  
 Mercaptobenztriazole 2.5 g  
 20 Ammonia water 7.3 ml  
 (made up to one liter with addition of water, and adjusted to pH as shown in Table 1 with acetic acid and ammonia water)

Further, with addition of silver powder, ferric diammonium ethylenediaminetetraacetate was reduced so  
 25 as to form 40 g of ferrous diammonium ethylenediaminetetraacetate, and again pH was adjusted as shown in Table 1.

30 [Alkali bath solution] Diethylenetriaminepentaacetic acid 2.0 g  
 Potassium carbonate 10 g  
 Borax 2.0 g  
 (made up to one liter with addition of water, and pH was adjusted as shown in Table 1 with potassium hydroxide or sulfuric acid)

35

[Stabilizing solution] Formalin (37% aqueous solution) 2 ml  
 Sodium diethylenetriaminepentaacetate 2 g  
 Konidax (produced by Konishiroku Photo Industry K.K.) 5 ml  
 40 Ammonium sulfate 1 g  
 (made up to one liter with addition of water, and pH adjusted to 3.0 with sulfuric acid)

45

50

55

Table 1

Experimental No.	Bleach-fixing solution pH	Alkali bath pH	
5	1-1 (Comparative)	4.0	6.0
	1-2 ( " )	"	7.0
	1-3 (This inv. )	"	8.0
10	1-4 ( " )	"	9.0
	1-5 ( " )	"	10.0
	1-6 ( " )	"	11.0
15	1-7 ( " )	"	12.0
	1-8 ( " )	"	13.0
	1-9 ( " )	"	14.0
20	1-10 (Comparative)	5.0	6.0
	1-11 ( " )	"	7.0
	1-12 (This inv. )	"	8.0
25	1-13 ( " )	"	9.0
	1-14 ( " )	"	10.0
	1-15 ( " )	"	11.0
	1-16 ( " )	"	12.0
30	1-17 ( " )	"	13.0
	1-18 ( " )	"	14.0
35	1-19 (Comparative)	6.0	6.0
	1-20 ( " )	"	7.0
	1-21 (This inv. )	"	8.0
	1-22 ( " )	"	9.0
40	1-23 ( " )	"	10.0
	1-24 ( " )	"	11.0
	1-25 ( " )	"	12.0
	1-26 ( " )	"	13.0
45	1-27 ( " )	"	14.0
50	1-28 (Comparative)	7.0	6.0
	1-29 ( " )	"	7.0
	1-30 (This inv. )	"	8.0
	1-31 ( " )	"	9.0
	1-32 ( " )	"	10.0
55	1-33 ( " )	"	11.0

Table 1 (cont'd)

5

	Experimental No.	Bleach-fixing solution pH	Alkali bath pH
10	1-34 (This inv. )	7.0	12.0
	1-35 ( " )	"	13.0
	1-36 ( " )	"	14.0
15	1-37 (Comparative)	8.0	6.0
	1-38 ( " )	"	7.0
	1-39 (This inv. )	"	8.0
	1-40 ( " )	"	9.0
20	1-41 ( " )	"	10.0
	1-42 ( " )	"	11.0
	1-43 ( " )	"	12.0
25	1-44 ( " )	"	13.0
	1-45 ( " )	"	14.0
	1-46 (Comparative)	9.0	6.0
30	1-47 ( " )	"	7.0
	1-48 (This inv. )	"	8.0
	1-49 ( " )	"	9.0
	1-50 ( " )	"	10.0
35	1-51 ( " )	"	11.0
	1-52 ( " )	"	12.0
	1-53 ( " )	"	13.0
40	1-54 ( " )	"	14.0
	1-55 (Comparative)	10.0	6.0
	1-56 ( " )	"	7.0
45	1-57 (This inv. )	"	8.0
	1-58 ( " )	"	9.0
	1-59 ( " )	"	10.0
	1-60 ( " )	"	11.0
50	1-61 ( " )	"	12.0
	1-62 ( " )	"	13.0
	1-63 ( " )	"	14.0

55

Following the above recipes, light-sensitive material samples were processed, and the residual silver amount (mg/dm<sup>2</sup>) at the maximum density portion in the sample after processing was measured by

fluorescent X-ray method. Further, after the cyan dye density was measured by use of Sakura photoelectric densitometer PDA-65 (produced by Konishiroku Photo Industry K.K.), and by use of this value, with the cyan dye density after processing of the same sample with a 3% red prussiate solution in a conventional manner at room temperature for 3 minutes as being 100, the color restoration ratio was calculated.

