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(54) Color developing solution for light-sensitive silver halide color photographic material and processing method.

(57) There are disclosed a color developing solution for a light-sensitive silver halide color photographic material which comprises a sulfite concentration of 1.0 x 10^{-3} mole or lower per liter of the color developing solution and containing 0.5 to 20 g/ℓ of a water-soluble surfactant and a processing method using the color developing solution.

COLOR DEVELOPING SOLUTION FOR LIGHT-SENSITIVE SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL AND PROCESSING METHOD

BACKGROUND OF THE INVENTION

This invention relates to a color developing solution for a light-sensitive silver halide color photographic material and a processing method using the same, more specifically, it relates to a color developing solution for a light-sensitive silver halide color photographic material capable of obtaining stable photographic characteristics even when a sulfite concentration of the color developing solution is low and overcome the problems of generation of contamination caused at a transport lack in a color developing processing tank or a roller portion, and a processing method using the same.

Processings of a light-sensitive material basically comprise two steps of color developing and desilvering, and the desilvering comprises a bleaching and a fixing step or a bleach-fixing step. As the additional processing steps, a linsing processing, stabilizing processing, etc. may be added.

In color developing, silver halide developed becomes silver by reduction and simultaneously an aromatic primary amine developing agent oxidized reacts with a coupler to form a dye. In this procedure, a halide ion generated by reduction of the silver halide is dissolved in a developing solution and accumulated therein. In addition, a component such as a restrainer contained in a light-sensitive silver halide photographic material is also dissolved and accumulated in the color developing solution. In the desilvering step, silver generated by developing is bleached by an oxidizing agent, and all the silver salts are removed away from the light-sensitive photographic material by a fixing agent as a soluble silver salt. A one-bath bleach-fixing processing step in which the bleaching step and the fixing step are carried out simultaneously has also been known.

In a color developing solution, a development inhibiting substance is accumulated in a developing solution by effecting developing processing of a light-sensitive photographic material as mentioned above. On the other hand, a color developing agent and benzyl alcohol are consumed or brought off by accumulating in the light-sensitive photographic material to be processed whereby concentrations of these components are gradually lowered. Accordingly, in the developing processing method in which a large amount of light-sensitive silver halide photographic material is continuously processed by using an automatic developing machine, it is required to have a means for maintaining components of a color developing solution in a constant concentration range in order to avoid fluctuation of development finished characteristics due to change in concentrations of the components. As such a means, a method of replenishing a replenishing solution in order to replenish lacked components and to dilute unnecessary components increased is generally employed. According to replenishing the replenishing solution, a large amount of overflow is necessarily generated and disposed, so that this method becomes great problems in view of economic and pollution. Therefore, in recent years, in order to decrease the above mentioned overflow solution, there have been proposed a regenerating method of a developing solution by an ion exchange resin method or an electrodialysis method, a concentrated less-replenishing method, or the method in which a regenerating agent is added to the overflow solution and the resulting solution is used again as a replenishing solution, and have been practiced.

Regeneration of a developing solution is carried out by removing a bromide which is an unnecessary accumulated component and replenishing a lacked component. However, this method (the ion exchange resin method and the electrodialysis method) has a defect that developing processing characteristics of the light-sensitive material are lost unless the composition of a developing solution should be determined by a chemical analysis and made constant, thus, it is substantially impossible to introduce the method in a small-sized photofinishing laboratory or mini-laboratory not having specific skill since complicated controls thereof are required.

Further, while the method in which an overflow solution is regenerated and used as a replenishing solution by adding a regenerating agent requires no specific skill, but a space for a stock tank and the like is required and it has a defect that the method is complicated for the photofinishing laboratory, whereby it is extremely difficult to introduce the method in a mini-laboratory. To the contrary, it can be said that the concentrated less-replenishing method is a particularly suitable method for a small-sized laboratory since a novel device is not specifically required and processing controls are easy. However, this method also has some defects. For example, accompanying with less-replenishing, dissolved-out materials from a light-sensitive material into a developing solution are accumulated with a great extent and a decomposed product of components in the color developing solution due to air oxidation is also accumulated with a large amount. Under such conditions, when developing processing is discontinuously carried out for a long period of time in a small-sized laboratory such as mini-laboratory in which processed amount is small, contamination at a rack or roller portion in the color developing processing tank of an automatic developing machine is generated so that a trouble of contaminating a light-sensitive material to be processed by the contamination is generated.

Also, a photofinishing laboratory propagandizing short time processing (one hour finishing) or so-called "One Hour Photo" has spread and this tendency is becoming more remarkable in recent years. Thus, a color paper containing a high content of silver chloride which is excellent in developing processing characteristics has been spread. However, in the color developing solution for processing the color paper mainly containing silver chloride, a large amount of sulfite cannot be added. In such a processing system containing a little amount of sulfite, contamination due to powder like material precipitated on a rack or roller portion in the color developing processing tank of an automatic developing machine becomes more marked and further a light-sensitive material is contaminated when continuous processing is carried out, particularly in a color printing material, it has been found that there is the problem that a white ground is colored and commercial value thereof is markedly lowered.

To the problems as mentioned above, there has been proposed a method in which a specific water-soluble surfactant is added to a color developing solution whereby contamination at a rack and roller portion in the color developing processing tank of an automatic developing machine is prevented as described in Japanese Provisional Patent Publications No. 42154/1987 and No. 42155/1987. However, when an amount of the surfactant added to the color developing solution is a little, a part of a material having a hydrophobic portion is oriented and adhered to the interface such as the rack or roller surface so that contamination due to deposition or adhering of powder-like material to the rack or roller cannot sufficiently be prevented, and further, when a concentration of sulfite is low, it becomes more difficult to prevent contamination of the rack or roller. Moreover, the method is indeed insufficient against deterioration of a white ground at continuous processing, and when a sulfite concentration is low, it is further insufficient.

Also, during continuous processing, as a method of preventing deterioration of a white ground particularly when processed with a color developing solution with low sulfite concentration, there have been disclosed a method of using an alkanolamine as described in Japanese Provisional Patent Publication No. 250444/1987, a method of using a dialkylhydroxylamine as described in Japanese Provisional Patent Publication No. 32547/1988 and a method of using a hydrazine derivative as described in Japanese Provisional Patent Publication No. 48548/1988. However, either of the methods does not have drastic effect and there are problems that one of which is insufficient in preventing deterioration at a white ground, or limited in a used amount because bad effect is caused in photographic performances so that effects are insufficient, or sludge is generated.

SUMMARY OF THE INVENTION

Accordingly, objects of the present invention is firstly to provide a color developing solution which is capable of effecting rapid processing and can provide stable photographic performances and a processing method, and secondly to provide a color developing solution which causes less contamination due to deposition or adhesion of powder-like material (sludge) to a rack or a roller whereby causing less contamination of a light-sensitive material and a processing method.

The present inventors have intensively studied to accomplish the above objects and as the results, they have completed the present invention.

That is, a color developing solution for a light-sensitive silver halide color photographic material according to the present invention comprises a sulfite concentration of 1.0×10^{-3} mole or less per liter of the color developing solution and containing 0.5 g/l to 20 g/l of a water-soluble surfactant.

As a preferred embodiment of the color developing solution for a light-sensitive silver halide color photographic material according to the present invention, said water-soluble surfactant is a nonionic surfactant and/or an anionic surfactant, and as the other preferred embodiment of the present invention, said water-soluble surfactant is contained in an amount of 1.0 g to 15 g per liter of the color developing solution. Further, more preferred embodiment of the present invention comprises containing a surfactant represented by the following formula (I):

$$R^1X(E^1)_{\ell 1}\text{-}(E^2)_{m1}\text{-}(E^3)_{n1}\text{-}R^2 \qquad (I)$$

wherein R^1 represents a hydrogen atom, an aliphatic group or an acyl group, R^2 represents a hydrogen atom or an aliphatic group, E^1 represents ethylene oxide, E^2 represents propylene oxide, E^3 represents ethylene oxide, X represents an oxygen atom or a $-R^3N-$ group where R^3 represents an aliphatic group, a hydrogen atom or $(E^1)_{\eta}$-$(E^2)_{m2}$-$(E^3)_{n2}$-R^4, where R4 represents a hydrogen atom or an aliphatic group, and ℓ1, ℓ2, ml, m2, n1 and n2 each represent a value of 0 to 300.

Also, a processing method of a light-sensitive silver halide color photographic material according to the present invention comprises processing the light-sensitive silver halide color photographic material with a color developing solution after imagewise exposure, the improvement wherein said color developing solution contains 1.0×10^{-3} mole or less of a sulfite per liter of the color developing solution and contains 0.5 to 20 g/ℓ of a water-soluble surfactant. Further, as the preferred embodiments of the present invention, said water-soluble surfactant is contained in an amount of 1.0 g to 15 g per liter of the color developing solution and said surfactant contains the surfactant represented by the above formula (I). Moreover, it is preferred that a replenishing amount of said color developing solution is 120 ml or less per 1 m² of the light-sensitive silver halide color photographic material.

That is, in the present invention, by using a remarkably large amount of a water-soluble surfactant than the amount conventionally and commonly used in the color developing solution, stain at unexposed portion or deposition of precipitates to a roller or lack during continuous processing which are likely generated in the color developing solution containing a low concentration of a sulfite can be prevented, which fact is entirely unexpected.

As described above, it has been known to use a water-soluble surfactant in a color developing solution, and in a color developing solution with high sulfite concentration, it has been practically sufficient with addition of a small amount of a water-soluble surfactant while it is insufficient and only a small amount thereof must be used in practical. That is, in a processing solution with a high sulfite concentration, prevention of oxidation of a color developing agent or reduction of a dye or a sensitizing dye can be carried out relatively smoothly so that deterioration of a color developing solution itself or the aforesaid problems which can be considered based on dissolved materials from a light-sensitive material are reduced. Also, in the conventional light-sensitive silver halide photographic material using an emulsion composed mainly of silver bromide, when a large amount of a surfactant is used, serious effects are caused in the photographic performances so that an amount to be used must be limited. However, in the case of using an emulsion composed mainly of silver chloride for rapid processing, an amount of a sulfite is depressed with a small amount which does not affect to developability. In such a developing solution with a low sulfite concentration, the above problems become more marked but by using a water-soluble surfactant with a high concentration, it has been found that the above problems have been solved and yet in the case of an emulsion composed mainly of silver chloride, substantially no effect occurs even when a water-soluble surfactant is used with a high concentration whereby accomplishing the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In the following, the present invention is described in more detail.

The water-soluble surfactant herein mentioned in the present specification means the water-soluble, having two groups of hydrophilic and hydrophobic groups which are opposed to each other in solubility to a solvent. The water-soluble surfactant is classified into an ionic surfactant and a nonionic surfactant by the reason that it shows ionic property in an aqueous solution or not, and the ionic surfactant is further classified into an anionic surfactant, a cationic surfactant and an amphoteric surfactant according to a kind of ion species at a portion of showing surface activity. Either of these surfactants can be used in order to accomplish the objects of the present invention and two or more kinds thereof may be used in combination.

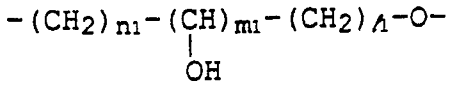
In the present invention, as a surfactant to be used other than the compound represented by the formula (I), there may be mentioned compounds represented by the following formulae (II) to (X) and (XI).

A_2-O-$(B)_m$-$(C)_n$-X_1 (II)

In the formula, A_2 represents a monovalent organic group such as an alkyl group having 6 to 50, preferably 6 to 35 carbon atoms (e.g. each group of hexyl, heptyl, octyl, nonyl, decyl, undecyl or dodecyl) and an aryl group substituted by an alkyl group having 3 to 35 carbon atoms or by an alkenyl group having 2 to 35 carbon atoms.

As the preferred substituents on the aryl group, there may be mentioned an alkyl group having 1 to 18 carbon atoms (e.g. unsubstituted alkyl group such as methyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl), a substituted alkyl group such as benzyl and phenethyl, or an alkenyl group having 2 to 20 carbon atoms (e.g. unsubstituted alkenyl groups such as oleyl, cetyl and allyl, and substituted alkenyl groups such as styryl). As the aryl group, there may be mentioned each group of phenyl, biphenyl and naphthyl, and preferably a phenyl group. As the position to be substituted on the aryl group, either of ortho, meta or para may be substituted and plural number of groups may be substituted.

B or C represents ethylene oxide or propylene oxide, or



$$-(CH_2)_{n_1}-(\underset{\displaystyle OH}{\underset{|}{CH}})_{m_1}-(CH_2)_{\ell_1}-O-$$

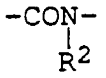
where n_1, m_1 and ℓ_1 each represent 0, 1, 2 or 3.

m and n each represent an integer of 0 to 100.

X_1 represents a hydrogen atom, an alkyl group, an aralkyl group or an aryl group, and for example, there may be mentioned groups as explained in A_2.

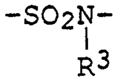
$$R^1 \text{—} (X\text{-}L)_{\ell} \text{—} COOM \qquad (III)$$

In the formula, R^1 represents an aliphatic group (e.g. a saturated or unsaturated, substituted or unsubstituted, straight or branched alkyl group), X represents



$$-CO\underset{\displaystyle R^2}{\underset{|}{N}}-$$

or

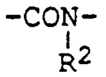


$$-SO_2\underset{\displaystyle R^3}{\underset{|}{N}}-$$

(where R^2 and R^3 each represent a hydrogen atom or the groups defined in R^1), ℓ is 0 or 1, M represents a hydrogen atom, an alkali metal (such as Na, K), an ammonium ion, an organic ammonium ion or a monovalent cation, and L represents an alkylene group.

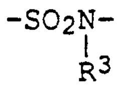
$$R^1 \text{—} (X\text{-}L)_{\ell} \text{—} (Y)_{m'} SO_3M \qquad (IV)$$

In the formula, R^1 represents an aliphatic group (e.g. a saturated or unsaturated, substituted or unsubstituted, straight or branched alkyl group), X represents



$$-CO\underset{\displaystyle R^2}{\underset{|}{N}}-$$

or

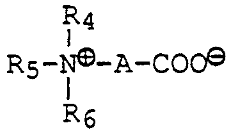


$$-SO_2\underset{\displaystyle R^3}{\underset{|}{N}}-$$

(where R^2 and R^3 each represent a hydrogen atom or the groups defined in R^1), ℓ and m' are each 0 or 1, L represents an alkylene group, Y represents an oxygen atom and M represents a hydrogen atom, an alkali metal (such as Na, K) or a monovalent cation.

A_2-O-$(CH_2CH_2O)_n$-SO_3M (V)

In the formula, M represents a hydrogen atom, an alkali metal (such as Na, K) or a monovalent cation, n is 1 to 100, A_2 represents a monovalent organic group such as an alkyl group having 6 to 20, preferably 6 to 12 carbon atoms (e.g. each group of hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl), or an aryl group substituted by an alkyl group having 3 to 20 carbon atoms, and as the substituents, there may be preferably mentioned an alkyl group having 3 to 12 carbon atoms (e.g. each group of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl), and as the aryl group, there may be mentioned each group of phenyl, tolyl, xylyl, biphenyl and naphthyl, preferably a phenyl group or a tolyl group. As the position of the alkyl group to be bonded on the aryl group, either of ortho, meta or para may be substituted.

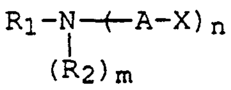


$$R_5-\overset{\displaystyle R_4}{\underset{\displaystyle R_6}{N^{\oplus}}}-A-COO^{\ominus} \qquad \text{(VI)}$$

In the formula, R_4, R_5 and R_6 each represent a substituted or unsubstituted alkyl group, and R_4 and R_5, or R_5 and R_6 may form a ring, respectively. A represents

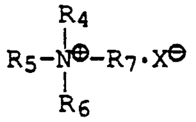
$$-(CH)_n-$$

(where n is an integer of 1, 2 or 3).



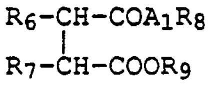
$$R_1-\underset{\displaystyle (R_2)_m}{N}-(-A-X)_n \qquad \text{(VII)}$$

In the formula, R_1 has the same meaning as A_2 in the formula (II), R_2 represents a hydrogen atom or an alkyl group (e.g. a methyl group and an ethyl group), m and n are each 0, 1 or 2, A represents an alkyl group or a substituted or unsubstituted aryl group and X is $-COOM$ or $-SO_3H$ where M is a hydrogen atom, an alkali metal (such as Na, K) or a monovalent cation.



