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(54) Method for processing a silver halide color photographic light-sensitive material

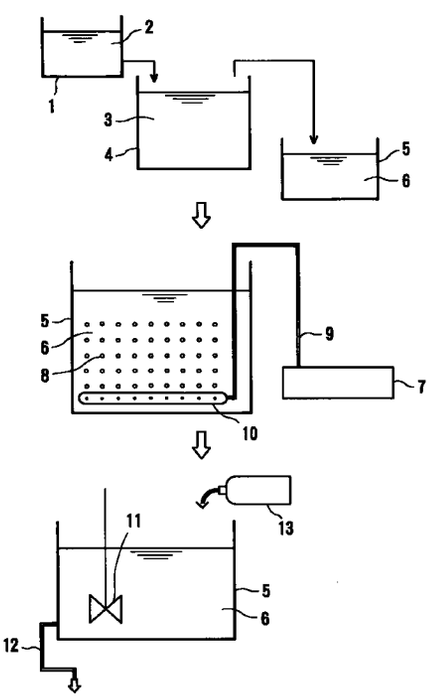
(57) There is disclosed a method for processing a silver halide color photographic light-sensitive material, which comprises after subjecting a silver halide color photographic light-sensitive material exposed to light imagewise, to color-development, bleaching the light-sensitive material, wherein the bleaching is carried out using a bleaching solution containing an iron(III) complex salt of an aminopolycarboxylic acid compound of the formula (I):

Formula (I):

$$R_1-N\begin{matrix}L_1-CO_2M_1\\ L_2-CO_2M_2\end{matrix}$$

wherein R_1 represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, or a heterocyclic group, L_1 and L_2 each represent an alkylene group, and M_1 and M_2 each represent a hydrogen atom or a cation, with the replenishment being made with a bleaching replenisher (2), and wherein after the overflow (6) from a bleaching bath (4) resulting from the replenishment is regenerated with a bleaching-solution-regenerating agent (13) in an amount smaller than the amount of the color developer, per square meter of the light-sensitive material to be processed, carried into the bleaching bath from a color-developing bath, the overflow is used as the bleaching replenisher (2). According to this method, when a regenerated bleaching solution is used, stain and fogging are suppressed, bubbling at the time of regeneration is suppressed, the efficiency of the regeneration operation is improved, and a bleaching solution can be regenerated and used without impairing the bleaching performance, with the load on the environment reduced.

Fig. 1



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Description

FIELD OF THE INVENTION

The present invention relates to a method for processing a silver halide color photographic light-sensitive material, and more specifically to a bleaching step that regenerates the overflow of a bleaching solution and recycles it.

BACKGROUND OF THE INVENTION

Generally, the processing of silver halide color photographic light-sensitive materials basically consists of a color-development step and a desilvering step, and the desilvering step is carried out in two steps, i.e., bleaching and fixing, or in one step, i.e., bleach-fixing, or in a step made up of a combination of these. Processing steps other than these include a washing step, a stabilizing step, a rinsing step, etc. In the bleaching step, developed silver that results from the reduction of a silver halide in the light-sensitive material in a developing bath with a developer, is oxidized with an oxidizing agent, called a bleaching agent, to a silver salt that can be fixed. At that time, the bleaching agent is reduced, in an amount equivalent to the silver that has been oxidized.

Since the bleaching agent that has been reduced by oxidizing silver loses bleaching capacity, in a usual processing, generally, the processing is carried out with a bleaching replenisher containing a fresh oxidizing agent be being added (replenished). However, the replenishment causes the bleaching solution to be discharged as a processing waste liquor, in an amount corresponding to the added amount of the replenisher. In recent years, reduction of the amount of processing waste liquor in view of problems, including water contamination, etc., has become an important demand in the market. To answer this, there are known a low-replenishment method, wherein the activity is maintained with a low replenishment rate by increasing the concentration of the replenisher, in order to reduce the processing waste liquor, and a regeneration utilization method, wherein the overflow of the bleaching solution is reused as a replenisher, so that processing liquor waste itself is not formed.

The latter regeneration of a bleaching solution is a method in which the overflow from a bleaching bath, which overflow will otherwise become waste liquor, is stored outside the bleaching solution tank, and bleaching solution components that have been reduced, for example, due to dilution with the carried-over solution from the preceding bath, consumption in the reaction, and the carryover to the succeeding bath by adhesion to the light-sensitive material, are supplied (replenished) to the stored overflow, so that it can be used as a replenisher again. Herein, as the method for replenishing bleaching solution components, a method is well known wherein, when the overflow is regenerated, out of the bleaching solution components, those that have been consumed, such as a bleaching agent and a rehalogenating agent in the bleaching solution, are added to the overflow from the bleaching bath. For the bleaching agent among them, in order to minimize the amount of the agent to be added freshly, a means is known wherein the bleaching agent whose bleaching capacity has been lost by the reaction of oxidizing developed silver is oxidized again, to make it regain its original bleaching capacity. Although one of such means is a technique wherein, by adding another oxidizing agent that is more powerful than the bleaching agent, the reduced bleaching agent is restored to a form capable of bleaching, so that the activity of the bleaching solution can be restored, the handling of the powerful oxidizing agent is inconvenient, and there is also a problem that the accumulation of the salt resulting from the addition of the agent hampers the bleaching speed. As another oxidation technique for restoring the activity of a bleaching agent, there is a method wherein air is bubbled through the bleaching solution, to allow the oxygen in the air to oxidize the bleaching agent. This method is simple and is used widely in the market.

This method causes less of an environmental pollution problem, and, as a bleaching agent that can be regenerated by a simple oxidation method, such as aeration, a ferric complex salt of ethylenediaminetetraacetic acid or 1,3-diaminopropanetetraacetic acid is used currently, in many cases. However, since the bleaching solution that uses the former has low oxidizing power, it is used in a high concentration or in combination with a bleaching accelerator, to secure bleaching speed. Therefore, as the regeneration of the bleaching solution progresses, there are sometimes an accumulation of developing solution components, formation of tar, which seems to be mainly the result of the oxidation of the developing agent owing to the condensation by evaporation, and formation of a precipitation that results from the deposition of the bleaching agent itself. These substances and phenomena cause such problems, for example, as that they adhere to the light-sensitive material being processed, to cause soil (hereinafter referred to as stain), or they cause clogging of the filter of the processor. Since the bleaching solution that uses the latter is high in bleaching speed in comparison with the former, and the latter can be used as a solution more dilute than that of the former, the occurrence of a precipitation resulting from the deposition of the bleaching agent itself can be avoided. However, since its oxidation power is great, when the color developer from the preceding bath adheres to the light-sensitive material and is carried into the bleaching solution, bleaching fogging owing to the oxidation of the developing agent is apt to occur. Further, in comparison with the former, the speed of the so-called reoxidation of the reducing-type ferrous complex salt to the ferric complex salt is low, and therefore it requires a longer period for the aeration, during which formation of tar that likely

results from the oxidation of the developing agent in the color developer inadvertently brought in, occurs. Thus, when it is used after the regeneration, the tar adheres to the light-sensitive material and can be seen as stain, which is a problem. Since stain and bleaching fogging can be easily detected by measuring the density of the minimum density section (Dmin) of the light-sensitive material, a bleaching solution with which stain and bleaching fogging can be minimized is desired.

A problem common to both of them is lowering of the operability due to the bubbling during the aeration. That is, surfactants and polymer components that mainly ooze from the light-sensitive material accumulate in the bleaching solution, causing such a problem as that the long-period aeration at the regeneration brings about violent bubbling from the vessel, to pollute the working environment or to cause part of the solution to flow out, making it impossible to secure the desired amount of the regenerated bleaching solution. Particularly, it is observed that, when the amount of the regeneration agent of the bleaching solution used at the regeneration is small, the bubbling is apt to increase, and therefore an operation of breaking the bubbles, such as interruption of the aeration, is needed. Although the foregoing problems exist clearly, suitable measures against them have not be taken up to now, and the current situation is such that the operator in charge of the regeneration operation takes measures in individual cases.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a method for processing a silver halide color photographic light-sensitive material, in which method, when a regenerated bleaching solution is used, stain and fogging are suppressed, bubbling at the time of regeneration is suppressed, the efficiency of the regeneration operation is improved, and a bleaching solution can be regenerated and used without impairing the bleaching performance, with the load on the environment reduced.

Other and further objects, features, and advantages of the invention will appear more fully from the following description, taken in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWING

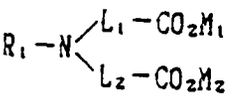
Fig. 1 shows a flow sheet of the method of the invention, which illustrates regenerating the overflow of a bleaching solution, to use it as a replenisher.

DETAILED DESCRIPTION OF THE INVENTION

The above object of the present invention has been attained by providing the following method:

(1) A method for processing a silver halide color photographic light-sensitive material, comprising after subjecting a silver halide color photographic light-sensitive material exposed to light imagewise, to color-development, bleaching the silver halide color photographic light-sensitive material, wherein the bleaching is carried out using a bleaching solution containing an iron(III) complex salt of an aminopolycarboxylic acid compound represented by the following formula (I):

Formula (I):



wherein R_1 represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, or a heterocyclic group, L_1 and L_2 each represent an alkylene group, and M_1 and M_2 each represent a hydrogen atom or a cation, with the replenishment being made with a bleaching replenisher, and wherein after the overflow from a bleaching bath resulting from the replenishment is regenerated with a bleaching-solution-regenerating agent in an amount smaller than the amount of the color developer, per square meter of the light-sensitive material to be processed, carried into the bleaching bath from a color-developing bath, the overflow is used as the bleaching replenisher;

(2) The method for processing as stated in the above (1), wherein the aminopolycarboxylic acid of the aminopolycarboxylic acid iron(III) complex salt in the bleaching solution comprises 1,3-diaminopropanetetraacetic acid or eth-

ylenediaminetetraacetic acid in an amount of 1/2 or less in terms of molar fraction;

(3) The method for processing as stated in the above (1) or (2), wherein a dicarboxylic acid, a hydroxycarboxylic acid, or a sulfocarboxylic acid is contained in the bleaching solution;

(4) The method for processing as stated in the above (1), (2), or (3), wherein a picolinic acid derivative is contained in the bleaching solution; and

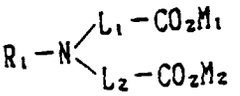
(5) The method for processing as stated in the above (1), (2), (3), or (4), wherein the pH of a washing bath after the bleaching is 3.5 to 8.0.

It is an unexpected surprising effect that, when the aminopolycarboxylic acid iron(III) complex salt represented by formula (I) for use in the present invention is used as a bleaching agent that will be regenerated and used, the above problems involved in the step of regenerating a bleaching solution can be overcome, and its effect is further increased by using it in combination with 1,3-diaminopropanetetraacetic acid, ethylenediaminetetraacetic acid, specific carboxylic acids, or picolinic acid derivatives. Details of the cause of the increase in the effect are not fully apparent, but it seems that an improvement of the chelate stability related to the bleaching performance of the aminopolycarboxylic acid iron(III) complex salt, and a change in the complex structure thereof facilitate the reoxidation reaction; that is, a so-called concerted effect is exhibited.

Further, the effect of preventing stain that contributes to a Dmin increase by controlling the pH of the washing bath after the bleaching, is distinctive when the aminopolycarboxylic acid iron(III) complex salt represented by formula (I) for use in the present invention is used. It is unexpected from the situation of the conventional use of ethylenediaminetetraacetic acid and 1,3-diaminopropanetetraacetic acid, that the simple method wherein pH is adjusted has opened an effective way of solving the problems.

The bleaching solution used in the present invention is characterized in that the ferric complex salt of the compound represented by formula (I) is regenerated, to be used in such a manner that the amount of a bleaching solution regenerating agent used, per square meter of the light-sensitive material to be processed, is smaller than the amount of the solution carried over from the color-developing bath, per that area. First, the compound represented by the following formula (I) is explained.

formula (I)



wherein R_1 represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, or a heterocyclic group; L_1 and L_2 each represent an alkylene group; and M_1 and M_2 each represent a hydrogen atom or a cation.

The number of carbon atoms hereinafter referred to means a number of carbon atoms, excluding that in a substituent moiety.

Examples of the aliphatic hydrocarbon group represented by R_1 include a straight-chain, branched, or cyclic alkyl group having preferably 1 to 12, more preferably 1 to 10, and still more preferably 1 to 8 carbon atoms; an alkenyl group having preferably 2 to 12, more preferably 2 to 10, and still more preferably 2 to 7 carbon atoms; and an alkynyl group having preferably 2 to 12, more preferably 2 to 10, and still more preferably 2 to 7 carbon atoms, each of which may be substituted with a substituent.

Examples of such a substituent include an aryl group having preferably 6 to 12, more preferably 6 to 10, and particularly preferably 6 to 8 carbon atoms (e.g. phenyl, p-methylphenyl); an alkoxy group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methoxy, ethoxy); an aryloxy group having preferably 6 to 12, more preferably 6 to 10, and particularly preferably 6 to 8 carbon atoms (e.g. phenyloxy); an acyl group having preferably 1 to 12, more preferably 2 to 10, and particularly preferably 2 to 8 carbon atoms (e.g. acetyl); an alkoxycarbonyl group having preferably 2 to 12, more preferably 2 to 10, and particularly preferably 2 to 8 carbon atoms (e.g. methoxycarbonyl); an acyloxy group having preferably 1 to 12, more preferably 2 to 10, and particularly preferably 2 to 8 carbon atoms (e.g. acetoxy); an acylamino group having preferably 1 to 10, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. acetylamino); a sulfonylamino group having preferably 1 to 10, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methanesulfonylamino); a sulfamoyl group having preferably

0 to 10, more preferably 0 to 6, and particularly preferably 0 to 4 carbon atoms (e.g. sulfamoyl and methylsulfamoyl); a carbamoyl group having preferably 1 to 10, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. carbamoyl and methylcarbamoyl); an alkylthio group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methylthio and ethylthio); a sulfonyl group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methanesulfonyl); a sulfinyl group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methanesulfinyl); a hydroxyl group, a halogen atom (e.g. fluorine, chlorine, bromine, and iodine), a cyano group, a sulfo group, a carboxyl group, a nitro group; and a heterocyclic group (e.g. imidazolyl, pyridyl). These groups may be further substituted. When there are two or more subsituents, they are the same or different.

Preferred among the above-listed substituents for the aliphatic hydrocarbon groups represented by R_1, are an alkoxy group, a carboxyl group, a hydroxyl group, and a sulfo group, and more preferred are a carboxyl group and a hydroxyl group.

Preferred among the aliphatic hydrocarbon groups represented by R_1, is an alkyl group, more preferably a chain alkyl group. Still more preferable examples thereof include methyl, ethyl, carboxymethyl, 1-carboxyethyl, 2-carboxyethyl, 1,2-dicarboxyethyl, 1-carboxy-2-hydroxyethyl, 2-carboxy-2-hydroxyethyl, 2-hydroxyethyl, 2-methoxyethyl, 2-sulfoethyl, 1-carboxypropyl, 1-carboxybutyl, 1,3-dicarboxypropyl, 1-carboxy-2-(4-imidazolyl)ethyl, 1-carboxy-2-phenylethyl, 1-carboxy-3-methylthiopropyl, 2-carbamoyl-1-carboxyethyl, and 4-imidazolylmethyl; and the particularly preferred are methyl, carboxymethyl, 1-carboxyethyl, 2-carboxyethyl, 1,2-dicarboxyethyl, 1-carboxy-2-hydroxyethyl, 2-carboxy-2-hydroxyethyl, 2-hydroxyethyl, 1-carboxypropyl, 1-carboxybutyl, 1,3-dicarboxypropyl, 1-carboxy-2-phenylethyl, and 1-carboxy-3-methylthiopropyl.

Preferred among the aryl groups represented by R_1, is an aryl group composed of a single ring or twin rings, each having 6 to 20 carbon atoms (e.g. phenyl and naphthyl); more preferred is an aryl group having 6 to 15 carbon atoms; and still more preferred is an aryl group having 6 to 10 carbon atoms.

The aryl group represented by R_1 may have a substituent, examples of which include an alkyl group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methyl and ethyl); an alkenyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. vinyl and allyl); and an alkynyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. propargyl), in addition to the above-listed groups as the substituents for the aliphatic hydrocarbon group represented by R_1.

Preferred among the substituents for the aryl group represented by R_1, are an alkyl group, an alkoxy group, a hydroxyl group, and a sulfo group; and more preferred are an alkyl group, a carboxyl group, and a hydroxyl group.

Specific examples of the aryl group represented by R_1 include 2-carboxyphenyl and 2-carboxymethoxyphenyl.

The heterocyclic group represented by R_1 is a residue of a 3- to 10-membered saturated or unsaturated heterocyclic compound containing at least one of N, O, and S atoms, which may be a single ring or a condensed ring with another ring.

Preferred among the heterocyclic groups, is a 5- or 6-membered aromatic heterocyclic group, with a more preferred example being a 5- or 6-membered nitrogen atom-containing aromatic heterocyclic group. Still more preferred is a 5- or 6-membered aromatic heterocyclic group containing one or two nitrogen atoms.

Specific examples of the heterocyclic group include pyrrolidinyl, piperidyl, piperazinyl, imidazolyl, pyrazolyl, pyridyl, and quinolyl. Preferred among these groups are an imidazolyl group and a pyridyl group.

The heterocyclic group represented by R_1 may have a substituent, examples of which include an alkyl group having preferably 1 to 8, more preferably 1 to 6, and particularly preferably 1 to 4 carbon atoms (e.g. methyl and ethyl); an alkenyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. vinyl and allyl); and an alkynyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. propargyl), in addition to the above-listed groups as the substituents for the aliphatic hydrocarbon group represented by R_1.

Preferred among the substituents for the heterocyclic group represented by R_1, are an alkyl group, an alkoxy group, a hydroxyl group, and a sulfo group; and more preferred are an alkyl group, a carboxyl group, and a hydroxyl group.

R_1 is preferably a hydrogen atom, or an alkyl group having 1 to 8 carbon atoms, and more preferred is a hydrogen atom, a methyl group, an ethyl group, a 1-carboxyethyl group, a 2-carboxyethyl group, a hydroxyethyl group, or a 2-carboxy-2-hydroxyethyl group. A hydrogen atom is especially preferred.

The alkylene groups represented by L_1 and L_2 are the same or different, and they may be straight chain, branched chain, or cyclic groups. Further, they may have a substituent, examples of which include an alkenyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. vinyl and allyl); and an alkynyl group having preferably 2 to 8, more preferably 2 to 6, and particularly preferably 2 to 4 carbon atoms (e.g. propargyl), in addition to the above-listed groups as the substituent for the aliphatic hydrocarbon group represented by R_1.

Preferred among the substituents for the alkylene groups represented by L_1 and L_2, are an aryl group, an alkoxy group, a hydroxy group, a carboxyl group, and a sulfo group; and more preferred are an aryl group, a carboxyl group,

and a hydroxyl group.

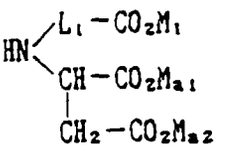
Preferred alkylene groups represented by L_1 and L_2 are groups whose alkylene moieties have 1 to 6 carbon atoms, and more preferably 1 to 4 carbon atoms. Still more preferred alkylene groups are substituted or unsubstituted methylene and ethylene groups.

Preferred specific examples of the alkylene group include methylene, ethylene, trimethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1,2-cyclohexylene, 1-carboxymethylene, carboxymethylmethylene, carboxyethylmethylene, hydroxymethylmethylene, 2-hydroxyethylmethylene, carbamoylmethylmethylene, phenylmethylene, benzylmethylene, 4-imidazolylmethylmethylene, and 2-methylthioethylmethylene; and more preferred are methylene, ethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1-carboxymethylene, carboxymethylmethylene, carboxyethylmethylene, hydroxymethylmethylene, benzylmethylene, 4-imidazolylmethylmethylene, and 2-methylthioethylmethylene; and still more preferred are methylene, ethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1-carboxymethylene, carboxymethylmethylene, hydroxymethylmethylene, and benzylmethylene.

The cation represented by M_1 or M_2 is an organic or inorganic cation, examples of which include an alkali metal ion (e.g. Li^+, Na^+, K^+, Cs^+), an alkali earth metal ion (e.g. Mg^{2+}, Ca^{2+}), an ammonium ion (e.g. ammonium, trimethylammonium, triethylammonium, tetramethylammonium, tetraethylammonium, tetrabutylammonium, 1,2-ethanediammonium), a pyridinium ion, an imidazolium ion, and a phosphonium ion (e.g. tetrabutylphosphonium). Preferred examples of M_1 and M_2 are an alkali metal ion and an ammonium ion, and more preferred are Na^+, K^+, and NH_4^+.

Preferred among the compounds represented by formula (I), are those represented by the following formula (I-a):

formula (I-a)



wherein L_1 and M_1 each have the same meanings as those in formula (I), and therefore their preferred ones are also same; M_{a1} and M_{a2} each have the same meanings as M_2 in formula (I).

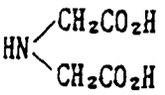
Preferred among the compounds represented by formula (I-a), are those in which L_1 is a substituted or unsubstituted methylene or ethylene group, and M_1, M_{a1}, and M_{a2} are any one of a hydrogen atom, an alkali metal, and an ammonium, respectively. More preferred compounds are ones in which L_1 is a substituted or unsubstituted methylene group, and M_1, M_{a1}, and M_{a2} are any one of a hydrogen atom, an alkali metal, and an ammonium, respectively. Particularly preferred compounds are ones in which L_1 is a substituted or unsubstituted methylene group having 1 to 10 total carbon atoms including its substituent, and M_1, M_{a1}, M_{a2} are any one of a hydrogen atom, Na^+, K^+, and NH_4^+, respectively.

Further, when the compound represented by formula (I) has asymmetric carbon atoms in the molecule, preferably at least one asymmetric carbon atom is in an L-form. When there are two or more asymmetric carbon atoms, the more numerous the L-form structures of the asymmetric carbon sections are, the more preferable it is.

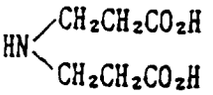
Specific examples of the compound represented by formula (I) are shown below, which do not limit the present invention.

Additionally, among the compounds, those compounds wherein L is annexed are ones wherein the asymmetric carbon section of the annexed part is in an L-form, and those wherein L is not annexed are mixtures of a D-form and a L-form.

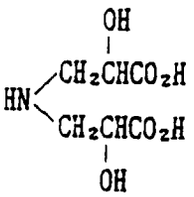
I－1



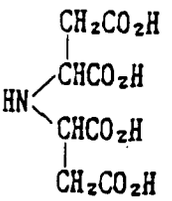
I－2



I－3



I－4



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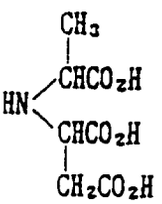
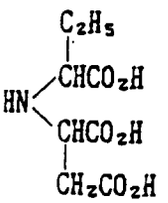


I－6



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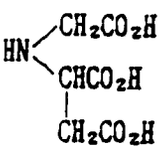

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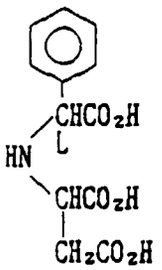

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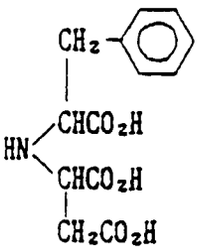
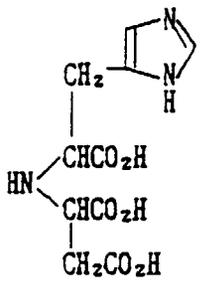


I－10



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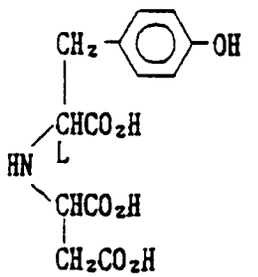

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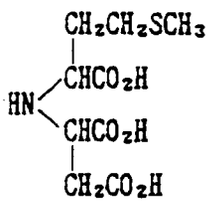

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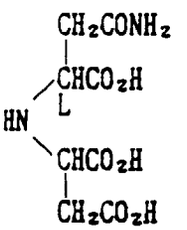

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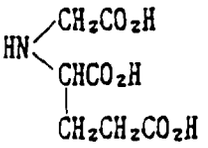

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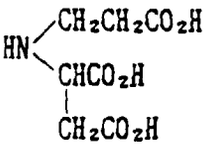

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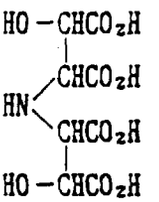

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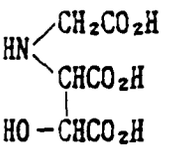

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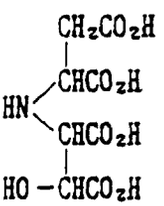

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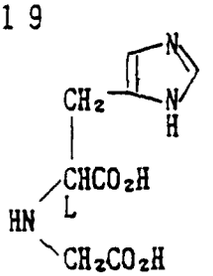

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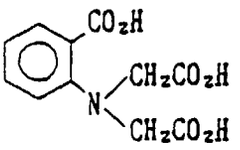

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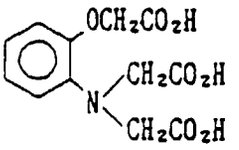

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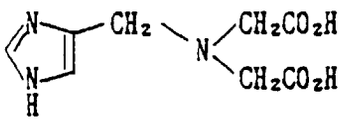

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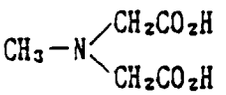

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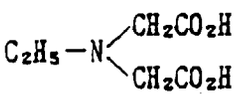

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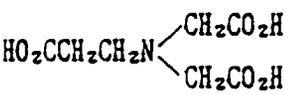

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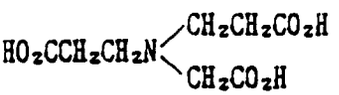

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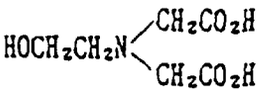

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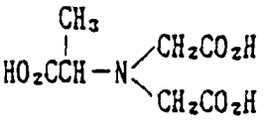

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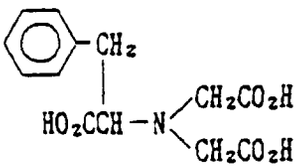

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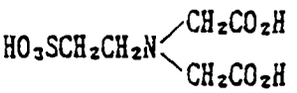

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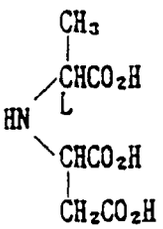

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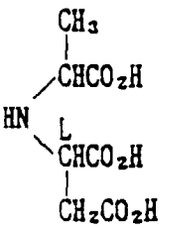

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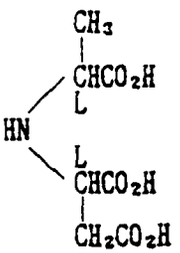

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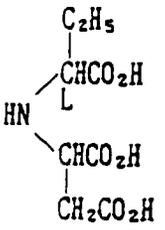

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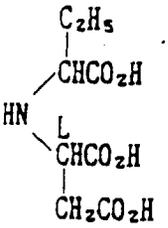

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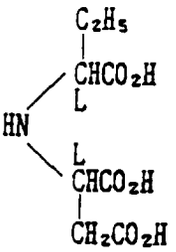

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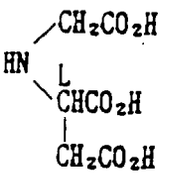

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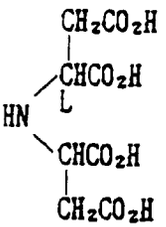

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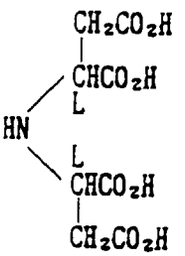

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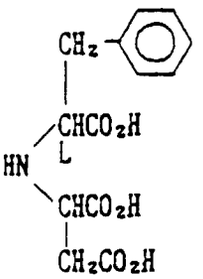

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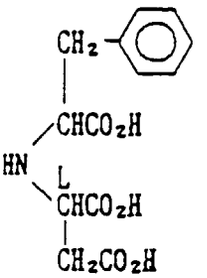

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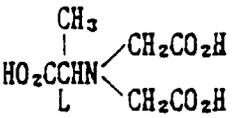

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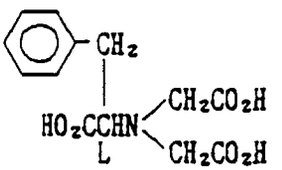

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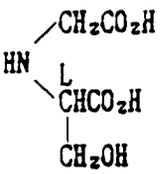

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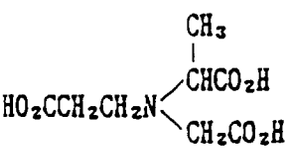
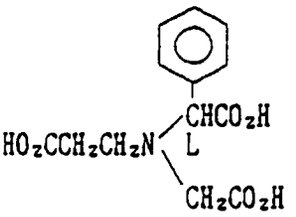


I-46



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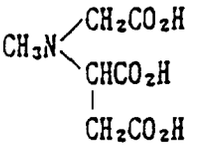

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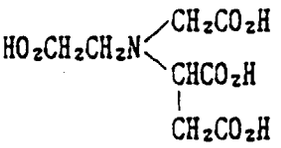

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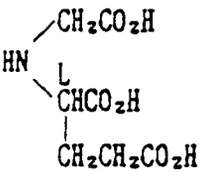

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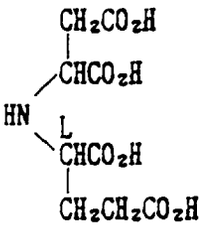

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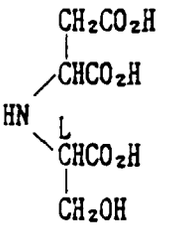

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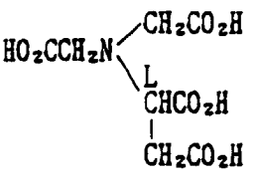
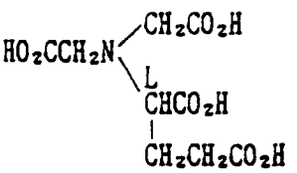


I-53



The above-listed compounds may be ones in which a hydrogen atom of the carboxyl group is substituted with a cation, respectively. In this case, the cation has the same meanings as defined for those represented by M_1 and M_2 in formula (I).

The compound represented by formula (I) for use in the present invention can be prepared according to the methods described in, for example, Journal of Inorganic and Nuclear Chemistry, Vol. 35, p. 523 (1973), Swiss patent No. 561504, DE-A-3912551(A1), DE-A-3939755(A1), DE-A-3939756(A1), JP-A-5-265159 ("JP-A" means unexamined published Japanese patent application), JP-A-6-59422 (methods for preparing L-forms of exemplified compounds I-42, I-43, I-46, I-52, and I-53 are described in the synthesis examples 1, 2, 3, 4 and 6), JP-A-6-95319 (methods for preparing L forms of exemplified compounds I-8, I-11, I-37, I-38, and I-40 are described in the synthesis examples 2 to 6), JP-A-6-161054, and JP-A-6-161065.

In the present invention, the replenisher is one that is added to each of the processing tanks, where processing is

carried out, in conformity with the processed amount of the light-sensitive material at the time of the development processing, to carry out the development processing continuously and stably. The components thereof are those that supplement exhausted components and consumed components.

In the present invention, the bleaching solution replenisher is prepared by adding a regenerating agent to the overflow. That is, the bleaching-solution replenisher comprises components required for the reuse of the overflow, which specifically include a bleaching agent, an organic acid, a pH adjustor, a rehalogenating agent, etc.

The bleaching regenerating agent solution constituting the present invention is added to the overflow from the bleaching bath for use in the present invention, to prepare the bleaching replenisher. The bleaching-regenerating-agent solution basically comprises components contained in the bleaching solution described in detail later. Specifically the bleaching-regenerating-agent solution can contain, a bleaching agent and an organic acid, as well as a rehalogenating agent, for example, a bromide, such as potassium bromide, sodium bromide, and ammonium bromide, or a chloride, such as potassium chloride, sodium chloride, and ammonium chloride. A plurality of rehalogenating agents can be used in combination. The concentration of the rehalogenating agent is generally 0.1 to 2 mol and preferably 0.2 to 1.5 mol, per liter of the bleaching solution. In addition, a nitrate, such as sodium nitrate and ammonium nitrate, boric acid, borax, sodium metaborate, acetic acid, sodium acetate, sodium carbonate, potassium carbonate, phosphorous acid, phosphoric acid, and such salts as sodium phosphate can be added. Further, a bleaching accelerator can be used in the bleaching-regenerating-agent solution for use in the present invention. As the bleaching accelerator, for example, can be mentioned various mercapto compounds described, for example, in US-A-3 893 858, GB-A-1 138 842, JP-A-53-141623, JP-A-53-95631, and JP-A-54-52534, disulfide compounds described in JP-A-53-95630, thiourea derivatives described in JP-B-45-8506 ("JP-B" means examined Japanese patent publication) and JP-B-49-42349, isothiourea derivatives described in JP-A-53-94927, thiazolidine derivatives described in JP-B-53-9854, thioamide compounds described in JP-A-42349, and dithiocarbamates described in JP-A-55-26506. The pH of the bleaching-regenerating-agent solution that is used in the present invention is generally in the range of 2.8 to 4.0, preferably 3.0 or higher but 4.0 or lower, and particularly preferably 3.1 to 3.9. As the pH adjustor, the above mentioned dicarboxylic acids as well as organic acids, inorganic acids, and alkalis can be used, and it is preferable to adjust the amount of acetic acid, nitric acid, sodium hydroxide, potassium hydroxide, ammonia, or the above mentioned dicarboxylic acids.

Generally, the regenerating agent is introduced into a separately provided storage tank for the overflow, where the solution thereof is prepared, and then it is transferred to a replenishment tank.

In the present invention, although the solution carried into the bleaching bath from the color-developing bath varies depending on the processor and the setting conditions, it is approximately constant, generally in the range of 30 to 100 ml/m^2, and preferably 40 to 90 ml/m^2.