5 The results are summarized in Table 2.

10

15

20

25

30

35

40

45

50

55



Table 2

Experimental No.	Residual silver amount (mg/dm <sup>2</sup> )	Color restoration ratio (%)
5	1-1 (Comparative)	none 11
	1-2 ( " )	" 19
10	1-3 (This inv. )	" 46
	1-4 ( " )	" 54
	1-5 ( " )	" 63
	1-6 ( " )	" 74
15	1-7 ( " )	" 89
	1-8 ( " )	" 97
	1-9 ( " )	" 100
20	1-10 (Comparative)	" 16
	1-11 ( " )	" 22
	1-12 (This inv. )	" 52
25	1-13 ( " )	" 61
	1-14 ( " )	" 76
	1-15 ( " )	" 85
	1-16 ( " )	" 99
30	1-17 ( " )	" 100
	1-18 ( " )	" 100
	1-19 (Comparative)	" 22
35	1-20 ( " )	" 26
	1-21 (This inv. )	" 64
	1-22 ( " )	" 78
40	1-23 ( " )	" 82
	1-24 ( " )	" 96
	1-25 ( " )	" 100
	1-26 ( " )	" 100
45	1-27 ( " )	" 100
	1-28 (Comparative)	" 36
	1-29 ( " )	" 41
50	1-30 (This inv. )	" 72
	1-31 ( " )	" 88
	1-32 ( " )	" 99
55	1-33 ( " )	" 100

Table 2 (cont'd)

Experimental No.	Residual silver amount (mg/dm <sup>2</sup> )	Color restoration ratio (%)
1-34 ( " )	none	100
1-35 ( " )	"	100
1-36 ( " )	"	100
1-37 (Comparative)	0.06	51
1-38 ( " )	0.06	63
1-39 (This inv. )	0.06	88
1-40 ( " )	0.06	99
1-41 ( " )	0.06	100
1-42 ( " )	0.06	100
1-43 ( " )	0.06	100
1-44 ( " )	0.06	100
1-45 ( " )	0.06	100
1-46 (Comparative)	0.12	84
1-47 ( " )	0.12	96
1-48 (This inv. )	0.13	100
1-49 ( " )	0.12	100
1-50 ( " )	0.11	100
1-51 ( " )	0.12	100
1-52 ( " )	0.12	100
1-53 ( " )	0.12	100
1-54 ( " )	0.13	100
1-55 (Comparative)	0.32	100
1-56 ( " )	0.31	100
1-57 (This inv. )	0.32	100
1-58 ( " )	0.30	100
1-59 ( " )	0.32	100
1-60 ( " )	0.33	100
1-61 ( " )	0.32	100
1-62 ( " )	0.33	100
1-63 ( " )	0.32	100

As is apparent from the results in Table 2, those processed in the alkali bath of pH 8.0 or more after the bleach-fixing process show markedly good effect of improvement in desilverizability and color restoration badness of cyan dyes.

As to the relation with pH of the bleach-fixing solution, it is seen that particularly preferable results are obtained when pH is 6 to 8. Also, when pH of the alkali bath is 9.0 or more, preferable results are shown.

5 Example - 2

An alkali bath solution having the following composition was prepared.

10

[Alkali solution] Diethylenetriaminepentaacetic acid 2.0 g  
Buffering agent (kind is indicated in Table 3) 10 g  
Bleach-fixing solution in Example - 1 100 ml  
Made up to 1 l with addition of water, and adjusted to pH as shown in Table - 3.)

15

By use of the above alkali bath solution, the same experiment and estimation as in Example 1 were made except for employing the bleach-fixing solution of pH 6.5.

Further, the alkali bath solution was stored in a glass beaker with an opening area of 15 cm<sup>2</sup> (opening area per one liter of alkali bath) at 50 °C for 5 days and 10 days, respectively, and thereafter the same  
20 processing as above was conducted by use of the respective stored alkali bath solutions, and deterioration after storage with lapse of time of the alkali bath solution was observed. The results are also shown in Table 3.