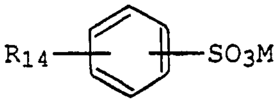
$$R_5-\overset{\displaystyle R_4}{\underset{\displaystyle R_6}{N^{\oplus}}}-R_7\cdot X^{\ominus} \qquad \text{(VIII)}$$

In the formula, R_4, R_5, R_6 and R_7 each represent a hydrogen atom, a substituted or unsubstituted alkyl group or a phenyl group, $X^{\ominus}$ represents an anion of a halogen atom, a hydroxyl group, a sulfate group, a carbonate group, a nitrate group, an acetate group or a p-toluenesulfonate group.

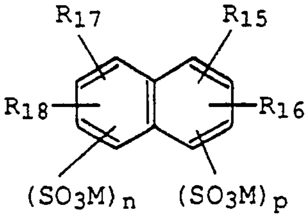


$$\begin{array}{l} R_6-CH-COA_1R_8 \\ \quad\;\; | \\ R_7-CH-COOR_9 \end{array} \qquad \text{(IX)}$$

In the formula, one of R_6 and R_7 represents a hydrogen atom or an alkyl group and the other represents a group represented by the formula: $-SO_3M$ (where M represents a hydrogen atom, an alkali metal (such as Na, K) or a monovalent cation), A_1 represents an oxygen atom or a group represented by the formula: $-NR_{10}-$ (where R_{10} represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms), and R_8 and R_9 each represent an alkyl group having 4 to 30 carbon atoms, provided that the alkyl group represented by R_8, R_9 or R_{10} may be substituted by a fluorine atom.



(X)



(XI)

In the formulae, R_{14}, R_{15}, R_{16}, R_{17} and R_{18} each represent a hydrogen atom or an alkyl group, M has the same meaning with M as defined in the formula (III), and n and p are each 0 or an integer of 1 to 4 and numbers satisfying $1 \leqq n + p \leqq 8$.

In the following, exemplary compounds represented by the formulae (I) to (X) and (XI) are enumerated but the present invention is not limited by these.

(Compounds represented by the formula (I))

I - 1

$C_{12}H_{25}COO-(C_2H_4O)_{10}-H$

I - 2

$C_9H_{19}COO-(C_2H_4O)_4-H$

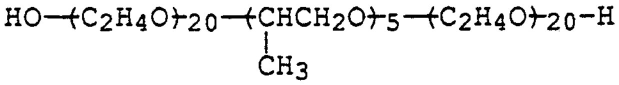
I - 3

$C_{12}H_{25}NH-(C_2H_4O)_{10}-H$

I - 4

$C_{12}H_{25}NH-(C_2H_4O)_{15}-H$

I - 5

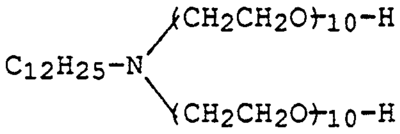


$HO-(C_2H_4O)_{20}-(\underset{CH_3}{\underset{|}{C}}HCH_2O)_5-(C_2H_4O)_{20}-H$

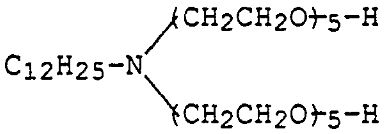
I - 6

$C_{12}H_{25}NHCH_2CH_2OH$

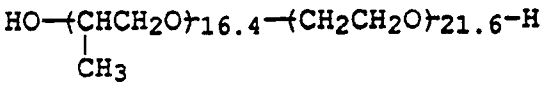
I - 7



I - 8

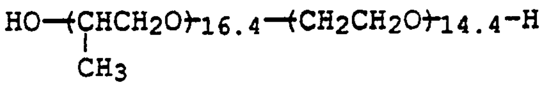


I - 9



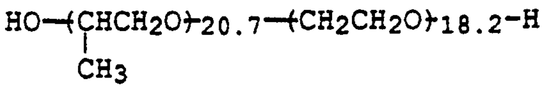
$$HO-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_{16.4}-(CH_2CH_2O)_{21.6}-H$$

I - 10



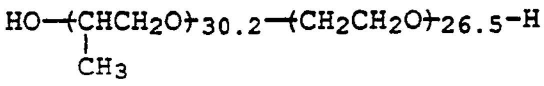
$$HO-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_{16.4}-(CH_2CH_2O)_{14.4}-H$$

I - 11



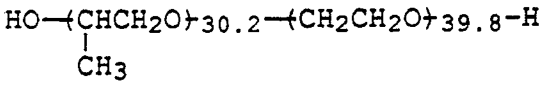
$$HO-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_{20.7}-(CH_2CH_2O)_{18.2}-H$$

I - 12



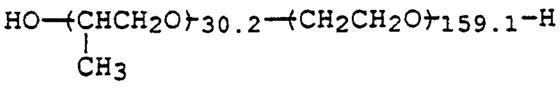
$$HO-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_{30.2}-(CH_2CH_2O)_{26.5}-H$$

I - 13



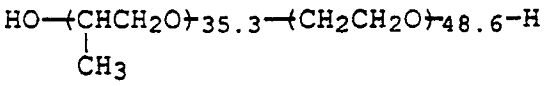
$$HO-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_{30.2}-(CH_2CH_2O)_{39.8}-H$$

I - 14



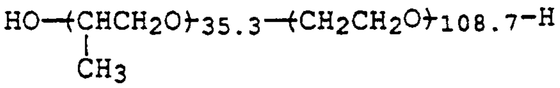
$$HO-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_{30.2}-(CH_2CH_2O)_{159.1}-H$$

I - 15



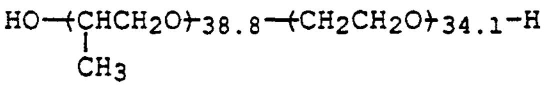
$$HO-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_{35.3}-(CH_2CH_2O)_{48.6}-H$$

I - 16



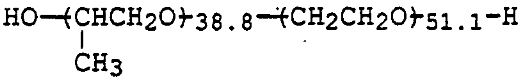
$$HO-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_{35.3}-(CH_2CH_2O)_{108.7}-H$$

I - 17



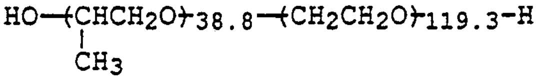
$$HO-(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_{38.8}-(CH_2CH_2O)_{34.1}-H$$

I - 18



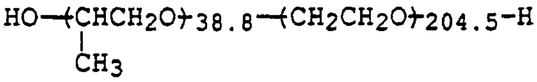
$$HO-(\underset{CH_3}{CH}CH_2O)_{38.8}-(CH_2CH_2O)_{51.1}-H$$

I - 19



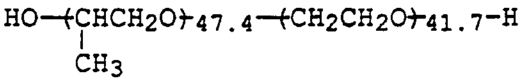
$$HO-(\underset{CH_3}{CH}CH_2O)_{38.8}-(CH_2CH_2O)_{119.3}-H$$

I - 20



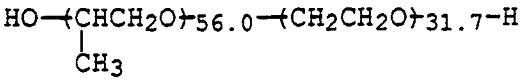
$$HO-(\underset{CH_3}{CH}CH_2O)_{38.8}-(CH_2CH_2O)_{204.5}-H$$

I - 21



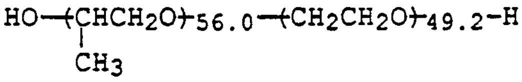
$$HO-(\underset{CH_3}{CH}CH_2O)_{47.4}-(CH_2CH_2O)_{41.7}-H$$

I - 22



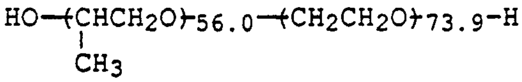
$$HO-(\underset{CH_3}{CH}CH_2O)_{56.0}-(CH_2CH_2O)_{31.7}-H$$

I - 23



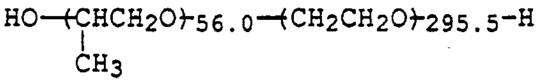
$$HO-(\underset{CH_3}{CH}CH_2O)_{56.0}-(CH_2CH_2O)_{49.2}-H$$

I - 24



$$HO-(\underset{CH_3}{CH}CH_2O)_{56.0}-(CH_2CH_2O)_{73.9}-H$$

I - 25



$$HO-(\underset{CH_3}{CH}CH_2O)_{56.0}-(CH_2CH_2O)_{295.5}-H$$

(Compound represented by the formula (II))

II - 1

$$C_{12}H_{25}-O-(C_2H_4O)_{10}-H$$

II - 2

$C_8H_{17}-O-(C_3H_6O)_{15}-H$

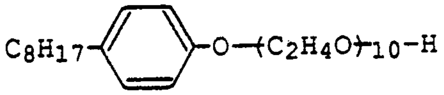
II - 3

$C_9H_{19}-O-(C_2H_4O)_4-H$

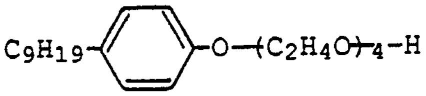
II - 4

$C_{10}H_{21}-O-(C_2H_4O)_{15}-H$

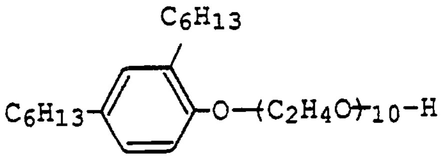
II - 5



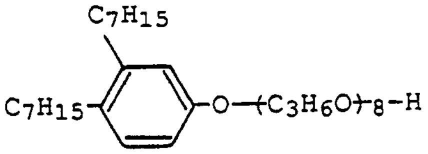
II - 6



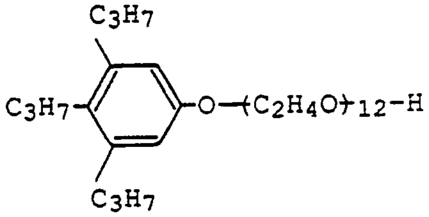
II - 7



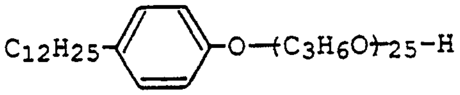
II - 8



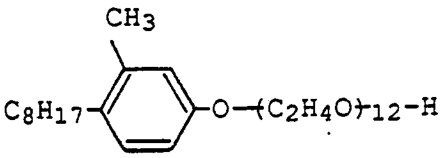
II - 9



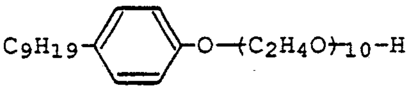
II - 10



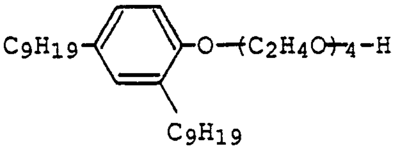
II - 11



II - 12



II - 13



II - 14

$C_{12}H_{25}O-(C_2H_4O)_4-H$

II - 15

$C_6H_{13}O-(C_2H_4O)_{10}-H$

II - 16

$C_8H_{17}O-(C_2H_4O)_{15}-H$

II - 17

$C_{10}H_{21}O-(C_2H_4O)_{10}-H$

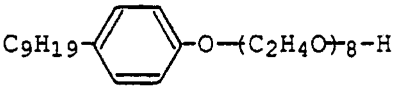
II - 18

$C_{12}H_{25}O-(C_2H_4O)_{15}-H$

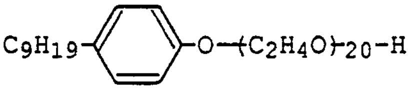
II - 19

$C_{14}H_{29}O-(C_2H_4O)_{15}-H$

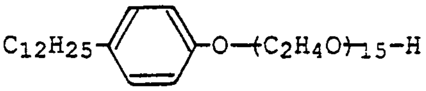
II - 20



II - 21



II - 22



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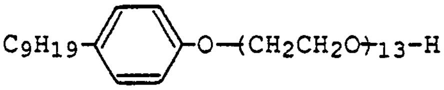
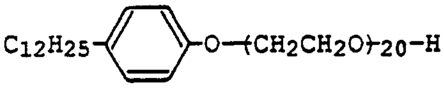
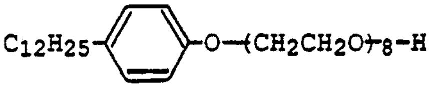


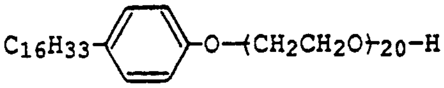
II - 24



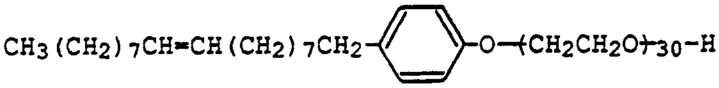
II - 25



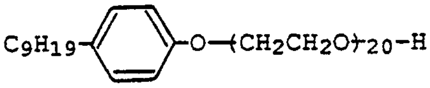
II - 26



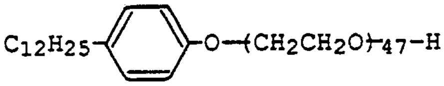
II - 27



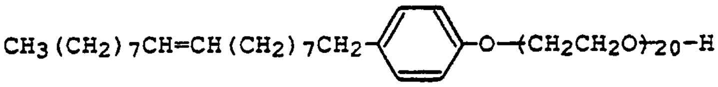
II - 28



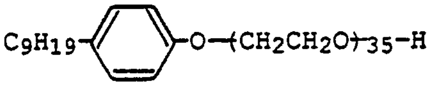
II - 29



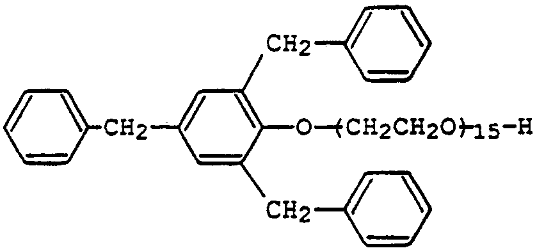
II - 30



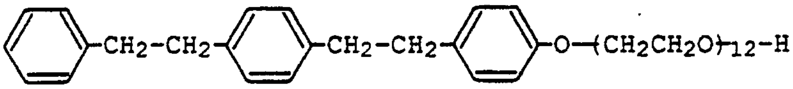
II - 31



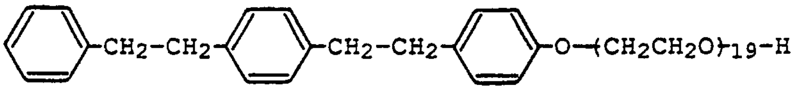
II - 32



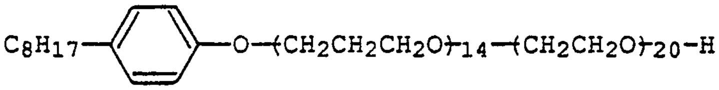
II - 33



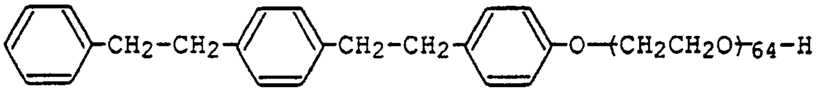
II - 34



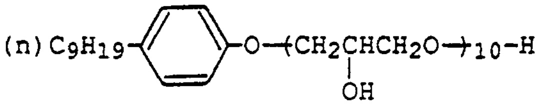
II - 35



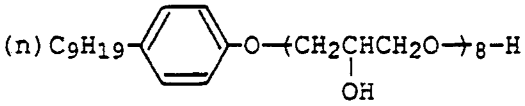
II - 36



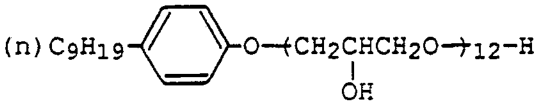
II - 37



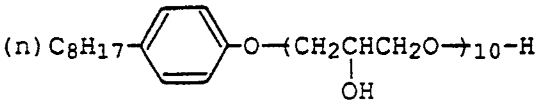
II - 38



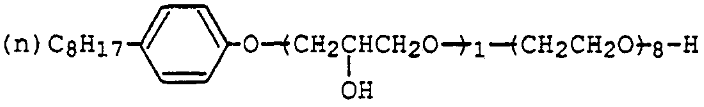
II - 39



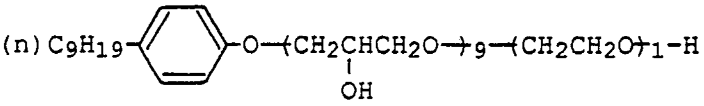
II - 40



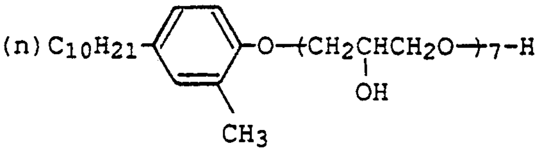
II - 41



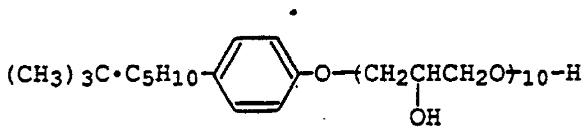
II - 42



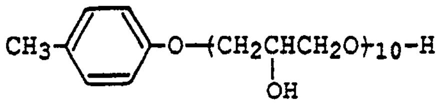
II - 43



II - 44



II - 45



II - 46 $(n)C_{13}H_{27}-O-(CH_2CH_2O)_5-H$

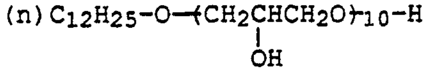
II - 47 $C_{12}H_{25}-O-(CH_2CH_2O)_{10}-H$