In the present invention, when the bleaching replenisher is prepared by adding the bleaching agent to the overflow from the bleaching bath that results from the replenishment, it is characterized in that the amount of the regenerating agent is made smaller than the amount of the solution carried into the bleaching bath from the above color-development bath. That is, it is characterized by the following relationship.

Letting the amount of the color developer carried into the bleaching bath from the color-development bath, per square meter of the light-sensitive material to be processed, be A, and the amount of the regenerating agent to be added in the preparation of the bleaching replenisher required in the processing of a square meter of the light-sensitive material to be processed, be B, the following relationship is to be held:

$$A > B$$

Herein, since the amount of the bleaching replenisher required in the processing of a square meter of the light-sensitive material to be processed is equal to the amount of the overflow from the bleaching bath that results from the processing of a square meter of the light-sensitive material to be processed, the amount of the replenisher can be calculated as follows:

The amount of the replenisher (ml/m^2) = (the total of the overflow of the bleaching solution that results from the processing (ml))/(the total square meter (m^2) of the processed light-sensitive material)

As is described above, when the replenisher is prepared, a regenerating agent is added; the amount to be added B of the regenerating agent will be described later.

In the present invention, a ferric (iron (III)) complex salt of a compound represented by formula (I) may be added in the form of an isolated compound. Alternatively, the compound of formula (I) and a ferric salt (e.g. ferric nitrate, ferric chloride) may be added in a solution to coexist therein, and subjected to a complex formation in a processing solution.

Further, the compound of formula (I) for use in the present invention may be used singly or in a combination of two

or more kinds thereof.

In the present invention, the compound of formula (I) may be used somewhat in excess of the amount necessary to form a complex salt of ferric ion (e.g. 0.5, 1, or 2 times the molar amount per the ferric ion). When the compound is used in such an excess amount, preferably the excess amount is generally regulated to the range of 0.01 to 15 mol%.

The amount of 1,3-diaminopropanetetraacetic acid and/or ethylenediaminetetraacetic acid in the aminopolycarboxylic acid(s) of the iron(III) complex salt of the aminopolycarboxylic acid compound in the bleaching solution used in the present invention is preferably 1/2 or less, but 0 or more, and more preferably 1/3 or less, but 0 or more, in terms of molar fraction.

A ferric complex salt of an organic acid contained in a processing solution having bleaching capacity for use in the present invention may be used in the form of an alkali metal salt or an ammonium salt. Example alkali metal salts are a lithium salt, a sodium salt, and a potassium salt. On the other hand, example ammonium salts are an ammonium salt and a tetraethylammonium salt. In the present invention, the concentration of an ammonium ion in a processing solution having bleaching capacity is preferably 0 to 0.4 mol/l, and especially preferably 0 to 0.2 mol/l.

In the present invention, as the bleaching agent, the above iron complex salts of organic acids can be used singly or in combination of two or more.

In the present invention, preferably the bleaching solution contains a dicarboxylic acid, a hydrocarboxylic acid, or a sulfocarboxylic acid. These acid compounds refer to saturated carboxylic acids, unsaturated carboxylic acids, and aromatic carboxylic acids, or their alkali metal salts and ammonium salts, that have, in the molecule, a carboxylic group and further one carboxylic group, a hydroxyl group, or a sulfo group. In the present invention, a dicarboxylic acid, a hydroxycarboxylic acid, or a sulfocarboxylic acid represented by the below-shown formula (D) and their salts are preferable:

$$X\text{-}L\text{-}COOH \qquad \text{Formula (D)}$$

wherein L represents a saturated or unsaturated aliphatic group having 1 to 4 carbon atoms, and X represents a carboxyl group, a hydroxy group, or a 1-sulfocarboxymethyl group.

A preferable amount of this acid to be added is generally in the range of 0.1 to 2.0 mol and more preferably 0.3 to 1.5 mol, per liter of the bleaching solution.

Preferable examples of these acids are mentioned below, but the present invention is not limited to them: oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, malic acid, tartaric acid, phthalic acid, glycolic acid, diglycolic acid, aspartic acid, glutamic acid, sulfosuccinic acid, and the like. Among these, malonic acid, succinic acid, glycolic acid, glutaric acid, and maleic acid are particularly preferable and preferably two or more of them are used in combination. Particularly a combination of succinic acid with maleic acid or a combination of glycolic acid with succinic acid or malonic acid is most preferable.

The bleaching solution constituting the present invention can contain, in addition to the bleaching agent and the above compounds, a rehalogenating agent, for example, a bromide, such as potassium bromide, sodium bromide, and ammonium bromide, and a chloride, such as potassium chloride, sodium chloride, and ammonium chloride. Two or more of the rehalogenating agents may be used in combination. The concentration of the rehalogenating agent is generally 0.1 to 2 mol and preferably 0.2 to 1.5 mol, per liter of the bleaching solution. In addition, a nitrate, such as sodium nitrate and ammonium nitrate, boric acid, borax, sodium metaborate, acetic acid, sodium acetate, sodium carbonate, potassium carbonate, phosphorous acid, phosphoric acid, and such salts as sodium phosphate can be added.

Further, a bleaching accelerator can be used in the bleaching solution for use in the present invention. As the bleaching accelerator, can be used, for example, various mercapto compounds described, for example, in US-A-3 893 858, GB-A-1 138 842, JP-A-53-141623, JP-A-53-95631, and JP-A-54-52534, disulfide compounds described in JP-A-53-95630, thiourea derivatives described in JP-B-45-8506 and JP-B-49-42349, isothiourea derivatives described in JP-A-53-94927, thiazolidine derivatives described in JP-B-53-9854, thioamide compounds described in JP-A-42349, and dithiocarbamates described in JP-A-55-26506.

Preferably the bleaching solution for use in the present invention contains at least one of 1,2-benzoisothiazolin-3-one or its derivatives. Specific examples of these compounds are given below, which do not limit the present invention:

1,2-benzoisothiazolin-3-one, 2-methyl-1,2-benzoisothiazolin-3-one, 2-ethyl-1,2-benzoisothiazolin-3-one, 2-(n-propyl)-1,2-benzoisothiazolin-3-one, 2-(n-butyl)-1,2-benzoisothiazolin-3-one, 2-(sec-butyl)-1,2-benzoisothiasolin-3-one, 2-(t-butyl)-1,2-benzoisothiazolin-3-one, 2-methoxy-1,2-benzoisothiazolin-3-one, 2-ethoxy-1,2-benzoisothiazolin-3-one, 2-(n-propyloxy)-1,2-benzoisothiazolin-3-one, 2-(n-butyloxy)1,2-benzoisothiazolin-3-one, 5-chloro-1,2-benzoisothiazolin-3-one, 5-methyl-1,2-benzoisothiazolin-3-one, 6-ethoxy-1,2-benzoisothiazolin-3-one, 6-cyano-1,2-benzoisothiazolin-3-one, and 5-nitro-1,2-benzoisothiazolin-3-one.

A preferable amount of these compounds to be added is 0.001 to 1 g, more preferably 0.01 to 0.5 g, and particularly preferably 0.02 to 0.2 g, per liter of the bleaching solution. These compounds may be added in the form of salts, and they may be added as a combination of two or more.

The bleaching solution for use in the present invention preferably contains various antibacteria agents and mildew-

proofing agents. These antibacteria agents and mildewproofing agents are preferably at least one of benzoimidazole compounds, alkylguanidine compounds, succinic acid imide compounds, sulfimide compounds, isothiazolone compounds, hydroxybenzoate ester compounds, phenoxyalcohol compounds, and quaternary ammonium salts described in JP-A-8-339063, or aminoglycocides selected from the group consisting of genatamicins, amikacin, tobramycin, dibekacin, arbekacin, micronomicin, isepamicin, sisomicin, netilmicin, and astromicin. Inter alia, benzoisothiazolone compounds are more preferable and particularly 1,2-benzoisothiazolin-3-one is preferable. Further, two or more of these antibacteria agents and mildewproofing agents can be used in combination in various ratios.

Further, the bleaching solution for use in the present invention preferably contains derivatives of picolinic acid. Examples of the picolinic acid derivatives include, in addition to picolinic acid, 2,6-pyridinedicarboxylic acid, 4-chloro-2,6-pyridinedicarboxylic acid, 4-hydroxy-2,6-pyridinedicarboxylic acid, 4-methoxy-2,6-pyridinedicarboxylic acid, 2,3-pyridinedicarboxylic acid, 2,4-pyridinedicarboxylic acid, and 2,5-pyridinedicarboxylic acid, and those described in JP-A-8-339063. Out of these, picolinic acid, 2,6-pyridinedicarboxylic acid, and 4-chloro-2,6-pyridinedicarboxylic acid are preferable, with particular preference given to 2,6-pyridinedicarboxylic acid. The amount of these compounds to be added is generallly suitably 0.005 to 3.0 mol/liter, preferably 0.01 to 2.0 mol/liter, and particularly preferably 0.05 to 1.50 mol/liter.

Further, in the bleaching solution for use in the present invention, preferably a sulfinic acid compound represented by the following formula (S) is used:

$$R\text{-}(SO_2M)_n$$

wherein R represents an alkyl group, an alkenyl group, an aralkyl group, a cycloalkyl group, an aryl group, or a heterocyclic group, M represents a cation, and n is 1 or 2.

It is already known to add sulfinic acid to a processing solution; for example, a processing method is described in JP-A-1-230039, wherein, when processing is carried out using an aromatic primary amine color-developing agent, at least one step of the processing steps contains sulfinic acid. In that method, it is described that sulfinic acid may be added to a bleaching solution, but it is not described that sulfinic acid is added in a bleaching solution itself, and stain and fogging that are problems addressed by the present invention are not described. In the present invention, it has been found that sulfinic acid compounds are effective with respect to stain and fogging. Details of the contents of its action are not fully clear, but as one reason, it is conjectured that generation of tar resulting from the oxidation of a developing agent, which generation seems to be a cause of stain, is prevented by its own reducing action. Further, since it is considered that the reducing action has naturally an effect of weakening the excess oxidising power that contributes to fogging, it seems that sulfinic acid compounds are particularly effective for achieving the object of the present invention.

Hereinbelow, the compound represented by formula (S) is described in detail.

R represents a substituted or unsubstituted alkyl group (e.g. methyl, ethyl, n-propyl, hydroxyethyl, sulfoethyl, carboxyethyl, and methoxyethyl), a substituted or unsubstituted alkenyl group (e.g. allyl and butenyl), a substituted or unsubstituted aralkyl group (e.g. benzyl, phenetyl, 4-carboxyphenylmethyl, and 3-sulfophenylmethyl), a substituted or unsubstituted cycloalkyl group (e.g. cyclohexyl), a substituted or unsubstituted aryl group (e.g. phenyl, 4-methylphenyl, naphthyl, 3-carboxyphenyl, 4-methoxyphenyl, 3-sulfophenyl, 4-carboxymethoxyphenyl, 3-carboxymethoxyphenyl, 4-carboxyethoxyphenyl, 4-sulfoethoxyphenyl, 4-carboxymethylphenyl, and 4-(N-carboxymethyl-N-methyl)phenyl), or a substituted or unsubstituted heterocyclic group (e.g. pyridyl, furyl, thienyl, pyrazolyl, and indolyl).

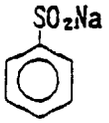
M represents a cation, for example, a hydrogen atom, an alkali metal, an alkali earth metal, a nitrogen-containing organic base, or ammonium group. The alkali metal includes Na, K, Li, and the like; and the alkali earth metal includes Ca, Ba, and the like; and the nitrogen-containing organic base includes usual amines capable of forming bases with sulfinic acid; and the ammonium group includes an unsubstituted ammonium group, a tetramethylammonium group, and the like.

In formula (S), when the group represented by R has a substituent, examples thereof are a nitro group, a halogen atom (e.g. chlorine and bromine), a cyano group, an alkyl group (e.g. methyl, ethyl, propyl, carboxymethyl, carboxyethyl, carboxypropyl, sulfoethyl, sulfopropyl, and dimethylaminoethyl), an aryl group (e.g. phenyl, naphthyl, carboxyphenyl, and sulfophenyl), an alkenyl group (e.g. allyl and butenyl), an aralkyl group (e.g. benzyl and phenetyl), a sulfonyl group (e.g. methanesulfonyl and p-toluenesulfonyl), an acyl group (e.g. acetyl and benzoyl), a carbamoyl group (e.g. unsubstituted carbamoyl and dimethylcarbamoyl), a sulfamoyl group (e.g. unsubstituted sulfamoyl, methylsulfamoyl, and dimethylsulfamoyl), a carbonamido group (e.g. acetamido and benzamido), a sulfonamido group (e.g. methanesulfonamido and benzenesulfonamido), an acyloxy group (e.g. acetyloxy and benzoyloxy), a sulfonyloxy group (e.g. methanesulfonyloxy), a ureido group (e.g. unsubstituted ureido), a thioureido group (e.g. unsubstituted thioureido and methylthioureido), a carboxylic acid or its salt, a sulfonic acid or its salt, a hydroxy group, an alkoxy group (e.g. methoxy, ethoxy, carboxyethoxy, carboxymethoxy, sulfoethoxy, and sulfopropyloxy), an alkylthio group (e.g. methylthio, carboxymethylthio, and sulfoethylthio), and an amino group (e.g. unsubstituted amino, dimethylamino, and N-carboxyethyl-

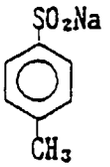
N-methylamino).

Specific examples of the compound represented by formula (S) are shown below.

S – 1



S – 2



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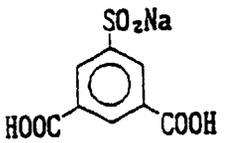
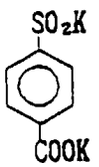
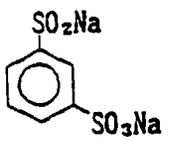


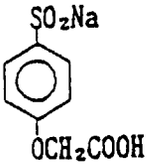
S – 4



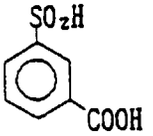
S – 5



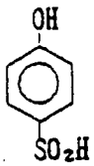
S-6



S-7



S-8



S-9

$CH_3SO_2NH_4$

S-10

$CH_3CH_2SO_2NH_4$

S-11

CH_3SO_2Na

S-12

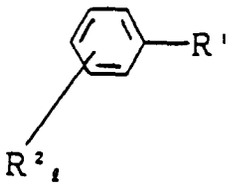
$CH_3CH_2SO_2Na$

Out of them, S-2, S-4, S-7, and S-11 are preferable, with particular preference given to S-7. A suitable amount of these compounds to be used is generally 0.005 to 0.1 mol, preferably 0.01 to 0.08 mol, and more preferably 0.015 to 0.05 mol, per liter of the bleaching solution. Two or more of them may be used in combination.

Further, in the bleaching solution for use in the present invention, preferably use is made of a surfactant selected from the group consisting of those represented by the following formulae (II) and (III):

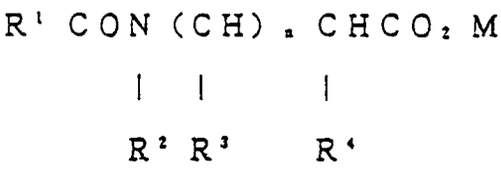
$$RO(CH_2CH_2O)_m[CH_2CH(OH)CH_2O]_nX \qquad \text{Formula (II)}$$

wherein R represents a straight-chain or branched and optionally substituted alkyl group having 8 to 25 carbon atoms or



in which R^1 represents a straight-chain or branched alkyl group having 6 to 20 carbon atoms, R^2 represents a hydrogen atom or a straight-chain or branched alkyl group having 1 to 20 carbon atoms, l is an integer of 0 to 4; and wherein when n is 0, m is 40 to 200, when n is 5 to 9, m is 10 to 100, when n is 10 or more, m is 0 to 100, n being 0 or an integer of 5 to 50, and X represents a hydrogen atom or SO_3M in which M represents a hydrogen atom or an alkali metal.

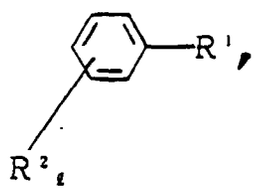
Formula (III):



wherein R^1 represents an optionally substituted alkyl group, alkenyl group, or alkoxyalkyl group, R^2 represents a hydrogen atom, an alkyl group, a hydroxyalkyl group, or an alkoxy group, R^3 and R^4 independently represent a hydrogen atom, a hydroxyl group, an optionally substituted alkyl group, or CO_2M^1, M and M^1 each represent a hydrogen atom or an alkali metal, and n is 0 or 1.

It is expected that surfactants have an effect of dispersing and solubilizing the above-described tar, to prevent the tar from adhering to the light-sensitive material to be processed, but it is an unexpected matter that surfactants have, in addition to the above effect, an effect of preventing fogging, which is one object of the present invention. Hereinbelow, surfactants that have shown a particularly high effect, that is, the compounds represented by formula (II) or (III), are described.

In formula (II), when R is a straight-chain or branched and optionally substituted alkyl group having 8 to 25 carbon atoms, preferably R has 9 to 18 carbon atoms and particularly preferably 10 to 16 carbon atoms. When R represents



R^1 represents a straight-chain or branched alkyl group having 6 to 20 carbon atoms, preferably 8 to 16 carbon atoms, and more preferably 9 to 12 carbon atoms. R^2 represents a straight-chain or branched alkyl group having 1 to 20 carbon atoms, and particularly preferably a methyl group, an ethyl group, an n- or i-propyl group, an n-, i-, or t-butyl group, a pentyl group, an n- or t-octyl group, or a nonyl group.

When n is 0, m is an integer of 40 to 200, preferably 50 to 150, and more preferably 80 to 130. When n is from 5 to 9, m is an integer of 10 to 100, preferably 20 to 80, and more preferably 30 to 70. When n is 10 or more, m is an integer of 0 to 100, preferably 5 to 50, and more preferably 10 to 40.

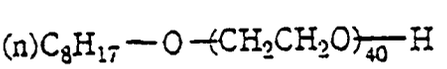
n is 0 or an integer of 5 to 50, preferably 0 or an integer of 5 to 30, and particularly preferably 0 or an integer of 10 to 20.

X represents a hydrogen atom or SO_3M, preferably a hydrogen atom, and M represents a hydrogen atom or an alkali metal, and preferably sodium.

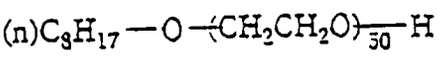
Preferable specific compound examples [II]-1 to [II]-52 of the compound (II) are shown below, but the surfactants

used in the present invention are not limited to them:

〔II〕 − 1



〔II〕 − 2



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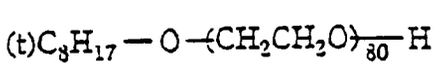
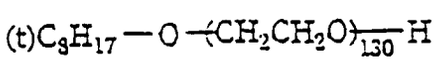
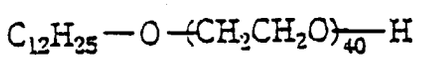


〔II〕 − 4



〔II〕 − 5



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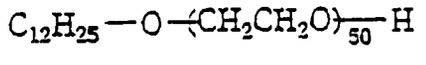
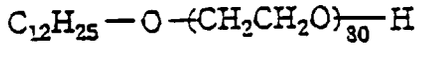
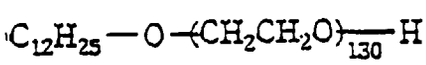


〔II〕 − 7



〔II〕 − 8



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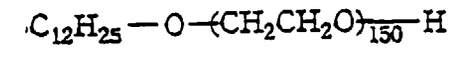

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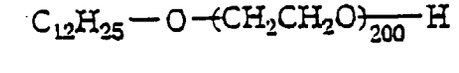
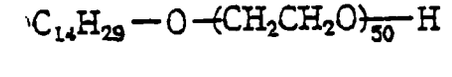


〔II〕 −11



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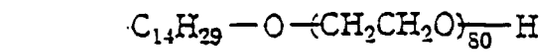
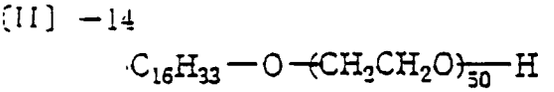


〔II〕 −13

〔II〕 −14

〔II〕 −15



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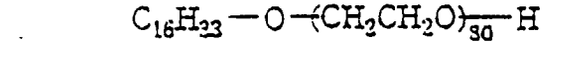
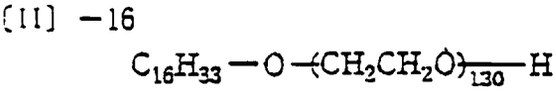
〔II〕 −17



〔II〕 −18



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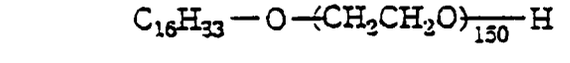
〔II〕 −20



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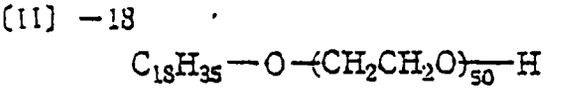

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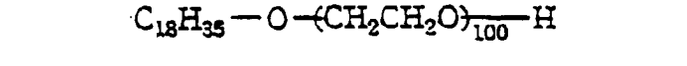
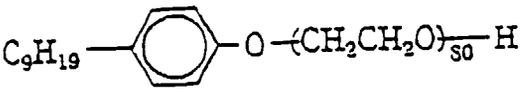
〔II〕 −23



〔II〕 −24



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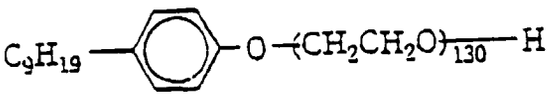

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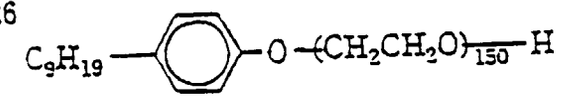

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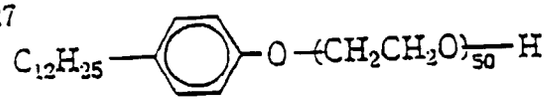

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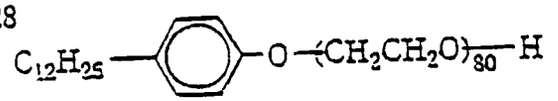

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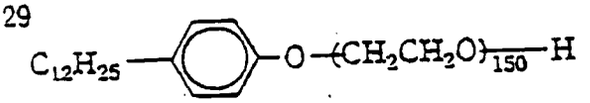

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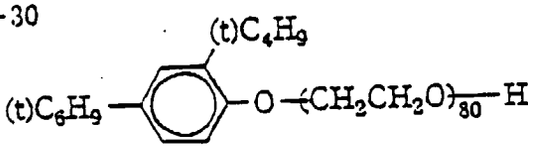

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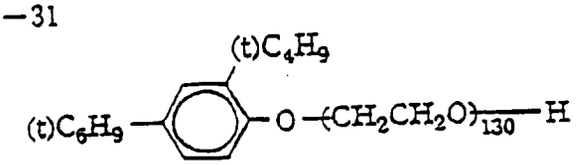

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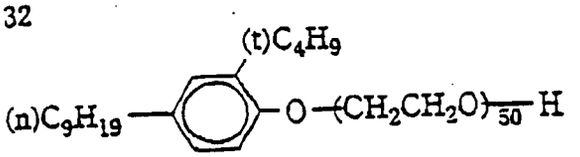

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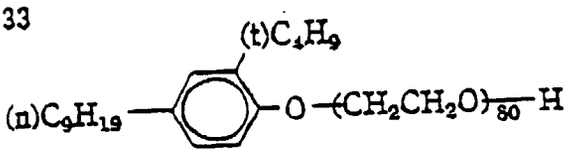

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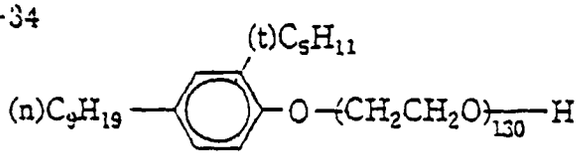

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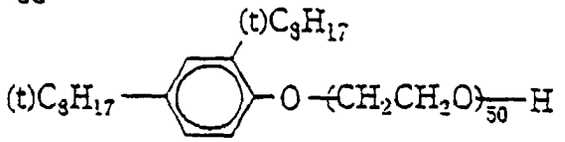

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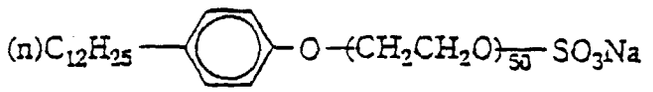

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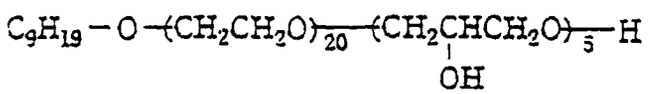

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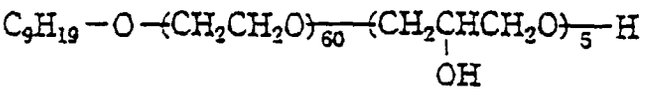

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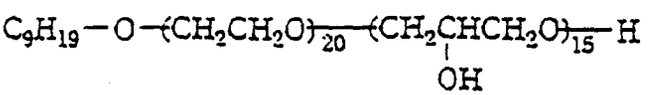

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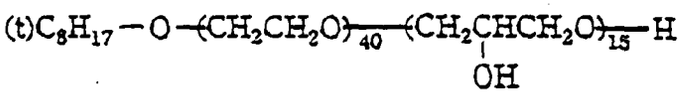

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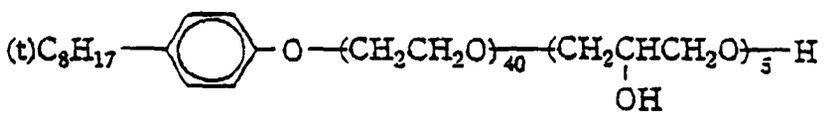

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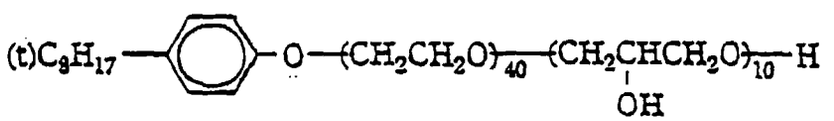

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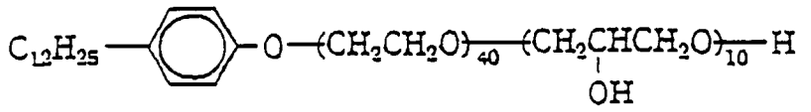

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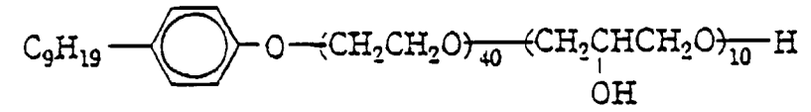

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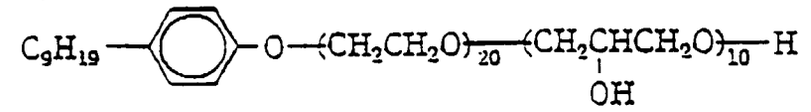

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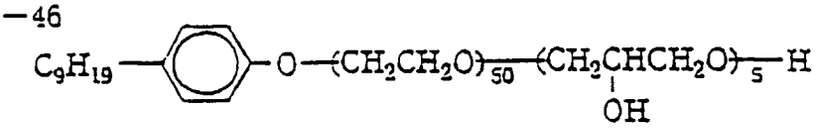

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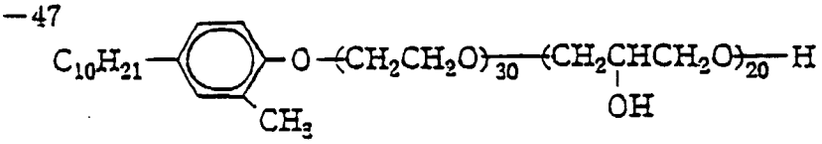

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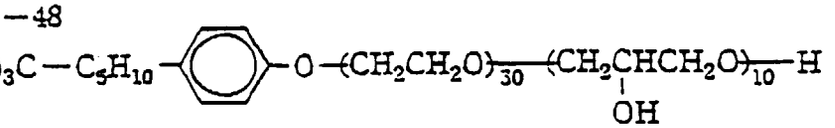

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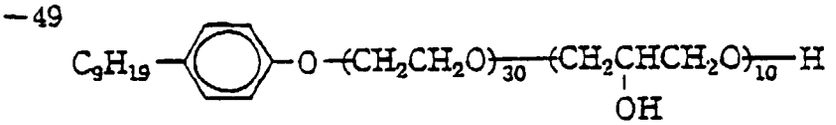

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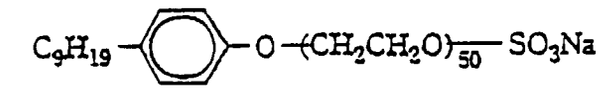

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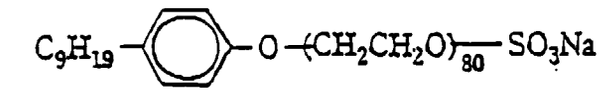
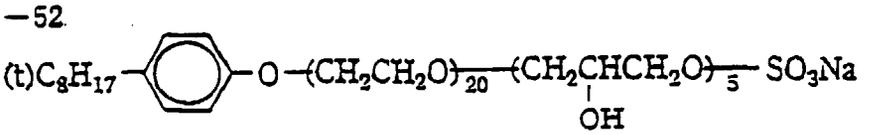


〔II〕 −52

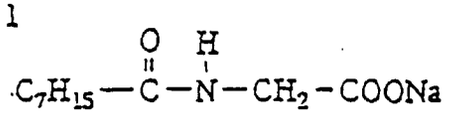


In formula (III), R^1 represents an optionally substituted alkyl group, alkenyl group, or alkoxyalkyl group having 3 to 30 carbon atoms, preferably 5 to 18 carbon atoms, and more preferably 8 to 16 carbon atoms. Preferable substituents thereof are, for example, an alkyl group, an alkenyl group, an alkoxyalkyl group, a carboxyalkyl group, a sulfoalkyl group, a dicarboxyalkyl group, and a sulfocaboxyalkyl group, and particularly preferable examples include a dicarboxymethyl group and a sulfocarboxymethyl group. R^2 represents a hydrogen atom, an alkyl group, a hydroxyalkyl group, an alkoxy

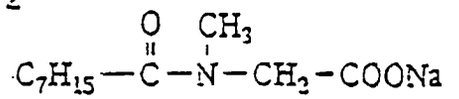
group, or an alkoxyalkyl group, R^2 and R^4 independently represent a hydrogen atom, a hydroxyl group, an optionally substituted alkyl group, such as a carboxyalkyl group, or CO_2M^1, M and M^1 each represent a hydrogen atom or an alkali metal, and n is 0 or 1. In particular, a lower carboxyalkyl group, such as a carboxymethyl group and a carboxyethyl group, and a lower alkyl group, such as a methyl group, an ethyl group, and a propyl group, are preferable.