25

30

35

40

45

50

55

5  
10  
15  
20  
25  
30  
35  
40  
45  
50

Table 3

Experimental No.	Buffering agent	Alkali bath pH before storage	Color restoration ratio after storage at 50°C		
			0 day	5 days	10 days
2-1 (Comp.)	Potassium carbonate	7.0	46	48	50
2-2 (Inve.)	Potassium carbonate	8.0	79	82	80
2-3 ( " )	Patassium carbonate	9.0	92	95	94
2-4 ( " )	Potassium carbonate	10.0	99	100	98
2-5 ( " )	Potassium carbonate	12.0	100	100	100
2-6 ( " )	Potassium bicarbonate	10.0	97	95	92
2-7 ( " )	Boric acid	10.0	98	95	91
2-8 ( " )	Borax	10.0	97	94	90
2-9 ( " )	Sodium metaborate	10.0	96	95	93
2-10 ( " )	Sodium phosphate	10.0	93	91	88
2-11 ( " )	Triethanolamine	10.0	97	91	86
2-12 ( " )	Diethanolamine	10.0	97	90	85
2-13 ( " )	Sulfosalicylic acid	10.0	96	93	90
2-14 (Comp.)	None (only KOH)	10.0	92	75	91

55 As is apparent from the results in Table 3, in all of the experiments No. 2 - 2 to 2 - 13 by use of the alkali bath of the present invention, improvement effect of color restoration badness can be markedly seen also after lapse of time, while in the comparative experiment No. 2 - 1 by use of an alkali bath with less than pH 8.0 is great in color restoration badness regardless of presence or absence of storage. Also, it can be

understood that, in the comparative experiment No. 2 - 14 in which no buffering agent is used, although pH may be adjusted to 10.0, the improvement effect of color restoration ratio can be satisfactory immediately after preparation of the alkali bath, but the color restoration will become insufficient with lapse of time, whereby no stable photographic image can be obtained.

5

Example - 3

The processing steps in Example - 1, namely the respective steps of 1. color developing, 2. bleach-fixing, 3. alkali bath and 4. stabilizing were replaced with the processing steps as shown in the following Table 4-1 and 4-2 to carry out experiments.

15

20

25

30

35

40

45

50

55

Table 4-1

Experimental No.	3-1 (Comp.)	3-2 (Comp.)	3-3 (Comp.)	3-4 (Inv.)	3-5 (Inv.)	3-6 (Inv.)	3-7 (Inv.)
Steps							
Color developing	3 min. 15 sec.	3 min. 15 sec.	3 min. 15 sec.	3 min. 15 sec.	3 min. 15 sec.	3 min. 15 sec.	3 min. 15 sec.
Bleaching	3 min.	-	1 min.	3 min.	-	1 min.	1 min.
Bleach-fixing	-	4 min.	3 min.	-	4 min.	3 min.	1 min.
Fixing	3 min.	-	-	3 min.	-	-	2 min.
Water washing	2 min.	2 min.	2 min.	-	-	-	-
Alkali bath	-	-	-	1 min.	1 min.	1 min.	1 min.
Alkali bath	-	-	-	1 min.	1 min.	1 min.	1 min.
Stabilization	1 min.	1 min.	1 min.	1 min.	1 min.	1 min.	1 min.

Table 4-2

5 Experimental No.	3-8 (This inv.)	Experimental No.	3-9 (This inv.)
10 Steps Color deve- loping	3 min.15 sec.	Steps Color deve- loping	3 min.15 sec.
15 Bleach-fixing	1 min.	Fixing	1 min.
Bleaching	1 min.	Bleaching	1 min.
Fixing	2 min.	Bleach-fixing	2 min.
20 Water washing	-	Water wasing	-
Alkali bath	1 min.	Alkali bath	1 min.
Alkali bath	1 min.	Alkali bath	1 min.
25 Stabilization	1 min.	Stabilization	1 min.

In the processing solutions used in the above processing steps, the bleach-fixing solution used was that of pH 6.5 in Example - 1, and the alkali bath used was similarly tht of pH 10.0.

Further, except for the bleaching solution and the fixing solution shown below, all are the same as in Example - 1.