II - 48 $C_{18}H_{37}-O-(CH_2CH_2O)_{10}-H$

II - 49 $(n)C_{10}H_{21}-O-(CH_2CH_2O)_4-H$

II - 50 $(n)C_{16}H_{33}-O-(CH_2CH_2O)_4-H$

II - 51



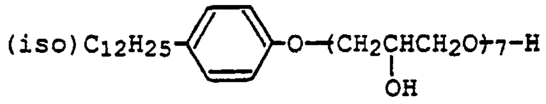
$(n)C_{12}H_{25}-O-(CH_2\underset{OH}{CH}CH_2O)_{10}-H$

II - 52

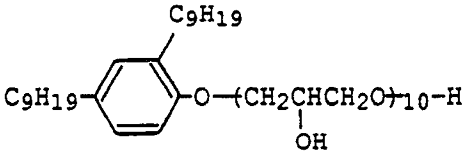
$(n)C_{12}H_{25}-O-(CH_2\underset{OH}{CH}CH_2O)_2-(CH_2CH_2O)_8-H$

II - 53 $(n)C_{13}H_{27}-O-(CH_2CH_2O)_4-H$

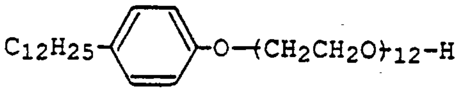
II - 54



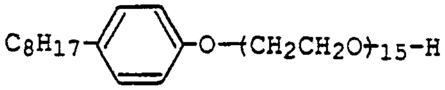
II - 55



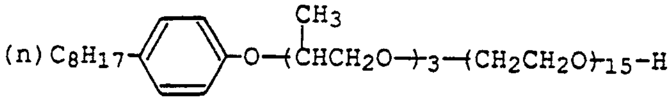
II - 56



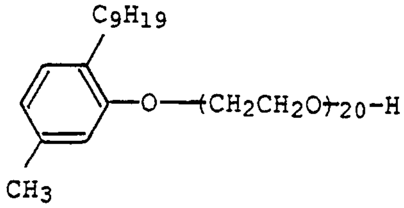
II - 57



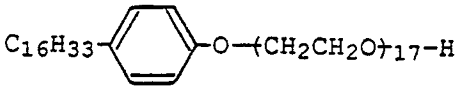
II - 58



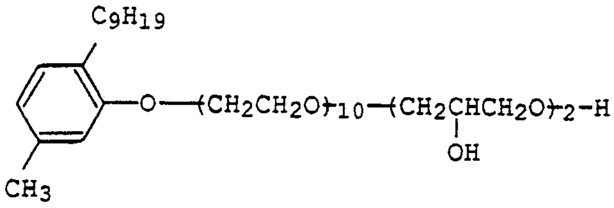
II - 59



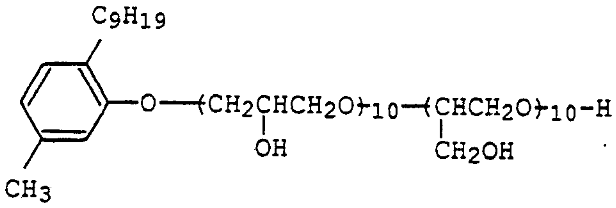
II - 60



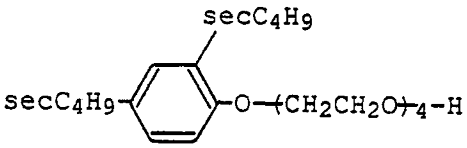
II - 61



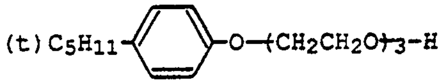
II - 62



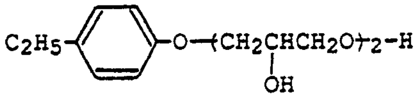
II - 63



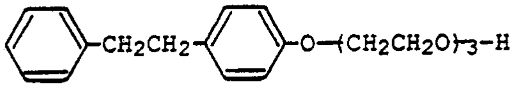
II - 64



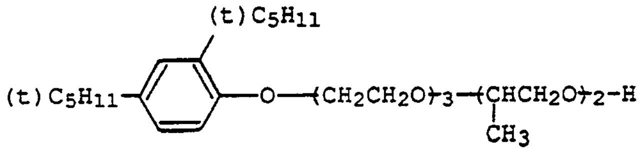
II - 65



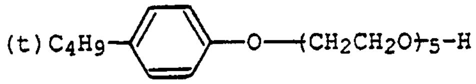
II - 66



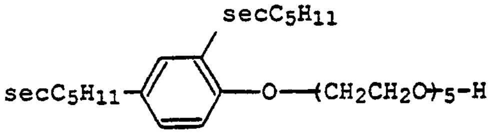
II - 67



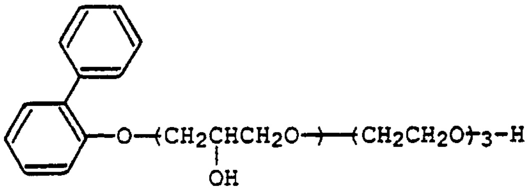
II - 68



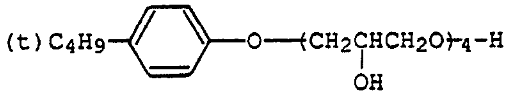
II - 69



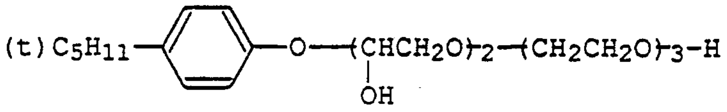
II - 70



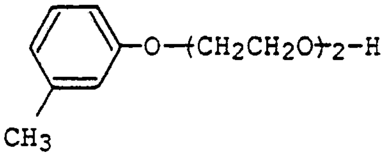
II - 71



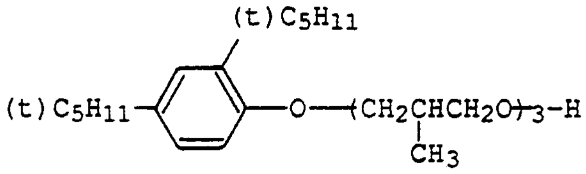
II - 72



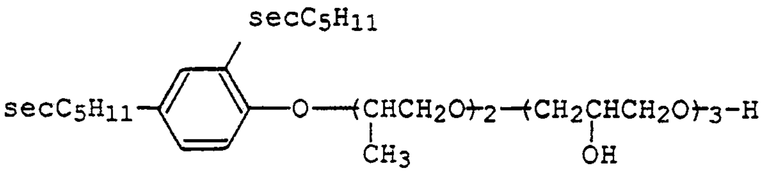
II - 73



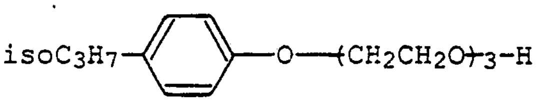
II - 74



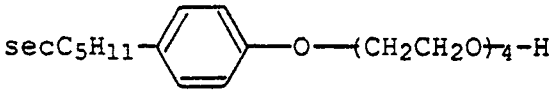
II - 75



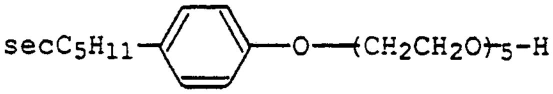
II - 76



II - 77



II - 78



(Compounds represented by the formula (III))

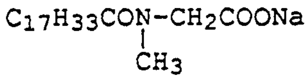
III - 1 $C_{12}H_{25}{-}SO_2NHCH_2CH_2COONa$

III - 2 $C_{12}H_{25}COONa$

III - 3 $C_{12}H_{25}COOK$

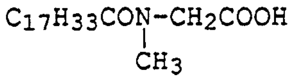
III - 4 $C_{17}H_{33}CONHCH_2CH_2COONa$

III - 5



$C_{17}H_{33}CO\underset{CH_3}{\underset{|}{N}}{-}CH_2COONa$

III - 6



$C_{17}H_{33}CO\underset{CH_3}{\underset{|}{N}}{-}CH_2COOH$

(Compounds represented by the formula (IV))

IV - 1 $C_{12}H_{25}SO_3Na$

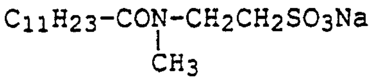
IV - 2 $C_{11}H_{23}CONHCH_2CH_2OSO_3Na$

IV - 3 $C_{12}H_{25}CONH{-}(CH_2CH_2O)_n{-}SO_3Na$

IV - 4 $C_{12}H_{25}OSO_3Na$

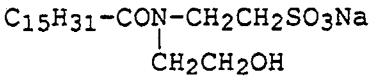
IV - 5 $C_{11}H_{23}COOCH_2CH(OH)CH_2OSO_3Na$

IV - 6



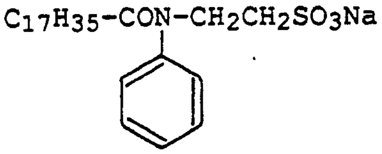
$C_{11}H_{23}{-}CO\underset{CH_3}{\underset{|}{N}}{-}CH_2CH_2SO_3Na$

IV - 7

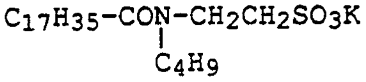


$C_{15}H_{31}{-}CO\underset{CH_2CH_2OH}{\underset{|}{N}}{-}CH_2CH_2SO_3Na$

IV - 8

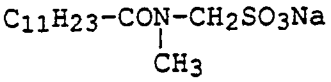


IV - 9



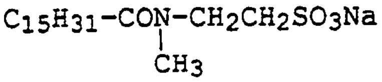
$C_{17}H_{35}-CO\underset{C_4H_9}{\underset{|}{N}}-CH_2CH_2SO_3K$

IV - 10



$C_{11}H_{23}-CO\underset{CH_3}{\underset{|}{N}}-CH_2SO_3Na$

IV - 11



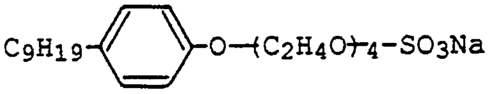
$C_{15}H_{31}-CO\underset{CH_3}{\underset{|}{N}}-CH_2CH_2SO_3Na$

(Compounds represented by the formula (V))

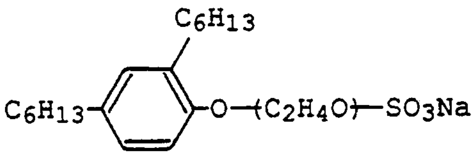
V - 1 $C_9H_{19}O(C_2H_4O)_4SO_3Na$

V - 2 $C_{10}H_{21}O(C_2H_4O)_{15}SO_3Na$

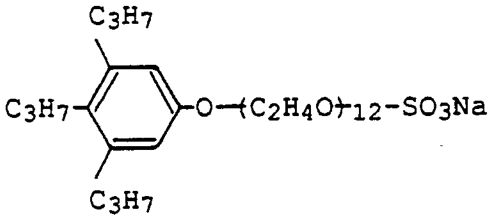
V - 3



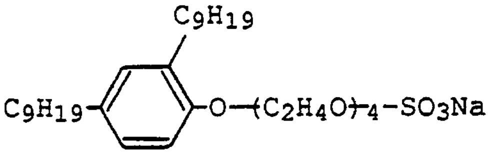
V - 4



V - 5



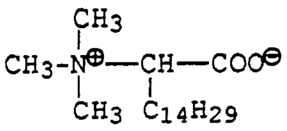
V - 6



V - 7 $C_{12}H_{25}O-(C_2H_4O)_4-SO_3Na$

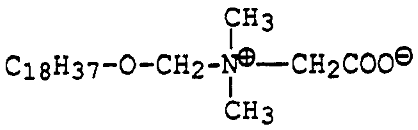
(Compounds represented by the formula (VI))

VI - 1



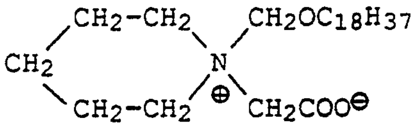
$$CH_3-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-\underset{C_{14}H_{29}}{CH}-COO^{\ominus}$$

VI - 2

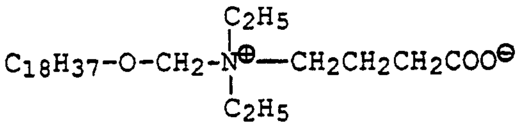


$$C_{18}H_{37}-O-CH_2-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_2COO^{\ominus}$$

VI - 3

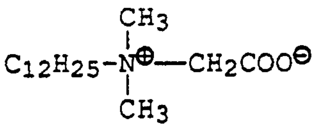


VI - 4



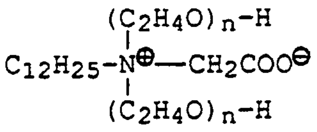
$$C_{18}H_{37}-O-CH_2-\overset{C_2H_5}{\underset{C_2H_5}{N^{\oplus}}}-CH_2CH_2CH_2COO^{\ominus}$$

VI - 5



$$C_{12}H_{25}-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_2COO^{\ominus}$$

VI - 6



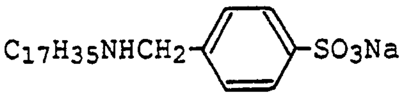
$$C_{12}H_{25}-\overset{(C_2H_4O)_n-H}{\underset{(C_2H_4O)_n-H}{N^{\oplus}}}-CH_2COO^{\ominus}$$

(Compounds represented by the formula (VII))

VII - 1 $C_{12}H_{25}-N-(CH_2CH_2COONa)_2$

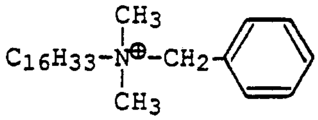
VII - 2 $C_{17}H_{35}NHCH_2CH_2SO_3Na$

VII - 3



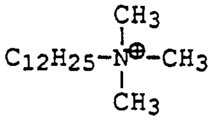
(Compounds represented by the formula (VIII))

VIII - 1



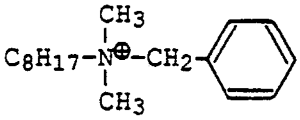
$Cl^{\ominus}$

VIII - 2



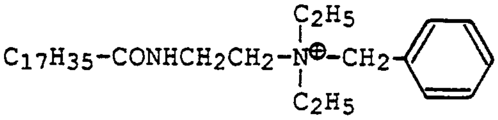
$$C_{12}H_{25}-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_3 \qquad Cl^{\ominus}$$

VIII - 3



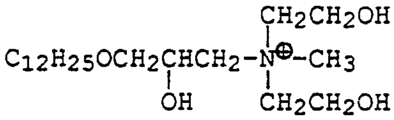
$Cl^{\ominus}$

VIII - 4



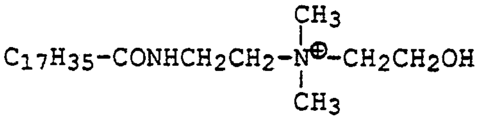
$Cl^{\ominus}$

VIII - 5



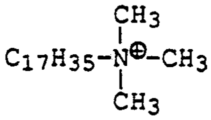
$$C_{12}H_{25}OCH_2\underset{OH}{C}HCH_2-\overset{CH_2CH_2OH}{\underset{CH_2CH_2OH}{N^{\oplus}}}-CH_3 \qquad CH_3SO_4^{\ominus}$$

VIII - 6



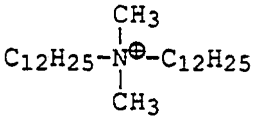
$$C_{17}H_{35}-CONHCH_2CH_2-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_2CH_2OH \qquad NO_2^{\ominus}$$

VIII - 7



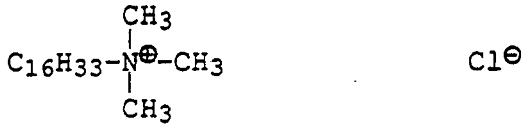
$$C_{17}H_{35}-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_3 \qquad Cl^{\ominus}$$