Preferable specific compound examples [III]-1 to [III]-56 of the compound (III) are shown below, but the surfactants used in the present invention are not limited to them:

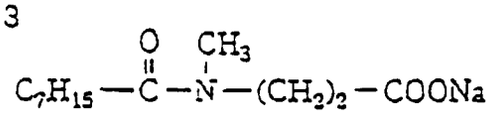
[III] − 1



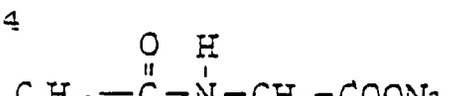
[III] − 2



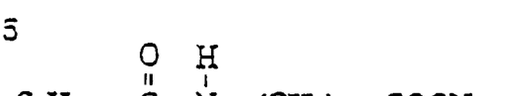
[III] − 3



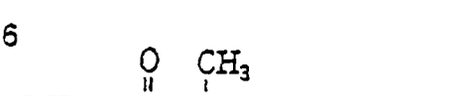
[III] − 4



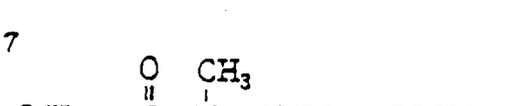
[III] − 5



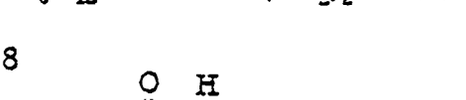
[III] − 6



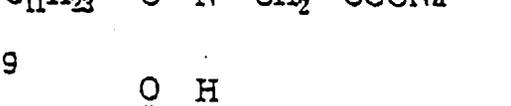
[III] − 7



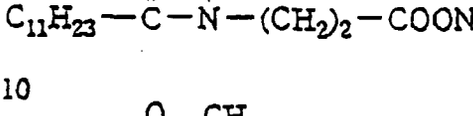
[III] − 8



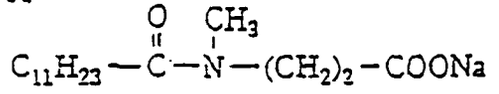
[III] − 9



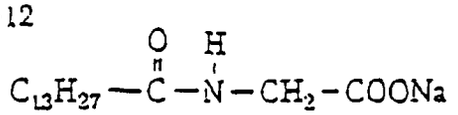
[III] − 10



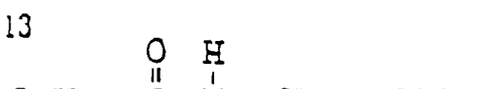
(III) -11



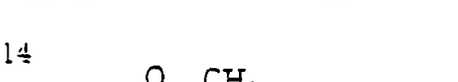
(III) -12



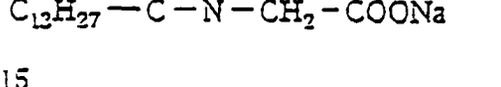
(III) -13



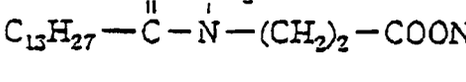
(III) -14



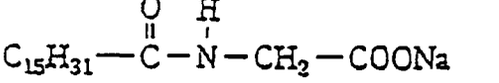
(III) -15



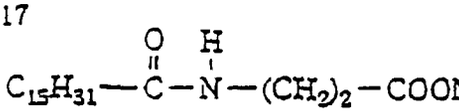
(III) -16



(III) -17



(III) -18



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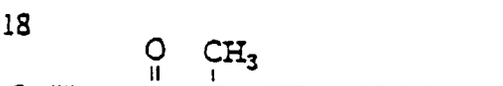
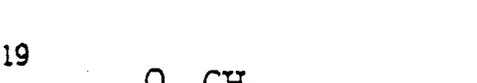


(III) -20



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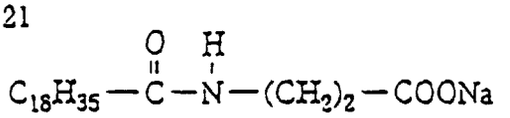

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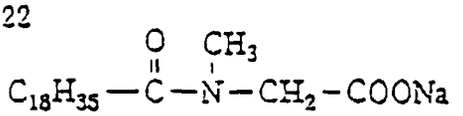

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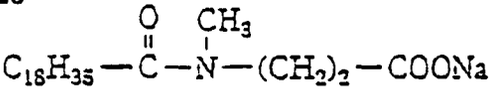

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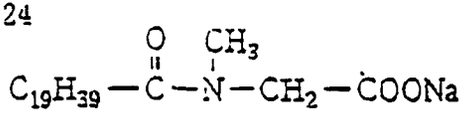

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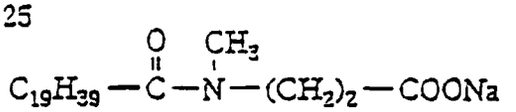

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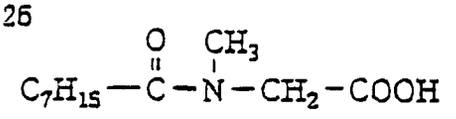

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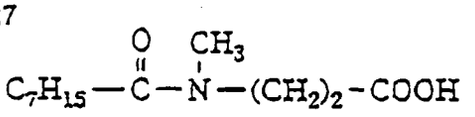

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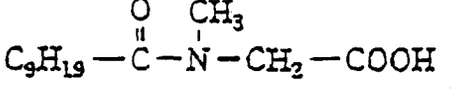

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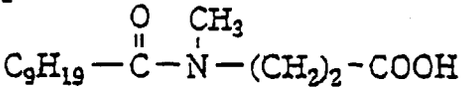

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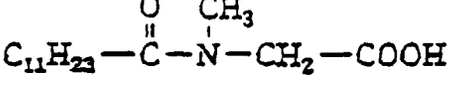

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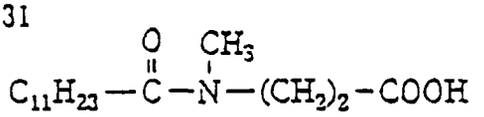

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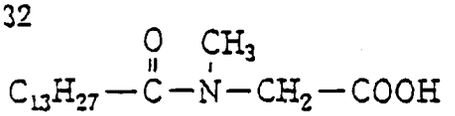

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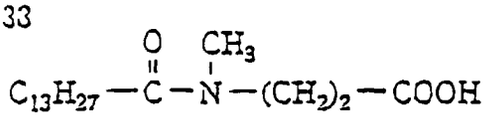

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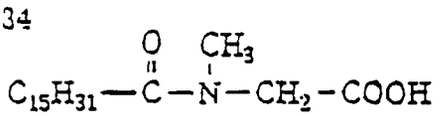

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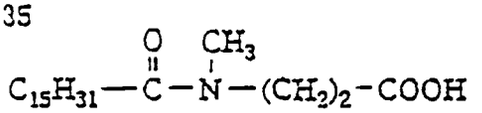

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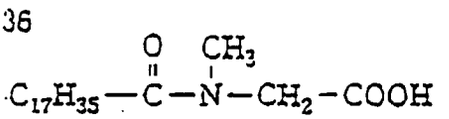

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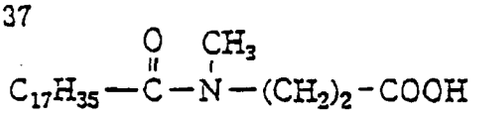

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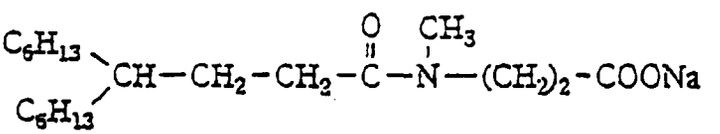

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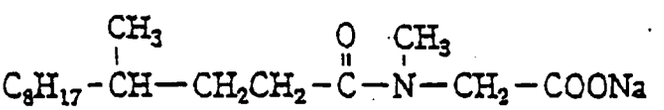

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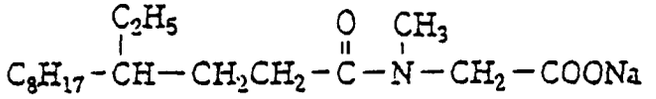

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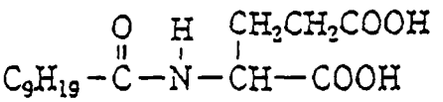

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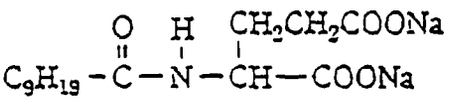

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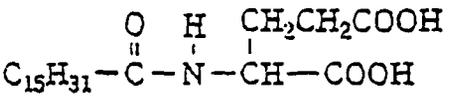

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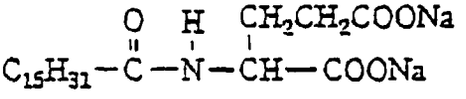

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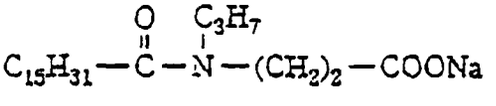

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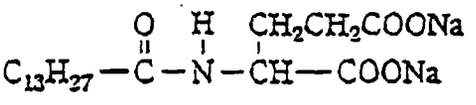

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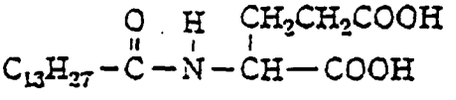

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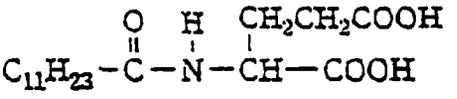

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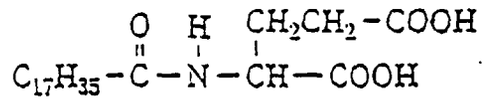

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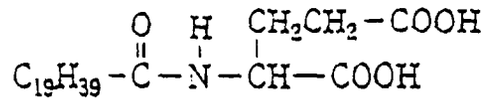

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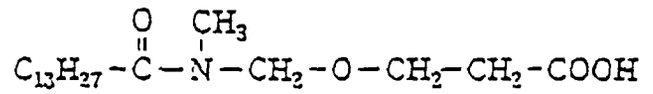

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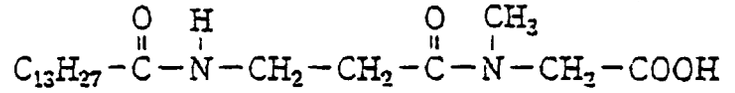

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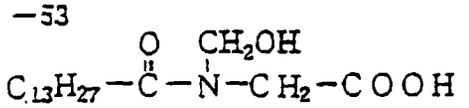

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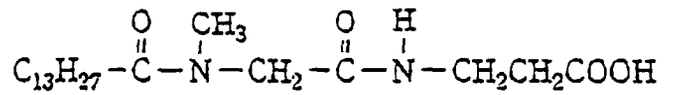

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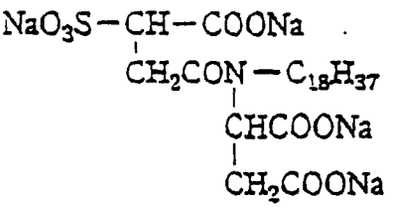

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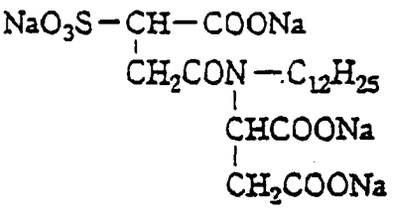


The amount of the surfactants of formula (II) or (III) to be added is generally 0.02 to 5 g, preferably 0.1 to 3 g, and more preferably 0.2 to 2 g, per liter of the bleaching solution. A combination of the surfactants of formulae (II) and (III) can increase the effect more, and in that case the amount of each of them to be added is generally 0.01 to 3 g, preferably 0.04 to 2 g, and more preferably 0.1 to 1 g, per liter of the bleaching solution, with the total amount being generally 0.02 to 5 g, preferably 0.1 to 3 g, and more preferably 0.2 to 2 g, per liter of the bleaching solution.

A replenishing solution for the solution having a bleach capacity, basically contains each of components in such a concentration as calculated according to the following equation:

$$C_R = C_T \times (V_1 + V_2)/V_1 + C_P$$

C_R: Concentration of a component in a replenishing solution,
C_T: Concentration of a component in a mother liquid (processing tank solution),
C_P: Concentration of a component consumed during a processing,
V_1: Replenishing amount (ml) of the replenishing solution having bleach capacity, per m^2 of the light-sensitive material,
V_2: Amount (ml) of solution carried into by m^2 of the light-sensitive material from a preceding bath to a subsequent bath.

Each of the concentrations of components in a mother liquid can be kept constant by the above-described replenishing solution.

In the present invention, the amount of the bleaching agent to be used is suitably generally 0.005 to 3.0 mol/l, preferably 0.02 to 2.0 mol/l, and particularly preferably 0.05 to 1.50 mol/l.

The pH of the solution is suitably in the range of generally 2.9 to 7.5, preferably 3.1 to 6.5, and particularly preferably 3.3 to 5.5.

As the pH adjustor, an organic or inorganic acid or alkali can be used, and it is preferable to adjust the amount of acetic acid, nitric acid, sodium hydroxide, potassium hydroxide, ammonia, or the above-mentioned dicarboxylic acids.

In the present invention, the longer, in time, the bleaching step is, the more remarkable the effect of the present invention is. In the case of color photographing materials, a suitable processing time is in the range of generally 40 sec to 10 min, preferably 1 min 30 sec to 8 min, and particularly preferably 2 to 7 min. In the case of print materials, a suitable processing time is in the range of generally 10 sec to 3 min, preferably 15 sec to 2 min, and more preferably 20 sec to 1 min 45 sec.

In the present invention, when the bleaching solution is processed continuously by replenishing it, preferably the pH value of the bleaching replenisher is set to be lower, by about 0.1 to 1.0, than that of the bleaching solution. Further, the replenishment is also preferably carried out by using a replenisher prepared by regenerating the overflow.

In the present invention, the amount of the overflow from the bleaching bath corresponds substantially to the replenishment rate to the bleaching bath, and it is, in the case of color photographing materials, generally 100 to 2,000 ml, preferably 150 to 1,500 ml, and more preferably 300 to 1,000 ml, per square meter of the light-sensitive material to be processed, and in the case of print materials, generally 20 to 900 ml, preferably 25 to 500 ml, and more preferably 30 to 200 ml. The term "overflow" means the bleaching solution taken out from the bleaching bath for the renewal involved in the replenishment of the solution described above, and it does not necessarily mean one that overflows in its phenomenon. The proportion of the overflow that is reused is generally 0.1 to 1, preferably 0.2 to 1, and more preferably 0.5 to 1, assuming the entirety to be 1.

Now, the regeneration of the overflow of the bleaching solution in the present invention is described.

In the bleaching process in the present invention, a bleaching-solution-regenerating-agent solution is added to the overflow, to make a bleaching replenisher, and when it is used as a replenisher, the effect of the present invention is remarkable. First, replenishment corresponding to the processed amount of the light-sensitive material is made for the processing tank, and an overflow corresponding to the replenishment rate is discharged from the bleaching tank. Although the overflow may be, for example, pumped out, the overflow can be taken out simply by forming a notch or hole in an upper part of the bleaching tank. The overflow is temporary stored in a tank outside the bleaching tank, and when a certain amount is stored, it is processed batchwise.

In the bleaching solution, developed silver that results from the reduction of the silver halide in the light-sensitive material with the developing agent in the developing bath, is oxidized with an oxidizing agent, called a bleaching agent, to silver ions. At that time, the bleaching agent is reduced in an amount equivalent to the oxidized silver. At the time of regeneration, the reduced bleaching agent is oxidized with oxygen in the air introduced into the bleaching solution by aeration, to turn (restore) the reduced bleaching agent into the original bleaching agent. This aeration step can be carried out in the processing tank directly.

For the aeration, a means known in the art can be used, and, for example, blowing of air into a liquid having a bleaching capacity, or absorption of air by using an ejector, can be used.

When air is blown, preferably air is discharged into the liquid through aeration tubes having fine pores.

For the aeration, those described in Z-121, Using Process, C-41, third edition, (1982), pages BL-1 to BL-2, published by Eastman Kodak Co., can be used.

The regeneration operation of the overflow of the bleaching solution can be carried out by adding the above-described bleaching-solution-regenerating agent to the overflow that has been subjected to the above aeration, and the resulting solution can be used as a replenisher. The bleaching-solution-regenerating agent is made up basically of the same components as the replenisher and the working solution, and the concentration thereof is generally higher than that of the replenisher. The addition of the bleaching-solution-regenerating agent makes the overflow that has been

subjected to aeration reusable as a replenisher.

In this case, the amount of the bleaching-solution-regenerating-agent solution is preferably 0.03 to 0.2 times, and more preferably 0.04 to 0.15 times, the amount of the overflow of the bleaching solution. In the case of color photographing materials, the amount of the bleaching-solution-regenerating-agent solution is preferably 0.03 to 0.1 times, and more preferably 0.04 to 0.09 times, the amount of the overflow of the bleaching solution. In the case of color print materials, the amount of the bleaching-solution-regenerating-agent solution is preferably 0.05 to 0.2 times, and more preferably 0.07 to 0.15 times, the amount of the overflow of the bleaching solution. If the amount is too small, the amount of the solution is decreased due to the concentration or the like, or the components of the developing solution are increased relatively, which likely leads to a risk of crystallization and precipitation. On the other hand, if the amount is too large, the solution is increased at the time of the regeneration, and the merit that the regeneration of the overflow reduces the waste liquor is lost.

Preferably the amount of the regenerating agent used, per square meter of the light-sensitive material to be processed, becomes smaller than the amount of the solution carried over from the color-developing bath, per that area. That is, the amount of the regenerating agent used, per square meter of the light-sensitive material to be processed, is preferably 0.96 times or less (the volume ratio B/A, wherein A and B are as defined above), more preferably 0.92 times or less, and particularly preferably 0.88 times or less, the amount of the solution carried over from the color-developing bath, per that area. As is described above, if the amount is too small, problems also arise, and therefore preferably the amount of the regenerating agent used, per square meter of the light-sensitive material to be processed, is 0.60 times or more, the amount of the solution carried over from the color-developing bath, per that area. The lower limit of the amount of the solution of the bleaching-solution-regenerating agent is preferably 18 ml or more, and more preferably 24 ml or more, per square meter of the light-sensitive material to be processed.

Generally, for the solution in the bleaching step, if the ammonium salts in the formulation accumulate in rivers, lakes, and ponds, it is known that the water is made eutrophic, to affect the environment. In the present invention, the ammonium salts can be replaced with alkali metal salts. Specifically, instead of the ammonium salts, the sodium salt and potassium salt of an organic acid ferric complex salt, potassium bromide, sodium bromide, potassium nitrate, sodium nitrate, and the like are preferably used.

Further, preferably the ammonia water used in adjusting the pH is changed to potassium hydroxide or sodium hydroxide.

Conventionally, the great reason why ammonium salts are used in a liquid having a bleaching capacity is to increase the bleaching speed. However, in the system containing a bleaching accelerator as in the present invention, since even alkali metal salts secure satisfactory speed, salts other than ammonium salts can be used without any problems.

In the present invention, preferably a processing step of washing is provided after the bleaching step. The pH of the processing step of washing is preferably 3.5 to 8.0, more preferably 3.8 to 7.0, and further more preferably 4.0 to 6.0.

The iron complex diffused in the light-sensitive layers of the light-sensitive material to be processed during the bleaching is washed out from the light-sensitive layers by this washing after the bleaching. At that time, the iron complex must be removed from the gelatin films forming the light-sensitive layers, with the complex structure kept stably. However, if the iron complex is low in stability, the complex dissociates in the films, and the remained iron causes stain.

The iron(III) complex of the monoamine compound represented by formula (I) for use in the present invention described above is less stable, that is, small in the stability constant of iron complex, in comparison with iron(III) complexes of ethylenediaminetetraacetic acid or 1,3-diaminopropanetetraacetic acid, which are hitherto widely used diamine compounds. The stability constant and magnitude thereof mentioned herein is described in detail in "Nyumon Chelate Kagaku", written by Kagehei Ueno (Nanko-do), page 122.

The present inventors have found that the above problems can be avoided only by controlling the pH of the washing bath after the bleaching step, as described above.

Further, it has been found that the effect obtained by controlling the pH is also effective in preventing the precipitation of iron hydroxide, which results from the dissociation of the iron complex in the washing bath, and which is unpreferable in view of the processing operation.

The control of the pH of the washing water may be carried out in any way known hitherto, and the method of controlling the pH of the washing water is not limited in the present invention. For example, there are a method wherein an acid or an alkali is used to control the pH, a method wherein an ion exchanger is used, and a method wherein an acid or an alkali produced by electrolysis is used. Particularly preferably the pH is controlled with an inorganic acid, such as sulfuric acid and nitric acid;, an organic acid, such as acetic acid and citric acid; an alkali metal salt, an alkali earth metal salt, or ammonia. This pH control is preferably carried out by automatic control using a pH-stat or the like.

Now, other processings used in the present invention are described in order.

Preferable processing steps in the present invention are listed below, but the present invention is not limited to them.

(1) Color-development - bleaching - fixing - washing - stabilizing - drying
(2) Color-development - bleaching - bleach-fix - fixing - washing - stabilizing - drying
(3) Color-development - bleaching - bleach-fix - washing - stabilizing - drying
(4) Color-development - bleaching - washing - fixing - washing - stabilizing - drying
(5) Color-development - bleach-fix - washing - stabilizing - drying
(6) Color-development - stopping - washing - bleaching - fixing - washing - stabilizing - drying

In the above processing steps, the washing step prior to the stabilization can be omitted. The final stabilizing bath can also be omitted.

The light-sensitive material that can be applied to the present invention may be any color light-sensitive materials, with preference given to color negative films, color reversal films, or color print papers.

If a color reversal light-sensitive material is processed, prior to the above steps, black-and-white development, reversal exposure or processing using a reversal bath, and, if necessary, a washing step are carried out.

For the processing solution used in processing color negative films or color reversal films, reference can be made to the description in JP-A-5-34887, column 81, line 8 to column 93, line 17.

Particularly, as the color developer, solutions containing, as a preservative, a substituted hydroxylamine, as described in JP-A-3-158849 or JP-A-3-174152 are preferable, and in particular, solutions containing a hydroxylamine having a sulfoalkyl group as a substitutent are preferable. Also solutions containing, as a chelating agent, diethylenetriaminepentaacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, or 4,5-dihydroxybenzene-1,3-disulfonic acid are preferable. The replenisher of the color developer is preferably one whose bromide ion concentration is lowered to 0.004 mol/liter or less and particularly preferably 0.002 mol/liter or less, in view of the reduction of the replenishment rate. As preferable examples of the color developer, can be mentioned color developers and color development replenishers of Process CN-16X, CN-16Q, and CN-16FA (trade name) manufactured by Fuji Photo Film Co., Ltd., a color developer and a color-development replenisher of Process CR-56P (trade name) manufactured by Fuji Photo Film Co., Ltd.

In the processing of the present invention, the color developer is preferably replenished with a color development replenisher. The color development replenisher contains the compounds contained in the color developer. The role of the color development replenisher is to replenish the color developer with compounds that have been decreased due to the processing of the light-sensitive material, and due to their deterioration with time in the automatic processor, and, in contrast with this, to keep the development performance constant by controlling the concentrations of compounds dissolving out of the light-sensitive material being processed. Accordingly, the concentrations of the former compounds are made higher than those in the color development tank solution, and the concentrations of the latter compounds are made lower than those in the color development tank solution. Examples of the former compounds include a color-developing agent and a preservative, and they are contained in the replenisher in amounts generally 1.1 to 2 times those in the tank solution. Examples of the latter compounds include a development inhibitor, represented by a halide (e.g. potassium bromide), and they are contained in the replenisher in amounts generally 0 to 0.6 times those of the tank solution. The concentration of the halide in the replenisher is generally 0.006 mol/liter or less, but it is required that the lower the replenishment rate is made, the more the concentration is decreased, and in some cases, the halide concentration is nil.

Further, compounds whose concentrations are hardly to change in the processing or with time are generally contained in the replenisher approximately in the same concentrations as those in the color-development tank solution. Examples of such compounds are chelating agents and buffers.

Further, the pH of the color-development replenisher is generally made higher than that of the tank solution, by about 0.05 to 0.5, in order to prevent the pH of the tank solution from being lowered by the processing. It is required that the difference in this pH be made higher if the replenishment rate is to be lowered. The replenishment rate of the color developer is generally 3000 ml or less, preferably 100 ml to 1500 ml, and most preferably 100 to 600 ml, per square meter of the light-sensitive material.

Suitably the processing temperature of the color developer is generally 20 to 55 °C, and preferably 30 to 50 °C. The processing time is suitably generally 20 sec to 5 min, preferably 30 sec to 3 min 30 sec, and more preferably 1 min to 3 min 20 sec.

Further, the color-developing bath is divided, if required, into two baths or more, and the replenishment with the color development replenisher may be made to the first bath or the last bath, to shorten the development time or to reduce further the replenishment rate.

The color developer may be regenerated, to be used as a processing solution again, by processing the used color developer with an anion exchange resin, subjecting the used color developer to electrodialysis, or adding a processing chemical called a regenerating agent to the used color developer, to increase the activity of the color developer. In this case, the regeneration rate (the rate of the overflow in the replenisher) is preferably 50% or more, and particularly preferably 70% or more. In the processing using the regenerated color developer, the overflow of the color developer is

regenerated, to be used as a color developer replenisher.

As a means for the regeneration, an anion exchange resin is preferably used. Particularly preferable compositions of anion exchange resins and methods for regenerating resins include those described in Diaion Manual (I), 14th edition (1986), published by Mitsubishi Chemical Industries Ltd. Among anionic exchange resins, resins having compositions described in JP-A-2-952 and JP-A-1-281152 are preferable.

The color-print-paper developer and the development replenisher contain a color-developing agent, and preferable examples are known aromatic primary amine color-developing agents, particularly p-phenylenediamine derivatives. Representative examples are shown below, but the present invention is not limited to them. Further, in recent years, among black-and-white light-sensitive materials, there are black-and-white light-sensitive materials wherein couplers are added to form black color, and a black and white image is formed by using a general-purpose usual color-developing solution. The color developing solution for use in the present invention can also be applied for the processing of this type of light-sensitive material.

1) N,N-diethyl-p-phenylenediamine
2) 4-amino-N,N-diehyl-3-methylaniline
3) 4-amino-N-(β-hydroxyethyl)-N-methylaniline
4) 4-amino-N-ethyl-N-(β-hydroxyethyl)aniline
5) 4-amino-N-ethyl-N-(β-hydroxyethyl)-3-methylaniline
6) 4-amino-N-ethyl-N-(3-hydroxypropyl)-3-methylaniline
7) 4-amino-N-ethyl-N-(4-hydroxybutyl)-3-methlaniline
8) 4-amino-N-ethyl-N-(β-methanesulfoneamidoethyl)-3-methylaniline
9) 4-amino-N,N,-diethyl-3-(β-hydroxyehyl)aniline
10) 4-amino-N-ethyl-N-(β-hydroxyethyl)-3-methylaniline
11) 4-amino-N-(β-ethoxyethyl)-N-ethyl-3-methylaniline
12) 4-amino-N-(3-carbamoylpropyl-N-n-propyl-3-methylaniline
13) 4-amino-N-(4-carbamoylbutyl-N-n-propyl-3-methylaniline
14) N-(4-amino-3-methylphenyl)-3-hydroxypyrrolidine
15) N-(4-amino-3-methylphenyl)-3-(hydroxymethyl)-pyrrolidine
16) N-(4-amino-3-methylphenyl)-3-pyrrolidinecarboxyamido

Out of the above p-phenylenediamine derivatives, Exemplified Compounds 5), 6), 7), 8), and 12) are particularly preferable, and among them Compounds 5) and 8) are preferable. Further, these p-phenylenediamine derivatives are generally in the form of sulfates, hydrochlorides, sulfites, and salts of naphthalenedisulfonic acid, p-toluenesulfonic acid, etc. when they are in the state of solid materials. The concentration of the aromatic primary amine developing agent in the developing solution or the replenisher is preferably 2 to 200 millimol, more preferably 12 to 200 millimol, and further more preferably 12 to 150 millimol, per liter of the developing solution, and the replenisher is designed to have a concentration higher than that of the developing solution due to the consumption in the development.

In the method for developing color print papers, depending on the type of the subject light-sensitive material, a small amount of sulfite ions is contained in the developing solution, or the developing solution is substantially free from sulfite ions, in some cases.

Further, depending on the type of the subject light-sensitive material, hydroxylamine is contained in the constitutional components of the composition, or it is not contained therein, in some cases. This is because hydroxylamine functions as a preservative of the developing solution, in addition to hydroxylamine itself having a silver development activity, and therefore this influences the photographic properties in some cases.

The developer composition for use in the present invention preferably contain inorganic preservatives, such as a sulfite ion, and organic preservatives. Herein the term "organic preservatives" refers generally to organic compounds that reduce the deterioration speed of the aromatic primary amine color-developing agent, when they are added to the processing solution of light-sensitive materials. That is, organic preservatives are organic compounds that have a function of preventing color-developing agents from being oxidized with air or the like; and particularly effective organic preservatives are hydroxylamine derivatives, hydroxamic acids, hydrazides, phenols, α-hydroxyketones, α-aminoketones, saccharides, monoamines, diamines, polyamines, quaternary ammonium salts, nitroxy radicals, alcohols, oximes, diamide compounds, and fused-ring-type amines. These are disclosed, for example, in JP-A-63-4235, JP-A-63-30845, JP-A-63-21647, JP-A-63-44655, JP-A-63-53551, JP-A-63-43140, JP-A-63-56654, JP-A-63-58346, JP-A-63-43138, JP-A-63-146041, JP-A-63-44657, and JP-A-63-44656, US-A-3,615,503 and US-A-2,494,903, JP-A-52-143020, and JP-B-48-30496.

Further, other preservatives that may be contained, if required, include, for example, various metals described in JP-A-57-44148 and JP-A-57-53749, salicylic acids described in JP-A-59-180588, alkanolamines described in JP-A-54-3532, polyethyleneimines described in JP-A-56-94349, and aromatic polyhydroxy compounds described in US-A-

3,746,544. Among the above, alkanolamines are effective to upgrade long term stability of a developer, a replenisher itself, and a composition in a condensed state to which the developer or the replenisher are provided as a processing agent.

Alkanolamines particularly effective in improving the long-term stability are, for example, triisopropanolamine, diisopropanolamine, monoisopropanolamine, and diethanolamine, and among them triisopropanolamine is preferable. In addition, triethanolamines can be preferably used.

The amount of the above alkanolamines to be added is generally 0.01 to 1 mol and preferably 0.02 to 0.2 mol, per liter of the processing solution.

In addition, hydroxylamine derivatives, such as substituted or unsubstituted dialkylhydroxylamines, for example, disulfoethylhydroxylamine and diethylhydroxylamine, or aromatic polyhydroxy compounds can be preferably added.

Among the above organic preservatives, hydroxylamine derivatives are particularly preferable and their details are described, for example, in JP-A-1-97953, JP-A-1-186939, JP-A-1-186940, and JP-A-1-187557.

Into the color-print-paper developing solution, chloride ions may be added, if necessary, and in many cases, generally chloride ions are contained in an amount of 3.5×10^{-2} to 1.5×10^{-1} mol/liter, but since chloride ions are released generally as a by-product of the development into the developing solution, they are not required to be added into the replenisher in many cases.

With respect to the inclusion of bromide ions, the same thing as that of chloride ions can be applied. In the processing of print materials, preferably the concentration of bromide ions is 1.0×10^{-3} mol/liter or less. In some cases, as required, bromide ions are added to the development replenisher so that the bromide ion concentration may fall in that range.

When these are added to the developing solution and, if necessary, to the replenisher, as a chloride-ion-supply substance, sodium chloride, potassium chloride, ammonium chloride, lithium chloride, nickel chloride, magnesium chloride, manganese chloride, or calcium chloride can be mentioned, with preference given to sodium chloride and potassium chloride.

As a bromide-ion-supply substance, sodium bromide, potassium bromide, ammonium bromide, lithium bromide, calcium bromide, magnesium bromide, manganese bromide, nickel bromide, cerium bromide, or thallium bromide can be mentioned, with preference given to potassium bromide and sodium bromide.

When the light-sensitive material to be subjected to development is a color print paper, since it is important for image quality that the background of the image area be white, it is important that short-wavelength light be converted to visible light (because it is generally difficult to make short-wavelength light be felt visually), by using a fluorescent whitening agent, to increase the quantity of light that can be visually perceived, and to finish it to be apparently white. The developing solution may contain a fluorescent whitening agent. As the fluorescent whitening agent, triazinyl-4,4-diaminostilbene compounds are preferable.

Further, stilbene fluorescent whitening agents can be added to the color-developing solution as well as to any of the desilvering solution or the light-sensitive material.

The developing solution or the replenisher used in color-print materials preferably has a pH of 9.5 to 13.0, and more preferably 9.8 to 12.5. To retain the above pH, it is preferable to use various buffers. As a buffer, potassium carbonate and sodium carbonate can be used. Other examples of the buffer are carbonates, phosphates, borates, tetraborates, hydroxybenzoates, glycil salts, N,N-dimethylglycine salts, leucine salts, norleucine salts, guanine salts, 3,4-dihydroxyphenylalanine salts, alanine salts, aminobutyrates, 2-amino-2-methyl-1,3-propandiol salts, valine salts, proline salts, trishydroxyaminomethane salts, and lysine salts. In particular, carbonates, phosphates, tetraborates, and hydroxybenzoates have such advantages that they are excellent in buffering function at a high pH region in pH of 9.0 or over, and that when they are added to the color-developing solution, the photographic performance is not adversely affected (e.g. fog), and that they are low in cost, so that these buffers are particularly preferably used.

Specific examples of these buffers include, in addition to sodium carbonate and potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, tripotassium phosphate, disodium phosphate, dipotassium phosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-suofosalicylate), and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate). However, the present invention is not limited to these compounds.

The amount of the buffers to be added, as the concentration in the color-developing replenisher, is preferably 0.04 to 2.0 mol/liter, and particularly preferably 0.1 to 0.4 mol/liter, assuming the amount to be the total of the buffers.

In the developer composition regarding the present invention, another color-developing-solution component that is, for example, a precipitation-preventing agent against calcium and magnesium, or is an agent for improving stability of the color-developing solution, various chelating agents can be used. Examples include nitrilotriacetic acid, diethylenetriaminepentaacetic acid, ethylenediaminetetraacetic acid, N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenesulfonic acid, ethylenediaminN,N-disuccinic acid, N,N-di(carboxylate)-L-aspartic acid, β-alaninedisussinic acid, ehylenediamine-N,N,N',N'-tetramethylenesulfonic acid, transcyclohexane-diaminetetraacetic

acid, 1,2-diaminopropanetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediamine orthohydroxyphenylacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid, and 1,2-dihydroxybenzene-4,6-disulfonic acid.

Two or more of these chelating agents may be used in combination, if necessary.

With respect to the amount of these chelating agents to be added, preferably the amount is enough to sequester the metal ions in the color-developing solution, and, generally, these chelating agents are used in a concentration in the developing solution or in the replenisher of 0.1 to 10 g per liter.

To the developing solution and the replenisher, any of development accelerators can be added, if necessary.

As the development accelerator, the following can be added as required: thioether compounds disclosed, for example, in JP-B-37-16088, JP-B-37-5987, JP-B-38-7826, JP-B-44-12380, JP-B-45-9019, and US-A-3 813 247; p-phenylenediamine compounds disclosed in JP-A-52-49829 and JP-A-50-15554, quaternary ammonium salts disclosed, for example, in JP-A-50-137726, JP-B-44-30074, JP-A-56-156826, and JP-A-52-43429; amine compounds described, for example, in US-A-2 494 903, US-A-3 128 182, US-A-4 230 796, US-A-3 253 919, JP-B-41-11431, US-A-2 482 546, US-A-2 596 926, and US-A-3 582 346; polyalkylene oxides disclosed, for example, in JP-B-37-16088, JP-B-42-25201, US-A-3 128 183, JP-B-41-11431, JP-B-42-23883, and US-A-3 532 501, as well as 1-phenyl-3-pyrazolidones, imidazoles, etc.

Further, if required, an arbitrary antifoggant can be added. As the antifoggant, the said alkali metal halide, such as sodium chloride, potassium bromide, and potassium iodide, and an organic antifoggant, can be used. Typical examples of the organic antifoggant include nitrogen-containing heterocyclic compounds, such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 2-thiazolyl-benzimidazole, 2-thiazolylmethyl-benzimidazole, indazole, hydroxyazaindolidine, and adenine.

Further, if necessary, various surfactants can be added. Specific examples of the surfactants include, for example, compounds of formula (I) or (II) described in JP-A-4-195037, and compounds of any of formulas (I) to (X) described in JP-A-4-81750.

Further, by adding the above compounds, preferably the surface tension of the color-developing solution and the color development replenisher is brought to 20 to 60 dyn/cm.

To prevent deposition in the processing tank and on the section where a rack, the processing solution, and the air come in contact with each other, and particularly to prevent deposition of the color-developing agent, particularly preferably a compound of formula (I) described in JP-A-5-333505 is added.