35 [Bleaching solution] Ammonium ethylenediaminetetraacetate 2.0 g  
 Ferric diammonium ethylenediaminetetraacetate 100 g  
 Ammonium bromide 130 g  
 Mercaptobenztriazole 1.5 g  
 Ammonia water 5.0 ml  
 40 (made up to one liter with addition of water, and adjusted to pH 6.0 with ammonia wate or acetic acid)

Similarly as in Example - 1, ferric diammonium ethylenediaminetetraacetate was reduced with silver powder to give 40 g of ferrous diammonium ethylenediaminetetraacetate.

45 [Fixing solution] Sodium sulfite 10 g  
 Aqueous ammonium thiosulfate solution (70%) 200 ml  
 Sodium bisulfite 5.0 g  
 50 (made up to one liter with addition of water, and adjusted to pH 7.0)

Except for the above processing steps, the same experiments as in Example - 1 were conducted and color restoration ratio and desilverizability were examined. The results are shown in Table 5.

55

Table 5

5	Experimental No.	Color restoration ratio (%)
	3-1 (Comparative)	82
10	3-2 ( " )	62
	3-3 ( " )	75
15	3-4 (This invention)	100
	3-5 ( " )	99
	3-6 ( " )	100
20	3-7 ( " )	100
	3-8 ( " )	100
25	3-9 ( " )	100

Remarks: as to residual silver amount, no problem occurred.

30 As is apparent from Table 5, it can be appreciated that color restoration badness can be remarkably improved by application of the alkali bath processing of the present invention, even when desilverization processing may be variously changed.

35 Example - 4

In the above Example - 1, pH of the bleach-fixing solution was changed to 6.5, pH of the alkali bath to 10.0, and further the ferric complex of the aminopolycarboxylic acid or aminopolyphosphonic acid shown in the following Table 6 was used in place of ferric diammonium ethylenediaminetetraacetate as the  
 40 aminopolycarboxylic acid in the bleach-fixing solution at the concentration shown in Table 6, and experiments were conducted following otherwise the same procedure as in Example - 1. The results are also shown in Table 6.

45

50

55



Table 6

5	Experi- mental No.	Ferric complex of compounds of the formula (I) or (II)	Density (g/liter)	Residual silver amount (mg/dm <sup>2</sup> )	Color restration amount (%)
10	4-1	A - 8	40	0.03	74
	4-2	A - 8	60	0.06	86
15	4-3	A - 8	80	none	92
	4-4	A - 8	100	none	100
	4-5	A - 8	120	none	100
20	4-6	A - 8	140	none	100
	4-7	A - 8	160	none	100
25	4-8	A - 8	200	none	100
	4-9	A - 8	150	none	100
	4-10	A - 8	150	none	100
30	4-11	A - 13	150	none	100
	4-12	A - 16	150	none	98
35	4-13	A - 17	150	none	99
	4-14	A - 19	150	none	100
	4-15	A - 22	150	none	100
40	4-16	A - 24	150	none	100
	4-17	A - 26	150	none	100
45	4-18	A - 3	150	none	98
	4-19	A - 15	150	none	94
	4-20	A - 11	150	none	94
50	4-21	A - 32	150	none	94

55 As is apparent from the results in Table 6, it can be appreciated that the effect of the present invention can be obtained even if the kind and the concentration of the bleaching agent used in the bleach-fixing solution may be varied.

## Example - 5

In the experiment No. 4-1 in Example - 4, further the additive shown in the following Table 7 was added in an amount of 10 g per 1 liter of the alkali bath, and the experiments were conducted following otherwise the same procedure. The results are also shown in Table 7.

Table 7

Experi- mental No.	Additives	Residual silver amount (mg/dm <sup>2</sup> )	Color restora- tion ratio(%)
5-1	Sodium ferric ethylenedi- amine tetraacetate	none	99
5-2	Sodium ferric diethylene- triaminepentaacetate	none	100
5-3	Sodium ferric cyclohexane- diaminetetraacetate	none	99
5-4	Sodium ferric hydroxyimino- diacetate	none	98
5-5	Sodium ferric glycoether- diaminetetraacetate	none	100
5-6	Hydrogene peroxide (36 % aqueous solution)	none	100
5-7	Potassium persulfate	0.08	100
5-8	Sodium carbonate (3/2 H <sub>2</sub> O <sub>2</sub> )	0.08	100
5-9	Sodium borate • H <sub>2</sub> O <sub>2</sub>	0.08	100
5-10	Ethylenediaminetetra- acetic acid	0.08	100
5-11	Diethylenetriaminepenta- acetic acid	none	100
5-12	Cyclohexanediaminetetra- acetic acid	none	100
5-13	Hydroxyiminodiacetic acid	none	100
5-14	Glycoetherdiaminetetra- acetic acid	none	100