VIII - 8



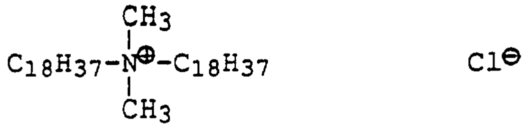
$$C_{12}H_{25}-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-C_{12}H_{25} \qquad Cl^{\ominus}$$

VIII - 9



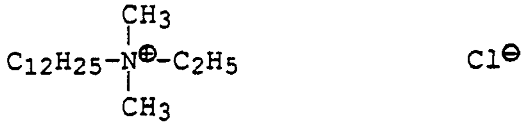
$$C_{16}H_{33}-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}-CH_3 \qquad Cl^{\ominus}$$

VIII - 10



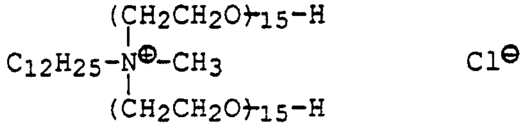
$$C_{18}H_{37}-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}-C_{18}H_{37} \qquad Cl^{\ominus}$$

VIII - 11



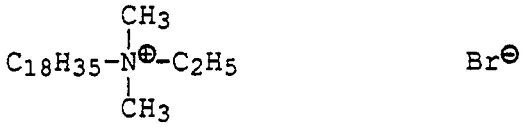
$$C_{12}H_{25}-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}-C_2H_5 \qquad Cl^{\ominus}$$

VIII - 12



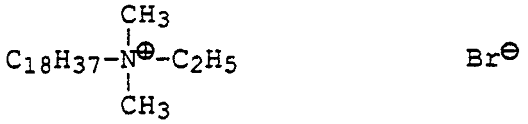
$$C_{12}H_{25}-\underset{(CH_2CH_2O)_{15}-H}{\overset{(CH_2CH_2O)_{15}-H}{N^{\oplus}}}-CH_3 \qquad Cl^{\ominus}$$

VIII - 13



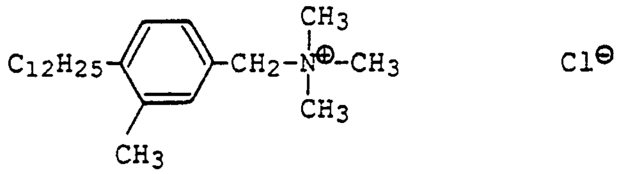
$$C_{18}H_{35}-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}-C_2H_5 \qquad Br^{\ominus}$$

VIII - 14

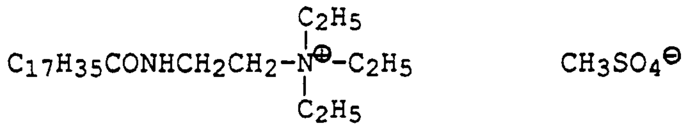


$$C_{18}H_{37}-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}-C_2H_5 \qquad Br^{\ominus}$$

VIII - 15

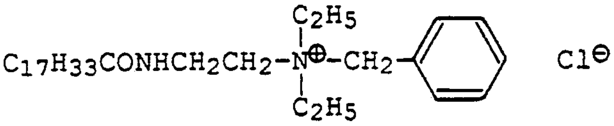


VIII - 16

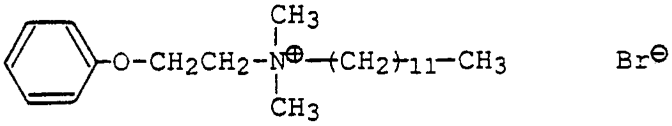


$$C_{17}H_{35}CONHCH_2CH_2-\underset{C_2H_5}{\overset{C_2H_5}{N^{\oplus}}}-C_2H_5 \qquad CH_3SO_4^{\ominus}$$

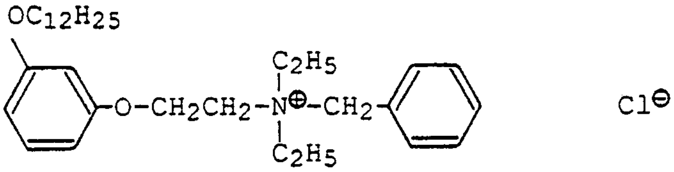
VIII - 17



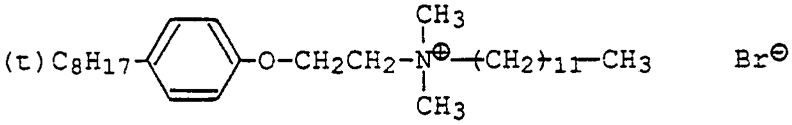
VIII - 18



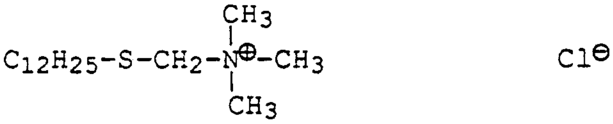
VIII - 19



VIII - 20

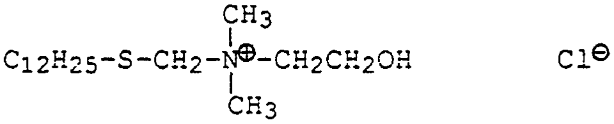


VIII - 21



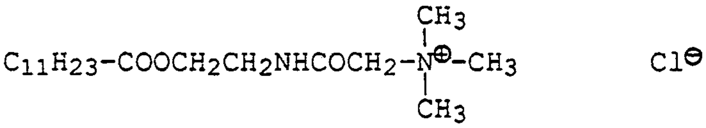
$$C_{12}H_{25}-S-CH_2-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_3 \qquad Cl^{\ominus}$$

VIII - 22



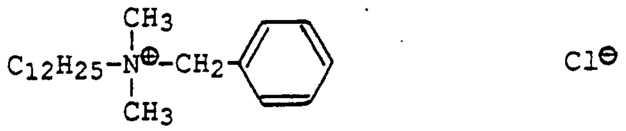
$$C_{12}H_{25}-S-CH_2-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_2CH_2OH \qquad Cl^{\ominus}$$

VIII - 23

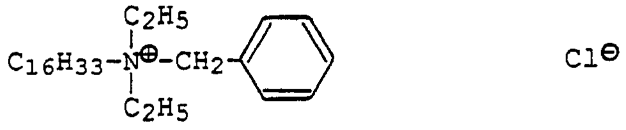


$$C_{11}H_{23}-COOCH_2CH_2NHCOCH_2-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_3 \qquad Cl^{\ominus}$$

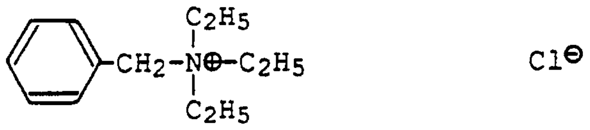
VIII - 24



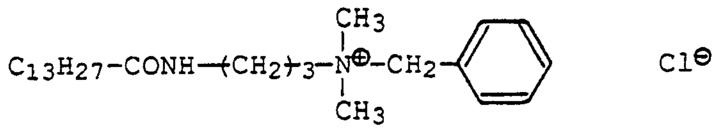
VIII - 25



VIII - 26

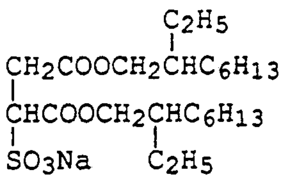


VIII - 27

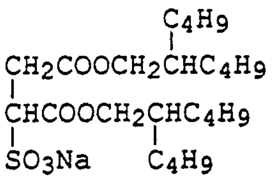


(Compound represented by the formula (IX))

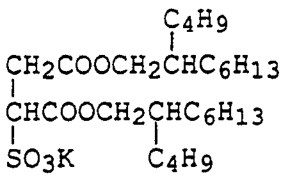
IX - 1



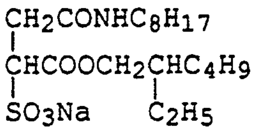
IX - 2



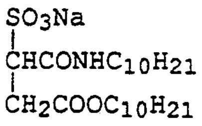
IX - 3



IX - 4

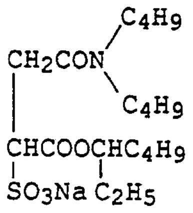


IX - 5

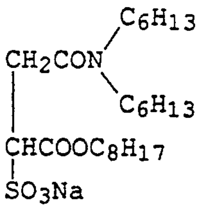


$$\begin{array}{l} SO_3Na \\ | \\ CHCONHC_{10}H_{21} \\ | \\ CH_2COOC_{10}H_{21} \end{array}$$

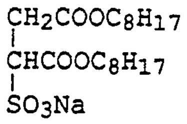
IX - 6



IX - 7

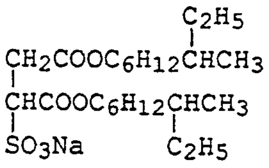


IX - 8



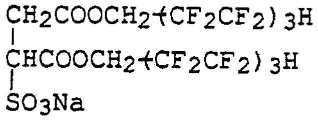
$$\begin{array}{l} CH_2COOC_8H_{17} \\ | \\ CHCOOC_8H_{17} \\ | \\ SO_3Na \end{array}$$

IX - 9



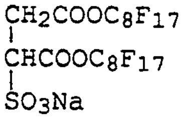
$$\begin{array}{ll} & C_2H_5 \\ & | \\ CH_2COOC_6H_{12} & CHCH_3 \\ | & \\ CHCOOC_6H_{12} & CHCH_3 \\ | & | \\ SO_3Na & C_2H_5 \end{array}$$

IX - 10



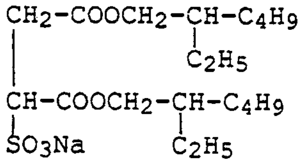
$$\begin{array}{l} CH_2COOCH_2(CF_2CF_2)_3H \\ | \\ CHCOOCH_2(CF_2CF_2)_3H \\ | \\ SO_3Na \end{array}$$

IX - 11



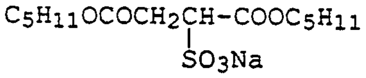
$$\begin{array}{l} CH_2COOC_8F_{17} \\ | \\ CHCOOC_8F_{17} \\ | \\ SO_3Na \end{array}$$

IX - 12



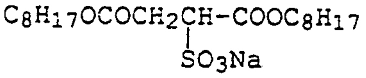
$$\begin{array}{ll} CH_2-COOCH_2- & CH-C_4H_9 \\ | & | \\ | & C_2H_5 \\ CH-COOCH_2- & CH-C_4H_9 \\ | & | \\ SO_3Na & C_2H_5 \end{array}$$

IX - 13



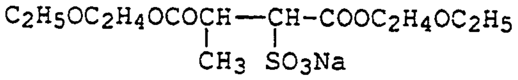
$$\begin{array}{ll} C_5H_{11}OCOCH_2 & CH-COOC_5H_{11} \\ & | \\ & SO_3Na \end{array}$$

IX - 14



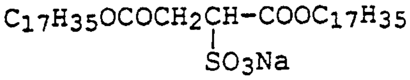
$$\begin{array}{ll} C_8H_{17}OCOCH_2 & CH-COOC_8H_{17} \\ & | \\ & SO_3Na \end{array}$$

IX - 15



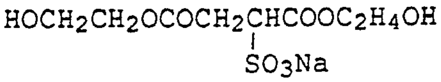
$$\begin{array}{lll} C_2H_5OC_2H_4OCO & CH— & CH-COOC_2H_4OC_2H_5 \\ & | & | \\ & CH_3 & SO_3Na \end{array}$$

IX - 16



$$C_{17}H_{35}OCOCH_2\underset{\displaystyle SO_3Na}{\underset{|}{C}}H-COOC_{17}H_{35}$$

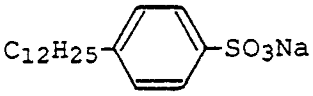
IX - 17



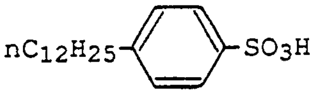
$$HOCH_2CH_2OCOCH_2\underset{\displaystyle SO_3Na}{\underset{|}{C}}HCOOC_2H_4OH$$

(Compound represented by the formula (X))

X - 1

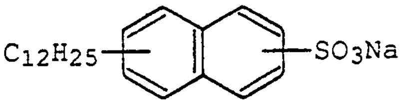


X - 2

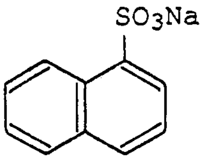


(Compound represented by the formula (XI))

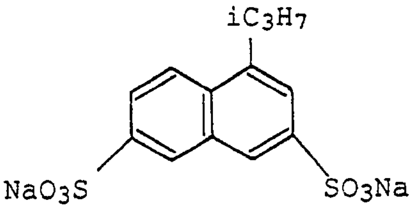
XI - 1



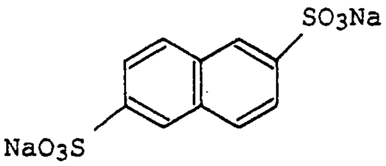
XI - 2



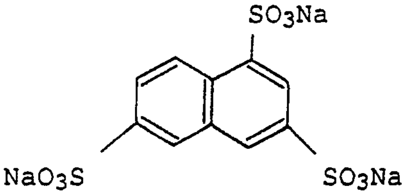
XI - 3



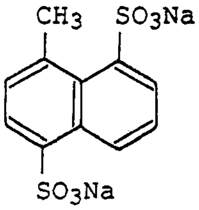
XI - 4



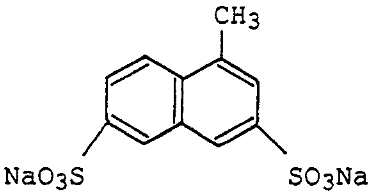
XI - 5



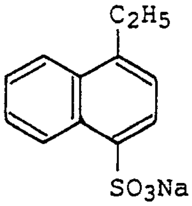
XI - 6



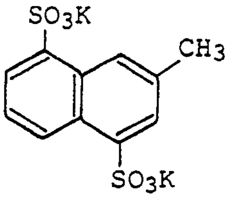
XI - 7



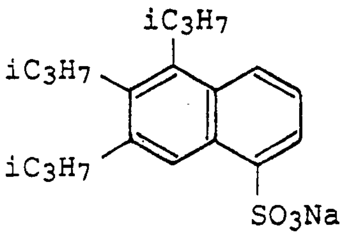
XI - 8



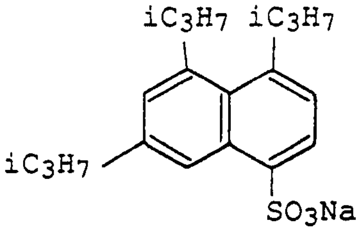
XI - 9



XI - 10



XI - 11



An amount of the water-soluble surfactant to be used in the color developing solution of the present invention is 0.5 to 20 g/ℓ, preferably 1.0 to 15 g/ℓ. If it is less than 0.5 g/ℓ, remarkable effect of the present invention in the color developing solution with low sulfite concentration cannot be expected, while if it exceeds 20 g, foam will likely caused so that it iS not practical.

Also, the water-soluble surfactant is contained in an amount of 0.5 to 20 g per liter of the color developing solution and it may be 0.5 to 20 g including the surfactant dissolved out from a light-sensitive silver halide color photographic material, but in order to accomplish the effect of the present invention as mentioned above, it is particularly preferred to previously add the above amount in the color developing solution. That is, the water-soluble surfactant dissolved out from a light-sensitive material is accumulated in the color developing solution according to the continuous processing while it is a small amount, but the effect thereof is markedly different from the case wherein it is previously added in the color developing solution.

The water-soluble surfactant to be used in the present invention should be contained at least one kind, but it may be contained 2 or more in combination, in summary, it is sufficient so long as it is contained in an amount of 0.5 to 20 g per liter of the color developing solution.

Preferred water-soluble surfactant to be used in the present invention is a nonionic surfactant and an anionic surfactant, and the water-soluble surfactant particularly preferably used in the present invention is the compound represented by the formula (I) or (II), most preferably the compound represented by the formula (I). The compound represented by the formula (I) scarcely affects to developing property and it shows less foaming property so that it can be used with a large amount. As the results, the effects of the present invention becomes more marked which is one of the preferred embodiments of the present invention.

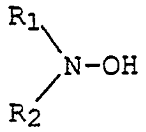
When the cationic surfactant is added in the color developing solution, deposition sometimes occur during continuous processing, the anionic surfactant is relatively low in solubility and the nonionic surfactant causes less problems mentioned above.

When an amount of the sulfurous acid (or sulfite) to be used in the present invention is 1 x 10^{-3} mole/liter or less, preferably 0, the effect of the present invention is remarkable.