When the light-sensitive material to be subjected to development is a color print material, the processing temperature at the color-development in the present invention is generally 30 to 55 °C, preferably 35 to 55 °C, and more preferably 38 to 45 °C. The development processing time is generally 5 to 90 sec, and preferably 15 to 60 sec, and the method of the present invention is suit to the extremely rapid processing of 10 to 30 sec. With respect to the replenishing rate, although a small amount is preferable, the replenishing rate is generally 20 to 600 ml, preferably 30 to 120 ml, and particularly preferably 15 to 60 ml, per m^2 of the photographic material.

In the present invention, the light-sensitive material that has been processed with the bleaching solution is processed with a processing solution having a fixing capacity. Herein, "the processing solution having a fixing capacity" means specifically a fixing solution and a bleach-fix solution. In the step of processing with a bleach-fix solution after the bleaching with the bleaching solution, the bleaching agent of the bleaching solution and the bleaching agent of the bleach-fix solution are the same or different. After the bleaching with the bleaching solution, a washing step may be provided prior to the processing with the bleach-fix solution.

The processing solution having a fixing capacity contains a fixing agent. As the fixing agent, can be mentioned thiosulfates, such as sodium thiosulfate, ammonium thiosulfate, sodium ammonium thiosulfate, and potassium thiosulfate, thiocyanates (rhodanates), such as sodium thiocyanate, ammonium thiocyanate, and potassium thiocyanate, thiourea, and thioethers. Ammonium thiosulfate is particularly preferably used inter alia. The amount of the fixing agent is generally 0.3 to 3 mol and preferably 0.5 to 2 mol, per liter of the processing solution having a fixing capacity.

Further, in view of the acceleration of the fixing, it is also preferable to use a thiosulfate in combination with ammonium thiocyanate (ammonium rhodanate), thiourea, a thioether (e.g. 3,6-dithia-1,8-octanediol), or a thiosulfonic acid (e.g. ammonium methanethiosulfonate). Out of these, a combination of a thiosulfate with a thiocyanate or a combination of a thiosulfate with a thiosulfonate is most preferable. In particular, a combination of ammonium thiosulfate with ammonium methanethiosulfonate is preferable. Suitably the amount of these compounds used in combination is generally 0.01 to 1 mol and preferably 0.1 to 0.5 mol, per liter of the processing solution having a fixing capacity, but in the case of a thiocyanate, the use of 1 to 3 mol can increase the fixing acceleration effect considerably. Further, in the case of a thiosulfonic acid, preferably the below-described sulfinic acid is used additionally.

The processing solution having a fixing capacity can contain, as preservatives, sulfites (e.g. sodium sulfite, potassium sulfite, and ammonium sulfite), hydroxylamines, hydrazines, bisulfite-addition compounds of aldehyde compounds (e.g. acetaldehyde sodium bisulfite and particularly preferably compounds described in Japanese patent application No. 1-298935), or sulfinic acid compounds described in JP-A-1-231051. Further, various fluorescent whitening agents,

anti-foaming agents, surfactants, polyvinyl pyrrolidones, and organic solvents, such as methanol, can be contained.

Further, to the processing solution having a fixing capacity, chelating agents, such as various aminopolycarboxylic acids and organic phosphonic acids, are preferably added in order to stabilize the processing solution. As preferable chelating agents, can be mentioned, for example, 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, nitrilotrimethylenephosphonic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, 1,2-propylenediaminetetraacetic acid, and 1,3-diaminopropanetetraaectic acid. Among them, 1-hydroxyethylidene-1,1-diphosphonic acid, 1,3-diaminopropanetetraacetic acid, and ethylenediaminetetraacetic acid are particularly preferable. The amount of the chelating agent to be added is generally 0.01 to 0.3 mol and preferably 0.03 to 0.2 mol, per liter of the processing solution.

The pH of the fixing solution is preferably 5 to 9 and more preferably 6 to 8. Further, the pH of the bleach-fix solution is preferably 4.0 to 7.0 and more preferably 5.0 to 6.5. To adjust the processing solution having a fixing capacity to such a pH range, a compound having a pKa in the range of 6.0 to 9.0 is preferably contained as a buffer. As this compound, imidazoles, such as imidazole and 2-methyl-imidazole, are preferable. The amount of the compound to be added is preferably 0.1 to 10 mol and more preferably 0.2 to 3 mol, per liter of the processing solution.

In addition, the bleach-fix solution can contain the above-described compounds that can be contained in the bleaching solution.

In the present invention, the bleach-fix solution (start solution) at the start of the processing is prepared by dissolving in water the above-described compounds that are to be used in the bleach-fix solution, or it may be prepared by mixing suitable amounts of a bleaching solution and a fixing solution that are prepared separately.

The replenishment rate of the fixing solution or the bleach-fix solution in the case of the use of a replenishing system is preferably 100 to 3,000 ml and more preferably 300 to 1,800 ml, per square meter of the light-sensitive material, in the case of color photographing materials. The above replenishment rate is generally 20 to 1,500 ml, preferably 30 to 600 ml, and more preferably 30 to 200 ml, per square meter of the light-sensitive material, in the case of color print materials. The replenishment with the bleach-fix solution may be carried out by the replenishment with a bleach-fix replenisher, or by using the overflow of the fixing solution and the bleaching solution, as described in JP-A-61-143755 or Japanese patent application No. 2-216389.

Further, in the present invention, the total processing time of the processing having a fixing capacity is generally 0.5 to 5 min, preferably 1.5 to 4 min, and particularly preferably 2 to 3.5 min, in the case of color photographing materials. The above total processing time is generally 5 sec to 2 min, preferably 10 sec to 1 min 40 sec, and more preferably 10 sec to 45 sec, in the case of color print materials.

The processing temperature of the processing solution having a fixing capacity for use in the present invention is generally 25 to 50 °C and preferably 35 to 45 °C.

From the processing solution having a fixing capacity for use in the present invention, silver can be recovered in the known manner, and the solution obtained by recovering the silver can be used for a regenerated solution. The solution having a fixing capacity in the case wherein silver is recovered is preferably the fixing solution. As the method for recovering silver, for example, an electrolysis method (described in FR-A-2 299 667), a precipitation method (described in JP-A-52-73037 or German patent No. 2,331,220), an ion exchange method (JP-A-51-17114 and German patent No. 2,548,237), and a metal replacement method (GB-A-1 353 805) are effective. Preferably, these silver recovering methods are carried out in an inline manner from the tank solution, because in that case the rapid processibility becomes more favorable.

It is preferable to carry out the electrolysis method out of these methods in an inline manner, and in that case, it is recommended that the concentration of silver in the solution having a fixing capacity is kept at generally 3 g/liter or less, and preferably 1 g/liter or less.

Further, in the case wherein silver is recovered in such a manner, the replenishment rate of the solution having a fixing capacity can be further reduced, and it is preferably 100 to 300 ml per square meter of the light-sensitive material in the case of color photographing materials.

In the present invention, after the bleach-fix or the fixing step, or between the bleaching step and the step having a fixing capacity, a processing step of washing, stabilizing, or the like that is generally carried out may be performed. Alternatively, after the processing with the processing solution having a fixing capacity, a simple processing method wherein stabilizing is carried out without carrying out substantial washing, can be used.

Particularly, when silver is recovered in a step having a fixing capacity, preferably there is a processing step of washing, rinsing, stabilizing, or the like, prior to the step having a fixing capacity.

The washing water used in the washing step may contain various surface-active agents, to prevent the processed light-sensitive material from being dried unevenly due to water droplets. Examples of the surface-active agents include polyethylene glycol-type nonionic surface-active agents, polyhydric alcohol-type nonionic surface-active agents, alkylbenzenesulfonate-type anionic surface-active agents, higher alcohol sulfate-type anionic surface-active agents, alkylnaphthalenesulfonate-type anionic surface-active agents, quaternary ammonium salt-type cationic surface-active agents, amine salt-type cationic surface-active agents, amino salt-type amphoteric surface-active agents, and betaine-

type amphoteric surface-active agents. Among these, since ionic surface-active agents sometimes combine with various ions introduced unintentionally along with the processing to form insoluble substances, nonionic surface-active agents are preferably used, with particular preference given to alkylphenol ethylene oxide adducts. The alkylphenol is particularly preferably octylphenol, nonylphenol, dodecylphenol, or dinonylphenol, and the addition molar number of ethylene oxide is particularly preferably 8 to 14 (mol). Further, a silicon-series surface-active agent high in antifoaming effect is also preferably used.

Further, the washing water can contain a variety of bacteria-proofing agents and mildew-proofing agents, to prevent the formation of scale or the existence of mildew occurring on processed light-sensitive materials. As the bacteria-proofing agents and mildew-proofing agents, can be used, for example, one or more of thiazorilbenzoimidazole compounds, as described in JP-A-57-157244 and JP-A-58-105145, isothiazolone compounds, as described in JP-A-57-8542, and general-purpose mildew-proofing agents described in "Journal Antibacteria and Antifungus Agents," Vol. 1, No. 5, pp 207 to 223 (1983), such as chlorophenol compounds, represented by trichlorophenol; bromophenol compounds, organotin compounds, organozinc compounds, thiocyanic acid compounds, isothiocyanic acid compounds, acid amide compounds, diazine compounds, triazine compounds, thiourea compounds, benzotriazolealkylguanidine compounds, quaternary ammonium salts, represented by benzalkonium chloride; or antibiotics, such as penicillins. Further, various fungicides described in JP-A-48-83820 can be used.

Further, preferably, various chelating agents are additionally used. Preferable compounds as the chelating agents include, for example, aminopolycarboxylic acids, such as ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid, organic phosphonic acids, such as 1-hydroxyethylidene-1,1-diphosphonic acid and ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, and hydrolyzates of maleic anhydride polymers, as described in EP-A-345 172 (A1).

Further, the above preservatives that can be contained in the fixing solution or the bleach-fix solution are preferably contained in the washing water.

The stabilizing solution used in the stabilizing step is a processing solution for stabilizing dye images. For example, a solution having a buffering function in the pH range of 3 to 6, such as a solution containing an aldehyde (e.g. formalin) can be used. Hereinbelow, stabilizing solutions preferably used in the present invention are described.

In the present invention, preferably the stabilizing solution is substantially free from formaldehyde. The term "substantially free from formaldehyde" means that the total amount of free formaldehyde and its hydrate is 0.003 mol or less, per liter of the stabilizing solution.

By using such a stabilizing solution, a formaldehyde vapor can be restrained from being scattered at the time of the processing.

In that case, for the purpose of stabilizing magenta dyes, preferably a formaldehyde-releasing compound is allowed to exist in the stabilizing solution, the bleaching solution, or a bath preceding it (e.g. an adjusting bath).

Compounds preferable as the formaldehyde-releasing compound are hexamethylenetetramine and its derivatives, formaldehyde-bisulfite adducts, azolylmethylamines, and N-methylol compounds.

These preferable compounds not only stabilize magenta dyes but also suppress the occurrence of yellow stain that will appear with time.

As hexamethylenetetramine and its derivatives, those compounds described in "Beilsteins Handbuch der Organishen Chemie," No. II enlarged edition, Vol. 26, pages 200 to 212 can be used, with particular preference given to hexamethylenetetramine.

Further, as the formaldehyde-bisulfite adducts, formaldehyde-sodium bisulfite is preferable.

As the azolylmethylamines, those obtained by reacting three compounds, i.e., an azole selected from among triazole, pyrazole, and imidazole, an amine selected from piperazine, morpholine, 4-hydroxyethylpiperidine, and 4-hydroxypiperidine, and formaldehyde are preferable. Among these, particularly N,N'-bis(1,2,4-triazol-1-ylmethyl)piperazine and N,N'-bis(pyrazol-1-ylmethyl)piperazine are preferable.

As the N-methylol compounds, particularly pyrazole and N-methylol compounds that are derivatives thereof, triazole and N-methylol compounds that are derivatives thereof, and urazol and N-methylol compounds that are derivatives thereof are preferable.

Specific examples of these N-methylol compounds include 1-hydroxymethylpyrazole, 1-hydroxymethyltriazole, and 1-hydroxymethylurazol.

Among these, the most preferable one is 1-hydroxymethylpyrazole.

These N-methylol compounds can be synthesized easily by reacting an amine compound having no methylol group with formaldehyde or paraformaldehyde.

Out of the above formaldehyde-releasing compounds, particularly preferable ones are hexamethylenetetramine, formaldehyde-sodium bisulfite, and the above preferable azolylmethylamines and N-methylol compounds.

Among them, N,N'-bis(1,2,4-triazol-1-ylmethyl)piperazine and N,N'-bis(pyrazol-1-ylmethyl)piperazine are most preferable.

When the above azolylmethylamines or N-methylol compounds are used, it is preferable to allow an amine com-

pound, such as triazole or pyrazole, to be present also in the processing solution, in a concentration 0.2 to 10 times that of the azolylmethylamine or the N-methylol compound in terms of molarity.

A preferable amount of the above formaldehyde-releasing compound to be added is 0.003 to 0.2 mol and preferably 0.005 to 0.05 mol, per liter of the processing solution.

These formaldehyde-releasing compounds may be used in combination of two or more in the bath.

The stabilizing solution can contain all compounds that can be added to the washing water, as well as ammonium compounds (e.g. ammonium chloride, ammonium sulfite), metal compounds (e.g. a bismuth compound, an aluminum compound), a fluorescent-whitening agent, a hardener; alkanolamines, as described in US-A-4,786,583, according to the occasion.

Further, the washing step and the stabilizing step are preferably of a multi-stage counter current system, and the number of stages is preferably 2 to 4. The replenishment rate is generally 1 to 50 times, preferably 2 to 30 times, and more preferably 2 to 15 times, the amount carried in from the preceding bath per unit area.

As the water used in the washing step or the stabilizing step, besides tap water, water deionized with ion exchange resins to bring the concentrations of Ca and Mg to 5 mg/liter or below, or water sterilized with a halogen lamp, an ultraviolet germicidal lamp, or the like, is preferably used. As the water to supplement the evaporation in the processing solutions, tap water can be used, but deionized water or sterilized water preferably used in the washing step or the stabilizing step, is preferably used.

Not only in the developing solution, the bleaching solution, the bleaching-fix solution, and the fixing solution, but also in other processing solutions, to correct the condensation due to the evaporation, it is preferable to supply a suitable amount of water, a replenisher, or a processing replenisher. For the correction related to the evaporation, methods described in Kokai-giho No. 94-4992 issued by Hatsumei-kyokai, page 1, right column, line 26 to page 3, left column, line 28 can be mentioned.

Further, the overflow of the washing step or the stabilizing step may be flowed into the preceding bath, that is, the bath having a fixing capacity, to reduce the amount of waste liquor.

As a developing apparatus for carrying out the present invention, commercially available one can be used. Examples of the developing apparatus preferably used for carrying out the present invention include FP230B, FP350, FP360B, FP560B, FP900, FNCP900, FNCP900II, FNCP900III, FNCP600II, and FNCP300II manufactured by Fuji Photo Film Co., Ltd., HM-55S, H8-440W-4, HM-60R, and HR4-8360 manufactured by Noritsu Koki Co., Ltd., AGFA CABOMATOR45, Hostert Fotomata, HOPE138, and HOPE2409V (manufactured by HOPE Co., USA). The stirring method, the materials, etc. of the developing apparatus are preferably those described in JP-A-4-130432.

Examples of the silver halide color photographic light-sensitive material to which the present invention is preferably applied includes photographing-light-sensitive materials, such as color reversal films and color negative films having a silver bromoiodide emulsion applied, and print light-sensitive materials, such as color print papers, with particular preference given to color negative films and, inter alia, those having a magnetic recording layer on a base.

Herein, as the photographing light-sensitive materials, those having a coating amount of silver of about 3 to 8 g/m^2 are preferably used, and for the halogen composition of the silver halide emulsion, silver bromoiodide (whose silver iodide content is 3 to 10 mol%) is preferable.

Further, as the print light-sensitive material, those having a coating amount of silver of 1 g/m^2 or less, and particularly preferably 0.3 to 0.8 g/m^2, are preferably used, and for the silver halide composition of the silver halide emulsion, high-silver chloride is preferable.

Now, silver halide color photographing photographic light-sensitive materials that are preferable in the processing of the present invention are described.

Now, light-sensitive materials having a magnetic recording layer that are preferably processed in accordance with the present invention are described.

The magnetic recording layer is a layer formed by coating on a base with an aqueous or organic solvent coating solution containing magnetic particles dispersed in a binder. To prepare the magnetic particles, use can be made of a ferromagnetic iron oxide, such as γFe_2O_3, Co-coated γFe_2O_3, Co-coated magnetite, Co-containing magnetite, ferromagnetic chromium dioxide, a ferromagnetic metal, a ferromagnetic alloy, hexagonal Ba ferrite, Sr ferrite, Pb ferrite, and Ca ferrite. A Co-coated ferromagnetic iron oxide, such as Co-coated γFe_2O_3, is preferable.

The shape may be any of a needle shape, a rice grain shape, a spherical shape, a cubic shape, a plate-like shape, and the like. The specific surface area is preferably 20 m^2/g or more, and particularly preferably 30 m^2/g or more, in terms of S_{BET}. The saturation magnetization (σs) of the ferromagnetic material is preferably 3.0×10^4 to 3.0×10^5 A/m, and particularly preferably 4.0×10^4 to 2.5×10^5 A/m. The ferromagnetic particles may be surface-treated with silica and/or alumina or an organic material. The surface of the magnetic particles may be treated with a silane coupling agent or a titanium coupling agent, as described in JP-A-6-161032. Further, magnetic particles whose surface is coated with an inorganic or an organic material, as described in JP-A-4-259911 and 5-81652, can be used.

As the binder used for the magnetic particles, as described in JP-A-4-219569, a thermoplastic resin, a thermal-setting resin, a radiation-setting resin, a reactive resin, an acid-degradable polymer, an alkali-degradable polymer, a bio-

degradable polymer, a natural polymer (e.g. a cellulose derivative and a saccharide derivative), and a mixture of these can be used. The above resins generally have a glass transition temperature Tg of -40 to 300 °C and a weight-average molecular weight of 2,000 to 1,000,000. Examples include vinyl copolymers, cellulose derivatives, such as cellulose diacetates, cellulose triacetates, cellulose acetate propionates, cellulose acetate butylates, and cellulose tripropionates; acrylic resins, and polyvinyl acetal resins; and gelatin is also preferable. Cellulose di(tri)acetates are particularly preferable. To the binder may be added an epoxy, aziridine, or isocyanate crosslinking agent, to harden the binder. Examples of the isocyanate crosslinking agent include isocyanates, such as tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, and xylylene diisocyanate; reaction products of these isocyanates with polyalcohols (e.g. a reaction product of 3 mol of tolylene diisocyanate with 1 mol of trimethylolpropane), and polyisocyanates produced by condensation of these isocyanates, which are described, for example, in JP-A-6-59357.

The method of dispersing the foregoing magnetic material in the foregoing binder is preferably one described in JP-A-6-35092, in which method use is made of a kneader, a pin-type mill, an annular-type mill, and the like, which may be used alone or in combination. A dispersant described in JP-A-5-088283 and other known dispersants can be used.

The thickness of the magnetic recording layer is generally 0.1 to 10 μm, preferably 0.2 to 5 μm, and more preferably 0.3 to 3 μm. The weight ratio of the magnetic particles to the binder is preferably from (0.5:100) to (60:100), and more preferably from (1:100) to (30:100). The coating amount of the magnetic particles is generally 0.005 to 3 g/m^2, preferably 0.01 to 2 g/m^2, and more preferably 0.02 to 0.5 g/m^2.

The magnetic recording layer used in the present invention can be provided to the undersurface of the photographic base by coating or printing through all parts or in a striped fashion. To apply the magnetic recording layer, use can be made of an air doctor, a blade, an air knife, squeezing, impregnation, a reverse roll, a transfer roll, gravure, kiss, cast, spraying, dipping, a bar, extrusion, or the like. A coating solution described, for example, in JP-A-5-341436 is preferable.

The magnetic recording layer may be provided with functions, for example, of improving lubricity, of regulating curling, of preventing electrification and adhesion, and of abrading a head, or it may be provided with another functional layer that is provided with these functions. An abrasive in which at least one type of particles comprises aspherical inorganic particles having a Moh's hardness of 5 or more, is preferable. The aspherical inorganic particles preferably comprise a fine powder of an oxide, such as aluminum oxide, chromium oxide, silicon dioxide, and titanium dioxide; a carbide, such as silicon carbide and titanium carbide; diamond, or the like. The surface of these abrasives may be treated with a silane coupling agent or a titanium coupling agent. These particles may be added to the magnetic recording layer, or they may form an overcoat (e.g. a protective layer and a lubricant layer) on the magnetic recording layer. As a binder used at that time, the above-mentioned binders can be used, and preferably the same binder as used in the magnetic recording layer is used. Light-sensitive materials having a magnetic recording layer are described in US-A-5 336 589, 5 250 404, 5 229 259, and 5 215 874, and EP-466 130.

The light-sensitive material that is processed by the present invention is preferably a light-sensitive material for photographing (shooting), and its base is preferably a polyester base. Polyester bases for use in the present invention are described in detail in Kokaigiho, Kogi No. 94-6023 (Hatsumei-kyokai; 15, 3, 1994) in detail.

Polyesters for use in the present invention are produced by using, as essential components, diols and aromatic dicarboxylic acids. Examples of the aromatic dicarboxylic acids include 2,6-, 1,5-, 1,4- and 2,7-naphthalene dicarboxylic acids; terephthalic acid, isophthalic acid, and phthalic acid; and examples of the diols include diethylene glycol, triethylene glycol, cyclohexanedimethanol, bisphenol A, and bisphenols. Examples of their polymers include homopolymers, such as polyethylene terephthlates, polyethylene naphthalates, and polycyclohexanedimethanol terephthalates. Polyesters comprising 2,6-naphthalenedicarboxylic acid as an acidic reaction component, at a content of 50 to 100 mol% of the total dicarboxylic acid component, are particularly preferable. Among them, polyethylene 2,6-naphthalates are particularly preferable. The average molecular weight is in the range of generally about 5,000 to 200,000. The Tg of the polyesters for use in the present invention is generally 50 °C or over, and preferably 90 °C or over.

Then the polyester base is heat-treated at a heat treatment temperature of generally 40 °C or over, but less than the Tg, and preferably at a heat treatment temperature of the Tg - 20 °C or more, but less than the Tg, so that it will hardly have core set curl. The heat treatment may be carried out at a constant temperature in the above temperature range, or it may be carried out with cooling. The heat treatment time is generally 0.1 hours or more, but 1,500 hours or less, and preferably 0.5 hours or more, but 200 hours or less. The heat treatment of the base may be carried out with the base rolled, or it may be carried out with it being conveyed in the form of web. The surface of the base may be made rough (unevenness, for example, by applying electroconductive inorganic fine particles, such as SnO_2 and Sb_2O_5), so that the surface state may be improved. Further, it is desirable to provide, for example, a rollette (knurling) at the both ends for the width of the base (both right and left ends towards the direction of rolling) to increase the thickness only at the ends, so that a trouble of deformation of the base will be prevented. The trouble of deformation of the base means that, when a base is wound on a core, on its second and further winding, the base follows unevenness of its cut edge of the first winding, deforming its flat film-shape. These heat treatments may be carried out at any stage after the production of the base film, after the surface treatment, after the coating of a backing layer (e.g. with an antistatic agent and a slipping agent), and after coating of an undercoat, with preference given to after coating of an antistatic agent.

Into the polyester may be blended (kneaded) an ultraviolet absorber. Further, prevention of light piping can be attained by blending dyes or pigments commercially available for polyesters, such as Diaresin (trade name, manufactured by Mitsubisi Chemical Industries Ltd.), and Kayaset (trade name, manufactured by Nippon Kayaku Co., Ltd.).

Further, in the light-sensitive material for use in the present invention, to adhere the base to the constitutional layers of light-sensitive material, a surface treatment is preferably carried out. A surface activation treatment can be mentioned, which includes a chemical treatment, a mechanical treatment, a corona discharge treatment, a flame treatment, an ultraviolet treatment, a high-frequency treatment, a glow discharge treatment, an active-plasma treatment, a laser treatment, a mixed-acid treatment, and an ozone oxidation treatment. Among the surface treatments, an ultraviolet irradiation treatment, a flame treatment, a corona treatment, and a grow treatment are preferable.

With respect to the undercoating technique, a single layer or two or more layers may be used. As the binder for the undercoat layer, for example, copolymers produced by using, as a starting material, a monomer selected from among vinyl chloride, vinylidene chloride, butadiene, methacrylic acid, acrylic acid, itaconic acid, maleic anhydride, and the like, as well as polyethylene imines, epoxy resins, grafted gelatins, nitrocelluloses, and gelatin, can be mentioned. As compounds that can swell the base, resorcin and p-chlorophenol can be mentioned. As gelatin hardening agents in the undercoat layer, chrome salts (e.g. chrome alum), aldehydes (e.g. formaldehyde and glutaraldehyde), isocyanates, active halogen compounds (e.g. 2,4-dichloro-6-hydroxy-s-triazine), epichlorohydrin resins, active vinyl sulfone compounds, and the like can be mentioned. SiO_2, TiO_2, inorganic fine particles, or polymethyl methacrylate copolymer fine particles (0.01 to 10 μm) may be included as a matting agent.

Further, in the light-sensitive material for use in the present invention, an antistatic agent is preferably used. As the antistatic agent, polymers, including carboxylic acids, carboxylates, and sulfonates; cationic polymers, and ionic surface-active compounds can be mentioned.

Most preferable antistatic agents are fine particles of at least one crystalline metal oxide selected from the group consisting of ZnO, TiO_2, SnO_2, Al_2O_3, In_2O_3, SiO_2, MgO, BaO, MoO_3, and V_2O_5, and having a specific volume resistance of 10^7 Ω • cm or less, and more preferably 10^5 Ω • cm or less and a particle size of 0.001 to 1.0 μm, or fine particles of their composite oxides (Sb, P, B, In, S, Si, C, etc.); as well as fine particles of the above metal oxides in the form of a sol, or fine particles of composite oxides of these. The content thereof in the light-sensitive material is preferably 5 to 500 mg/m^2, and particularly preferably 10 to 350 mg/m^2. The ratio of the amount of the electroconductive crystalline oxide or its composite oxide to the amount of the binder is preferably from 1/300 to 100/1, and more preferably from 1/100 to 100/5.

The light-sensitive material for use in the present invention preferably has slipperiness. Preferably the slipping-agent-containing layer is provided on both the side of the light-sensitive layer, and the side of the backing layer. Preferable slipperiness is 0.25 or less, but 0.01 or more, in terms of coefficient of dynamic friction. In this case, the value is obtained in the measurement wherein a sample is transferred at 60 cm/min against a stainless steel ball of a diameter 5 mm, at 25 °C and 60% RH. In this evaluation, if it is replaced with the light-sensitive layer surface as the partner material, the value will be almost on the same level.

Examples of the slipping agent that can be used in the present invention, include, for example, polyorganosiloxanes, higher fatty acid amides, higher fatty acid metal salts, and esters of higher fatty acids with higher alcohols; and polyorganosiloxanes that can be used include polydimethylsiloxane, polydiethylsiloxane, polystyrylmethylsiloxane, and polymethylphenylsiloxane. The layer to which the slipping agent is added is preferably the outermost layer of the light-sensitive emulsion layers, or the backing layer. In particular, polydimethylsiloxanes, and esters having a long-chain alkyl group are preferable.

The light-sensitive material for use in the present invention preferably have a matting agent. When a matting agent is used, the matting agent may be added to either the side of the light-sensitive emulsions or the side of the backing layer, and particularly preferably it is added to the outermost layer on the side of the light-sensitive emulsions. The matting agent may or may not be soluble in the processing solution, and preferably a matting agent soluble in the processing solution and a matting agent insoluble in the processing solution are used together. For example, polymethyl methacrylate, poly(methyl methacrylate/methacrylic acid = 9/1 or 5/5 (molar ratio)), and polystyrene particles are preferably used. Preferably the particle diameter is 0.8 to 10 μm. The narrower the particle diameter distribution is, the more preferable it is. Preferably 90% or more of all the particles is within 0.9 to 1.1 times the average particle diameter.

To enhance the matte feature, it is also preferable at the same time to add fine particles of 0.8 μm or below, and examples are polymethyl methacrylates (0.2 μm), poly(methyl methacrylate/methacrylic acid = 9/1 (molar ratio)) (0.3 μm), polystyrene particles (0.25 μm), and colloidal silica (0.03 μm).

The light-sensitive materials used in the present invention are preferably those described in JP-A-4-125558, from page 14, upper left column, line 1, to page 18, lower left column, line 11. Particularly, as the silver halide emulsion, a silver bromoiodide emulsion having an average silver iodide content of 3 to 20 mol% is preferable, whose silver halide grains are preferably tabular grains having an aspect ratio of 5 or more, or double-structure grains wherein the inside and the outside are different in halogen composition. Further, the grains may be ones wherein the inside and the outside constitute clear layer structures. Particularly the aspect ratio is preferably from 5 to 20, and more preferably from 6

to 12.

Further, monodisperse emulsions described in US-A-3 574 628 and US-A-3 655 394 are also preferable.

The light-sensitive material used in the present invention has preferably a layer containing a non-light-sensitive fine grain silver halide having an average grain diameter of 0.02 to 0.2 μm. The fine grain silver halide is made preferably of silver bromide having a silver iodide content of 0.5 to 10 mol%.

Additives used in the light-sensitive material for use in the present invention are described below.

	Additive	RD 17643	RD 18716	RD 307105
1	Chemical sensitizers	p.23	p.648 (right column)	p.866
2	Sensitivity-enhancing agents	_	p.648 (right column)	-
3	Spectral sensitizers and Supersensitizers	pp.23-24	pp.648 (right column) -649 (right column)	pp.866-868
4	Brightening agents	p.24	p.648 (right column)	p.868
5	Light absorbers, Filter dyes, and UV Absorbers	pp.25-26	pp.649 (right column) -650 (left column)	P.873
6	Binders	p.26	p.651 (left column)	pp.873-874
7	Plasticizers and Lubricants	p.27	p.650 (right column)	p.876
8	Coating aids and Surface-active agents	pp.26-27	p.650 (right column)	pp.875-876
9	Antistatic agents	p.27	p.650 (right column)	pp.876-877
10	Matting agents	-	-	pp.878-879

In the light-sensitive material for use in the present invention, various dye-forming couplers can be used, and particularly preferable couplers are the following:

Yellow couplers: couplers represented by formula (I) or (II) of EP-A-502,424; couplers represented by formula (1) or (2) of EP-A-513,496 (particularly Y-28 on page 18); couplers represented by formula (I) in claim 1 of EP-A-568,037; couplers represented by formula (I) of US-A-5 066 576, column 1, lines 45 to 55; couplers represented by formula (I) of JP-A-4-274425, paragraph number 0008; couplers claimed in claim 1 of EP-A-498,381(A1), page 40 (particularly D-35 on page 18); couplers represented by formula (Y) of EP-A-447,969(A1), page 4 (particularly Y-1 on page 17 and Y-54 on page 41); and couplers represented by any of formulae (II) to (IV) of US-A-4 476 219, column 7, lines 36 to 58 (particularly II-17, 19 (column 17) and II-24 (column 19).

Magenta couplers: JP-A-3-39737 (L-57 (page 11, lower right part), L-68 (page 12, lower right part), and L-77 (page 13, lower right part); A-4 -63 (page 134) and A-4 -73, and -75 (page 139) of EP-456,257; M-4 and -6 (page 26) and M-7 (page 27) of EP-486,965; M-45 (page 19) of EP-A-571,959; (M-1) (page 6) of JP-A-5-204106 and M-22 of JP-A-4-362631 (paragraph number 0237).

Cyan couplers: CX-1, 3, 4, 5, 11, 12, 14, and 15 (pages 14 to 16) of JP-A-4-204843 ; C-7 and 10 (page 35), 34 and 35 (page 37), and (I-1) and (I-17) (pages 42 to 43) of JP-A-4-43345; and couplers represented by formula (Ia) or (Ib) in claim 1 of JP-A-6-67385.

Polymer couplers: P-1 and P-5 (page 11) of JP-A-2-44345.

As couplers whose color-formed dyes have suitable diffusibility, those described in US-A-4 366 237, GB 2 125 570, EP-B-96,873, and DE 3,234,533 are preferable.

Couplers for correcting undesired absorption of color-formed dyes are preferably yellow-colored cyan couplers represented by formula (CI), (CII), (CIII), or (CIV) (particularly YC-86 on page 84) described in EP-A-456,257(A1), page 5; yellow-colored magenta couplers ExM-7 (page 202), EX-1 (page 249), and EX-7 (page 251) described in EP-A-456,257(A1); magenta-colored cyan couplers CC-9 (column 8) and CC-13 (column 10) described in US-A-4 833 069; (2) (column 8) of US-A-4 837 136; and colorless masking couplers (particularly, exemplified compounds on pages 36 to 45) represented by formula (A) in claim 1 of WO 92/11575.

Now, containers (e.g. film patrones (magazines)), into which the light-sensitive material to be processed according to the method of the present invention can be housed, are described. The major material of the patrone to be used may be metal or synthetic plastic, with preference given to plastic materials, such as polystyrenes, polyethylenes, polyprop-

ylenes, polyphenyl ethers, and the like.

Further, the patrone for use in the present invention may contain various antistatic agents, and preferably, for example, carbon black, metal oxide particles; nonionic, anionic, cationic, and betaine surface-active agents, or polymers can be used. These antistatic patrones are described in JP-A-1-312537 and JP-A-1-312538. In particular, the resistance of the patrone at 25 °C and 25% RH is preferably 10^{12} Ω or less. Generally, plastic patrones are made of plastics with which carbon black or a pigment has been kneaded, to make the patrones screen light. The size of the patrone may be size 135, that is currently used, and, to make cameras small, it is effective to change the diameter of the 25-mm cartridge of the current size 135, to 22 mm or less. Preferably the volume of the case of the patrone is 30 cm^3 or less, and more preferably 25 cm^3 or less. The weight of the plastic to be used for the patrone or the patrone case is preferably 5 to 15 g.