As is apparent from the results in Table 7, it can be appreciated that, when a chelating agent with a stabilization constant with iron of 6 or more is contained in the alkali bath in the processing method of the present invention, and also when the ferric complex of the compound of the present invention is contained at a certain concentration or higher, and further when an oxidizing agent is contained, the improvement effects of color restoration badness can be further marked, respectively.

Example - 6

In Example - 1, the light-sensitive materials shown in the following Table 8 with various film thicknesses of the light-sensitive materials to be processed (film thickness was changed by varying only gelatin amount) and coated silver amounts, and the experiments were conducted following otherwise the same procedure as in the experiment No. 1 - 24. However, experiments were also conducted for comparison using no alkali bath. The results are also shown in Table 8.

Table 8

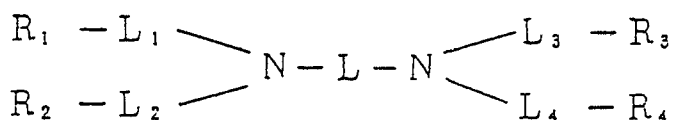
Experimental No.	Light-sensitive material		Residual silver amount <sub>2</sub> (mg/dm <sup>2</sup> )	Color restoration ratio (%)	
	Film thickness (μm)	Coated silver amount <sub>2</sub> (mg/100 cm <sup>2</sup> )			
6-1		10	60	none	84
6-2	No	13	60	none	72
6-3	alkali	16	60	none	61
6-4	bath	20	60	none	41
6-5	(Compa-	25	60	none	22
6-6	rative)	30	60	none	14
6-7	Alkali	10	60	none	100
6-8	bath	13	60	none	100
6-9	pH 11.0	16	60	none	98
6-10	(This	20	60	none	98
6-11	inven-	25	60	none	96
6-12	tion)	30	60	none	96
6-13	No	25	20	none	89
6-14	alkali	25	40	none	60
6-15	bath	25	60	none	22
6-16	(Compa-	25	80	none	16
6-17	rative)	25	100	none	8
6-18	Alkali bath	25	20	none	100
6-19	pH 11.0	25	40	none	100
6-20	(This	25	60	none	99
6-21	inven-	25	80	none	92
6-22	tion)	25	100	none	89

As is apparent from the results in Table 8, in the processing method of the present invention, the effect is not greatly affected by the film thickness of the light-sensitive material and the coated silver amount, and good effect of color restoration badness improvement can be obtained at a film thickness of 13 μm or more (color restoration badness is small at a film thickness of 13 μm or less). It can be appreciated that particularly great improvement effect can be obtained in the case of a film thickness of 16 μm or more, while greater improvement effect can be obtained as the coated silver amount is more.

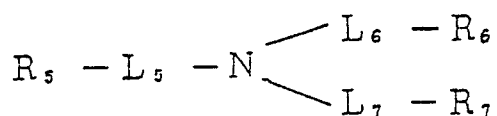
## Claims

1. A method for processing a light-sensitive silver halide color photographic material, which comprises subjecting an exposed light-sensitive silver halide color photographic material to color developing processing and then applying at least desilverization processing, characterized in that the processing bath to be used in said desilverization processing contains a ferric complex of at least one compound selected from the compounds represented by the formula (I) and the formula (II) shown below, and after said desilverization processing, processing with an alkali bath having a pH of 8.0 or more and containing a buffering agent is performed,

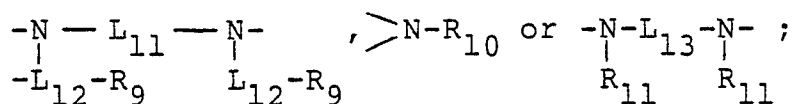
Formula (I)