When a light-sensitive material composed mainly of silver chloride is processed, the sulfite concentration is preferably substantially 0 in view of developability, but in order to prevent oxidation of the color developing solution for making kids, it may be added with a small amount of 1.0 x 10^{-3} mole/liter or less.

Also, in order to heighten the effect of the surfactant according to the persent invention, a substance generally called as a builder can be used in combination. As the builder, there may be mentioned an inorganic builder represented by carbonates such as sodium carbonate and sodium bicarbonate, silicates such as sodium metasilicate, sodium orthosilicate and sodium sesquisilicate, and phosphate such as sodium pyrophosphate, sodium tripolyphosphate and sodium tetraphosphate, and an organic builder represented by carboxymethyl cellulose, methyl cellulose, hydroxyethyl cellulose and carboxymethyl starch. Any of the builders may be used, but in oder to accomplish the effect of the present invention, the organic builder is preferably used. It has been known that a solution containing a surfactant generally foams, but in the case of a processing solution for photography, foaming phenomenon causes many inconvenient problem so that a defoaming agent may be used, if necessary.

In the color developing solution, in place of hydroxylamine which has heretofore been used as a preservative, an organic preservative such as hydroxylamine derivatives described in Japanese Provisional Patent Publications No. 146043/1988, No. 146042/1988, No. 146041/1988, No. 146040/ 1988, No. 135938/1988 and No. 118748/1988, hydroxamic acids, hydazides, phenols, α-hydroxyketones, α-aminoketones, saccharides, monoamines, diamines, quaternary ammonium salts, nitroxy radicals, alcohols, oximes, diamides and fused ring system amines as described in Japanese Provisional Patent Publication No. 62639/1989 can be preferably used. Particularly, it is preferred to add the compound represented by the following formula (A) and hydrazines for rapid processing and deminishing bluing. Also, by employing the above compounds, precipiration of crystals at the surface of the color developing solution becomes good and other effects can be accomplished so that it can be mentioned as one of the preferred embodiments of the present invention.

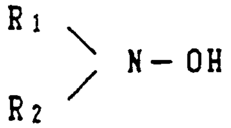


(A)

In the formula R_1 and R_2 each represent an alkyl group or a hydrogen atom, provided that both of R_1 and R_2 do not represent hydrogen atoms at the same time. Also, R_1 and R_2 may be formed a ring combinedly.

In the formula (A), R_1 and R_2 each represents an alkyl group or a hydrogen atom both of which are not hydrogen atoms at the same time, and the alkyl group represented by R_1 and R_2 may be the same or different, and an alkyl group having 1 to 3 carbon atom is preferred. The alkyl group of R_1 and R_2 may include those having a substituent, and R_1 and R_2 may be combined to form a ring and also form a heterocyclic ring such as piperidine or morpholine.

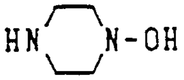
Specific compounds of the hydroxylamine type compound represented by the formula (A) are described in U.S. Patents No. 3,287,125, No. 3,293,034 and No. 3,287,124, but preferred exemplary compounds are set forth below.



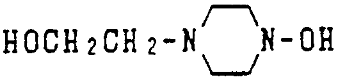
$$\begin{matrix} R_1 \diagdown \\ \qquad N-OH \\ R_2 \diagup \end{matrix}$$

Exemplary compound No.	R_1	R_2
A - 1	$-C_2H_5$	$-C_2H_5$
A - 2	$-CH_3$	$-CH_3$
A - 3	$-C_3H_7(n)$	$-C_3H_7(n)$
A - 4	$-C_3H_7(i)$	$-C_3H_7(i)$
A - 5	$-CH_3$	$-C_2H_5$
A - 6	$-C_2H_5$	$-C_3H_7(i)$
A - 7	$-CH_3$	$-C_3H_7(i)$
A - 8	$-H$	$-C_2H_5$
A - 9	$-H$	$-C_3H_7(n)$
A - 10	$-H$	$-CH_3$
A - 11	$-H$	$-C_3H_7(i)$
A - 12	$-C_2H_5$	$-C_2H_4OCH_3$
A - 13	$-C_2H_4OH$	$-C_2H_4OH$
A - 14	$-C_2H_4SO_3H$	$-C_2H_5$
A - 15	$-C_2H_4COOH$	$-C_2H_4COOH$

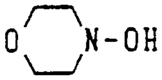
A − 16



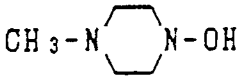
A − 17



A − 18

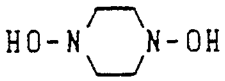


A − 19



Exemplary compound No.	R_1	R_2
A − 20	$-CH_3$	$-C_2H_4OCH_3$
A − 21	$-C_2H_4OCH_3$	$-C_2H_4OCH_3$
A − 22	$-C_2H_4OC_2H_5$	$-C_2H_4OC_2H_5$
A − 23	$-C_3H_6OCH_3$	$-C_3H_6OCH_3$
A − 24	$-C_2H_5$	$-C_2H_4OC_2H_5$
A − 25	$-C_3H_7$	$-C_2H_4OCH_3$
A − 26	$-CH_3$	$-C_2H_4OC_2H_5$
A − 27	$-CH_3$	$-CH_2OCH_3$
A − 28	$-C_2H_5$	$-CH_2OC_2H_5$
A − 29	$-CH_2OCH_3$	$-CH_2OCH_3$
A − 30	$-C_2H_5$	$-C_2H_4OC_3H_7$
A − 31	$-C_3H_6OC_3H_7$	$-C_3H_6OC_3H_7$

A − 32

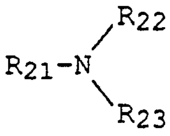


These compounds are used generally in the form of a free amine, hydrochloride, sulfate, p-toluenesulfonate, oxalate, phosphate or acetate.

A concentration of the compound represented by the formula (A) in the color developing solution is generally 0.2 g/ℓ to 50 g/ℓ, preferably 0.5 g/ℓ to 30 g/ℓ, more preferably 1 g/ℓ to 15 g/ℓ.

Also, a hydroxylamine conventionally used and the aforesaid organic preservative may be used in combination with the compound represented by the formula (A), but preferably not using the hydroxylamine in view of developability.

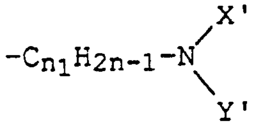
In the color developing solution according to the present invention, a compound represented by the following formula is preferably added since air oxidation resistance of the solution can be improved and even if it is mixed in a bleach-fixing solution, no bad effect occurs.



$$R_{21}-N(R_{22})(R_{23})$$

(B)

In the formula, R21 represents a hydroxyalkyl group having 2 to 6 carbon atoms, R22 and R23 each represent a hydrogen atom, an alkyl group having 1 to 6 cabron atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, a benzyl group or a group represented by



$$-C_{n_1}H_{2n-1}-N(X')(Y')$$

where n_1 is an integer of 1 to 6, X' and Y' each represent a hydrogen atom, an alkyl group having 1 to 6 carbon atoms or a hydroxyalkyl group having 2 to 6 carbon atoms.

Preferred specific examples of the compound represented by the above formula (B) are as follows.

(B - 1) Ethanolamine
(B - 2) Diethanolamine
(B - 3) Triethanolamine
(B - 4) Di-isopropanolamine
(B - 5) 2-Methylaminoethanol
(B - 6) 2-Ethylaminoethanol
(B - 7) 2-Dimethylaminoethanol
(B - 8) 2-Diethylaminoethanol
(B - 9) 1-Diethylamino-2-propanol
(B - 10) 3-Diethylamino-1-propanol
(B - 11) 3-Dimethylamino-1-propanol
(B - 12) Isopropylaminoethanol
(B - 13) 3-Amino-1-propanol
(B - 14) 2-Amino-2-methyl-1,3-propanediol
(B - 15) Ethylenediaminetetraisopropanol
(B - 16) Benzyldiethanolamine
(B - 17) 2-Amino-2-(hydroxymethyl)-1,3-propanediol

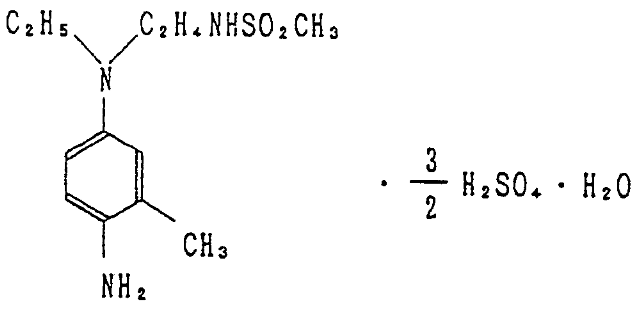
The compound represented by the above formula (B) is preferably used in an amount of 1 g to 100 g, more preferably 2 g to 30 g per liter of the color developing solution in view of prevention of air oxidation.

The color developing agent to be used in the color developing solution of the present invention is preferably a p-phenylenediamine type compound having a water-soluble group and the water-soluble group is possesed at least one on an amino group or a benzene nucleus of the p-phenylenediamine compound. Specific water-soluble group may include: $-(CH_2)n-CH_2OH$, $-(CH_2)_m-NHSO_2-(CH_2)_n-CH_3$,$-(CH_2)_m-O-(CH_2)_n-CH_3$, $-(CH_2CH_2O)_n-C_mH_{2m+1}$ (wherein m and n each represent an integer of 0 or more), -COOH group and $-SO_3H$ group.

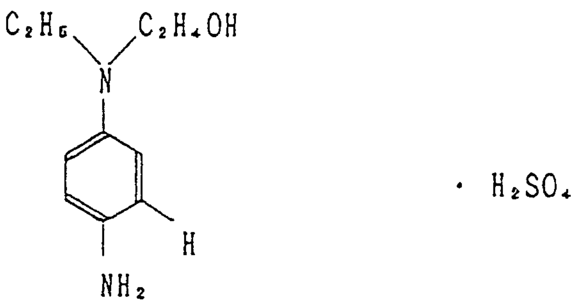
Exemplary compounds of the color developing agent to be preferably used in the present invention are enumerated below.

(Color developing agent)

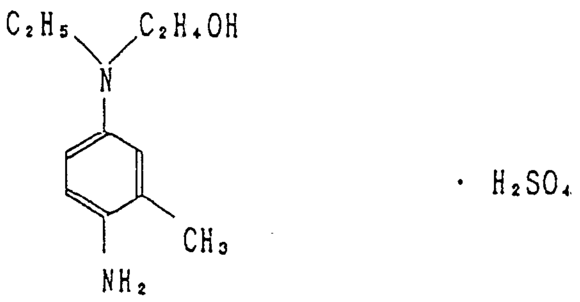
(A－1)



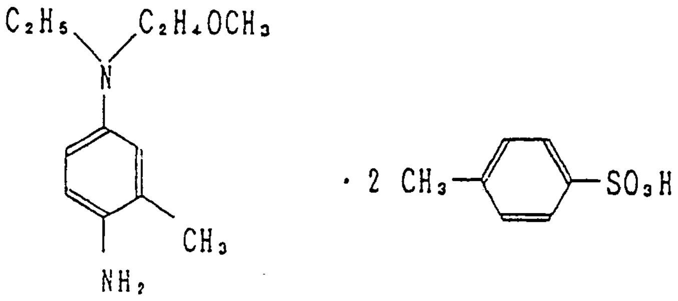
(A－2)



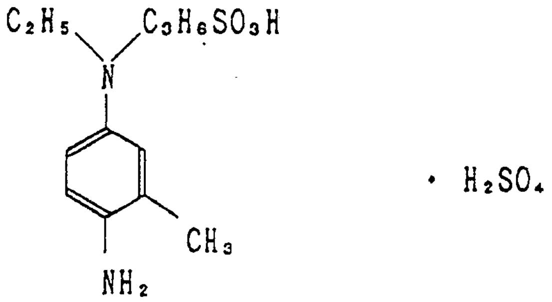
(A－3)



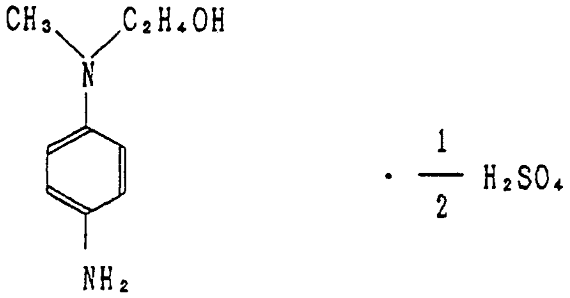
(A－4)



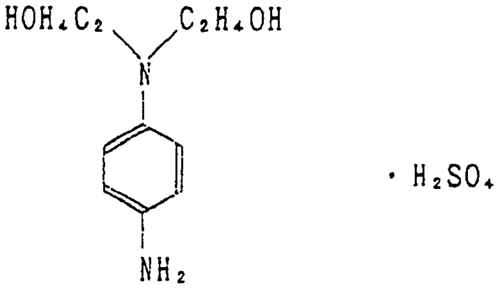
(A－5)


C₂H₅
C₃H₆SO₃H
N
CH₃
NH₂
· H₂SO₄

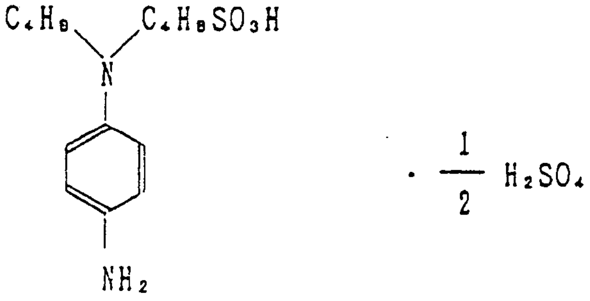
(A－6)


CH₃
C₂H₄OH
N
NH₂
· 1/2 H₂SO₄

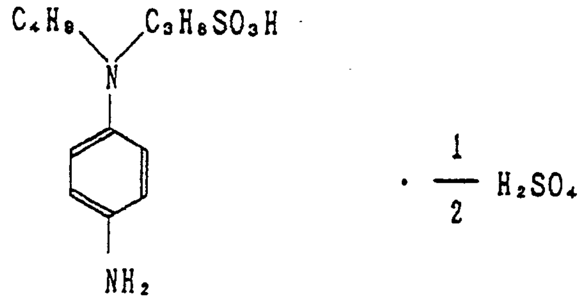
(A－7)


HOH₄C₂
C₂H₄OH
N
NH₂
· H₂SO₄

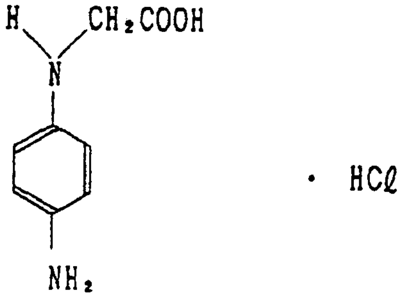
(A－8)


C₄H₉
C₄H₈SO₃H
N
NH₂
· 1/2 H₂SO₄

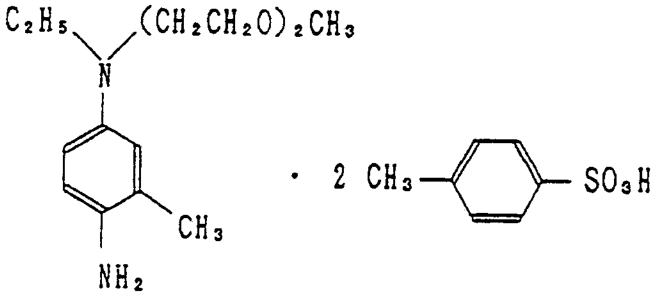
(A－9)



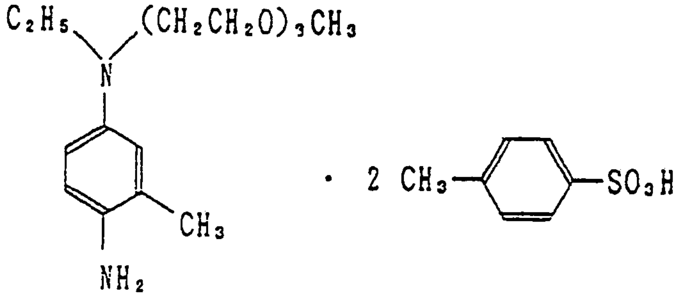
(A－10)



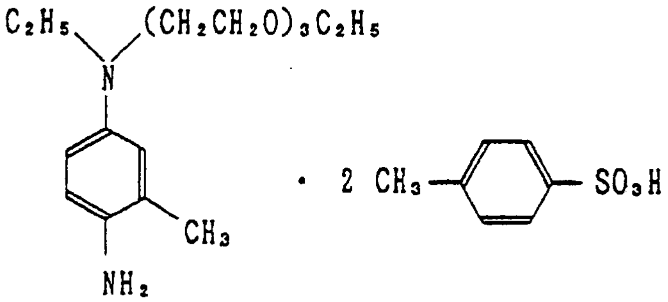
(A－11)



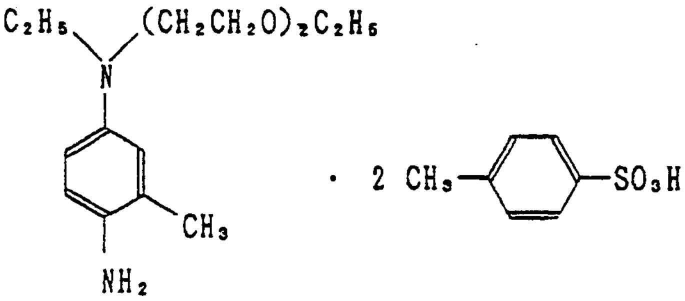
(A－12)



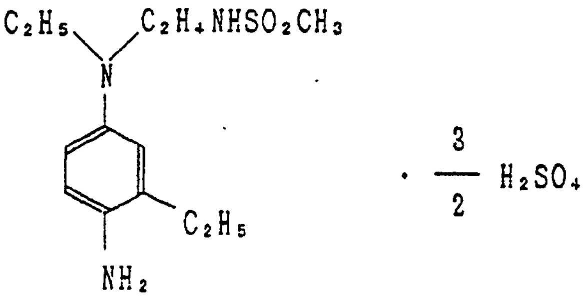
(A - 13)



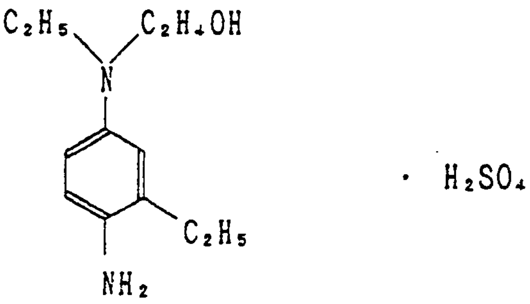
(A - 14)



(A - 15)



(A - 16)



Of these color developing agent exemplified above, preferred in the present invention are compounds represented by Exemplary No. (A - 1), (A - 2), (A - 3), (A - 4), (A - 6), (A - 7) and (A - 15), and particularly preferred is No. (A - 1).