Further, the patrone may be one in which a spool is rotated to deliver a film. Also the structure may be such that the forward end of film is housed in the patrone body, and by rotating a spool shaft in the delivering direction, the forward end of the film is delivered out from a port of the patrone. These patrones are disclosed in US-A-4,834,306, US-A-5,226,613, and US-A-5,296,887. The light-sensitive material that has been subjected to development, can be housed in a patrone again. In that case, the patrone that is used may or may not be the same as that for the light-sensitive material before the processing.

Specific examples of film formats are preferably those as described in "FUJIFILM ADVANCED PHOTO SYSTEM LAB SYSTEM GUIDE," pages 3 to 5, published by Fuji Photo Film Co., Ltd., wherein a light-sensitive material having a film width of 24 mm and provided with a magnetic recording function is housed in a plastic small-sized cartridge.

Further, to the light-sensitive material used in the present invention, are preferably applied those described in JP-A-4-62543, from page 6, upper right column, line 17, to page 10, upper right column, line 17.

Further, to prevent photographic performance from being deteriorated with formaldehyde gas, compounds capable of reacting with formaldehyde to immobilize it that are described in US-A-4 411 987 and US-A-4 435 503, are preferably added to the light-sensitive material.

The light-sensitive material for use in the present invention can contain compounds described in JP-A-60-107029, JP-A-60-252340, JP-A-1-44940, and JP-A-1-45687 that can undergo the oxidation-reduction reaction with the oxidized product of a developing agent to release a fogging agent, a development accelerator, a silver halide solvent, etc.

Preferably, the light-sensitive material for use in the present invention contains mercapto compounds described, for example, in US-A-4 740 454, JP-A-62-018539, US-A-4 788 132, and JP-A-1-283551.

The light-sensitive material for use in the present invention can contain compounds described, for example, in JP-A-1-106052 that release a fogging agent, a development accelerator, a silver halide solvent, or their precursor independently of the amount of developed silver resulting from development processing.

In the light-sensitive material for use in the present invention, can be preferably contained dyes that are dispersed by methods described in International Publication No. WO 88/04794 and JP-T-1-502912 ("JP-T" means a published searched patent publication), and dyes described, for example, in European Patent EP-0,317,308 (A2), US-A-4 420 555, and JP-A-1-259358.

In the light-sensitive material for use in the present invention, are preferably added various antiseptics and mildew-proofing agents, such as n-butyl, p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol, 2-(4-thiazolyl)benzimidazole, and 1,2-benzisothiazolin-3-on, as described in JP-A-63-257747, JP-A-62-272248, and JP-A-1-80941, and phenetyl alcohol.

Specific examples of preferable light-sensitive materials to which the present invention is applied are listed below: light-sensitive materials that can be subjected to C-41 processing of Eastman Kodak Co. or CN-16 processing of Fuji Photo Film Co., Ltd. are preferably used, such as

FUJICOLOR SUPER G100,
FUJICOLOR SUPER G200,
FUJICOLOR SUPER G400,
FUJICOLOR SUPER HG1600,
FUJICOLOR REALA,
FUJICOLOR Utsurundesu Super 800,
FUJICOLOR 160 PROFESSIONAL NS, and
FUJICOLOR 160 PROFESSIONAL L (trade names), each of which is manufactured by Fuji Photo Film Co., Ltd., and
Kodak SUPERGOLD 100,
Kodak SUPERGOLD 200,
Kodak Gold 400,
Kodak Gold 1600,
Kodak EKTAR 25,

Kodak EKTAR 100,
Kodak EKTAR 1000,
Vericolor III PROFESSIONAL FILM Type S, and
Vericolor III PROFESSIONAL FILM Type L (trade names), each of which is manufactured by Eastman Kodak Co., and
Konica Color Super DD100,
Konica Color Super DD200,
Konica Color XG400, and
Konica Color GX3200 (trade names), each of which is manufactured by Konica Corporation.

Light-sensitive materials for color photographic prints to which the present invention is applied are described. The method of the present invention can be applied to light-sensitive materials for both amateurs and professionals.

The method of the present invention can also effectively be applied to silver halide color photographic light-sensitive materials containing a pyrrolotriazole derivative as a cyan coupler. The use of pyrrolotriazole derivatives as cyan couplers is disclosed, for example, in JP-A-5-150423, JP-A-5-255333, JP-A-202004, JP-A-7-48376, and JP-A-9-189988.

Hereinbelow, the constitution of the light-sensitive material other than the above pyrrolotriazole-type cyan coupler is described.

The light-sensitive silver halide emulsion in the light-sensitive material as a positive material, such as a color paper, is preferably made up of silver halide grains that have a silver chloride content of at least 95 mol% with the rest being silver bromide and are substantially free from silver iodide. Herein, the term "substantially free from silver iodide" means that the silver iodide content is generally 1 mol% or less, preferably 0.2 mol% or less, and more preferably 0 mol%. In view of the rapid processibility, the above silver halide emulsion is preferably a silver halide emulsion particularly having a silver chloride content of 98 mol% or more. Among such silver halides, silver halide grains having a silver bromide localized phase on the surface of silver chloride grains are particularly preferable, because a high sensitivity can be obtained and the photographic performance can be stabilized.

The silver halide emulsion contained in at least one light-sensitive silver halide emulsion layer is preferably a monodisperse emulsion wherein the deviation coefficient of the grain size distribution (obtained by dividing the standard deviation of the grain size distribution by the average grain size) is preferably 15% or less and more preferably 10% or less. Further, for the purpose of obtaining a wide latitude, two or more of such monodisperse emulsions are mixed and are used in the same layer, preferably. In that case, the monodisperse emulsions are different in the average grain size preferably by 15% or more, more preferably 20 to 60%, and further particularly preferably 25 to 50%. Further, the monodisperse emulsions are different in sensitivity preferably by 0.15 to 0.50 log E (log E is the logarithmic exposure amount), more preferably 0.20 to 0.40 log E, and further more preferably 0.25 to 0.35 log E.

In the positive light-sensitive material to which the present invention is applied, it is effective to use a silver halide emulsion wherein silver bromochloride, having a silver chloride content of 95 mol% or more and substantially free from silver iodide, contains an iron and/or ruthenium and/or osmium compound in an amount of 1×10^{-5} to 1×10^{-3} mol per mol of the silver halide, and wherein a silver bromide localized phase contains an iridium compound in an amount of 1×10^{-7} to 1×10^{-5} mol per mol of the silver halide.

As the silver halide emulsion, generally one is used that is physically ripened and/or chemically ripened and spectrally sensitized. Additives used in such steps are described in RD Nos. 17643, 18716, and 307105, and the pertinent sections thereof are collected in the table below. In the light-sensitive material for use in the present invention, two or more emulsions different in at least one of the following properties: that are the grain size of the light-sensitive silver halide emulsion, the grain size distribution, the halogen composition, the shape of the grains, and the sensitivity, can be mixed for use in the same layer. Silver halide grains whose surfaces are fogged, described in US-A-4 082 553; silver halide grains whose insides are fogged, described in US-A-4 626 498 and JP-A-59-214852; or colloidal silver, is preferably applied in the light-sensitive silver halide emulsion layer and/or the substantially non-light-sensitive hydrophilic colloid layer. The term "silver halide grains whose insides or surfaces are fogged" means silver halide grains whose entire exposed part and unexposed part of the light-sensitive material can be subjected to development uniformly (unimagewise), and the method of preparing them is described in US-A-4 626 498 and JP-A-59-214852. The silver halide that forms the inside nuclei of the core/shell-type silver halide grains whose insides are fogged, may be made different in the silver halide composition. As the silver halide whose grains' insides or surfaces are fogged, any of silver chloride, silver bromochloride, silver bromoiodide, and silver bromoiodochloride can be used. The average grain size of these fogged silver halide grains is preferably 0.01 to 0.75 μm, and particularly preferably 0.05 to 0.6 μm. The shape of the grains may be regular, and the emulsion may be a polydisperse emulsion, but it is preferably a monodisperse emulsion (wherein at least 95% of the number of the silver halide grains or the weight of the silver halide grins falls within grains whose diameters are the average grain diameter ± 40%).

For the silver halide photographic light-sensitive material for printing or photographing to which the invention is applied, conventionally known photographic materials and additives can be used.

For example, as the photographic base, a transmission-type base or a reflective-type base can be used. As the transmission-type base, a transparent film, such as a cellulose nitrate film and a polyethylene terephthalate film, and one wherein a film, for example, of a polyester of 2,6-naphthalenedicarboxylic acid (NDCA) with ethylene glycol (EG) or a polyester of NDCA, terephthalic acid, and EG, is provided with an information recording layer, such as a magnetic layer, are preferably used. For the purpose of the present invention, a reflective-type base is preferably used, and particularly preferably a reflective-type base, wherein a laminate has a plurality of polyethylene layers or polyester layers and wherein at least one of such water-resistant resin layers (laminated layers) contains a white pigment, such as titanium oxide, is used.

Preferably the above water-resistant resin layers contain a fluorescent whitening agent. Further, a fluorescent whitening agent may be dispersed in the hydrophilic colloid layer of the light-sensitive material. As the fluorescent whitening agent, preferably a benzoxazole-series fluorescent whitening agent, a cumarin-series fluorescent whitening agent, or a pyrazoline-series fluorescent whitening agent can be used, and more preferably a benzoxazolylnaphthalene-series fluorescent whitening agent or a benzoxazolylstilbene-series fluorescent whitening agent is used. The amount to be used is not particularly limited, but preferably it is 1 to 100 mg/m^2. When it is mixed with a water-resistant resin, preferably the mixing proportion is 0.0005 to 3% by weight, and more preferably 0.001 to 0.5% by weight, to the resin.

A hydrophilic colloid layer containing a white pigment may be applied on the base.

Further, the reflective-type base may be a base having a specular reflective or a second-type diffusion reflective metal surface.

In the light-sensitive material according to the present invention, in order to improve the sharpness or the like of images, preferably the hydrophilic colloid layer contains a dye that can be decolored by processing (an oxonol dye inter alia), as described in European Patent EP-A-0,337,490(A2), pages 27 to 76, so that the optical reflection density of the light-sensitive material at 680 nm may be 0.70 or more, or preferably the water-resistant resin layer of the base contains 12% by weight or more (more preferably 14% by weight or more) of titanium oxide whose surface has been treated with a bivalent to tetravalent alcohol (e.g. trimethylolethane).

Further, it is preferable to add a mildewproofing agent as described in JP-A-63-271247 to the light-sensitive material according to the present invention, in order to prevent the proliferation of various mildew and fungus that will otherwise proliferate in the hydrophilic colloid layer to deteriorate images.

The light-sensitive material according to the present invention may be exposed to visible light or infrared radiation. The method of exposure may be of low-intensity exposure or high-intensity short-period exposure, and particularly, in the latter case, a laser scanning exposure system is preferable, wherein the exposure time per pixel is shorter than 10^{-4} sec.

In the light-sensitive material to which the present invention is applied, when the above pyrrolotriazole-type coupler is contained, the effect of the present invention in improving the whiteness of the white background is great, but the method of the present invention can be applied also to light-sensitive materials containing another cyan coupler besides the above coupler.

Preferably, the cyan coupler, the magenta coupler, or the yellow coupler is impregnated into a loadable latex polymer (e.g. US-A-4 203 716) in the presence (or absence) of a high-boiling organic solvent shown in the above table, or the coupler is dissolved together with a water-insoluble and organic-solvent-soluble polymer, and the resulting solution is emulsified and dispersed in an aqueous hydrophilic colloid solution.

Preferable water-insoluble and organic-solvent-soluble polymers are homopolymers or copolymers described in US-A-4 857 449, columns 7 to 15, and International Publication WO 88/00723, pages 12 to 30. In particular, methacrylate polymers and acrylamide polymers are particularly preferable, in view of image dye stability and the like.

In the light-sensitive material to which the present is applied, preferably a dye-image-preservability-improving compound as described in European Patent EP-A-0,277,589(A2) is used in combination with a pyrazoloazole coupler, the above pyrrolotriazole coupler, or an acylacetamide-type yellow coupler.

As the cyan coupler, in addition to phenol-type couplers and naphthol-type couplers as described in the known documents in the above table, cyan couplers, as described in JP-A-2-33144, European Patent EP-A-0,333,185(A2), JP-A-64-32260, European Patent EP-A-0,456,226(A1), European Patent EP-A-0,484,909, European Patent EP-A-0,488,248, and EP-A-0,491,197(A1), can be used.

As the magenta coupler used in the present invention, in addition to 5-pyrazolone-series magenta couplers as described in the known documents in the above table, those described in International Publication WO 92/18901, WO 92/18902, and WO 92/18903 are also preferable. In addition to these 5-pyrazolone magenta couplers, known pyrazoloazole-type couplers can be used in the present invention, and among them, pyrazoloazoles described in JP-A-61-65245, JP-A-61-65246, JP-A-61-14254, and European Patents EP-A-226,849, and EP-A-294,785 are preferably used in view of the hue, the image stability, the color-forming property, and the like.

As the yellow coupler, known acylacetanilide-type couplers are preferably used, and among them, couplers described in European Patent EP-A-0,447,969, JP-A-5-107701, JP-A-5-113642, European Patent EP-A-0,482,552, and EP-A-0,524,540 are preferably used.

As couplers whose color-formed dyes have a suitable diffusibility, those described in US-A-4 366 237, GB-A-2 125 570, EP-A-96 873, and DE 3 234 533 are preferable. Couplers for correcting undesired absorption of color-formed dyes are preferably yellow-colored cyan couplers represented by formula (CI), (CII), (CIII), or (CIV) (particularly YC-86 on page 84) described in EP-A-456,257(A1), page 5; yellow-colored magenta couplers ExM-7 (page 202), EX-1 (page 249), and EX-7 (page 251) described in EP-A-456,257(A1); magenta-colored cyan couplers CC-9 (column 8) and CC-13 (column 10) described in US-A-4 833 069; (2) (column 8) of US-A-4 837 136, and colorless masking couplers (particularly, exemplified compounds on pages 36 to 45) represented by formula (A) in claim 1 of WO 92/11575.

As a compound (including a coupler) that reacts with the oxidized product of a developing agent to release a residue of a photographically useful compound, the following can be listed:

Development-inhibitor-releasing compounds: compounds represented by formula (I), (II), (III), or (IV) described in EP-A-378,236(A1), page 11 (particularly, T-101 (page 30), T-104 (page 31), T-113 (page 36), T-131 (page 45), T-144 (page 51), and T-158 (page 58)); compounds represented by formula (I) described in EP-A-436,938(A2), page 7 (particularly D-49 (page 51)), compounds represented by formula (1) described in EP-A-568,037 (particularly (23) (page 11)), and compounds represented by formula (I), (II), or (III) described in EP-A-440,195(A2), pages 5 to 6 (particulaly I-(1) on page 29);
bleaching-accelerator-releasing compounds: compounds represented by formula (I) or (I') described in page 5 of EP-A-310,125(A2) (particularly (60) and (61) on page 61) and compounds represented by formula (C) in claim 1 of JP-A-6-59411 (particularly (7) (page 7); ligand-releasing compounds: compounds represented by LIG-X recited in claim 1 in US-A-4 555 478 (particularly compounds, in column 12, lines 21 to 41); leuco-dye-releasing compounds: compounds 1 to 6 in columns 3 to 8 in US-A-4 749 641; fluorescent-dye-releasing compounds: compounds represented by COUP-DYE in claim 1 in US-A-4 774 181 (particularly Compounds 1 to 11 in columns 7-10); development-accelerator- or fogging-agent-releasing compounds: compounds represented by formula (1), (2), or (3) in column 3 of US-A-4 656 123 (particularly (I-22) in column 25), and ExZK-2 in EP-A-450,637(A2), page 75, lines 36 to 38; and compounds that do not release groups capable of forming dyes until they are split off: compounds represented by formula (I) of claim 1 of US-A-4 857 447 (particularly Y-1 to Y-19 in columns 25 to 36).

As additives other than the couplers, the following are preferable:

Dispersion mediums of oil-soluble organic compounds: P-3, 5, 16, 19, 25, 30, 42, 49, 54, 55, 66, 81, 85, 86, and 93 (pages 140 to 144) of JP-A-62-215272; latexes for impregnation of oil-soluble organic compounds: latexes described in US-A-4 199 363; scavengers for the oxidized products of developing agents: compounds represented by formula (I) in column 2, lines 54 to 62 of US-A-4 978 606 (particularly I-, (1), (2), (6), and (12) (columns 4 to 5), compounds represented by formulae in column 2, lines 5 to 10 of US-A-4 923 787 (particularly compound 1 (column 3); antistaining agents: compounds represented by any of formulae (I) to (III) on page 4, lines 30 to 33 of EP-A-298,321 (particularly I-47, 72, III-1, and 27 (pages 24 to 48); antifading agents: compounds A-6, 7, 20, 21, 23, 24, 25, 26, 30, 37, 40, 42, 48, 63, 90, 92, 94, and 164 (pages 69 to 118) of EP-A-298,321, compounds II-1 to III-23 in columns 25 to 38 of US-A-5 122 444 (particularly III-10), compounds I-1 to III-4 on pages 8 to 12 of EP-A-471,347 (particularly II-2), and compounds A-1 to 48 in columns 32 to 40 of US-A-5 139 931 (particularly A-39 and 42); materials for reducing the usage of color-formation enhancing agents or color-mixing inhibitors: compounds I-1 to II-15 on pages 5 to 24 of EP-A-411,324 (particularly I-46); formalin scavengers: compounds SCV-1 to 28 on pages 24 to 29 of EP-A-477,932 (particularly SCV-8);
hardeners: compounds H-1, 4, 6, 8, and 14 on page 17 of JP-A-1-214845, compounds (H-1 to 54) represented by any of formulae (VII) to (XII) in columns 13 to 23 of US-A-4 618 573, compounds (H-1 to 76) represented by formula (6) shown in the lower right part on page 8 of JP-A-2-214852 (particularly H-14) and compounds recited in claim 1 of US-A-3 325 287; development-inhibitor precursors: compounds P-24, 37, and 39 (pages 6 to 7) of JP-A-62-168139 and compounds recited in claim 1 of US-A-5 019 492 (particularly 28 and 29 in column 7); antiseptics and mildewproofing agents: compounds I-1 to III-43 in columns 3 to 15 of US-A-4 923 790 (particularly II-1, 9, 10, and 18 and III-25); stabilizers and antifogging agents: compounds I-1 to (14) in columns 6 to 16 of US-A-4 923 793 (particularly I-1, 60, (2), and (13)) and compounds 1 to 65 in columns 25 to 32 of US-A-4 952 483 (particularly 36); chemical sensitizers: triphenylphosphine selenides, and compound 50 of JP-A-5-40324;
dyes: compounds a-1 to b-20 on pages 15 to 18 of JP-A-3-156450 (particularly a-1, 12, 18, 27, 35, 36, and b-5) and compounds V-1 to 23 on page 27 to 29 of JP-A-3-156450 (particularly V-1), compounds F-I-1 to F-II-43 on pages 33 to 55 of EP-A-445,627 (particularly F-I-11 and F-II-8), compounds III-1 to 36 on pages 17 to 28 of EP-A-457,153 (particularly III-1 and 3), fine crystal dispersions of Dye-1 to 124 of 8 to 26 of WO 88/04794, compounds 1 to 22 on pages 6 to 11 of EP-A-319,999 (particularly compound 1), compounds D-1 to 87 represented by any of formulas (1) to (3) (pages 3 to 28) of EP-A-519,306, compounds 1 to 22 represented by formula (I) (columns 3 to 10) of US-A-4 268 622, and compounds (1) to (31) represented by formula (I) (columns 2 to 9) of US-A-4 923 788;

UV absorbers: compounds (18b) to (18r) and 101 to 427 represented by formula (1) (pages 6 to 9) of JP-A-46-3335, compounds (33) to (66) represented by formula (I) (pages 10 to 44) and compounds HBT-1 to 10 represented by formula (III) (page 14) of EP-A-520,938, and compounds (1) to (31) represented by formula (1) (columns 2 to 9) of EP-A-521,823.

According to the processing method of the silver halide color photographic light-sensitive material of the present invention, even when a processing solution is regenerated repeatedly with the used amount of its regenerating agent lessened, to recycle it, such excellent effects can be attained that no stain occurs, that good bleaching can be effected, and that the load on the environment can be decreased.

The present invention is described in more detail with reference to the following examples, but the present invention is not limited thereto.

EXAMPLES

Example 1

Layers having the below-shown compositions were formed on a cellulose triacetate film support (base), that had been provided an undercoat, to prepare a multi-layer color photographic light-sensitive material.

(Compositions of Light-sensitive Layers)

Main materials used in each layer were classified as follows:

ExC: Cyan coupler	UV: Ultraviolet ray absorbent
ExM: Magenta coupler	HBS: High-boiling organic solvent
ExY: Yellow coupler	H: Gelatin hardening agent
ExS: Sensitizing dye	

Figures corresponding to each component represents the coating amount in terms of g/m^2, and for silver halide in terms of silver. With respect to sensitizing dyes, the coating amount is shown in mol, per mol of silver halide in the same layer.

First Layer (Halatation-prevention layer)

Black colloidal silver	silver 0.09
Gelatin	1.60
ExM-1	0.12
ExF-1	2.0 x 10^{-3}
Solid disperse dye ExF-2	0.030
Solid disperse dye ExF-3	0.040
HBS-1	0.15
HBS-2	0.02

Second Layer (Intermediate layer)

Silver bromoiodide emulsion M	silver 0.065
ExC-2	0.04
Polyethyl acrylate latex	0.20

(continued)

Gelatin	1.04

Third Layer (Low-sensitivity red-sensitive emulsion layer)

Silver bromoiodide emulsion A	silver 0.25
Silver bromoiodide emulsion B	silver 0.25
ExS-1	6.9×10^{-5}
ExS-2	1.8×10^{-5}
ExS-3	3.1×10^{-4}
ExC-1	0.17
ExC-3	0.030
ExC-4	0.10
ExC-5	0.020
ExC-6	0.010
Cpd-2	0.025
HBS-1	0.10
Gelatin	0.87

Fourth Layer (Medium-sensitivity red-sensitive emulsion layer)

Silver bromoiodide emulsion C	silver 0.70
ExS-1	3.5×10^{-4}
ExS-2	1.6×10^{-5}
ExS-3	5.1×10^{-4}
ExC-1	0.13
ExC-2	0.060
ExC-3	0.0070
ExC-4	0.090
ExC-5	0.015
ExC-6	0.0070
Cpd-2	0.023
HBS-1	0.10
Gelatin	0.75

Fifth Layer (High-sensitivity red-sensitive emulsion layer)

Silver bromoiodide emulsion D	silver 1.40

(continued)

ExS-1	2.4×10^{-4}
ExS-2	1.0×10^{-4}
ExS-3	3.4×10^{-4}
ExC-1	0.10
ExC-3	0.045
ExC-6	0.020
ExC-7	0.010
Cpd-2	0.050
HBS-1	0.22
HBS-2	0.050
Gelatin	1.10

Sixth Layer (Intermediate layer)

Cpd-1	0.090
Solid disperse dye ExF-4	0.030
HBS-1	0.050
Polyethyl acrylate latex	0.15
Gelatin	1.10

Seventh Layer (Low-sensitivity green-sensitive emulsion layer)

Silver bromoiodide emulsion E	silver 0.15
Silver bromoiodide emulsion F	silver 0.10
Silver bromoiodide emulsion G	silver 0.10
ExS-4	3.0×10^{-5}
ExS-5	2.1×10^{-4}
ExS-6	8.0×10^{-4}
ExM-2	0.33
ExM-3	0.086
ExY-1	0.015
HBS-1	0.30
HBS-3	0.010
Gelatin	0.73

Eighth Layer (Medium-sensitivity green-sensitive emulsion layer)

Silver bromoiodide emulsion H	silver 0.80
ExS-4	3.2×10^{-5}
ExS-5	2.2×10^{-4}
ExS-6	8.4×10^{-4}
ExC-8	0.010
ExM-2	0.10
ExM-3	0.025
ExY-1	0.018
ExY-4	0.010
ExY-5	0.040
HBS-1	0.13
HBS-3	4.0×10^{-3}
Gelatin	0.80

Ninth Layer (High-sensitivity green-sensitive emulsion layer)

Silver bromoiodide emulsion I	silver 1.25
ExS-4	3.7×10^{-5}
ExS-5	8.1×10^{-5}
ExS-6	3.2×10^{-4}
ExC-1	0.010
ExM-1	0.020
ExM-4	0.025
ExM-5	0.040
Cpd-3	0.040
HBS-1	0.25
Polyethyl acrylate latex	0.15
Gelatin	1.33

Tenth Layer (Yellow filter layer)

Yellow colloidal silver	silver 0.015
Cpd-1	0.16
Solid disperse dye ExF-5	0.060
Solid disperse dye ExF-6	0.060

(continued)

Oil-soluble dye ExF-7	0.010
HBS-1	0.60
Gelatin	0.60

Eleventh Layer (Low-sensitivity blue-sensitive emulsion layer)

Silver bromoiodide emulsion J	silver 0.09
Silver bromoiodide emulsion K	silver 0.09
ExS-7	8.6×10^{-4}
ExC-8	7.0×10^{-3}
ExY-1	0.050
ExY-2	0.22
ExY-3	0.50
ExY-4	0.020
Cpd-2	0.10
Cpd-3	4.0×10^{-3}
HBS-1	0.28
Gelatin	1.20

Twelfth Layer (High-sensitivity blue-sensitive emulsion layer)

Silver bromoiodide emulsion L	silver 1.00
ExS-7	4.0×10^{-4}
ExY-2	0.10
ExY-3	0.10
ExY-4	0.010
Cpd-2	0.10
Cpd-3	1.0×10^{-3}
HBS-1	0.070
Gelatin	0.70

Thirteenth Layer (First protective layer)

UV-1	0.19
UV-2	0.075
UV-3	0.065

(continued)

HBS-1	5.0×10^{-2}
HBS-4	5.0×10^{-2}
Gelatin	1.8

Fourteenth Layer (Second protective layer)

Silver bromoiodide emulsion M	silver 0.10
H-1	0.40
B-1 (diameter: 1.7 μm)	5.0×10^{-2}
B-2 (diameter: 1.7 μm)	0.15
B-3	0.05
S-1	0.20
Gelatin	70

Further, in order to improve preservability, processability, pressure resistance, antimold and antibacterial properties, antistatic property, and coating property, compounds of W-1 to W-3, B-4 to B-6, and F-1 to F-17, and salts of iron, lead, gold, platinum, palladium, iridium, and rhodium were suitably added in each layer.

Details of emulsions used in this Example are shown in Table 1.

Table 1

	Average content of AgI (%)	Deviation coefficient regarding AgI content among grains (%)	Average grain-diameter corresponding to sphere (μm)	Deviation coefficient regarding grain-diameter (%)	Diameter in projected area corresponding to circle (μm)	Ratio of diameter/thickness
Emulsion A	1.7	10	0.46	15	0.56	5.5
B	3.5	15	0.57	20	0.78	4.0
C	8.9	25	0.66	25	0.87	5.8
D	8.9	18	0.84	26	1.03	3.7
E	1.7	10	0.46	15	0.56	5.5
F	3.5	15	0.57	20	0.78	4.0
G	8.8	25	0.61	23	0.77	4.4
H	8.8	25	0.61	23	0.77	4.4
I	8.9	18	0.84	26	1.03	3.7
J	1.7	10	0.46	15	0.50	4.2
K	8.8	18	0.64	23	0.85	5.2
L	14.0	25	1.28	26	1.46	3.5
M	1.0	—	0.07	15	—	1

In Table 1,

(1) Emulsions J to L were subjected to a reduction sensitization using thiourea dioxide and thiosulfonic acid at the time of preparation of grains, according to the Example described in JP-A-2-191938.

(2) Emulsions A to I were subjected to a gold sensitization, a sulfur sensitization, and a selenium sensitization under the presence of respective sensitizing dyes described in each layer and sodium thiocyanate, according to the Example described in JP-A-3-237450.

(3) At the preparation of tabular grains, low-molecular-weight gelatin was used, according to the Example described in JP-A-1-158426.

(4) Tabular grains were observed a rearrangement line by a high-pressure electron microscope, as described in JP-A-3-237450.

(5) Emulsion L contained double-structure grains, whose grains' had a core high in iodide content, as described in JP-A-60-143331.

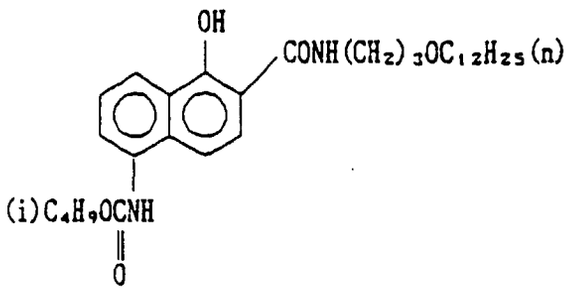
Preparation of a dispersion of an organic solid disperse dye

ExF-2 illustrated below was dispersed in the manner as described below.

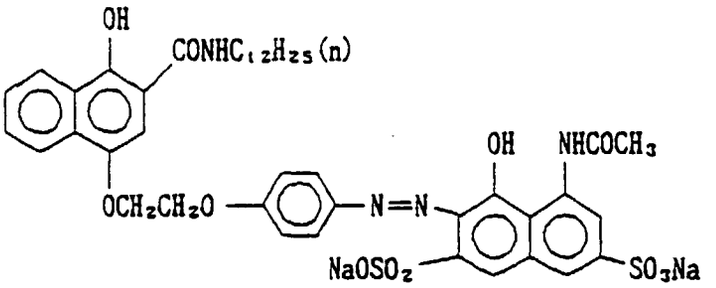
Into 700-ml pot mill, were placed 21.7 ml of water, 3 ml of a 5% aqueous solution of sodium p-octylphenoxyethoxyethoxyethanesulfonate, and 0.5 g of a 5% aqueous solution of p-octylphenoxypolyoxyethylene ether having a degree of polymerization of 10, followed by addition of 5.0 g of the dye ExF-2 and 500 ml of zirconium oxide beads having a diameter of 1 mm. The resulting mixture was dispersed for 2 hrs. The dispersion was conducted by means of a BO-type vibration ball mill, manufactured by Chuo-Koki Co. After the dispersion, the content was recovered, and added into 8 g of 12.5% aqueous gelatin solution. Then the beads were removed by filtration, and a gelatin dispersion of the dye was obtained. The average grain diameter of the fine grains of the dye was 0.44 μm.

Dispersions of ExF-3, ExF-4, and ExF-6 in the form of solid fine grains were obtained in the same manner as above. Average grain diameters of the fine grains of the dye were 0.24 μm, 0.45 μm and 0.52 μm, respectively. ExF-5 was dispersed by the microprecipitation dispersion method as described in Example 1 of EP-A-549,489. The average grain diameter of the fine grains of ExF-5 was 0.06 μm.