Formula (II)



wherein L represents an alkylene group, a cycloalkylene group, a phenylene group,  $-L_8-O-L_8-O-L_8-$  or  $-L_8-Z-L_8-$ ; where Z represents  $\begin{array}{c} \diagdown \\ \diagup \end{array} N-L_{10}-R_8$ ,



L<sub>1</sub> to L<sub>3</sub>, each represent an alkylene group; R<sub>1</sub> to R<sub>4</sub>, each represent a hydrogen atom, a hydroxyl group, a carboxylic acid group (including its salt) or a phosphonic acid group (including its salt); with proviso that at least two of R<sub>1</sub> to R<sub>4</sub> are carboxylic acid groups (including salts thereof) or phosphonic acid groups (including salts thereof), and at least one of R<sub>5</sub> to R<sub>7</sub> is a carboxylic acid group (including its salt) or a phosphonic acid group (including its salt).

2. The method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein the pH of the alkali processing solution is within the range of 8.5 to 12.0.

3. The method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein said compounds represented by the formula (I) and the formula (II) is at least one of compounds shown below:

- A-1 Ethylenediaminetetraacetic acid
- A-2 Disodium ethylenediaminetetraacetate
- A-3 Diammonium ethylenediaminetetraacetate
- A-8 Ammonium diethylenetriaminepentaacetate
- A-13 Ammonium propylenediaminetetraacetate
- A-14 Disodium propylenediaminetetraacetate
- A-17 Cyclohexanediaminetetraacetic acid
- A-18 Disodium cyclohexanediaminetetraacetate
- A-19 Iminodiacetic acid
- A-22 Glycol ether diaminetetraacetic acid
- A-24 Ammonium 1,2-diaminopropanetetraacetate
- A-25 Sodium 1,2-diaminopropanetetraacetate

A-26 Ammonium hydroxyiminodiacetate

A-27 Sodium hydroxyiminodiacetate.

4. The method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein said compounds represented by the formula (I) and the formula (II) is contained in a solution having bleaching ability in an amount of 0.05 to 2 mol % per 1 liter of said solution.

5. The method for processing a light-sensitive silver halide color photographic material according to Claim 4, wherein said compounds represented by the formula (I) and the formula (II) is contained in a solution having bleaching ability in an amount of 0.2 to 0.6 mol % per 1 liter of said solution.

6. The method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein said buffering agent is at least one of inorganic salts, amines, amino acids and organic compounds.

7. The method for processing a light-sensitive silver halide color photographic material according to Claim 6, wherein the buffering agent is at least one of sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, ammonium carbonate, ammonium bicarbonate, boric acid, borax, sodium metaborate, sodium phosphate, potassium phosphate, sodium primary phosphate, ethanolamine, ethylenediamine, methylamine, trimethylamine, propylamine, hydroxyproline, leucine, glycine, alanine, aspartic acid,  $\gamma$ -aminobutylic acid, sulfosalicylic acid, piperazine and guanidine.

8. The method for processing a light-sensitive silver halide color photographic material according to Claim 7, wherein the buffering agent is at least one of sodium carbonate, potassium carbonate, potassium bicarbonate, boric acid, borax, sodium metaborate, sodium phosphate, potassium phosphate, sodium primary phosphate and sulfosalicylic acid.

9. The method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein the buffering agent contained in an amount ranging from 0.2 to 50 g per one liter of the alkali bath.

10. The method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein the alkali processing solution contains a chelating agent with a chelate stability constant with iron ions ( $\log K_{\text{MMA}}$ ) of 6 or more in the alkali processing solution.

11. The method for processing a light-sensitive silver halide color photographic material according to Claim 10, wherein the chelating agent is at least one of ethylenediamine diortho-hydroxyphenylacetic acid, diaminopropanetetraacetic acid, nitrilotriacetic acid, hydroxyethylethylenediaminetriacetic acid, dihydroxyethylglycine, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, iminodiacetic acid, diethylenetriaminepentaacetic acid, hydroxyethyliminodiacetic acid, diaminopropanoltraacetic acid, trans-cyclohexanediaminetetraacetic acid, ethylenediaminetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediaminetetrakis(methylenephosphonic acid), nitrilotrimethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, 1,1-diphosphonoethane-2-carboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxy-1-phosphonopropane-1,2,3-tricarboxylic acid, catechol-3,5-disulfonic acid, sodium pyrophosphate, sodium tetrapolyphosphate and sodium hexametaphosphate.