The above color developing agent is generally used in the form of a salt such as hydrochloride, sulfate and p-toluenesulfonate.

In the present invention, an amount of the p-phenylenediamine type compounds having a water-soluble group to be preferably used in the present invention is 0.5 x 10^{-2} mole or more, more preferably 1.0 x 10^{-2}

to 1.0 x 10^{-1} mole per liter of the color developing solution.

In the color developing solution to be used in the present invention, the following components for the developing solution may be contained in addition to the above components.

As an alkali agent, for example, sodium hydroxide, potassium hydroxide, silicates, sodium metaborate, potassium metaborate, trisodium phosphate, tripotassium phosphate and borax may be used alone or in combination of two or more in the range where no deposition is generated and pH stabilization effect can be maintained. Further, for necessity from preparation, or in order to heighten ion strength, various salts such as disodium hydrogen phosphate, dipotassium hydrogen phosphate, sodium bicarbonate, potassium bicarbonate and borates may be used.

Also, if necessary, inorganic and organic antifoggants may be added.

Furthermore, if necessary, a development accelerator may be used. As the development accelerator, there may be mentioned various kinds of pyridinium compounds specifically disclosed in U.S. Patents No. 2,648,604 and No. 3,671,247, and Japanese Patent Publication No. 9503/1969, or other cationic compound, a cationic dye such as phenosaphranine, a nutral salt such as tallium nitrate, polyethylene glycol or derivatives thereof as disclosed in U.S. Patents No. 2,533,990, No. 2,531,832, No. 2,950,970 and No. 2,577,127 and Japanese Patent Publication No. 9504/1969, a nonionic compound such as polythioethers, also a phenethyl alcohol as disclosed in U.S. Patent No. 2,304,925, and acetylene glycol, methyl ethyl ketone, cyclohexanone, thioethers, pyridine, ammonia, hydrazine and amines.

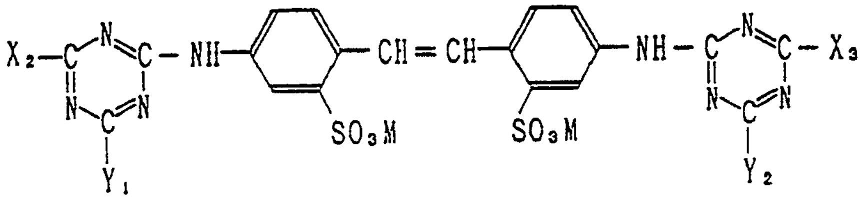
Benzyl alcohol is not preferably used in the present invention and as for an organic solvent with poor solubility represented by phenethyl alcohol, it is desired to not use it in view of accomplishing the object of the present invention effectively. If it is used, tar is likely caused by the use for a long period of term of the color developing solution, particularly in low replenishing system. Generation of such tar sometimes causes serious defect that commercial value is markedly impaired by adhering to a paper light-sensitive material to be processed.

Also, the organic solvent with poor solubility is bad in solubility to water so that troublesome of requiring a stirring device for preparation of the color developing solution itself. Further, even if such a stirring device is used, development accelerating effect is limited due to its bad solibility.

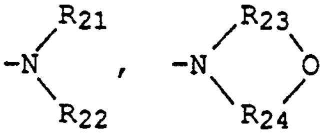
Moreover, an orgnic solvent with poor solubility has problems that a pollution loading value such as biochemical oxygen demand (BOD) is large so that it cannot be disposed in a sewer or a river and for its waste liquor processing, many labour and costs are required. Therefore, not only benzyl alcohol but also other organic solvent with poor solubility are preferably reduced or eliminated their amount used.

In the color developing solution of the present invention, a triazinylstylbene type optical brightening agent is preferably added.

As the triazinylstylbene type optical brightening agent, that represented by the following formula is preferred.



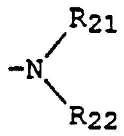
In the formula, X_2, X_3, Y_1 and Y_2 each represent a hydroxyl group, a halogen atom such as chlorine and bromine, an alkyl group (e.g. methyl and ethyl), an aryl group (e.g. phenyl and methoxyphenyl),



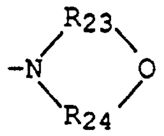
or $-OR_{25}$. Here, R_{21} and R_{22} each represent a hydrogen atom, an alkyl group which may have a substituent(s), or an aryl group which may have a substituent(s), R_{23} and R_{24} each represent an alkylene group which may have a substituent(s), R_{25} represents a hydrogen atom, an alkyl group which may have a substituent(s) or an aryl group which may have a substituent(s), and M represents a cation (e.g. sodium, potassium, lithium and ammonium).

The alkyl groups represented by R_{21}, R_{22} and R_{25} are preferably those having 1 to 6 carbon atoms and the alkylene groups represented by R_{23} and R_{24} are preferably those having 1 to 2 carbon atoms.

As the substituent for the alkyl groups represented by R_{21}, R_{22} and R_{25} and that for the alkylene groups represented by R_{23} and R_{24}, a hydroxyl group, a sulfo group, a sulfoamino group and a carboxyamino group are preferred. Specific examples of

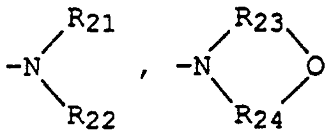


may include an amino group, an alkylamino group (e g. methylamino, ethylamino, propylamino, dimethylamino, cyclohexylamino, β-hydroxyethylamino, di(β-hydroxyethyl)amino, β-sulfoethylamino, N-(β-sulfoethyl)-N'-methylamino and N-(β-hydroxyethyl-N'-methylamino), and an arylamino group (e.g. anilino, o-, m-, p-sulfoanilino, o-, m-, p-chloroanilino, o-, m-, p-toluidino, o-, m-, p-carboxyanilino, o-, m-, p-hydroxyanilino, o-, m-, p-aminoanilino and o-, m-, p-anidino), and specific examples of

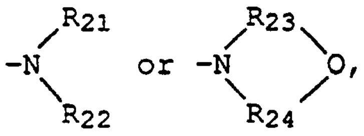


may include morpholino group, and specific examples of $-OR_{25}$ may include an alkoxy group (e.g. methoxy, ethoxy and methoxyethoxy) and an aryloxy group (e.g. phenoxy and p-sulfophenoxy).

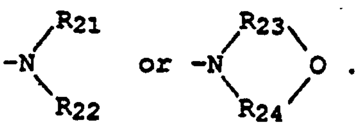
Of these optical brightening agent represented by the above formula, preferred compounds are those wherein all the X_2, X_3, Y_1 and Y_2 are



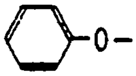
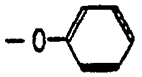
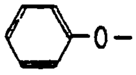
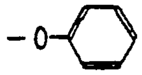
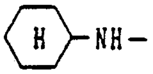
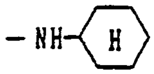
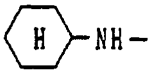
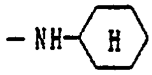
or $-OR_{25}$ and most preferred compound is that wherein one of X_3 and Y_1 is $-OR_{25}$ and the other is

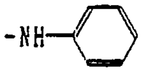
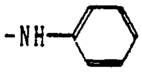
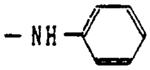
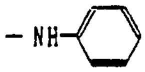
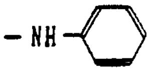
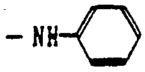
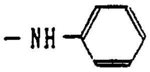
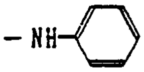
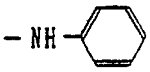
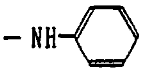
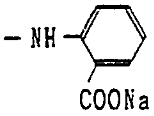
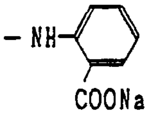
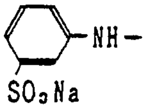
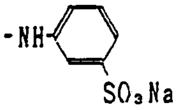
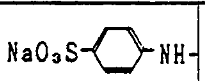
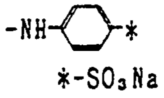
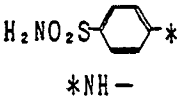
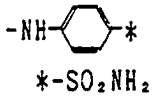
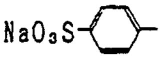
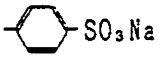


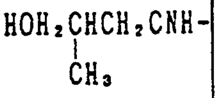
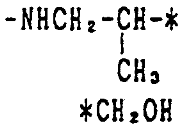
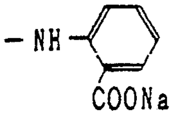
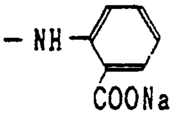
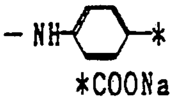
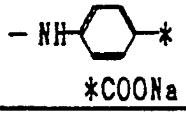
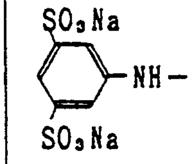
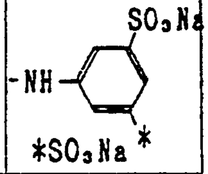
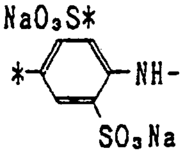
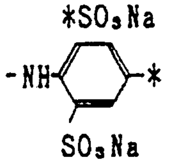
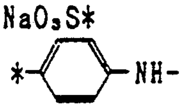
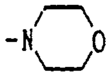
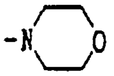
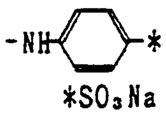
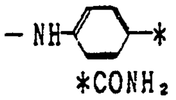
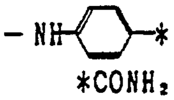
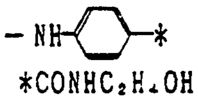
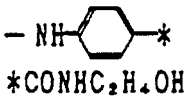
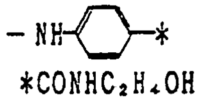
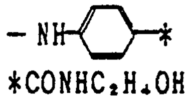
and one of X_3 and Y_2 is $-OR_{25}$, the other is

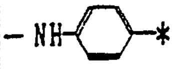
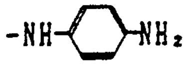
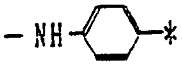
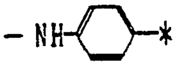
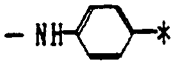
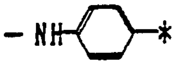
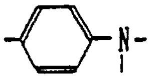
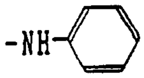
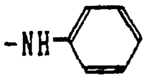
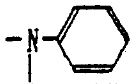
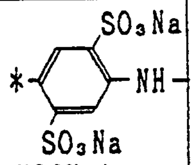
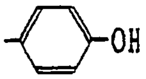
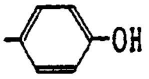
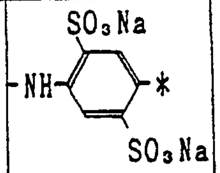
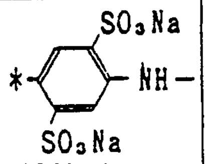
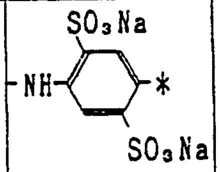
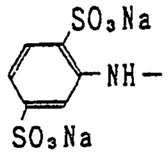
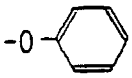
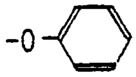
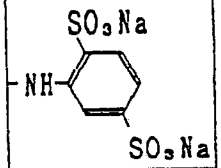
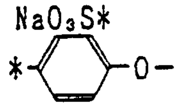
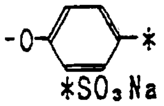


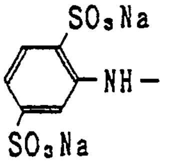
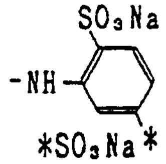
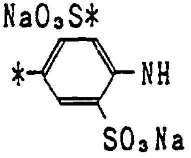
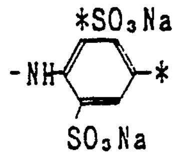
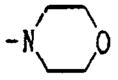
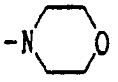
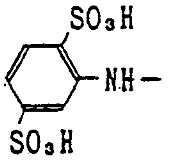
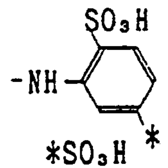
More specifically, the following compounds can be mentioned, but the present invention is not limited by these.