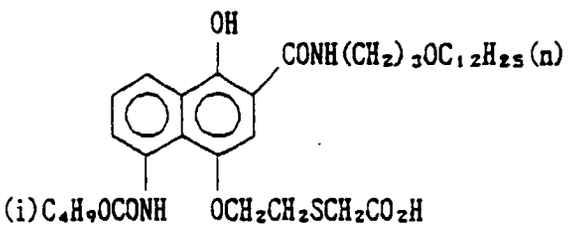
Ex C－1



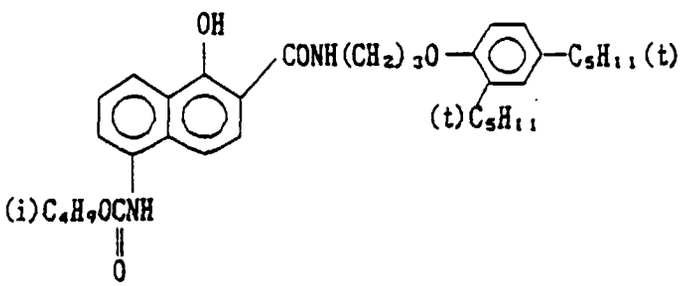
Ex C－2



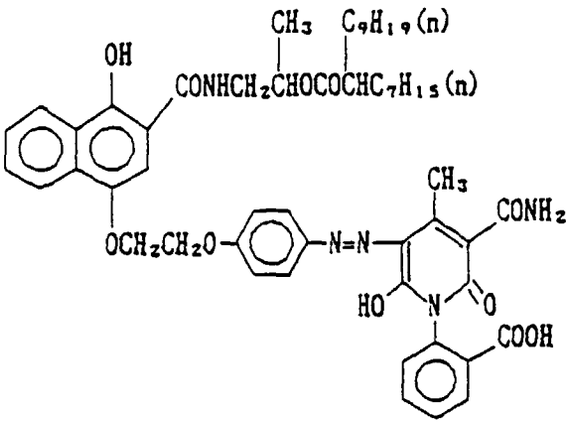
Ex C－3



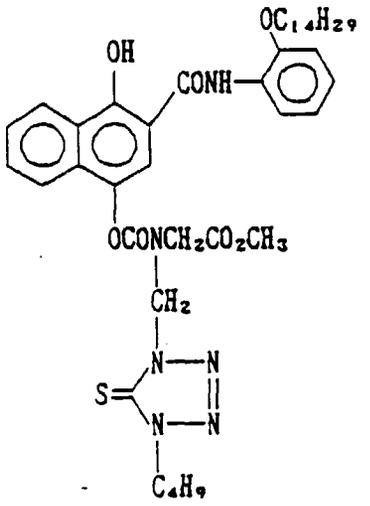
Ex C－4



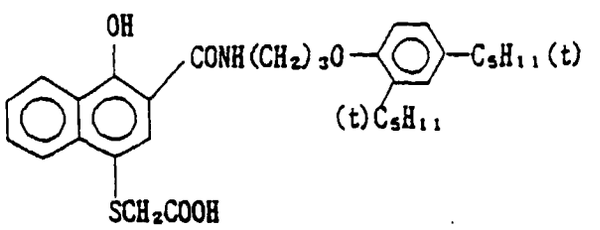
Ex C-5



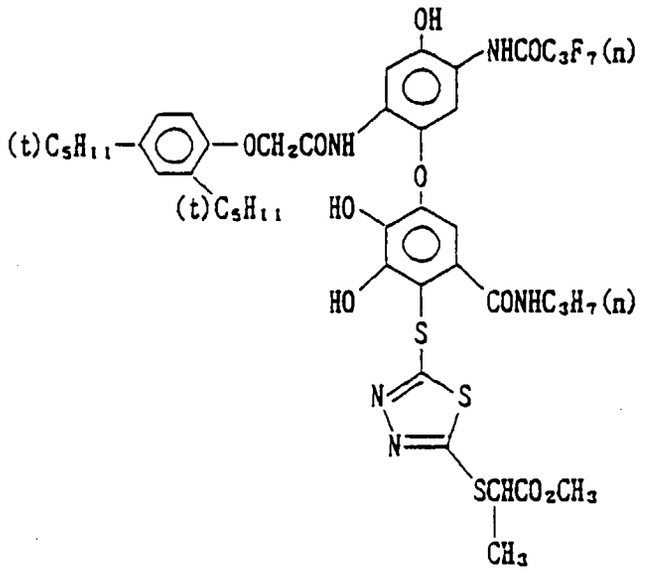
Ex C-6



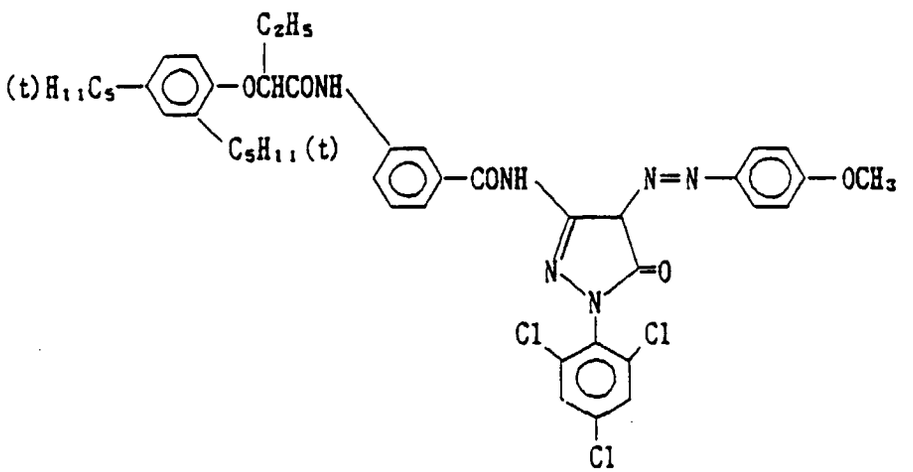
Ex C-7



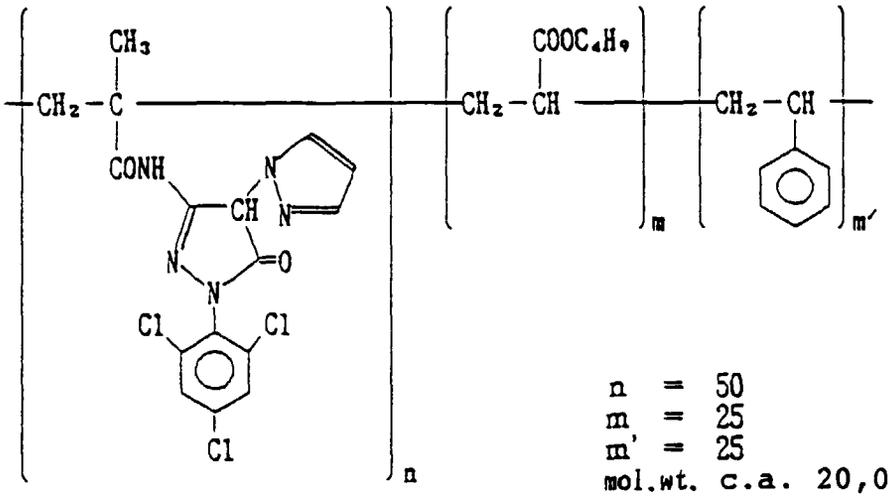
Ex C-8


OH
NHCOC3F7(n)
(t)C5H11
OCH2CONH
(t)C5H11
O
HO
HO
CONHC3H7(n)
S
N
S
N
SCHCO2CH3
CH3

Ex M-1

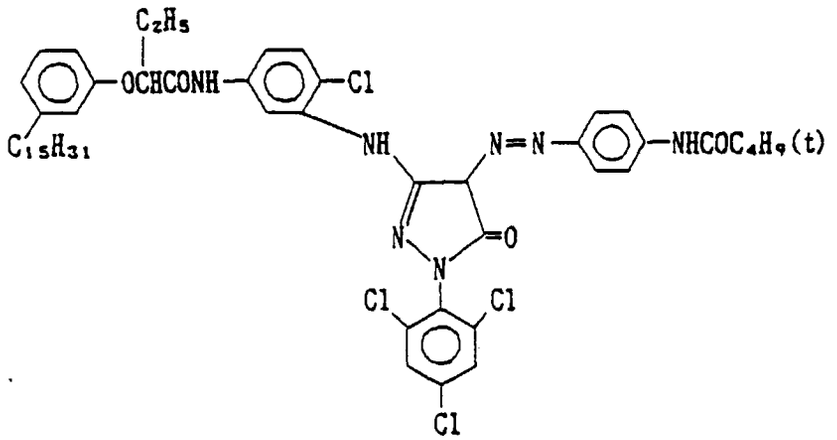

C2H5
(t)H11C5
OCHCONH
C5H11(t)
CONH
N=N
OCH3
N
N
=O
Cl
Cl
Cl

Ex M－2

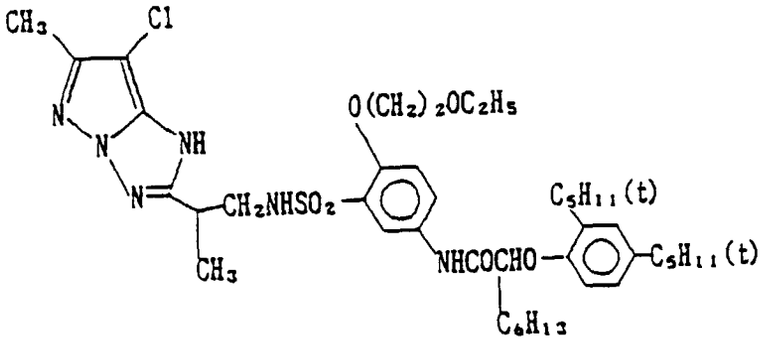


n = 50
m = 25
m' = 25
mol.wt. c.a. 20,000

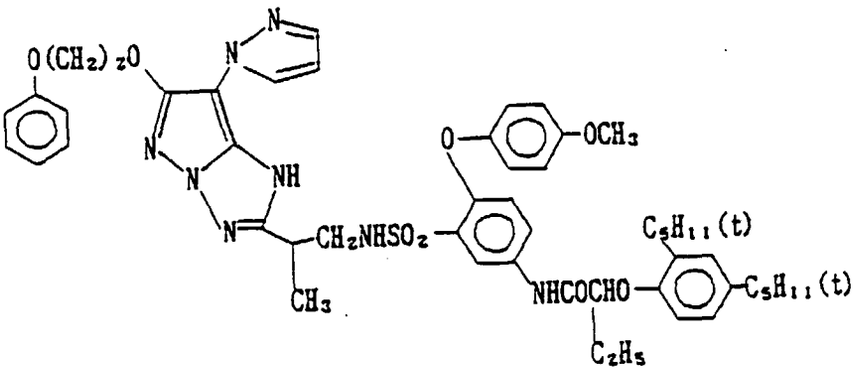
Ex M－3



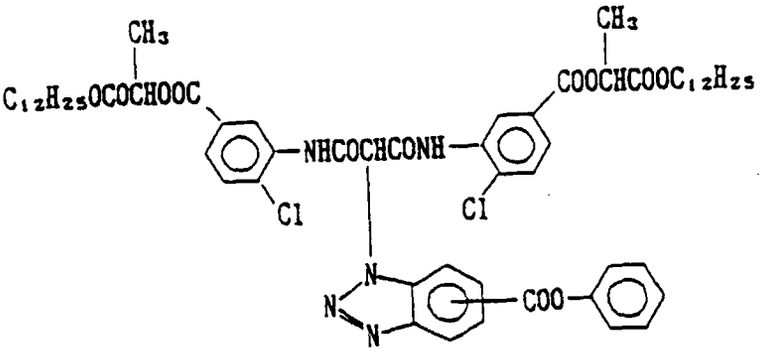
Ex M－4



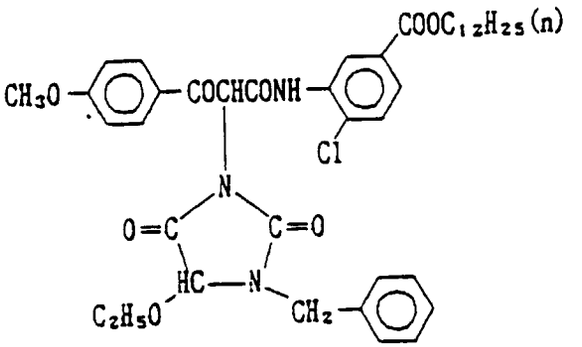
Ex M－5



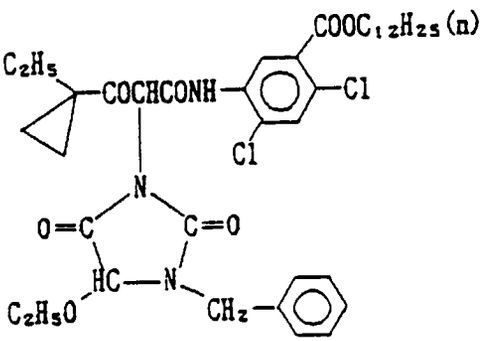
Ex Y－1



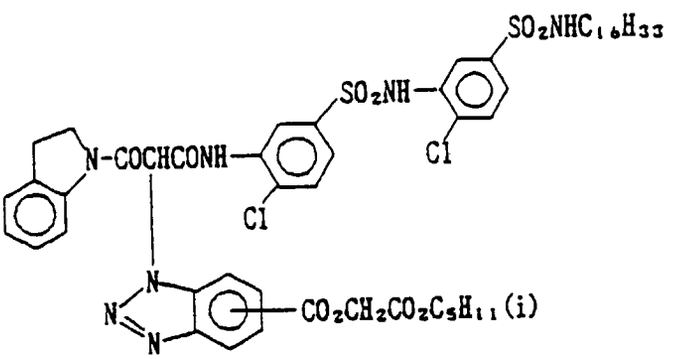
Ex Y－2



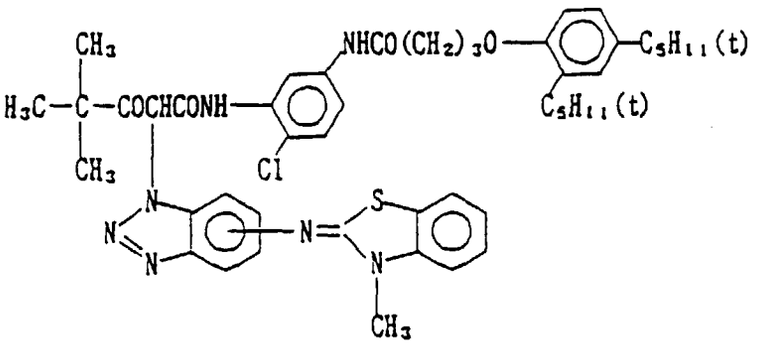
Ex Y－3



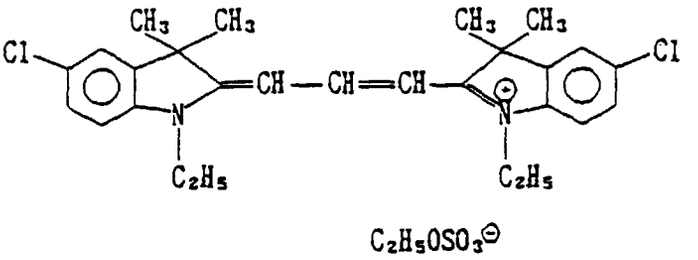
Ex Y－4



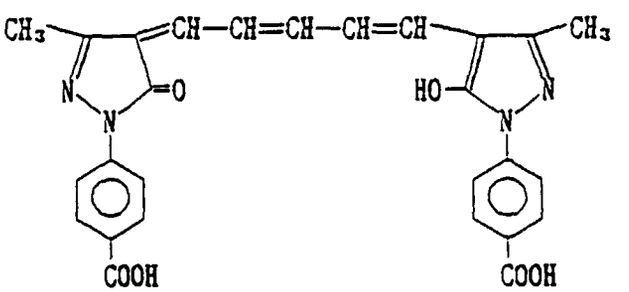
Ex Y-5



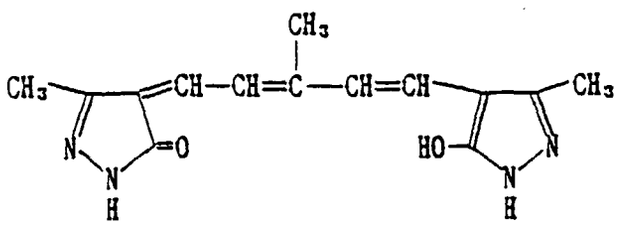
Ex F-1



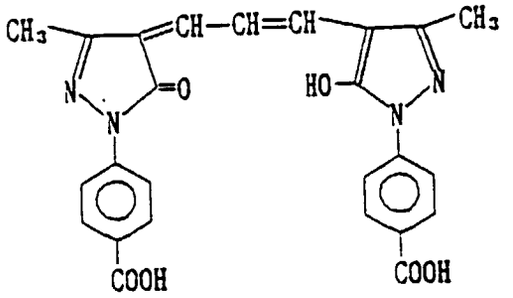
Ex F-2



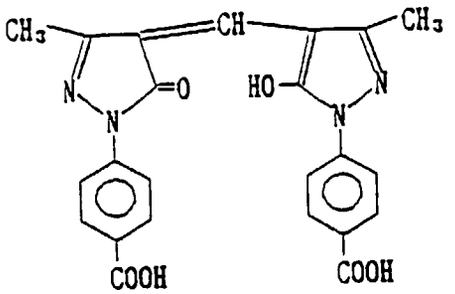
Ex F-3



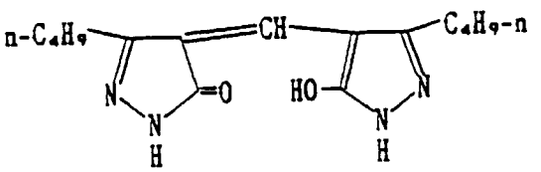
Ex F－4



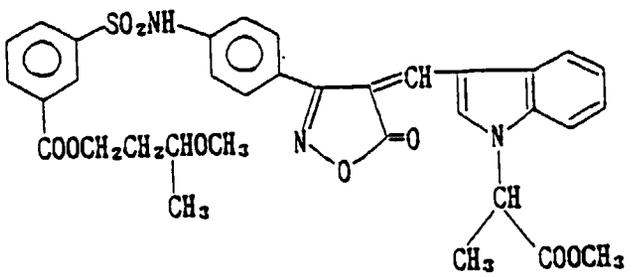
Ex F－5



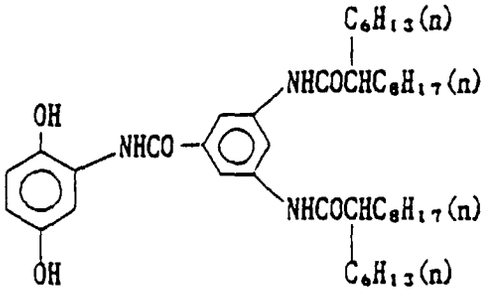
Ex F－6



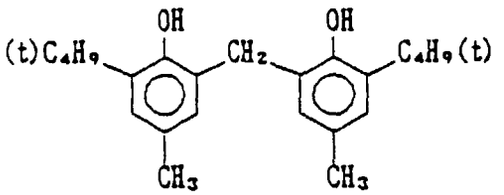
Ex F－7



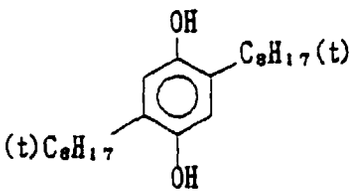
Cpd-1



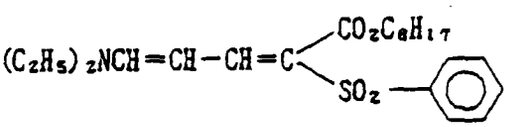
Cpd-2



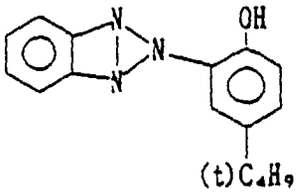
Cpd-3



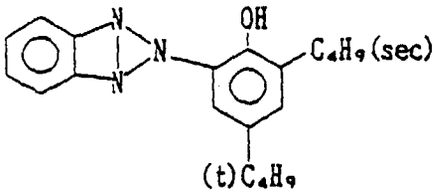
UV-1



UV-2



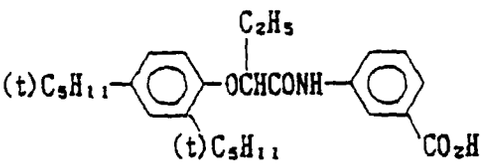
UV-3



HBS-1 tricresyl phosphate

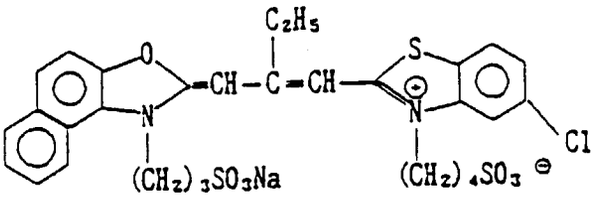
HBS-2 di-n-butyl phthalate

HBS-3

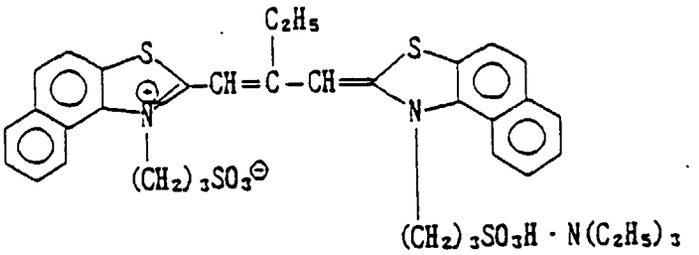


HBS-4 tri(2-ethylhexyl) phosphate

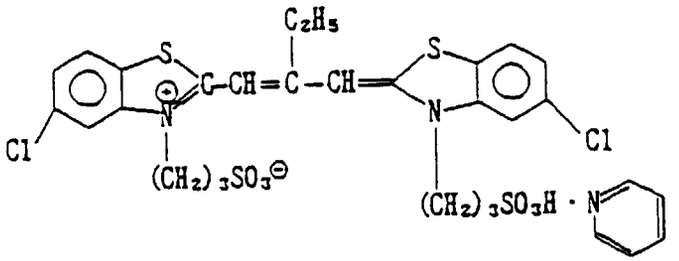
Ex S－1



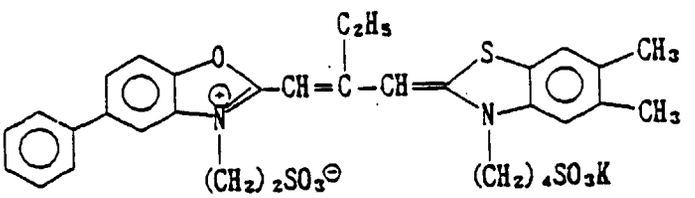
Ex S－2



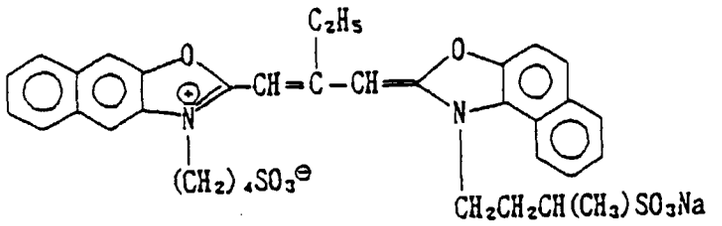
Ex S－3



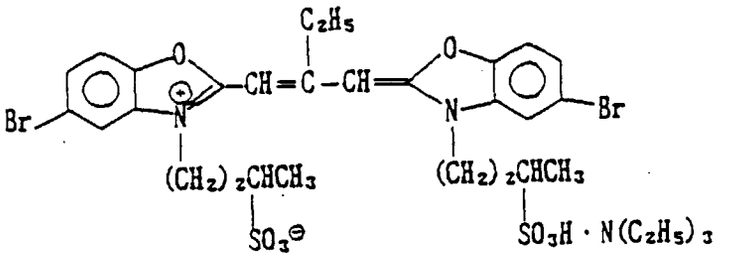
Ex S－4



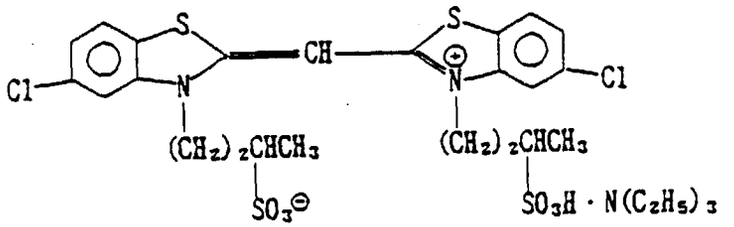
Ex S－5



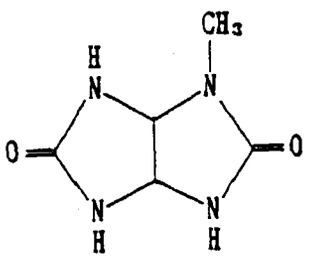
Ex S－6



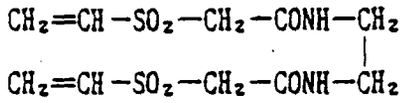
Ex S－7



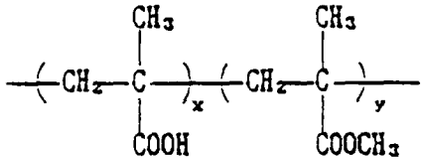
S－1



H－1



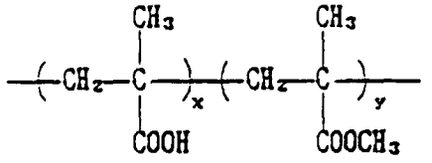
B－1



x/y=10/90 (weight ratio)

average molecular weight:c.a. 35,000

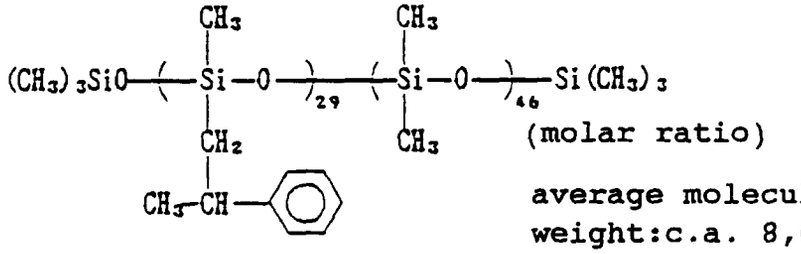
B－2



x/y=40/60 (weight ratio)

average molecular weight:c.a. 20,000

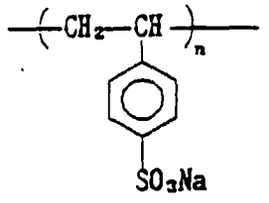
B－3



(molar ratio)

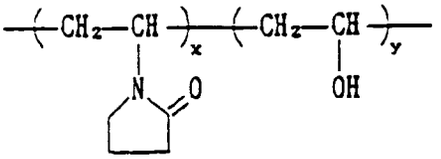
average molecular weight:c.a. 8,000

B－4



average molecular weight:c.a. 750,000

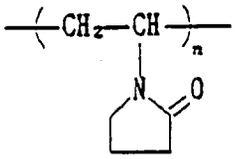
B－5



x/y=70/30 (weight ratio)

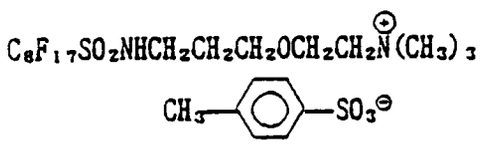
average molecular weight:c.a. 17,000

B－6

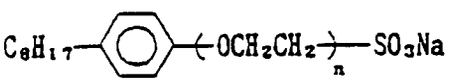


average molecular weight:c.a. 10,000

W－1

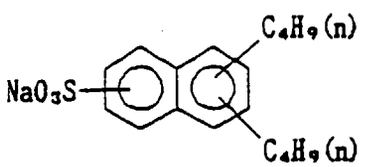


W－2

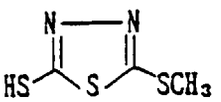


n＝2 ～ 4

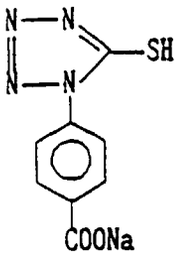
W－3



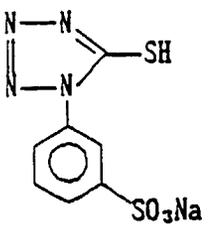
F－1



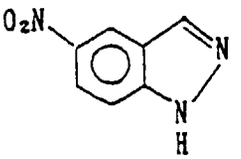
F－2



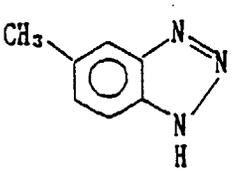
F－3



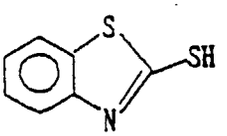
F－4



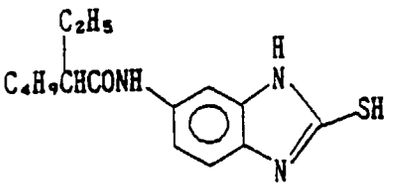
F－5



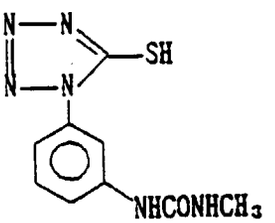
F－6



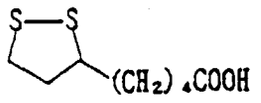
F－7



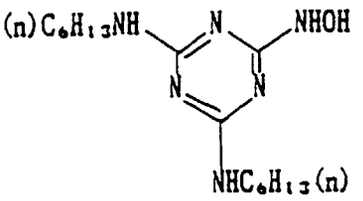
F－8



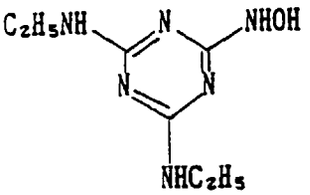
F－9



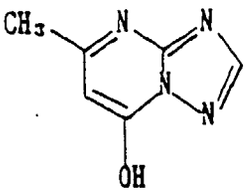
F－10



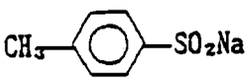
F－11



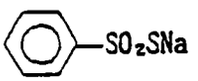
F－12



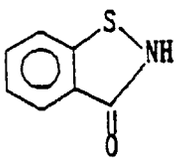
F－13



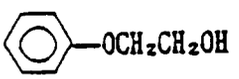
F－14



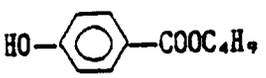
F－15



F－16



F－17



The above light-sensitive material was cut into the size of the 135 film stipulated by JIS standard "JIS K-7519 (1982)," which was named Sample 101.

Sample 101 was exposed to light imagewise and was continuously processed with processing solutions that were prescribed as shown below, until the cumulative total of the replenishment rate of the bleaching solution reached 8,000 ml. In the bleaching step, the overflow was regenerated every 100 liters. As shown in the chart in Fig. 1, the regeneration was carried out in such a manner that a bleaching replenisher 2, from a replenishing tank 1, was supplied to a bleaching solution 3, in a bleaching tank 4, and the overflow 6 from the bleaching bath 4 was stored in a stock tank 5. Every time the overflow accumulated in an amount of 100 liters, air 8 was blown through the stored overflow 6 by an air

pump 7, for 4 hours. Thereafter, the below-described bleaching-solution-regenerating agent 13 was added in the amount shown in Table 3, to prepare a regenerated replenisher, and the regenerated replenisher was used as a bleaching replenisher from the next time, to continue the processing. In the figure, 9 is a pipe of air from the air pump 7 to an air-blowing part 10 in the stock tank 5; 11 is a stirrer; and 12 is a pipe of the regenerated replenisher to the replenishing tank. Further, an experiment wherein the time of the blowing of the air 8 to restore the oxidizing power of the overflow 6 was 2 hours, was also carried out. In the bleaching step, air was supplied from the bottom of the tank through aeration tubes, in an amount of 500 ml per min, during the processing.

Processing step				
Processing step	Processing		Replenishing rate*1	Tank Volume /liter
	time	temperature		
Color-developing	3 min 15 sec	38.0 °C	630 ml	2
Bleaching	3 min 00 sec	38.0 °C	715 ml	2
Washing (1)	30 sec	38.0 °C	430 ml	2
Fixing	3 min 00 sec	38.0 °C	430 ml	2
Washing (2)	1 min 00 sec	38.0 °C	770 ml	2
Stabilizing	30 sec	38.0 °C	570 ml	2
Drying	3 min	50.0 °C	-	-

*1 the replenishment rate was the amount per m^2 of the light-sensitive material

Washing (1) was separated to 2 tanks, and washing (2) was separated to 3 tanks, and each washing was carried out in a counter current mode from back side to forward. Further, in each step, the carried over amount of tank solution to the next step were respectively 60 ml, per m^2 of the light-sensitive material. Each crossover time was 3 sec which was included in the processing time of the preceding step.

The composition of each processing solution was as follows, respectively:

(Color-developer)

	Mother Solution (g)	Replenisher (g)
Diethylenetriaminepentaacetic acid	1.2	1.2
1-Hydroxyethylidene-1,1-diphosphonic acid	2.7	3.3
Potassium hydroxide	1.72	1.9
Sodium sulfite	3.84	4.8
Sodium bicarbonate	1.8	-
Potassium carbonate	31.7	39.0
Potassium bromide	1.4	0.37
Potassium iodide	1.3 mg	-
Hydroxylamine sulfate	2.5	3.1
4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.044	-
2-Methyl-4-[N-ethyl-N-(β-hydroxyethyl)-amino]aniline sulfate	4.7	5.9

(continued)

	Mother Solution (g)	Replenisher (g)
Water to make	1.0 liter	1.0 liter
pH	10.05	10.15

(Start bleaching replenisher)

Bleaching agent (*)	shown in Table 2
Maleic acid	33 g
Succinic acid	36 g
Ammonium nitrate	7 g
Potassium bromide	60 g
Water to make	1.0 liter
pH (pH was adjusted by aqueous ammonia)	4.9

* Each of ferric complex salts of compounds shown in Table 2 was used in Experimant Nos. 1 to 3, as the bleaching agent.

(Start tank solution)

The start replenisher was diluted to 1.1 times, and pH was adjusted to 5.0 with aqueous ammonia, to use as a start tank solution.

(Bleaching-solution-regenerating agent)

Bleaching agent (**)	shown in Table 2
Maleic acid	56 g
Succinic acid	60 g
Ammonium nitrate	14 g
Potassium bromide	80 g
Water to make	1.0 liter
pH (pH was adjusted by aqueous ammonia)	3.8

** Each of ferric complex salts of compounds shown in Table 2 was used in Experiment Nos. 1 to 3, as the

Table 2

No		Start bleaching replenisher	Bleaching-solution-regenerating agent
1	I - 15	28 g	54 g
2	1,3-diaminopropanetetraacetic acid	35 g	62 g
3	Ethylenediamine-N,N'-disuccinic acid	34 g	61 g

(Fixing solution)

	Mother solution (g)	Replenisher (g)
Ammonium sulfite	21	23
Aqueous ammonium thiosulfate solution (750 g/liter)	288	320 ml
Ethylenediaminetetraacetic acid	0.6	0.68
Water to make	1.0 liter	1.0 liter
pH (pH was adjusted by aqueous ammonia and acetic acid)	6.8	6.8

(Washing water)

Tap water was treated by passage through a mixed bed ion-exchange column filled with H-type strong acidic cation exchange resin (Amberlite IR-120B, trade name, made by Rohm & Haas) and OH-type strong basic anion exchange resin (Amberlite IRA-400, the same as the above) so that the concentrations of Ca ions and Mg ions in water were both made to decrease to 3 mg/liter or below, followed by adding 20 mg/liter of sodium dichlorinated isocyanurate and 150 mg/liter of sodium sulfate. The pH of this water was in the range of 6.5 to 7.5.

(Stabilizing solution and stabilizing replenisher)

	(g)
Triazole	1.5
N,N'-bis(1,2,4-triazole-1-ylmethyl)piperazine	0.5
Sodium p-toluenesulfinate	0.05
Polyoxyethylene-p-monononylphenylether (av. polymerization degree: 10)	0.2
Disodium ethylenediaminetetraacetate	0.05
Water to make	1.0 liter
pH	8.0

Sample 101 that was exposed to light of 20 CMS, and Sample 101 that was not exposed to light, were processed with the solution with which the continuous processing had been made, the residual amount of silver in the unexposed part was measured by a fluorescent X-ray spectrometer, and with respect to the unexposed part, to measure the extent of the stain/fogging, the yellow transmission density (referred to as Dmin) was measured by using a Photographic Densitometer FSD103, manufactured by Fuji Photo Film Co., Ltd. Further, the state of bubbling due to the blowing of air at the time of regeneration of the bleaching solution was also recorded.

The results are shown in Table 3.