12. The method for processing a light-sensitive silver halide color photographic material according to Claim 11, wherein the chelating agent is at least one of diaminopropanetetraacetic acid, diethylenetriaminepentaacetic acid, hydroxyethyliminodiacetic acid, diamino propanoltraacetic acid and ethylenediaminetetraacetic acid and salts thereof.

13. The method for processing a light-sensitive silver halide color photographic material according to Claim 10, wherein the chelating agent is contained in an amount ranging from 0.01 to 50 g.

14. The method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein the alkali processing solution contains  $1 \times 10^{-3}$  mol or more of ferric complex of an aminopolycarboxylic acid per 1 liter of the alkali processing solution.

15. The method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein the alkali processing solution contains an oxidizing agent.

16. The method for processing a light-sensitive silver halide color photographic material according to Claim 15, wherein the oxidizing agent is at least one of hydrogen peroxide, sodium percarbonate, sodium perborate, potassium persulfate, ammonium persulfate, sodium perchlorate, sodium hypochlorite, potassium hydrobromide, ammonium hydrobromide and sodium hydrobromide.

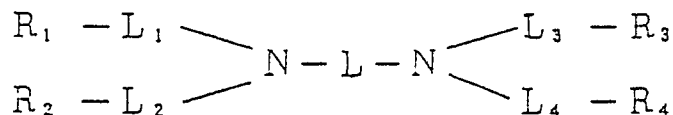
17. The method for processing a light-sensitive silver halide color photographic material according to Claim 15, wherein the oxidizing agent is contained in an amount ranging from 0.01 g to 30 g/liter of the alkali processing solution.

18. The method for processing a light-sensitive silver halide color photographic material according to Claim 1, wherein the light-sensitive silver halide color photographic material contains silver on a support thereof in an amount of 20 mg/100  $\text{cm}^2$  of the support.

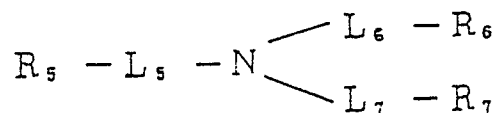
19. The method for processing a light-sensitive silver halide color photographic material according to Claim 18, wherein the amount of silver on the support is within the range of 30 mg/100 cm<sup>2</sup> to 80 mg/100 cm<sup>2</sup> of the support.

20. A processing solution for light-sensitive silver halide color photographic material, which is an alkali processing solution to be used after an exposed light-sensitive silver halide color photographic material is subjected to color developing processing and desilverization processing by use of a ferric complex of at least one compound selected from the compounds represented by the formula (I) and the formula (II) shown below, said alkali processing solution having a pH of 8.0 or more and containing a buffering agent,

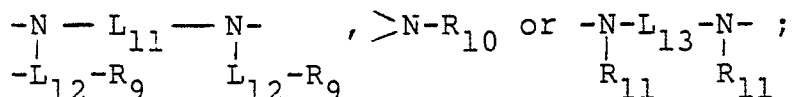
Formula (I)



Formula (II)



wherein L represents an alkylene group, a cycloalkylene group, a phenylene group, -L-O-L-O-L- or -L-Z-L-; where Z represents  $\begin{array}{c} \diagup \\ \diagdown \end{array} N-L_8-R_8$ ,



L<sub>1</sub> to L<sub>13</sub> each represent an alkylene group; R<sub>1</sub> to R<sub>11</sub> each represent a hydrogen atom, a hydroxyl group, a carboxylic acid group (including its salt) or a phosphonic acid group (including its salt); with proviso that at least two of R<sub>1</sub> to R<sub>4</sub> are carboxylic acid groups (including salts thereof) or phosphonic acid groups (including salts thereof), and at least one of R<sub>5</sub> to R<sub>7</sub> is a carboxylic acid group (including its salt) or a phosphonic acid group (including its salt).

21. The method for processing a light-sensitive silver halide color photographic material according to Claim 20, wherein the pH of the alkali processing solution is within the range of 8.5 to 12.0.