Compound No.	M	X_2	Y_1	X_3	Y_2
E - 1	Na		-NHC$_2$H$_4$OH	-NHC$_2$H$_4$OH	
E - 2	Na	HOC$_2$H$_4$NH-	-NHC$_2$H$_4$OH	-NHC$_2$H$_4$OH	-NHC$_2$H$_4$OH
E - 3	Na		-N(C$_2$H$_4$OH)$_2$	-N(C$_2$H$_4$OH)$_2$	
E - 4	Na	(HOC$_2$H$_4$)$_2$N-	-OCH$_3$	-OCH$_3$	-NHC$_2$H$_4$SO$_3$Na
E - 5	Na	HOHCH$_2$CNH-	-N(C$_2$H$_4$OH)$_2$	-N(C$_2$H$_4$OH)$_2$	 $\text{-NHCH}_2\underset{\text{CH}_2\text{OH}}{\underset{\mid}{\text{CHOH}}}$
E - 6	Na	(HOC$_2$H$_4$)$_2$N-	-N(C$_2$H$_4$OH)$_2$	-N(C$_2$H$_4$OH)$_2$	-N(C$_2$H$_4$OH)$_2$
E - 7	Na		-NHC$_2$H$_4$OH	-NHC$_2$H$_4$OH	
E - 8	Na		-N(C$_2$H$_4$OH)$_2$	-N(C$_2$H$_4$OH)$_2$	

Compound No.	M	X_2	Y_1	X_3	Y_2
E－9	Na	HO-			-OH
E－10	Na	H_2N-			$-NH_2$
E－11	Na	CH_3O-			$-OCH_3$
E－12	Na	HOC_2H_4NH-			$-NHC_2H_4OH$
E－13	Na	$-(HOC_2H_4)_2N$			$-N(C_2H_4OH)_2$
E－14	Na	HOC_2H_4NH-			$-NHC_2H_4OH$
E－15	Na		$-N(C_2H_4OH)_2$	$-N(C_2H_4OH)_2$	
E－16	Na		$-N(C_2H_4OH)_2$	$-N(C_2H_4OH)_2$	
E－17	Na		$-N(C_2H_4OH)_2$	$-N(C_2H_4OH)_2$	
E－18	Na		$-N(C_2H_4OH)_2$	$-N(C_2H_4OH)_2$	

Compound No.	M	X_2	Y_1	X_3	Y_2
E-19	Na	 $HOH_2\underset{CH_3}{C}HCH_2CNH-$	$-CH_3O$	$-CH_3O$	 $-NHCH_2-\underset{CH_3}{CH}-*$ $*CH_2OH$
E-20	Na	$(HOC_2H_4)_2N-$			$-N(C_2H_4OH)_2$
E-21	Na	HOC_2H_4NH-			$-NHC_2H_4OH$
E-22	Na		$-NHC_2H_5$	$-NHC_2H_5$	
E-23	Na		$-NHCH_3$	$-NHCH_3$	
E-24	Na				
E-25	Na	HOC_2H_4NH-			$-NHC_2H_4OH$
E-26	Na	HOC_2H_4NH-			$-NHC_2H_4OH$
E-27	Na	$(HOC_2H_4)_2N-$			$-N(C_2H_4OH)_2$

Compound No.	M	X_2	Y_1	X_3	Y_2
E-28	Na	HOC_2H_4NH-	 $*SO_2NH_2$		$-NHC_2H_4OH$
E-29	Na	HOC_2H_4NH-	 $*SO_2NHC_2H_4OH$	 $*SO_2NHC_2H_4OH$	$-NHC_2H_4OH$
E-30	Na	$(HOC_2H_4)_2N-$	 $*SO_2NHC_2H_4OH$	 $*SO_2NHC_2H_4OH$	$-N(C_2H_4OH)_2$
E-31	Na	 $*C_2H_4OH$			 C_2H_4OH
E-32	Na	 $HOCH_2*$			 $*CH_2OH$
E-33	Na	 $HOCH_2*$	$-NHC_2H_5$	$-NHC_2H_5$	 $*CH_2OH$
E-34	Na	CH_3O-	$-NHCH_2CH(OH)CH_3$	$-NHCH_2CH(OH)CH_3$	$-OCH_3$
E-35	Na				
E-36	Na		$-N(C_2H_4OH)_2$	$-N(C_2H_4OH)_2$	

Compound No.	M	X_2	Y_1	X_3	Y_2
E - 37	Na		$-N(C_2H_5)_2$	$-N(C_2H_5)_2$	
E - 38	Na		$-NHCH_3$	$-NHCH_3$	
E - 39	Na	CH_3O-	$-NH-CH(CH_2OH)CH_3$	$-NH-CH(CH_2OH)CH_3$	$-OCH_3$
E - 40	Na	CH_3O-	$-N(C_2H_4OH)_2$	$-N(C_2H_4OH)_2$	$-OCH_3$
E - 41	Na	CH_3O-	$-NHC_2H_4SO_3Na$	$-NHC_2H_4SO_3Na$	$-OCH_3$
E - 42	Na	CH_3O-	$-NH(C_2H_4OH)$	$-NH(C_2H_4OH)$	$-OCH_3$
E - 43	Na	CH_3O-			$-OCH_3$
E - 44	K	CH_3O-	$-NHC_2H_4SO_3K$	$-N(C_2H_4OH)_2$	$-OCH_3$
E - 45	H		$-N(C_2H_5)_2$	$-N(C_2H_5)_2$	

The triazinylstylbene type brightening agent to be preferably used in the present invention can be synthesized by the conventional method as described in, for example, "Optical Brightening agent" edited by Chemical Products Industry Association (published in August, 1976), p. 8.

Of these exemplary compounds, particularly preferably used are E - 34, E - 35, E - 36, E - 37 and E - 42.

The triazinylstylbene type brightening agent is preferably added in an amount of 0.2 g to 6 g, more preferably in the range of 0.4 g to 3 g per liter of the color developing solution.

Further, in the color developing solution to be used in the present invention, if necessary, ethylene glycol, methyl cellosolve, methanol, acetone, dimethylformamide, b-cyclodexytrin, and other compounds as disclosed in Japanese Patent Publications No. 33378/1972 and No. 9509/1969 as an organic solvent for increasing solubility of the color developing agent.

Further, an auxiliary developer may be used in combination with the color developing agent. As the auxiliary developer, there have been known, for example, N-methyl-p-aminophenolsulfate (Metol), phenidone, N,N'-diethyl-p-aminophenol hydrochloride and N,N,N',N'-tetramethyl-p-phenylenediamine hydrochloride, and as an amount thereof to be added, 0.01 g to 1.0 g per liter of the color developing solution is generally preferred.

Furthermore, various additives such as stain preventives, sludge preventives and interlayer effect accelerating agents may be used.

Also, in the color developing solution of the present invention, to add a chelating agent represented by the formula (I) to (XV) disclosed in Japanese Provisional Patent Publication No. 48548/1988 is preferred in view of accomplishing the effect of the present invention more effectively.

The color developing solution of the present invention can be prepared by adding the above respective components successively to a predetermined amount of water and stirring. In this case, a component(s) having low solubility to water may be added by mixing with the above organic solvent such as triethanol amine. Also, in general, a condensed aqueous solution or a solid in which a plural number of components can be stably existed, respectively, is previously prepared in a small apparatus and added in water and the mixture is stirred to prepare the color developing solution of the present invention

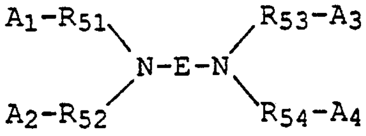
In the present invention, the above color developing solution can be used in an optional pH range, but in view of rapid processing, it is preferred to use in a pH of 9.5 to 13.0, more preferably a pH of 9.8 to 12.0. The processing temperature is generally 30 °C or higher, preferably 33 °C or higher, particularly preferably 35 °C to 65 °C, and the processing time is preferably within 90 seconds, more preferably 3 sec to 60 sec, particularly preferably 3 sec to 45 sec.

In the present invention, the effect of the present invention can be effectively accomplished when the system is low replenishing so that the replenishing amount of the color developing solution is preferably 120 ml/m^2 or less, more preferably 110 ml/m^2 or less, particularly preferably 100 ml/m^2 or less.

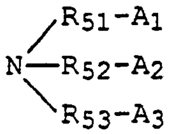
In the present invention, various processing systems can be employed including one bath treatment, and other various methods such as a spray system in which a processing solution is atomized, a web system using a carrier in which a processing solution is impregnated to contact therewith, or a developing method due to a viscous processing solution.

In the present invention, after the color development processing, bleaching, fixing or bleach-fixing processing with one bath is carried out.

In a bleaching solution or a bleach-fixing solution, an organic acid ferric complex salt such as aminopolycarboxylic acid is used and as an organic acid constituting said organic acid ferric complex salt may preferably include an amonocarboxylic acid type compound and aminophosphonic acid type compound, and each represents an amino compound having at least one carboxylic acid group and an amino compound having at least one phosphonic acid group, more preferably the compounds represented by the following formulae (1) and (2).



(1)



(2)

In the formula, E represents a substituted or unsubstituted alkylene group, a cycloalkylene group, a phenylene group, $-R_{55}OR_{55}OR_{55}-$ or $-R_{55}ZR_{55}-$ where Z represents $>N-R_{55}-A_5$ or $>N-A_5$, R_{51} to R_{55} each represent a substituted or unsubstituted alkylene group, A_1 to A_5 each represent a hydrogen atom, -OH, -COOM or $-PO_3M_2$ where M represents a hydrogen atom or an alkali metal atom.

Next, preferred exemplary compounds of the compounds represented by the formulae (1) and (2) are enumerated below.

(Exemplary compound)

(1 - 1) Ethylenediaminetetraacetic acid
(1 - 2) Diethylenetriaminepentaacetic acid
(1 - 3) Ethylenediamie-N-(β-hydroxyethyl)-N,N',N'-triacetic acid
(1 - 4) 1,3-Propylenediaminetetraacetic acid

(1 - 5) Triethylenetetraminehexaacetic acid
(1 - 6) Cyclohexanediaminetetraacetic acid
(1 - 7) 1,2-Diaminopropanetetraacetic acid
(1 - 8) 1,3-Diaminopropan-2-ol-2-tetraacetic acid
(1 - 9) Ethyletherdiaminetetraacetic acid
(1 - 10) Glycoletherdiaminetetraacetic acid
(1 - 11) Ethylenediaminetetrapropionic acid
(1 - 12) Phenylenediaminetetraacetic acid
(1 - 13) Ethylenediaminetetraacetic acid disodium salt
(1 - 14) Ethylenediaminetetraacetic acid tetra(trimethylammonium) salt
(1 - 15) Ethylenediaminetetraacetic acid tetrasodium salt
(1 - 16) Diethylenetriaminepentaacetic acid pentasodium salt
(1 - 17) Ethylenediamine-N-(β-hydroxyethyl)-N,N',N'-triacetic acid sodium salt
(1 - 18) Propylenediaminetetraacetic acid sodium salt
(1 - 19) Ethylenediaminetatramethylenephosphonic acid
(1 - 20) Cyclohexanediaminetetraacetic acid sodium salt
(1 - 21) Diethylenetriaminepentamethylenediphosphonic acid
(1 - 22) Cyclohexanediaminetetramethylenephosphonic acid
(2 - 1) Nitrilotriacetic acid
(2 - 2) Iminodiacetic acid
(2 - 3) Hydroxyethyliminodiacetic acid
(2 - 4) Nitrilotripropionic acid
(2 - 5) Nitrilotrimethylenephosphonic acid
(2 - 6) Iminodimethylenephosphonic acid
(2 - 7) Hydroxyethyliminodimethylenephosphonic acid
(2 - 8) Nitrilotriacetic acid trisodium salt

Of these aminocarboxylic acid type compounds and aminophosphonic acid type compounds, compounds which are particularly preferably used in view of accomplishing the effect of the present invention are (1 - 1), (1 - 2), (1 - 4), (1 - 5), (1 - 6), (1 - 7), (1 - 8), (1 - 10), (1 - 19), (2 - 1), (2 - 3) and (2 - 5).

Of these aminocarboxylic acid type compounds and aminophosphonic acid type compounds, particularly preferred are (1 - 1), (1 - 2), (1 - 4), (1 - 6), (1 - 8) and (1 - 10) since they are high bleaching ability and rapid processing.

Also, these ferric complex salts may be used at least one, but may be used in combination of two or more.

These bleaching agent is preferably used in an amount of 5 to 450 g/ℓ, more preferably 20 to 250 g/ℓ. From the viewpoint of rapid processing and stain prevention, it is particularly preferred to use 60 g/ℓ or more, most preferably 80 g/ℓ to 250 g/ℓ.

To the bleaching solution or the bleach-fixing solution, a silver halide fixing agent may be added in addition to the bleaching agent as mentioned above and, if necessary, a solution having a composition containing a sulfite as a preservative may be applied.

As a halide, in addition to ammonium bromide, hydrochloric acid, hydrobromic acid, lithium bromide, sodium bromide, potassium bromide, sodium iodide, potassium iodide and ammonium iodide may be used.

As the silver halide fixing agent as mentioned above to be contained in the bleaching solution or the bleach-fixing solution, there may be specifically mentioned a compound which forms a water-soluble complex reacting with silver halide to be used in the usual fixing processing, for example, thiosulfates such as potassium thiosulfate, sodium thiosulfate and ammonium thiosulfate, thiocyanates such as potassium thiocyanate, sodium thiocyanate and ammonium thiocyanate, thiourea and thioether. Also, ammonium salts are effective since they have rapid diffusion rate. These fixing agents are used in an amount of 5 g/ℓ or more to an amount within the range of capable of being dissolved, and generally 50 g/ℓ to 250 g/ℓ. In the point of rapid processing, 70 g/ℓ to 250 g/ℓ is preferred.

To the bleaching solution or the bleach-fixing solution, various buffering agent such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide may be added singly or in combination of two or more.

Furthermore, various optical brightening agents or defoaming agents, or surfactants may be contained. Also, preservatives such as bisulfite adducts of hydroxylamine, hydrazine and aldehyde compound, an organic solvent such as methanol, dimethylsulfoamide and dimethylsulfoxide can be optionally added.

To the bleaching solution or the bleach-fixing solution, various bleach accelerators as disclosed in

Japanese Provisional Patent Publication No. 280/1971, Japanese Patent Publications No. 8506/1970 and No. 556/1971, Belgium Patent No. 770,910, Japanese Patent Publications No. 8836/1970 and No. 9854/1978, Japanese Provisional Patent Publications No. 71634/1979 and No. 42349/1974 may be added.

A pH of the bleach-fixing solution to be used is generally in the range of 4.0 to 9.5, desirably 4.5 to 8.5, and most preferably 5.0 to 8.0. In the case of the bleaching solution, it is preferably 1 to 7.0, more preferably 1.5 to 6.0, particularly preferably 2.0 to 5.5. A pH of the fixing solution is preferably 5.0 to 9.0, more preferably 5.5 to 8.5. A temperature of the processing is 80 °C or lower, desirably 35 °C to 70 °C while depressing evaporation. If it exceeds 70 °C, it is not preferred in view of dryness, while if it is less than 35 °C, it is also not preferred in view of rapid processing. A processing time of the bleaching or bleach-fixing is preferably 2 sec to 50 sec, more preferably 3 sec to 40 sec, most preferably 5 sec to 30 sec. A fixing processing time is preferably 5 sec to 3 min, more preferably 7 sec to 2 min.

After the fixing processing or bleach-fixing processing which is preferably employed in the present invention, it is preferred to employ a stabilizing processing due to a stabilizing solution.

In the stabilizing solution, a sulfite is preferable contained. Said sulfite is not limited either an organic compound or an inorganic compound so long as it releases a sulfite ion, but preferably an inorganic salt. Preferred specific examples thereof may include sodium sulfite, potassium sulfite, ammonium sulfite, ammonium bisulfite, potassium bisulfite, sodium bisulfite, sodium metabisulfite, potassium metabisulfite, ammonium metabisulfite and hydrosulfite. The above sulfite is preferably added to the stabilizing solution in an amount of at least 1 x 10^{-3} mole/liter, more preferably to be added in an amount of 5 x 10^{-3} mole/liter to 10^{-1} mole/liter whereby the effect of the present invention, particularly stain preventive effect becomes remarkable and such an embodiment is preferably used in the present invention. As a method of addition, it may be added directly to the stabilizing solution, but to add it to a stabilizing replenishing solution is preferred.

As the compound particularly desired compound to be added to the stabilizing solution, there may be specifically mentioned ammonium hydroxide, ammonium bromide, ammonium carbonate, ammonium chloride, ammonium hypophosphite, ammonium phosphate, ammonium phosphite, ammonium fluoride, acidic ammonium fluoride, ammonium fluoroborate, ammonium arsenate, ammonium hydrogen carbonate, ammonium hydrogen fluoride, ammonium hydrogen sulfate, ammonium sulfate, ammonium iodide, ammonium nitrate, ammonium pentaborate, ammonium acetate, ammonium adipate, ammonium laurintricarboxylate, ammonium benzoate, ammonium carbamate, ammonium citrate, ammonium diethyldithiocarbamate, ammonium formate, ammonium hydrogen malate, ammonium hydrogen oxalate, ammonium phthalate, ammonium hydrogen tartrate, ammonium thiosulfate, ammonium sulfite, ammonium ethylenediaminetetraacetate, ferric ammonium ethylenediaminetetraacetate, ammonium lactate, ammonium malate, ammonium maleate, ammonium oxalate, ammonium picrate, ammonium pyrolidinedithiocarbamate, ammonium salicylate, ammonium succinate, ammonium sulfanylate, ammonium tartrate, ammonium thioglycolate and ammonium 2,4,6-trinitrophenol. They may be used singly or in combination of two or more.

An amount of the ammonium compound to be added is preferably in the range of 0.001 mole to 1.0 mole, more preferably in the range of 0.002 mole to 2.0 mole per liter of the stabilizing solution.

In the stabilizing solution, it is preferred to contain a chelating agent having a chelate stability constant of 8 or more to accomplish the object of the present invention. Here, the chelate stability constant is a well known constant by, for example, written by L.G. Sillen & A.E. Martell, "Stability constants of Metal-ion Complexes", The Chemical Society, London (1964), and written by S.Chaberek & A.E. Martell, "Organic Sequestering Agents", Wiley (1959).