Table 3

		No. 1					
		I-15					
Added amount of regenerating agent		2 hours of air blowing			4 hours of air blowing		
per 100 liters of the overflow	per m² of the light-sensitive material processed	D_{min}	Bubbling	Residual silver mg/m²	D_{min}	Bubbling	Residual silver mg/m²
7 liters	50.0 ml	0.801	○	22	0.811	○	20
8 liters	57.2 ml	0.810	○	20	0.820	○	19
9 liters	64.4 ml	0.882	○	25	0.890	○	24
10 liters	71.5 ml	0.991	○	30	0.998	○	28

(Note) 1) Within the bold lines, this invention

2) Evaluation standard on bubbling

× : Bubbles overflowed from the stock tank.

△ : Many bubbles occurred, although they did not overflow from the stock tank.

○ : Small amount of bubbles occurred on the solution surface.

Table 3 (continued)

No. 2								
	1,3-diaminopropanetetraacetic acid							
Added amount of regenerating agent		2 hours of air blowing			4 hours of air blowing			
per 100 liters of the overflow	per m² of the light-sensitive material processed	D_{min}	Bubbling	Residual silver mg/m²	D_{min}	Bubbling	Residual silver mg/m²
7 liters	50.0 ml	0.880	×	50	1.012	×	45
8 liters	57.2 ml	0.981	△	55	1.101	×	47
9 liters	64.4 ml	1.101	△	57	1.205	△	50
10 liters	71.5 ml	1.211	○	60	1.223	△	51

Table 3 (continued)

No. 3								
	Ethylenediamine-N,N'-disuccinic acid							
	Added amount of regenerating agent		2 hours of air blowing			4 hours of air blowing		
	per 100 liters of the overflow	per m^2 of the light-sensitive material processed	D_{min}	Bubbling	Residual silver mg/m^2	D_{min}	Bubbling	Residual silver mg/m^2
	7 liters	50.0 ml	0.891	×	70	1.037	×	62
	8 liters	57.2 ml	0.973	△	73	1.111	×	64
	9 liters	64.4 ml	1.002	△	75	1.221	×	67
	10 liters	71.5 ml	1.102	○	80	1.281	△	70

As is shown in the results in Table 3, it can be seen that, according to the method of the present invention, there was no bubbling at the time of regeneration of the bleaching solution, stain/fogging was less, and an improvement in desilvering due to quick reoxidation was identified.

Example 2

The support and the backing layer of the light-sensitive material were prepared as described below, and the light-sensitive layers as described in the above Example 1 were coated on the support, to prepare a light-sensitive material

Sample 102.

1) Support

The support that was used in this example was prepared as follows:

100 weight parts of polyethylene-2,6-naphthalate polymer, and 2 weight parts of Tinuvin P. 326 (trade name, manufactured by Ciba-Geigy Co.), as an ultraviolet absorbing agent, were dried, then melted at 300 °C; subsequently they were extruded through a T-type die, and stretched 3.3 times in the lengthwise direction at 140 °C, and then 3.3 times in the width direction at 130 °C; and further they were thermally fixed for 6 seconds at 250 °C, and PEN film having a thickness of 90 μm was obtained. To the PEN film, appropriate amounts of a blue dye, a magenta dye, and a yellow dye (I-1, I-4, I-6, I-24, I-26, I-27, II-5, as described in Kokai Giho: Kogi No. 94-6023) were added. Further, this film was wound around a stainless steel core (spool) having a diameter of 20 cm, and thermal history was imparted thereto at 110 °C for 48 hours, to obtain a support having suppressed core-set-curl.

2) Coating of an undercoat layer

After both surfaces of the said support were subjected to corona discharge, UV discharge, and glow discharge treatments, each side of the support was coated with undercoat solution having a composition of 0.1 g/m^2 of gelatin, 0.01 g/m^2 of sodium α-sulfo-di-2-ethylhexylsuccinate, 0.04 g/m^2 of salicylic acid, 0.2 g/m^2 of *p*-chlorophenol, 0.012 g/m^2 of $(CH_2=CHSO_2CH_2CH_2NHCO)_2CH_2$, and 0.02 g/m^2 of polyamideepichlorohydrin polycondensation product (10 cc/m^2, a bar coater was used). The undercoat layer was provided on the side that was heated at a higher temperature at the time of stretching. Drying was carried out at 115 °C for 6 minutes (the roller and the transportation apparatus in the drying zone all were set at 115 °C).

3) Coating of a backing layer

An antistatic layer, a magnetic recording layer, and a slippling layer, each having the compositions mentioned below, were coated on one side of the above support coated with the undercoat layer, as a backing layer.

3-1) Coating of an antistatic layer

0.2 g/m^2 of a dispersion of fine grain powder of a composite of stannic oxide-antimony oxide having an average grain size of 0.005 μm, and the specific resistance of 5 Ω • cm (secondary aggregation grain size of about 0.08 μm) was coated with 0.05 g/m^2 of gelatin, 0.02 g/m^2 of $(CH_2=CHSO_2CH_2CH_2NHCO)_2CH_2$, 0.005 g/m^2 of poly(polymerization degree: 10)oxyethylene-*p*-nonylphenol, and resorsine.

3-2) Coating of a magnetic recording layer

3-Poly(polymerization degree: 15)oxyethylene-propyloxytrimethoxysilan (15 weight%)-coated Co-γ-iron oxide (specific surface area, 43 m^2/g; major axis, 0.14 μm; minor axis, 0.03 μm; saturation magnetization, 89 emu/g, Fe^{2+}/Fe^{3+} = 6/94; the surface was treated with 2 wt% respectively, based on iron oxide, of aluminum oxide and silicon oxide) (0.06 g/m^2), diacetylcellulose (a dispersion of the iron oxide was carried out by an open kneader and a sand mill) (1.2 g/m^2), and the hardener $C_2H_5C(CH_2OCONH\text{-}C_6H_3(CH_3)NCO)_3$ (0.3 g/m^2) were coated using acetone, methylethylketone, and cyclohexanone, as solvents, by means of a bar coater, to obtain a magnetic recording layer having a thickness of 1.2 μm. Silica grains (0.3 μm), as a matting agent, and 3-poly(polymerization degree: 15) oxyethylene-propyloxytrimethoxysilan (15 weight%)-coated aluminum oxide (0.15 μm), as an abrasive, were each added thereto, to give a coverage of 10 mg/m^2. Drying was conducted at 115 °C for 6 min (the roller and the transportation apparatus in the drying zone all were set at 115 °C). The increment of the color density of D^B of the magnetic recording layer was about 0.1 when X-light (blue filter) was used. The saturation magnetization moment of the magnetic recording layer was 4.2 emu/g, the coercive force was 7.3 x 10^4 A/m, and the squareness ratio was 65%.

3-3) Preparation of a slipping layer

Diacetyl cellulose (25 mg/m^2), and a mixture of $C_6H_{13}CH(OH)C_{10}H_{20}COOC_{40}H_{81}$ (Compound a, 6 mg/m^2) and $C_{50}H_{101}O(CH_2CH_2O)_{16}H$ (Compound b, 9 mg/m^2) was coated. When adding the mixture, the mixture was dissolved in a solution of xylene and propyleneglycol monomethylether (1/1) at 105 °C, and this solution was poured into a 10-fold volume of propyleneglycol monomethylether (normal temperature) and finely dispersed. This was further dispersed in acetone, and the obtained dispersion (average grain diameter: 0.01 μm) was added to the coating solution. Silica grains

(0.3 μm), as a matting agent, and 3-poly(polymerization degree, 15) oxyethylene-propyloxytrimethoxysilan (15 weight%)-coated aluminum oxide (0.15 μm), as an abrasive, were each added thereto, to give a coverage of 15 mg/m^2. The slipping layer was dried at 115 °C for 6 minutes (the roller and the transportation apparatus in the drying zone all were set at 115 °C). The slipping layer showed excellent performances of the coefficient of dynamic friction: 0.06 (a stainless steel hard ball of 5 mm∅, diameter, load: 100 g, speed: 6 cm/min), and of the static friction coefficient: 0.07 (clip method). The sliding property of the slipping layer with the surface of the emulsion, which will be described below, was also excellent, such that the coefficient of dynamic friction was 0.12.

The thus-prepared Sample 102 was cut into a strip having a length of 160 cm and a width of 24 mm. Two perforations of 2 mm square were made at intervals of 5.8 mm, located at the position of 0.7 mm in the width direction and at one side in the lengthwise direction of the light-sensitive material, respectively. Further, sets of such two perforations were made at intervals of 32 mm. The sample was encased in a plastic film cartridge, as illustrated in Fig. 1 to Fig. 7 of US-A-5,296,887.

The sample 102 was set in a camera with a built-in magnetic recording device having a headgap of 5 μm, a turn number of 50, and made of permalloy. A digital saturation recording using a recording wavelength of 50 μm and photographing were conducted with the camera.

Tte thus-photographed Sample 102 was continuously processed with processing solutions and processing methods as shown below until the cumulative total of the replenishment rate of the bleaching solution reached 6,000 ml.

In the bleaching step, the overflow was regenerated every 1 liter. As shown in the chart in Fig. 1, the regeneration was carried out in such a manner that a bleaching replenisher 2, from a replenishing tank 1, was supplied to a bleaching solution 3, in a bleaching tank 4, and the overflow 6 from the bleaching tank 4 was stored in a stock tank 5. Every time the overflow accumulated in an amount of 1 liter, air 8 was blown through the stored overflow 6 by an air pump 7, for 4 hours. Thereafter, 50 ml of the below-described bleaching-solution-regenerating agent 13 was added, to prepare a regenerated replenisher, and the regenerated replenisher was used as a bleaching replenisher from the next time, to continue the processing.

Processing step				
Processing step	Processing		Replenishing rate*1	Tank Volume /liter
	time	temperature		
Color-developing	3 min 15 sec	38.0 °C	630 ml	2
Bleaching	3 min 00 sec	38.0 °C	715 ml	2
Washing (1)	30 sec	38.0 °C	430 ml	2
Fixing	3 min 00 sec	38.0 °C	430 ml	2
Washing (2)	1 min 00 sec	38.0 °C	770 ml	2
Stabilizing	30 sec	38.0 °C	570 ml	2
Drying	3 min	50.0 °C	-	-

*1 the replenishment rate was the amount per m^2 of the light-sensitive material

Washing (1) was separated to 2 tanks, and washing (2) was separated to 3 tanks, and each washing was carried out in a counter current mode from back side to forward. Further, in each step, the carried over amount of tank solution to the next step were respectively 60 ml, per m^2 of the light-sensitive material. Each crossover time was 3 sec which was included in the processing time of the preceding step.

The composition of each processing solution was as follows, respectively:

The color-developer, the fixing solution, and the washing water used were the same as those in the above Example 1, for both the mother solution and the replenisher.

(Bleaching-solution-regenerating agent)

Bleaching agent	shown in Table 4

(continued)

Organic acid	shown in Table 4
Iron nitrate	110 g
Aqueous ammonia (27%)	70 g
Picolinic acid derivative	shown in Table 4
Ammonium bromide	95 g
1,2-benzoisothiazolin-3-one	0.01 g
Water to make	1.0 liter
pH (pH was adjusted by aqueous ammonia)	3.5

(Start bleaching replenisher)

Use was made of the above bleaching-solution-regenerating agent diluted to 0.4 times, and pH was adjusted to 3.4 with nitric acid.

(Start tank solution)

Use was made of the above regenerating agent diluted to 0.35 times, and pH was adjusted to 3.6 with aqueous ammonia.

Table 4

No	Bleaching agent and its added amount (g) of bleaching-regenerating agent				Kind of organic acid and its added amount (g) of bleaching-regenerating agent					Kind of picolinic acid derivative and its added amount (g)		Remarks
1	EDTA	100	—	—	acetic acid	60	—	—	—	—	—	Comparative example
2	PDTA	65	—	—	acetic acid	60	—	—	—	—	—	Comparative example
3	I-15	140	—	—	acetic acid	70	—	—	—	—	—	This invention
4	I-15	140	—	—	glycollic acid	80	—	—	—	—	—	This invention
5	I-15	140	—	—	glycollic acid	60	succinic acid	40	malonic acid	25	—	This invention
6	I-15	140	—	—	sulfo-succinic acid	60	—	—	—	—	—	This invention
7	I-15	105	EDTA	35	glycollic acid	70	succinic acid	50	—	—	—	This invention
8	I-15	105	PDTA	35	glycollic acid	70	succinic acid	50	—	—	—	This invention
9	I-15	105	PDTA	35	glycollic acid	70	succinic acid	40	malonic acid	25	—	This invention
10	I-15	105	PDTA	35	acetic acid	80	—	—	—	—	—	This invention

Table 4 (continued)

No	Bleaching agent and its added amount (g) of bleaching-regenerating agent				Kind of organic acid and its added amount (g) of bleaching-regenerating agent					Kind of picolimic acid derivative and its added amount (g)		Remarks
11	I-15	140	–	–	acetic acid	80	–	–	–	2,6-pyridine-dicarboxylic acid	20	This invention
12	I-15	140	–	–	glycollic acid	80	–	–	–	2,6-pyridine-dicarboxylic acid	20	This invention
13	I-15	140	–	–	glycollic acid	60	succinic acid	40	malonic acid	25	20	This invention
14	I-15	105	PDTA	35	glycollic acid	70	succinic acid	40	malonic acid	25	20	This invention
15	I-15	140	–	–	glycollic acid	60	succinic acid	40	malonic acid	25	18	This invention
16	I-15	105	PDTA	35	glycollic acid	70	succinic acid	40	malonic acid	25	18	This invention
17	I-7	130	–	–	glycollic acid	60	succinic acid	40	malonic acid	25	–	This invention
18	I-23	300	–	–	glycollic acid	60	succinic acid	40	malonic acid	25	–	This invention
19	I-25	140	–	–	glycollic acid	60	succinic acid	40	malonic acid	25	–	This invention

EDTA : ethylenediaminetetraacetic acid iron (III) ammonium·dihydrate

PDTA : 1,3-diaminopropanetetraacetic acid iron (III) ammonium·dihydrate

Sample 102 that was exposed to light of 20 CMS, and Sample 102 that was not exposed to light, were processed with the solution with which the continuous processing had been made, the residual amount of silver in the unexposed

part was measured by a fluorescent X-ray spectrometer, and with respect to the unexposed part, to measure the extent of the stain/fogging, the yellow transmission density (referred to as Dmin) was measured by using a Photographic Densitometer FSD103, manufactured by Fuji Photo Film Co., Ltd. Further, the state of bubbling due to the blowing of air at the time of regeneration of the bleaching solution was also recorded.

The results are shown in Table 5.

Table 5

No	Dmin	State of bubbling	Amount of residual silver mg/m^2	Remarks
1	1.242	X	107	Comparative example
2	1.209	X	53	Comparative example
3	0.880	○	33	This invention
4	0.877	○	30	This invention
5	0.865	○	22	This invention
6	0.871	△	29	This invention
7	0.870	○	28	This invention
8	0.822	○	20	This invention
9	0.823	○	20	This invention
10	0.855	○	25	This invention
11	0.863	△	29	This invention
12	0.812	○	13	This invention
13	0.810	○	11	This invention
14	0.810	○	12	This invention
15	0.817	○	17	This invention
16	0.812	○	15	This invention
17	0.844	○	24	This invention
18	0.867	○	33	This invention
19	0.870	△	32	This invention

(Note) Evaluation standard on bubbling
X : Bubbles overflowed from the stock tank.
△ : Many bubbles occurred, although they did not overflow from the stock tank.
○ : Small amount of bubbles occurred on the solution surface.

Example 3

The experiments of Example 1 were carried out in the same manner as in Example 1, except that a Developing Apparatus FNCP900II, manufactured by Fuji Photo Film Co., Ltd., was used. In addition to the four levels of experiments in Example 1, in which the added amount of the bleaching-solution-regenerating agent per 100 liters of the overflow was changed in four (4) levels, another level of experiment was carried out in this Example. That is, in the another level of experiment, the added amount of the bleaching-solution-regenerating agent per 100 liters of the overflow was further reduced to 4 liters, which meant that the regenerating agent was used in an amount of 28.6 ml per square meter of the processed light-sensitive material. As a result, at the levels of 7, 8, 9, and 10 liters, results almost the same as those of Example 1, shown in Table 3, were obtained. Even at the level of 4 liters of the regenerating agent, the following results were obtained, demonstrating the effects of the present invention.

Regenerating agent used	Air bubbling for 2 hours			Air bubbling for 4 hours		
	D_{min}	Bubbling	Residual silver (mg/m^2)	D_{min}	Bubbling	Residual silver (mg/m^2)
I-15	0.798	○	21	0.800	○	20
1,3-diaminopropane-tetraacetic acid	0.870	X	49	1.001	X	44
Ethylenediamine-N,N'-disuccinic acid	0.887	X	68	1.021	X	60

Example 4

The experiments of Example 2 were conducted using a Developing Apparatus FNCP900II, manufactured by Fuji Photo Film Co., Ltd. This example was conducted in the same manner as in Example 2, except that the added amount of the bleaching-solution-regenerating agent was reduced from 50 ml to 39 ml, per liter of the overflow. As a result, results almost the same as those of Example 2 were attained.

Example 5

The experiments were conducted in the same manner as Example 4, except that the bleaching agent was changed to Compounds I-1, I-8, I-19, I-20, I-26, I-31, I-32, I-37, and I-52, respectively. As a result, it was identified that the excellent bleach processing could be attained, according to the method of the present invention.

Example 6

In Experiment Nos. 3 to 19 of Example 2, the pH of the washing bath after the bleaching bath was controlled to the values shown in Table 6, and its effect was investigated. To control the pH of the washing bath, a pH Controller FC-10, manufactured by Tokyo Rikakiki Co., was used. Further, the pH of the washing water had previously been brought to the specified pH, with nitric acid, and the resulting water came to flow in. When the processing of 10 m^2 of the light-sensitive material was completed, the D_{min} of the light-sensitive material that was processed last was measured. The state of the formation of the precipitation of iron hydroxide in the washing bath was checked, by visually observing the amount of an orange precipitate settled on a circular filter paper, with a diameter of 5 cm, placed on the bottom of the washing bath after the processing, after allowing the precipitate to stand for 48 hours. The results are shown in Table 6.

Table 6

	This invention				Comparative example	
pH	6.0		8.0		9.0	
No	D_{min}	Precipitation	D_{min}	Precipitation	D_{min}	Precipitation
3	0.778	○	0.879	△	0.983	X
4	0.777	○	0.876	○	0.990	X
5	0.765	○	0.866	○	0.970	X
6	0.771	○	0.871	△	0.981	X
7	0.769	○	0.870	○	0.983	X
8	0.720	○	0.821	○	0.933	X
9	0.722	○	0.824	○	0.935	X
10	0.760	○	0.857	△	0.979	X

Table 6 (continued)

	This invention				Comparative example	
pH	6.0		8.0		9.0	
No	D_{min}	Precipitation	D_{min}	Precipitation	D_{min}	Precipitation
11	0.759	○	0.862	○	0.981	X
12	0.719	○	0.821	○	0.919	X
13	0.711	○	0.811	○	0.908	△
14	0.709	○	0.810	○	0.910	△
15	0.717	○	0.818	○	0.932	△
16	0.712	○	0.813	○	0.928	△
17	0.740	○	0.843	○	0.942	X
18	0.770	○	0.868	○	0.977	X
19	0.766	○	0.867	○	0.980	X

(Note) Evaluation standard on precipitation amount
X : Precipitation on allover the filter paper
△ : A little precipitation on the filter paper
○ : No precipitation at all

As is apparent from the results in Table 6, it can be understood that, by bringing the pH to 8 or less, not only an effect of reducing stain but also suppression of the amount of a precipitation could be secured, and in particular no precipitation occurred at a pH of 6 or less.

Example 7

[Preparation of samples of a light-sensitive material]

A paper base both surfaces of which had been coated with a polyethylene resin, was subjected to surface corona discharge treatment; then it was provided with a gelatin undercoat layer containing sodium dodecylbenzensulfonate, and it was successively coated with the first to seventh photographic constitutional layers, to prepare two kind samples of a silver halide color photographic light-sensitive material (Sample A and Sample B) having the layer configuration shown below. The coating solutions for each photographic constitutional layer were prepared as follows. The below shown "average grain size of emulsion" means an average value of an estimate diameter calculated from the area of grains measured with a so-called projection-area method.

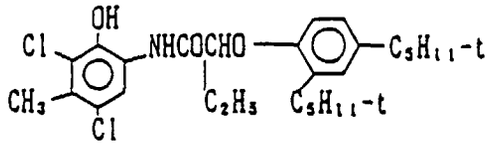
[Preparation of coating solutions]

(Preparation of Fifth-Layer Coating Solution)

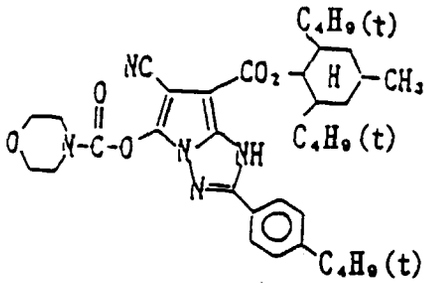
300 g of a cyan coupler (the below-shown acylaminophenol coupler (Sample A) or pyrrolotriazole coupler (Sample B) was used, respectively), 250 g of a color-image-stabilizer (Cpd-1), 10 g of a color-image-stabilizer (Cpd-9), 10 g of a color-image-stabilizer (Cpd-10), 20 g of a color-image-stabilizer (Cpd-12), 14 g of an ultraviolet absorbing agent (UV-1), 50 g of an ultraviolet absorbing agent (UV-2), 40 g of an ultraviolet absorbing agent (UV-3), and 60 g of an ultraviolet absorbing agent (UV-4) were dissolved in 230 g of a solvent (Solv-6) and 350 ml of ethyl acetate, and the resulting solution was emulsified and dispersed in 6500 g of a 10% aqueous gelatin solution containing 200 ml of 10% sodium dodecylbenzensulfonate, to prepare an emulsified dispersion C.

Cyan coupler

SampleA ;



SampleB ;



On the other hand, a silver chlorobromide emulsion C (cubes, a mixture of a large-size emulsion C having an average grain size of 0.50 μm, and a small-size emulsion C having an average grain size of 0.41 μm (1 : 4 in terms of mol of silver), the deviation coefficients of the grain size distributions being 0.09 and 0.11 respectively, and each emulsion having 0.5 mol % of silver bromide locally contained in part of the grain surface whose substrate was made up of silver chloride) was prepared.

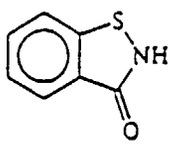
To the large-size emulsion C of this emulsion, had been added 6.0 x 10^{-5} mol, per mol of silver, of each of red-sensitive sensitizing dyes G, and H shown below, and to the small-size emulsion C of this emulsion, had been added 9.0 x 10^{-5} mol, per mol of silver, of each of red-sensitive sensitizing dyes G, and H shown below. The chemical ripening of this emulsion was carried out optimally with a sulfur sensitizer and a gold sensitizer being added.

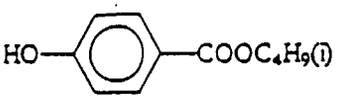
The above emulsified dispersion C and this silver chlorobromide emulsion C were mixed and dissolved, and a fifth-layer coating solution was prepared so that it would have the composition shown below. The coating amount of the emulsion is in terms of silver.

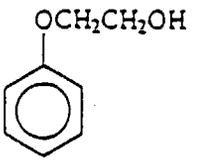
The coating solutions for the first layer to forth layer and the sixth layer to seventh layer were prepared in the similar manner as that for the fifth layer coating solution. As the gelatin hardener for each layer, 1-oxy-3,5-dichloro-s-triazine sodium salt was used.

Further, to each layer, were added Ab-1, Ab-2, Ab-3, and Ab-4, so that the total amounts would be 15.0 mg/m^2, 60.0 mg/m^2, 5.0 mg/m^2, and 10.0 mg/m^2, respectively.

(Ab-1)Antiseptic (Ab-2) Antiseptic (Ab-3) Antiseptic

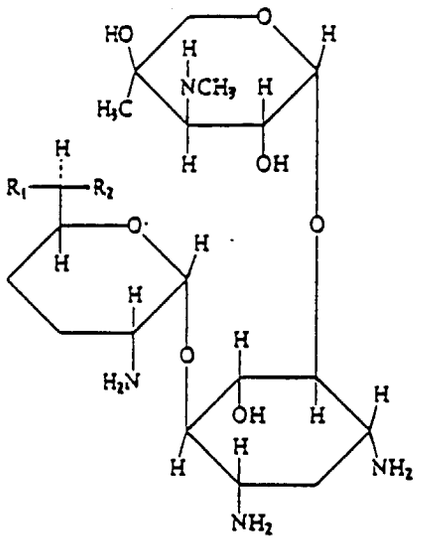






(Ab-4) Antiseptic

1:1:1:1 mixture of a, b, c and d

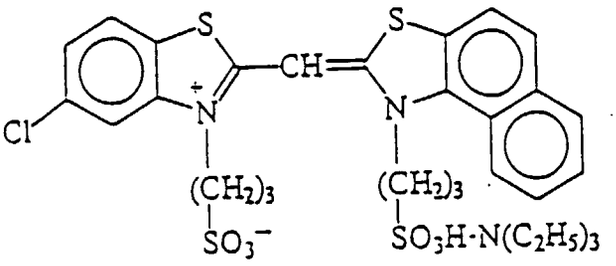


	R_1	R_2
a	$-CH_3$	$-NHCH_3$
b	$-CH_3$	$-NH_2$
c	$-H$	$-NH_2$
d	$-H$	$-NHCH_3$

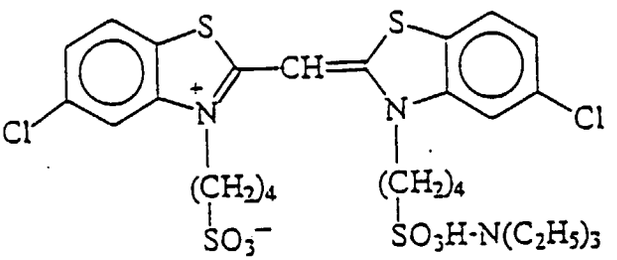
For the silver chlorobromide emulsion of each photosensitive emulsion layer, the following spectral sensitizing dyes were used.

(Blue-Sensitive Emulsion Layer)

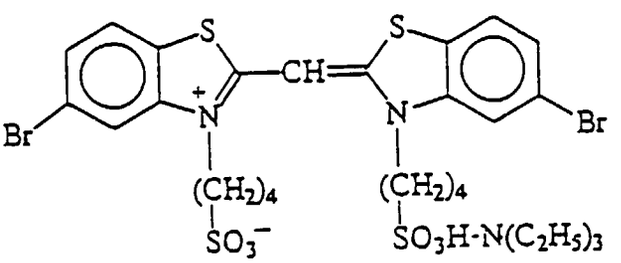
(Sensitizing dye A)



(Sensitizing dye B)



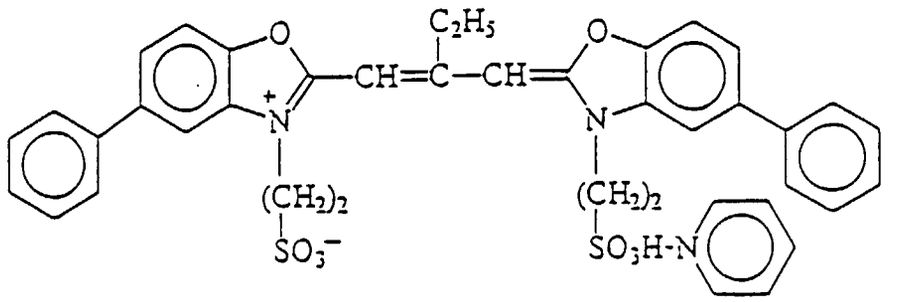
(Sensitizing dye C)



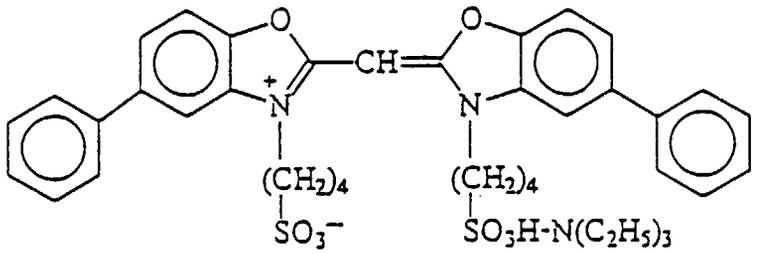
(The sensitizing dyes A, B, and C were added, respectively, to the large-size emulsion, in an amount of 1.4×10^{-4} mol per mol of the silver halide, and to the small-size emulsion in an amount of 1.7×10^{-4} per mol of the silver halide.)

(Green-Sensitive Emulsion Layer)

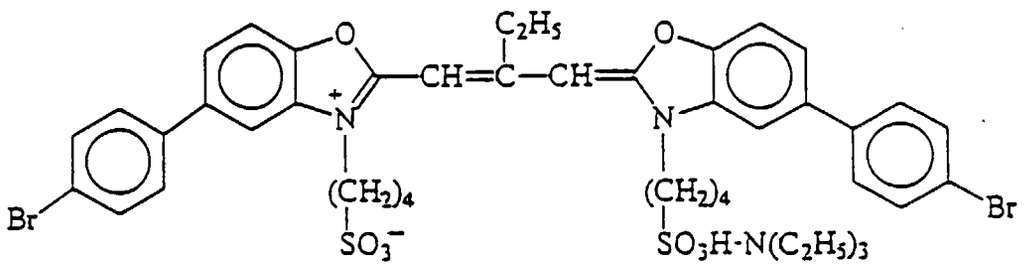
(Sensitizing dye D)



(Sensitizing dye E)



(Sensitizing dye F)

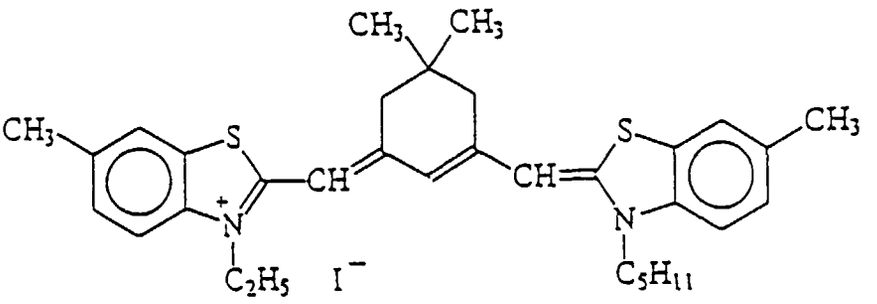


(The sensitizing dye D was added to the large-size emulsion in an amount of 3.0×10^{-4} mol per mol of the silver halide, and to the small-size emulsion in an amount of 3.6×10^{-4} mol per mol of the silver halide; the sensitizing dye E was added to the large-size emulsion in an amount of 4.0×10^{-5} mol per mol of the silver halide, and to the small-size emulsion in an amount of 7.0×10^{-5} mol per mol of the silver halide; and the sensitizing dye F was added to the large-

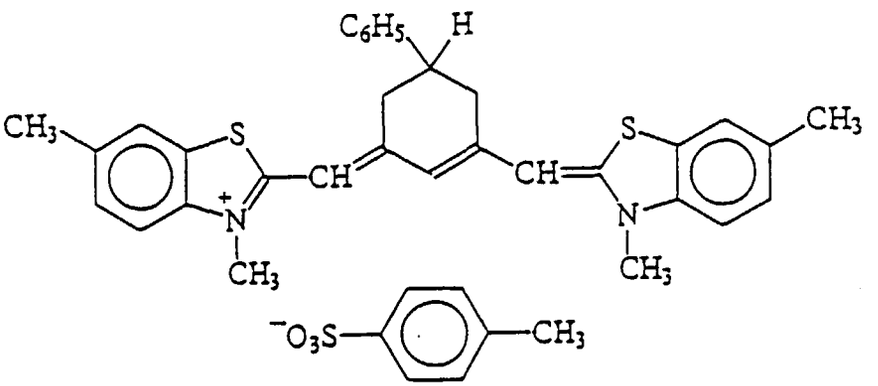
size emulsion in an amount of 2.0 x 10^{-4} mol per mol of the silver halide, and to the small-size emulsion in an amount of 2.8 x 10^{-4} mol per mol of the silver halide.)

(Red-Sensitive Emulsion Layer)

(Sensitizing dye G)



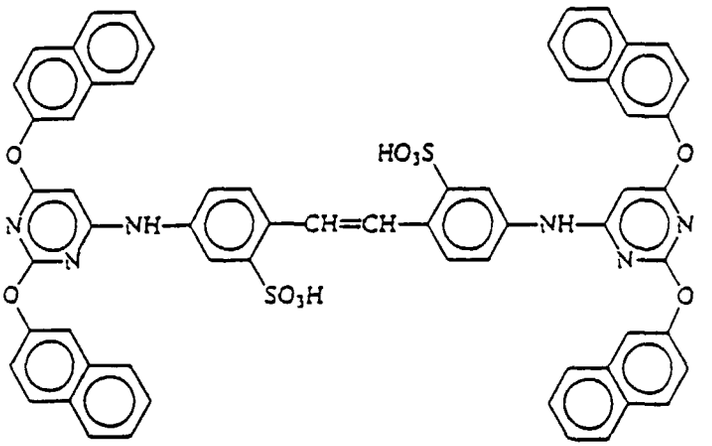
(Sensitizing dye H)



(The sensitizing dyes G and H were added, respectively, to the large-size emulsion, in an amount of 6.0 x 10^{-5} mol per mol of the silver halide, and to the small-size emulsion in an amount of 9.0 x 10^{-5} per mol of the silver halide.)

Further, the following compound I was added in the red-sensitive emulsion layer in an amount of 2.6 x 10^{-3} mol per mol of the silver halide.

(Compound I)



Further, to the blue-sensitive emulsion layer, the green-sensitive emulsion layer, and the red-sensitive emulsion layer, was added 1-(3-methylureidophenyl)-5-mercaptotetrazole in amounts of 3.3×10^{-4} mol, 1.0×10^{-3} mol, and 5.9×10^{-4} mol, per mol of the silver halide, respectively.

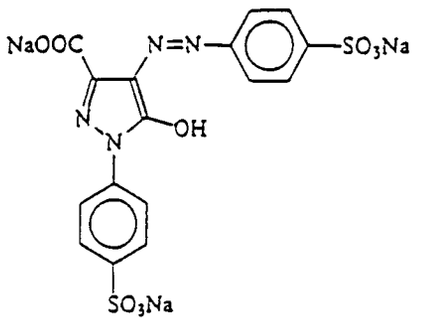
Further, to the second layer, the fourth layer, the sixth layer, and the seventh layer, it was added in amounts of 0.2 mg/m^2, 0.2 mg/m^2, 0.6 mg/m^2, and 0.1 mg/m^2, respectively.

Further, to the blue-sensitive emulsion layer and the green-sensitive emulsion layer, was added 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene in amounts of 1×10^{-4} mol and 2×10^{-4} mol, respectively, per mol of the silver halide.

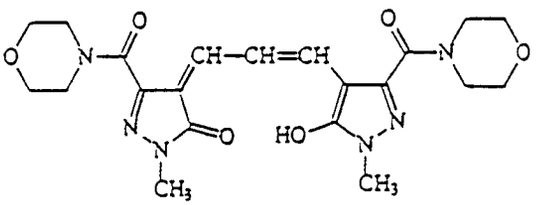
To the red-sensitive emulsion layer, was added a copolymer of methacrylic acid and butyl acrylate (1 : 1 in weight ratio; average molecular weight, 200,000 to 400,000) in an amount of 0.05g/m^2.

Further, to the second layer, the fourth layer, and the sixth layer, was added disodium catechol-3,5-disulfonate in amounts of 6 mg/m^2, 6 mg/m^2, and 18 mg/m^2, respectively.

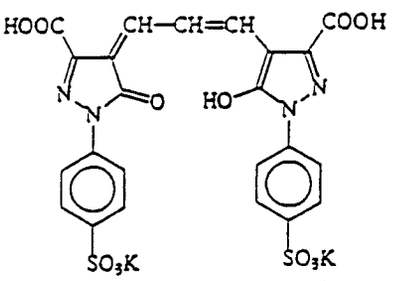
Further, to neutralize irradiation, the following dyes were added to the emulsion layers (the coating amount is shown in parentheses).



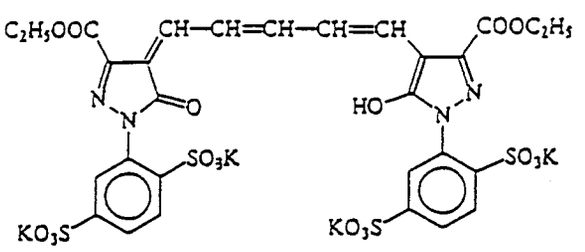
(10mg/m²)



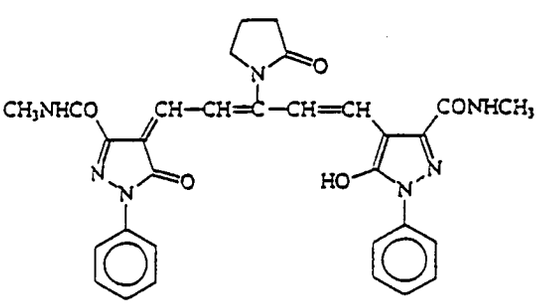
(20mg/m²)



(5mg/m²)



(20mg/m²)



(20mg/m²)

(Layer Constitution)

The composition of each layer is shown below. The numbers show coating amounts (g/m^2). In the case of the silver halide emulsion, the coating amount is in terms of silver.

Base

Polyethylene resin-Laminated Paper
[The polyethylene resin on the first layer side contained a white pigment (TiO_2: content of 16 wt%, ZnO: content of 4 wt%), a fluorescent whitening agent (4,4-bis(5-methylbenzoxazoryl)stilbene: content of 0.05 wt%), and a blue dye (ultramarine)]

First Layer (Blue-Sensitive Emulsion Layer)

A silver chlorobromide emulsion: cubes, a mixture of a large-size emulsion A having an average grain size of 0.72 μm, and a small-size emulsion A having an average grain size of 0.60 μm (3 : 7 in terms of mol of silver). The deviation coefficients of the grain size distributions were 0.08 and 0.10, respectively, and each emulsion had 0.3 mol % of AgBr locally contained in part of the grain surface whose substrate was made up of silver chloride.	0.26
Gelatin	1.35
Yellow coupler (ExY)	0.62
Color-image stabilizer (Cpd-1)	0.08
Color-image stabilizer (Cpd-2)	0.04
Color-image stabilizer (Cpd-3)	0.08
Solvent (Solv-1)	0.23

Second Layer (Color-Mixing Inhibiting Layer)

Gelatin	0.99
Color-mixing inhibitor (Cpd-4)	0.09
Color-mixing inhibitor (Cpd-5)	0.018
Color-mixing inhibitor (Cpd-6)	0.13
Color-mixing inhibitor (Cpd-7)	0.01
Solvent (Solv-1)	0.06
Solvent (Solv-2)	0.22

Third Layer (Green-Sensitive Emulsion Layer)

A silver chlorobromide emulsion B: cubes, a mixture of a large-size emulsion B having an average grain size of 0.45 μm, and a small-size emulsion B having an average grain size of 0.35 μm (1 : 3 in terms of mol of silver). The deviation coefficients of the grain size distributions were 0.10 and 0.08, respectively, and each emulsion had 0.4 mol % of AgBr locally contained in part of the grain surface whose substrate was made up of silver chloride.	0.14

(continued)

Gelatin	1.36
Magenta coupler (ExM)	0.15
Ultraviolet absorbing agent (UV-1)	0.05
Ultraviolet absorbing agent (UV-2)	0.03
Ultraviolet absorbing agent (UV-3)	0.02
Ultraviolet absorbing agent (UV-4)	0.04
Color-image stabilizer (Cpd-2)	0.02
Color-image stabilizer (Cpd-4)	0.002
Color-image stabilizer (Cpd-6)	0.09
Color-image stabilizer (Cpd-8)	0.02
Color-image stabilizer (Cpd-9)	0.03
Color-image stabilizer (Cpd-10)	0.01
Color-image stabilizer (Cpd-11)	0.0001
Solvent (Solv-3)	0.11
Solvent (Solv-4)	0.22
Solvent (Solv-5)	0.20

Fourth Layer (Color-Mixing Inhibiting Layer)

Gelatin	0.71
Color-mixing inhibitor (Cpd-4)	0.06
Color-image stabilizer (Cpd-5)	0.013
Color-image stabilizer (Cpd-6)	0.10
Color-image stabilizer (Cpd-7)	0.007
Solvent (Solv-1)	0.04
Solvent (Solv-2)	0.16

Fifth Layer (Red-Sensitive Emulsion Layer)

A silver chlorobromide emulsion C: cubes, a mixture of a large-size emulsion C having an average grain size of 0.50 μm, and a small-size emulsion C having an average grain size of 0.41 μm (1 : 4 in terms of mol of silver). The deviation coefficients of the grain size distributions were 0.09 and 0.11, respectively, and each emulsion had 0.5 mol % of silver bromide locally contained in part of the grain surface whose substrate was made up of silver chloride.	0.20
Gelatin	1.11
Cyan coupler (A or B)	0.30
Ultraviolet absorbing agent (UV-1)	0.14
Ultraviolet absorbing agent (UV-2)	0.05

(continued)

Ultraviolet absorbing agent (UV-3)	0.04
Ultraviolet absorbing agent (UV-4)	0.06
Color-image stabilizer (Cpd-1)	0.25
Color-image stabilizer (Cpd-9)	0.01
Color-image stabilizer (Cpd-10)	0.01
Color-image stabilizer (Cpd-12)	0.02
Solvent (Solv-6)	0.23

Sixth Layer (Ultraviolet Absorbing Layer)

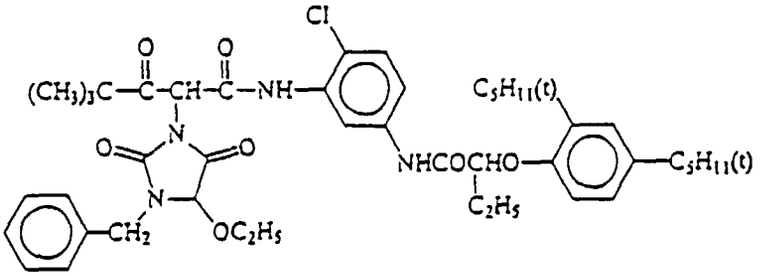
Gelatin	0.66
Ultraviolet absorbing agent (UV-1)	0.19
Ultraviolet absorbing agent (UV-2)	0.06
Ultraviolet absorbing agent (UV-3)	0.06
Ultraviolet absorbing agent (UV-4)	0.05
Ultraviolet absorbing agent (UV-5)	0.09
Solvent (Solv-7)	0.25

Seventh Layer (Protective Layer)

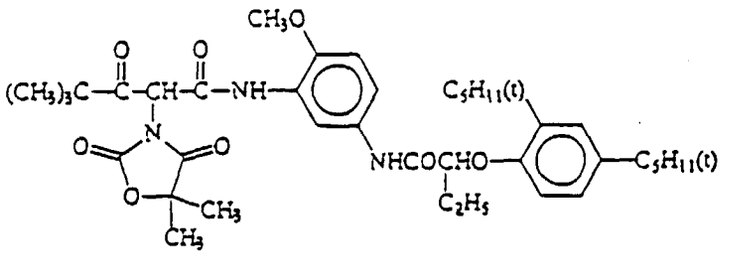
Gelatin	1.00
Acryl-modified copolymer of polyvinyl alcohol (modification degree: 17 %)	0.04
Liquid paraffin	0.02
Surface-active agent (Cpd-13)	0.01

(E x Y) Yellow coupler

60:40 mixture (molar ratio) of

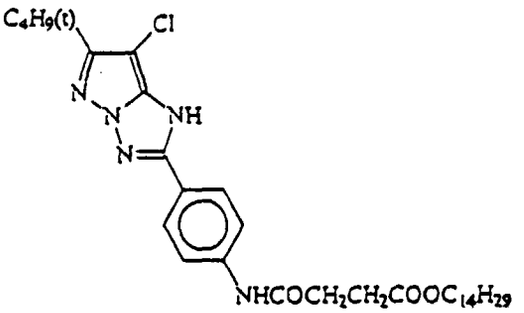


and



(E x M) Magenta coupler

60:40 mixture (molar ratio) of



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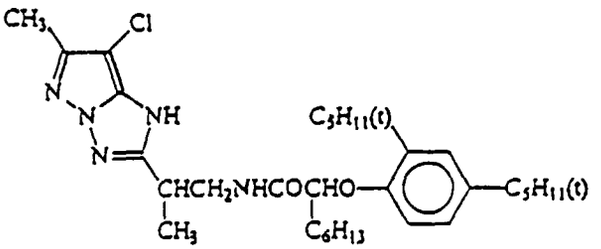
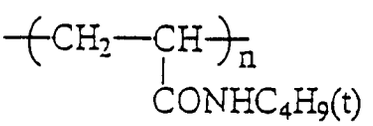
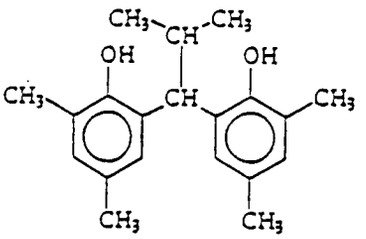


(Cpd-1) Color-image stabilizer

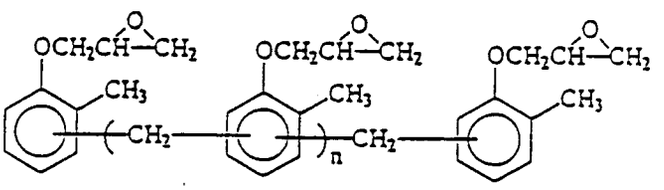


number-average molecular weight 60,000

(Cpd-2) Color-image stabilizer



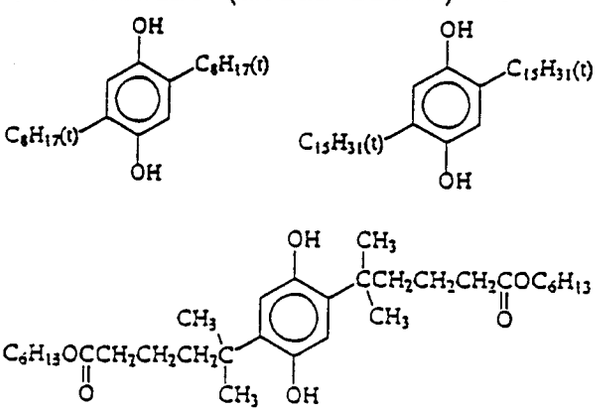
(Cpd-3) Color-image stabilizer



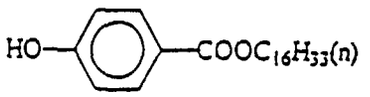
n = 7 ~ 8 (average value)

(Cpd-4) Color-mixing inhibitor

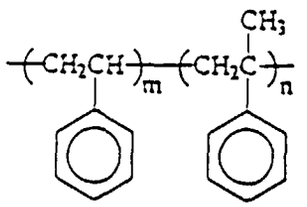
1:1:1 mixture (molar ratio) of



(Cpd-5) Color-mixing inhibiting auxiliary



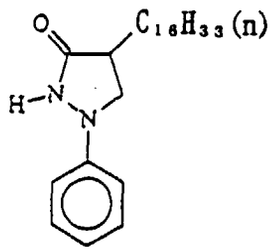
(Cpd-6) Stabilizer



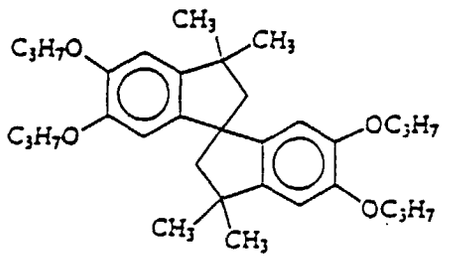
number-average molecular weight 600

m/n=10/90

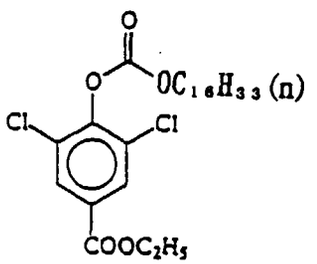
(Cpd-7) Color-mixing inhibitor



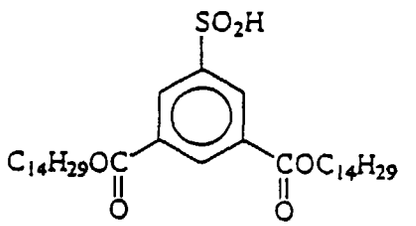
(Cpd-8) Color-image stabilizer



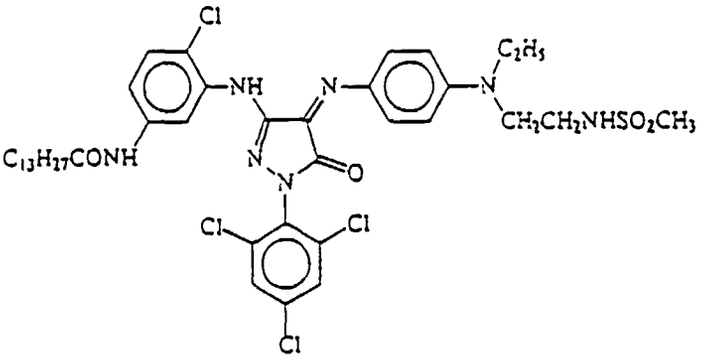
(Cpd-9) Color-image stabilizer



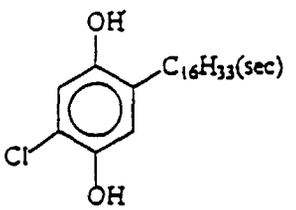
(Cpd-10) Color-image stabilizer



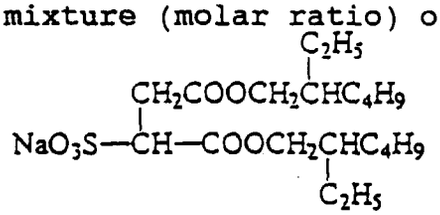
(Cpd-11)



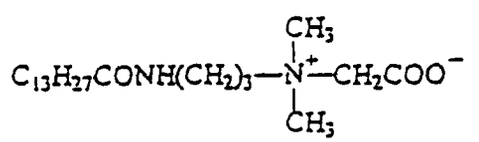
(Cpd-12) Color-image stabilizer



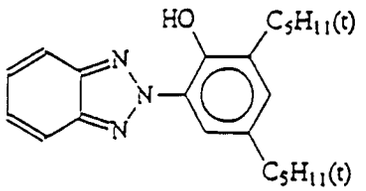
(Cpd-13) Surface-active agent
7:3 mixture (molar ratio) of



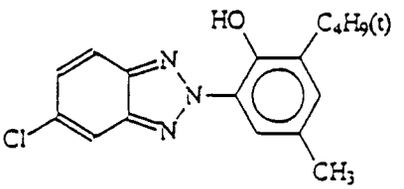
and



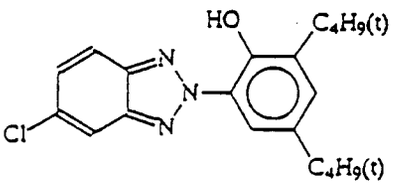
(UV-1) Ultraviolet absorbing agent



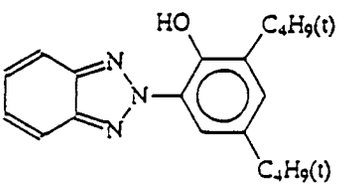
(UV-2) Ultraviolet absorbing agent



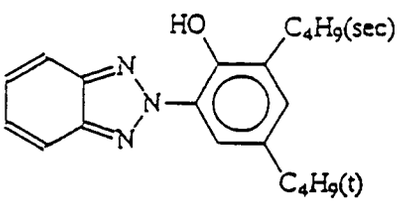
(UV-3) Ultraviolet absorbing agent



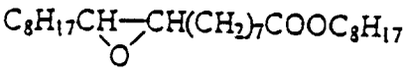
(UV-4) Ultraviolet absorbing agent



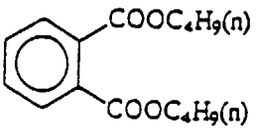
(UV-5) Ultraviolet absorbing agent



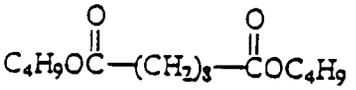
(Solv-1)



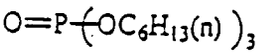
(Solv-2)



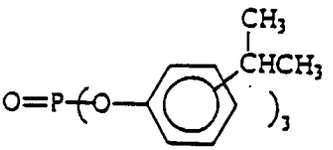
(Solv-3)



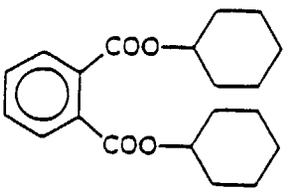
(Solv-4)



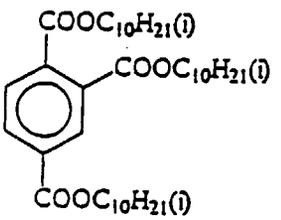
(Solv-5)



(Solv-6)



(Solv-7)



The thus-prepared color photographic light-sensitive material was formed into a roll with a width of 127 mm, it was exposed to light imagewise by an automatic printer, and it was processed using an automatic processor in the way described below, until the accumulative total of the replenishing rate of the bleaching solution reached 3 times the tank volume of the bleaching solution.

[Processing method]				
Processing step	Processing		Replenisher*	Tank Volume
	time	temperature		
Color-developing	45 sec	32 °C	45 ml	20 liter
Stopping	15 sec	32 °C	150 ml	20 liter
Washing	15 sec	32 °C	1.5 liter	10 liter
Bleaching	1 min 15 sec	32 °C	100 ml	40 liter
Washing (1)	20 sec	32 °C	counter-current piping system from tank (2) to tank (1)	10 liter
Washing (2)	20 sec	32 °C	1.5 liter	10 liter
Fixing	3 min 00 sec	32 °C	55 ml	30 liter
Washing (3)	45 sec	32 °C	counter-current piping system from tank (4) to tank (3)	10 liter
Washing (4)	45 sec	32 °C	2.0 liter	10 liter
Drying	1 min 20 sec	80 °C		

Note: * Replenisher amount (ml) per m^2 of the photographic material.

In the bleaching step, the overflow was regenerated every 10 liters. The regeneration was carried out in the same way as in Example 1, and the blowing of air at the regeneration was carried out for 2 hours. The regenerating agent used therein is shown below.

In passing, the amount carried over from the preceding bath by the light-sensitive material was 80 ml.

The composition of each processing solution was as follows, respectively:

(Color-developer)

	Tank Solution	Replenisher
Water	800.0ml	800.0 ml
Dimethylpolysiloxane-series surface active agent (Silicone KF351A, trade name: manufactured by Shinetsu Kagaku Kogyo Co.)	0.1 g	0.1 g
Triisopropanolamine	15.0 g	15.0 g
Ethylenediaminetetraacetic acid	4.0 g	4.0 g
Sodium 4,5-dihydroxybenzene -1,3-disulfonate	0.5 g	0.5 g
Potassium chloride	10.0 g	-
Potassium bromide	0.04 g	0.01 g
Fluorescent whitening agent (Blankophor BSU-PN, trade name: manufactured by Bayer AG)	5.0 g	15.0 g
Fluorescent whitening agent (Hakkol BRK, trade name: manufactured by Showa Kagaku Co.)	0.5 g	2.0 g
Sodium sulfite	0.1 g	0.1 g
Disodium-N,N-bis(sulfonatoethyl)hydroxylamine	8.5 g	11.1 g

(continued)

	Tank Solution	Replenisher
N-Ethyl-N-(β-methanesulfonamidoethyl) -3-methyl-4-aminoaniline • 3/2 sulfuric acid • monohydrate	5.0 g	14.5 g
Potassium carbonate	26.3 g	26.3 g
Water to make	1000 ml	1000 ml
pH (at 25 °C / pH was adjusted by KOH and sulfuric acid)	10.15	12.50

(Stopping solution)

0.7% aqueous acetic acid solution was used.

(Washing water)

The same washing water as in Example 1 was used.

(Start bleaching replenisher)

The start bleaching replenisher was prepared by diluting the bleaching-regenerating agent shown below 4 times, and its pH was adjusted to 3.2 by 20% sulfuric acid.

(Start tank solution)

The below-shown bleaching-regenerating agent was diluted 6 times, and its pH was adjusted to 3.4 in the same manner as in the replenisher.

(Bleaching-regenerating agent)

Bleaching agent (described in Table 7, the ferric complex salt of each compound was used)	
1,3-Diaminopropanetetraacetic acid	63 g
25% Aqueous ammonia	30 g
70% Glycolic acid	20 g
75% Acetic acid	60 g
Ferric nitrate • nonahydrate	167 g
Ammonium bromide	110 g
Water to make	1.0 liter
pH (pH was adjusted by using aqueous ammonia)	3.2

Table 7

No		Start bleaching replenisher	Bleaching-regenerating agent
1	I - 15	27 g	52 g
2	1,3-diaminopropanetetraacetic acid	34 g	59 g
3	Ethylenediamine-N,N'-disuccinic acid	33 g	58 g

(Fixing solution)

	Mother solution (g)	Replenisher (g)
Metha sodium bisulfite	1.8	2.3
75% ammonium thiosulfate	170	213
Sodium sulfite anhydride	28	35
Disodium ethylenediaminetetraacetate dihydrate	3	3.8
Water to make	1.0 liter	1.0 liter
pH (pH was adjusted by ammonia or acetic acid)	7.56	7.57

The residual amounts of silver in the exposed parts of each of Samples A and B after processing were determined by a fluorescent X-ray apparatus, and the yellow reflection densities (referred to as D_{min}) of the unexposed parts were measured by using a Densitometer 310-model, manufactured by X-Rite Co. The results for Sample A are shown in Table 8.

Table 8

		No 1		No 2		No 3	
Added amount of regenerating agent		I-15		1,3-diaminopropane-tetraacetic acid		Ethylenediamine-N,N'-disuccinic acid	
per 10 liters of the overflow	per m² of the light-sensitive material processed	D_{min}	Residual silver mg/m²	D_{min}	Residual silver mg/m²	D_{min}	Residual silver mg/m²
1 liter	10ml	0.10	2.21	0.13	3.31	0.14	3.42
5 liters	50ml	0.12	2.98	0.15	3.45	0.16	3.56
10 liters	100ml	0.19	3.80	0.20	4.57	0.21	4.61

Note) Within the bold lines, this invention

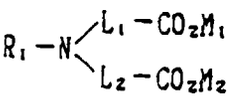
Further, with respect to the Sample B, similar results were obtained, which identified the effects of the invention.

Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

Claims

1. A method for processing a silver halide color photographic light-sensitive material, comprising after subjecting a silver halide color photographic light-sensitive material exposed to light imagewise, to color-development, bleaching the silver halide color photographic light-sensitive material, wherein the bleaching is carried out using a bleaching solution containing an iron(III) complex salt of an aminopolycarboxylic acid compound represented by the following formula (I):

Formula (I):

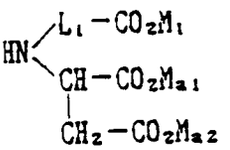


wherein R_1 represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, or a heterocyclic group, L_1 and L_2 each represent an alkylene group, and M_1 and M_2 each represent a hydrogen atom or a cation, with the replenishment being made with a bleaching replenisher, and wherein after the overflow from a bleaching bath resulting from the replenishment is regenerated with a bleaching-solution-regenerating agent in an amount smaller than the amount of the color developer, per square meter of the light-sensitive material to be processed, carried into the bleaching bath from a color-developing bath, the overflow is used as the bleaching replenisher.

2. The method for processing as claimed in claim 1, wherein the aminopolycarboxylic acid of the aminopolycarboxylic acid iron(III) complex salt in the bleaching solution comprises 1,3-diaminopropanetetraacetic acid or ethylenediaminetetraacetic acid in an amount of 1/2 or less in terms of molar fraction.

3. The method for processing as claimed in claim 1 or 2, wherein the aminopolycarboxylic acid compound is represented by the following formula (I-a):

formula (I-a)



wherein L_1 represents an alkylene group, M_1 represents a hydrogen atom or a cation, and M_{a1} and M_{a2} each represent a hydrogen atom or a cation.

4. The method for processing as claimed in claim 1, 2, or 3, wherein a dicarboxylic acid, a hydroxycarboxylic acid, or a sulfocarboxylic acid is contained in the bleaching solution.

5. The method for processing as claimed in claim 4, wherein the amount of the dicarboxylic acid, the hydroxycarboxylic acid, or the sulfocarboxylic acid to be added in the bleaching solution is in the range of 0.1 to 2.0 mol, per liter of the bleaching solution.

6. The method for processing as claimed in claim 1, 2, 3, 4, or 5, wherein a picolinic acid derivative is contained in the bleaching solution.

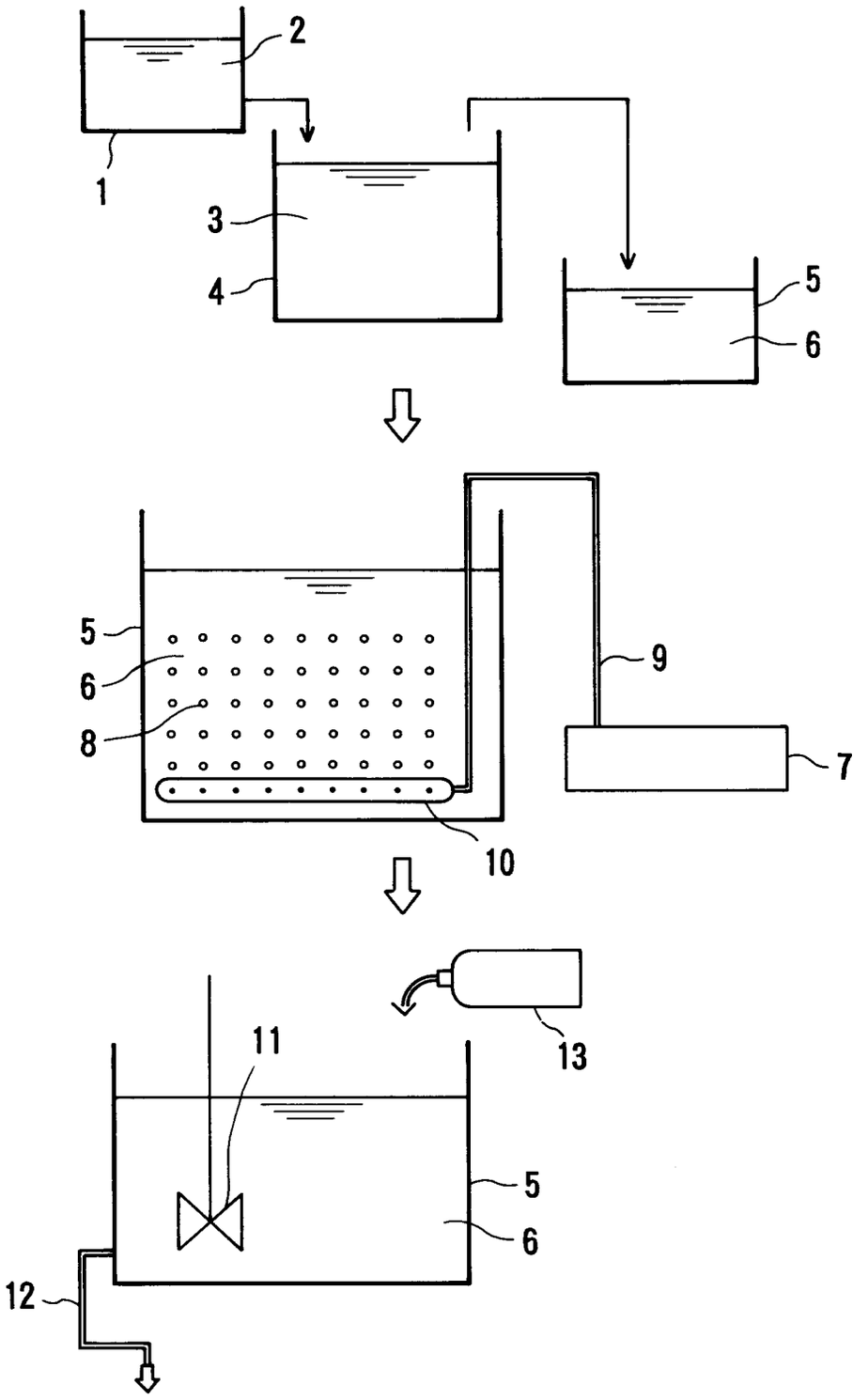
7. The method for processing as claimed in claim 6, wherein the amount of the picolinic acid derivative to be added in the bleaching solution is 0.005 to 3.0 mol/liter.

8. The method for processing as claimed in claim 1, 2, 3, 4, 5, 6, 7, or 8, wherein the pH of a washing bath after the bleaching is 3.5 to 8.0.

9. The method for processing as claimed in claim 1, 2, 3, 4, 5, 6, 7, or 8, wherein the amount of the bleaching agent to be used is 0.005 to 3.0 mol/liter.

10. The method for processing as claimed in claim 1, 2, 3, 4, 5, 6, 7, 8, or 9, wherein the amount of the bleaching-solution-regenerating-agent solution is 0.03 to 0.2 times, the amount of the overflow of the bleaching solution.

Fig. 1



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 10 6286

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 580 705 A (UEDA YUTAKA ET AL) 3 December 1996 * column 2, line 14 - column 9, line 8 * * column 11, line 27 - line 38 * * column 12, line 26 - column 14, line 11 * * column 51, line 1 - column 53, line 5 * * column 53, line 36 - line 56 * * claims 1-12 * ---	1-5,9,10	G03C5/395 G03C5/44 G03C7/44
X	US 5 153 111 A (YOSHIDA KAZUAKI ET AL) 6 October 1992 * example 5 * * column 76, line 66 - column 78, line 31 * ---	1,9,10	
X	US 4 923 785 A (FRANK KARL) 8 May 1990 * column 1, line 23 - line 48 * * column 4, line 3 - line 5 * ---	1,9,10	
A	EP 0 329 088 A (KONISHIROKU PHOTO IND) 23 August 1989 * page 3, line 44 - line 48 * * page 9, line 41 - page 15, line 57 * * page 19, line 26 - line 28 * * page 47, line 30 - page 49, line 49 * * page 52; table 3 * * claims 1-14 * ---	1,2,4-7,9	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C
A	EP 0 488 233 A (FUJI PHOTO FILM CO LTD) 3 June 1992 * page 2, line 47 - page 3, line 11 * * page 4, line 8 - line 25 * * page 8, line 46 - line 47 * --- -/--	1,8	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	15 July 1998	Lindner, T

CATEGORY OF CITED DOCUMENTS

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L : document cited for other reasons

& : member of the same patent family, corresponding document

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EUROPEAN SEARCH REPORT

Application Number
EP 98 10 6286

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	COOLEY A ET AL: "FACTORS LIMITING THE RECOVERY, REGENERATION, AND REUSE OF PHOTOGRAPHIC PROCESSING SOLUTIONS" JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY, vol. 37, no. 6, 1 November 1993, pages 603-606, XP000422491 * p. 604, chapter "Squeegee Efficiency" *	1,8	
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 352 (P-1248), 6 September 1991 & JP 03 134664 A (FUJI PHOTO FILM CO LTD), 7 June 1991, * abstract *	1,8	
A	PATENT ABSTRACTS OF JAPAN vol. 096, no. 005, 31 May 1996 & JP 08 006220 A (FUJI PHOTO FILM CO LTD), 12 January 1996, * abstract *	1-5	
A	EP 0 512 318 A (AGFA GEVAERT AG) 11 November 1992 * examples 1,2 *	1,10	TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	15 July 1998	Lindner, T

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