As the chelating agent having a chelate stability constant with ferric ion being 8 or more, the following compounds may be mentioned, but not limited by these. That is, there may be mentioned ethylenediaminediorthohydroxyphenylacetic acid, diaminpropanetetraacetic acid, nitrilotriacetic acid, hydroxyethylenediaminetriacetic acid, dihydroxyethylglycin, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, iminodiacetic acid, diethylenetriaminepentaacetic acid, hydroxyethyliminodiacetic acid, diaminopropanoltetraacetic acid, transcyclohexanediaminetetraacetic acid, glycoletherdiaminetetraacetic acid, ethylenediaminetetraxismethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, 1,1-diphosphonoethane-2-carboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxy-1-phosphonopropane-1,2,3-tricarboxylic acid, catecol-3,5-diphesphonic acid, sodium pyrophosphate, sodium tetrapolyphosphate and sodium hexametaphosphate, particularly preferably diethylenetriaminepentaacetic acid, nitrilotriacetic acid, nitrilotrimethylenephosphonic acid and 1-hydroxyethylidene-1,1-diphosphonic acid, and of these, 1-hydroxyethylidene-1,1-diphosphonic acid is most preferred.

An amount of the above chelating agent to be used is preferably 0.01 to 50 g, more preferably in the range of 0.05 to 20 g per liter of the stabilizing solution to give good results.

As the other compounds which are generally known and can be added to the stabilizing solution, there may be mentioned polyvinylpyrrolidone (PVP K-15, K-30 and K-90, all trade names), organic acid salts (salt of citric acid, acetic acid, succinic acid, oxalic acid and benzoic acid), pH adjusting agents (phosphates, borates, hydrochloric acid and sulfuric acid), mildewproofing agents (phenol derivatives, catechol derivatives, imidazole derivatives, triazole derivatives, cyabendazole derivatives, organic halide compounds, and other mildewproofing agents which have been known as a slime controller for paper-pulp industry), or optical brightening agents, surfactants, antispectic agents, metal salts of a metal such as Bi, Mg, Zn, Ni, Al, Sn, Ti and Zr. These compounds may be optionally used in either of combinations thereof so long as causing any bad effect against stability of a color photographic image during preservation and occurrence of deposition.

A processing temperature for the stabilizing processing is 15 °C to 70 °C, preferably in the range of 20 °C to 55 °C. Also, a processing time is preferably 120 sec or shorter, more preferably 3 sec to 90 sec, most preferably 6 sec to 50 sec whereby the effect of the present invention can be accomplished more effectively

After stabilizing processing, washing processing is not entirely required, but rinse or surface washing with a small amount of water within extremely minute time can be optionally carried out, if necessary. It is preferred to exist a soluble iron salt in the stabilizing solution to accomplish the effect of the present invention. As the soluble iron salts, there may be mentioned inorganic iron salts such as ferric chloride, ferrous chloride, ferric phosphate, ferric bromide, ferric nitrate and ferrous nitrate, and organic acid iron salts such as ferric ethylenediaminetetraacetate, ferric 1-hydroxyethylidene-1,1-diphosphonate, ferrous 1-hydroxyethylidene-1,1-diphosphonate, ferrous ethylenediaminetetraacetate, ferric diethylenetriaminepentaacetate, ferrous diethylenetriaminepentaacetate, ferric citrate, ferric ethylenediaminetetramethylenephosphonate, ferrous ethylenediaminetetramethylenephosphonate, ferric nitrilotrimethylenephosphonate, ferric nitrilotriacetate and ferrous nitrilotriacetate. These organic acid iron salts may be either a free acid type or a sodium salt, a potassium salt, an ammonium salt, a lithium salt or an alkylammonium salt (triethanolammonium salt, trimethylammonium salt or tetramethylammonium salt). These soluble iron salts are preferably used in a concentration of at least 5×10^{-3} mole/liter, more preferably in the range of 8×10^{-3} to 150×10^{-3} mole/liter, further preferably in the range of 12×10^{-3} to 100×10^{-3} mole/liter in the stabilizing solution. Also, these soluble iron salts may be added to the stabilizing solution (tank solution) by adding in a replenishing solution for the stabilizing solution, or may be added to the stabilizing solution (tank solution) by dissolving out from a light-sensitive material in the stabilizing solution, or may be added to the stabilizing solution (tank solution) by adhering to a light-sensitive material from the previous bath and bring it into the stabilizing solution tank.

Also, in the present invention, a stabilizing solution which is made a calcium ion or magnesium ion concentration 5 ppm or less by subjecting to treatment by using an ion exchange resin may be used, or it may be used by further adding the above antispectic agent or halogen ion releasing compound.

A pH of the stabilizing solution is preferably in the range of 5.5 to 10.0. A pH adjusting agent which may be contained in the stabilizing solution may be any of an alkali agent or an acid agent generally known.

The amount to be replenished of the stabilizing solution is preferably 0.1- to 50-fold, particularly preferably 0.5- to 30-fold of the amount brought in from the previous bath (bleach-fixing solution) per unit area of a light-sensitive material in the points of rapid processing and preservability of a dye image.

The stabilizing tank for stabilizing processing is preferably 1 to 5 tanks, particularly preferably 1 to 3 tanks, most preferably 1 tank in view of desilvering property and rapid processing.

Next, a light-sensitive material to which the present invention is preferably applied is to be described.

Silver halide grains to be preferably used in the light-sensitive material are silver halide grains composed mainly of silver chloride containing at least 80 mole % or more of silver chloride, more preferably 90 mole % or more, particularly preferably 95 mole % or more, most preferably 99 mole % or more. By having such a composition, good effects can be obtained with respect to rapid processing and prevention of stain so that it is preferred embodiment of the present invention to process the light-sensitive material using silver halide emulsion composed mainly of silver chloride.

The above silver halide emulsion composed mainly of silver chloride may contain silver bromide and/or silver iodide as a silver halide composition, and in this case, an amount of silver bromide is preferably 20 mole % or less, more preferably 10 mole % or less, further preferably 3 mole % or less, and also when silver iodide exists, it is preferably 1 mole % or less, more preferably 0.5 mole % or less, most preferably 0. The silver halide grains composed mainly of silver chloride with 80 mole % or more of silver chloride may be applied to at least one layer of silver halide emulsion layers, but preferably they are applied to all of the silver halide emulsion layers.

Crystal habit of the above silver halide grains may be normal crystal, twin crystal or other crystals, and any ratio of [1.0.0] face to [1.1.1] face can be employed as desired. Further, a crystalline structure of the silver halide grains may be either a structure which is uniform from an inner portion to an outer portion or a layer structure in which an inner portion and an outer portion are heterogeneous (core/shell type). Further, the silver halide grains may be of the type in which a latent image is formed mainly on the grain surface or of the type in which a latent image is formed internally of the grain. Also, plane silver halide grains (see Japanese Provisional Patent Publications No. 113934/1983 and No. 47959/1986) can be used.

The silver halide grains to be used in the present invention may be those obtained by any preparation method such as an acidic method, a neutral method or an ammoniacal method.

Further, for example, there may be employed a method in which seed grains are formed by an acidic method, and grown to a predetermined size according to an ammoniacal method by which grains can be grown quickly. When the silver halide grains are grown, it is preferred to control pH and pAg in a reaction vessel, and, for example, it is preferred to add and mix successively or simultaneously silver ions and halide ions in an amount which is adjusted corresponding to a growth speed of the silver halide grains disclosed in Japanese Provisional Patent Publication No. 48521/1979.

The silver halide emulsion layer of the light-sensitive material to be processed by the present invention contains a color coupler. These color coupler forms a non-diffusive dye by reacting with an oxidized product of a color developing agent. The color coupler is advantageously contained in a light-sensitive layer in a non-diffusive state or combined therein by closely adjacent thereto.

Thus, a red-sensitive layer may contain, for example, a non-diffusive color coupler forming a cyan part color image, generally phenol or α-naphthol type coupler. A green-sensitive layer may contain at least one non-diffusive color coupler forming a magenta part color image, generally 5-pyrazolone type coupler and pyrazolotriazole. A blue-sensitive layer may contain at least one non-diffusive coupler forming a yellow part color image, generally a color coupler having an open-chain ketomethylene group. The color couplers may be, for example, 6-, 4- or 2-equivalent coupler.

In the present invention, 2-equivalent coupler is particularly preferred.

Suitable couplers are disclosed, for example, in the following publications: "Color coupler" written by W. Pelz in Research Report by Agfa (Mitteilunglnausden Forschungslaboratorien der Agfa), Leverkusaen/München, Vol. III. p. 111 (1961); "The chemistry of Synthetic Dyes" written by K. Venkataraman, Vol. 4, pp. 341 to 387, Academic Press; "The Theory of the Photographic Process", 4th Edition, pp. 353 to 362; and "Research Disclosure", No. 17643, Section VII.

In the present invention, 5-pyrazolone type and pyrazoloazole type compounds disclosed in U.S. Patents No. 4,310,619 and No. 4,351,897, European Patent No. 73,636, Research Disclosures No. 24220 and No. 24230, Japanese Provisional Patent Publication No. 43659/1985 and WO 88/04795 are preferred, and particularly, to use the magenta coupler represented by the formula (M - 1) described at page 26 of Japanese Provisional Patent Publication No. 106655/1988 (as the specific exemplary magenta couplers thereof, those of No. 1 to No. 77 described at pages 29 to 34 of Japanese Provisional Patent Publication No. 106655/-1988 may be mentioned.), the cyan coupler represented by the formula (C - I) or (C - II) described at page 34 of the same (as the specific exemplary cyan couplers thereof, those of (C' - 1) to (C' - 82) and (C" - 1) to (C" - 36) described at pages 37 to 42 of the same may be mentioned.) and the high speed yellow coupler described at page 20 of the same (as the specific exemplary yellow couplers thereof, those of (Y' - 1) to (Y' - 39) described at pages 21 to 26 of the same may be mentioned.) are preferred in view of accomplishing the effects of the present invention.

When a nitrogen-containing heretocyclic mercapto compound is used in a light-sensitive material using an emulsion composed mainly of silver chloride, not only accomplishing the effect of the present invention more effectively but also accomplishing the other effect that an influence in photographic performance caused by being mixed the bleach-fixing solution into the color developing solution can be made extremely slight so that it can be mentioned as one of the preferred embodiments of the present invention.

Specific examples of these nitrogen-containing heterocyclic mercapto compounds may include (I' - 1) to (I' - 87) described at pages 42 to 45 of Japanese Provisional Patent Publication No. 106655/1988.

The silver halide emulsion composed mainly of silver chloride with a silver chloride content of 80 mole % or more can be prepared according to the conventional method (for example, single influent or double influent method with constant or accelerated rapid rate of materials). Particularly, the preparation method of the double influent method while adjusting a pAg is preferred (see Research Disclosure No. 17643, Sections I and II).

The emulsion composed mainly of silver chloride can be chemically sensitized . As the sensitizer, sulfur-containing compounds such as allylisothiocyanate, allylthiourea and thiosulfate are particularly preferred. A reducing agent can be also used as a chemical sensitizer and it may include, for example, a silver compound as disclosed in Belgium Patents No. 493,464 and No. 568,687, and a polyamine such as diethylenetriamine or aminomethylsulfinic acid derivative as disclosed in Belgium Patent No. 547,323. Noble metals such as gold, platinum, palladium, iridium, ruthenium and rhodium, and noble metal compounds are also suitable sensitizers. The chemical sensitizing method is described in the literature of "Zeitschrift für Wissenshaftliche Photography", written by R. Koslovsky, vol. 46, pp. 65 to 72 (also see the above "Research Disclosure", No. 17643, Section III).

The emulsion composed mainly of silver chloride can be sensitized by using an optically well-known method, for example, using usual polymethyne dye such as neutrocyanine, basic or acidic carbocyanine, rhodacyanine and hemicyanine, styryl dye, oxonol and derivatives thereof (see "The Cyanine Dyes and related Compounds" written by F. M. Hamer (1964) published by Ullmanns Enzyklpadie der technischen Chemie, fourth edition, vol. 18, p. 431 and et seq. and the above "Research Disclosure", No. 17643, Section IV).

In the emulsion composed mainly of silver chloride, the conventionally used antifoggants and stabilizers can be used. Azaindenes are particularly suitable stabilizer and tetra- and pentaazaindene are preferred, and those substituted by a hydroxyl group or an amino group are particularly preferred. This kinds of compounds are described in the literature written by Birr, "Zeitschrift für Wissenshaftliche Photography", vol. 47, pp. 2 to 58 (1952) and the above "Research Disclosure", No. 17643, Section IV.

Components of the light-sensitive material can be contained generally according to the conventional method. For example, components of the light-sensitive material such as a coupler and UV absorber may be contained in the form of a charged latex (see West German Provisional Patent Publication (OLS) 2,541,274 and European Patent Publication (A) No. 14,921 which corresponds to U.S. Patents No. 4,237,194 and No. 4,308,332). These components may be also fixed in the light-sensitive material as a polymer (see, for example, West German Provisional Patent Publication (OLS) 2,044,992 and U.S. Patents No. 3,370,952 and No. 4,080,211.

As a support of the light-sensitive material, usual support may be used and it may include, for example, a support of a cellulose ester such as cellulose acetate, and a support of a polyester. In the present invention, a reflective support such as a paper is most suitable, and it may be coated by a polyolefin, particularly polyethylene or polypropylene. Concerning the above, refer to the above "Research Disclosure", No. 17643, Section VI.

In the present invention, as a light-sensitive material, any of the light-sensitive material which is processed by the so-called inner type development system, which light-sensitive material contains a coupler therein may be used and the color developing solution can be applied to optional light-sensitive material such as a color paper, a color negative film, a color positive film , a color reversal film for slide, a color reversal film for movie, a color reversal film for television and a reversal color paper, but most preferably to apply it to a color paper composed mainly of silver chloride.

According to the present invention, a color developing solution which is capable of effecting rapid processing and stable in photographic performances, and a processing method can be provided. Also, a color developing solution which is less contamination at a rack or roller portion due to deposition or adhesion of sludge and easy in maintenance and a processing method can be provided.

EXAMPLES

In the following, the present invention will be described in more detail by referring to Examples, but the present invention is not limited by these Examples at all.

Example 1

On a paper support one surface of which is laminated with a polyethylene and the other surface of which is laminated with a polyethylene containing titanium oxide as a first layer, each layer having a constitution as mentioned below was coated to prepare a multi-layer light-sensitive silver halide color photographic material (1). The coating solutions are prepared as shown below.

First layer coating solution

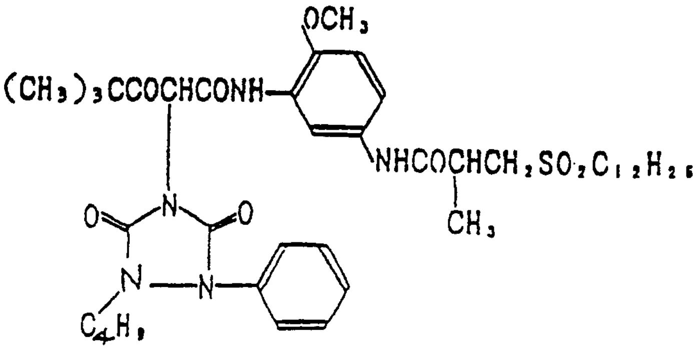
To 6.67 g of a high boiling point organic solvent (DNP) were added 26.7 g of a yellow coupler (Y - 1), 10.0 g of a dye image stabilizer (ST - 1), 6.67 g of the same (ST - 2) and 0.67 g of an additive (HQ - 1), and the mixture was dissolved by adding 60 ml of ethyl acetate. The solution was emulsified in 220 ml of a 10 % gelatin aqueous solution containing 7 ml of a 20 % surfactant (SU - 1) by using an ultrasonic homogenizer to prepare a yellow coupler dispersion. This dispersion was mixed with a blue-sensitive silver halide emulsion (containing 10 g of silver) prepared by the following conditions to prepare a first layer coating solution.

The second layer to the seventh layer coating sclutions are also prepared in the same manner as in the above first layer coating solution.

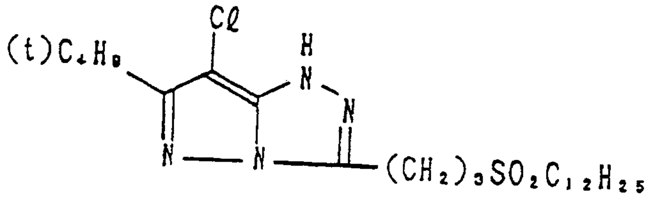
Layer	Constitution	Amount added (g/m2)
Seventh layer (Protective layer)	Gelatin	1.0
Sixth layer (UV ray absorbing layer)	Gelatin	0.4
	UV absorber (UV - 1)	0.10
	UV absorber (UV - 2)	0.04
	UV absorber (UV - 3)	0.16
	Antistain agent (HQ - 1)	0.01
	DNP	0.2
	PVP	0.03
	Irradiation preventive dye (AI - 2)	0.02
Fifth layer (Red-sensitive layer)	Gelatin	1.30
	Red-sensitive silver chloro-bromide emulsion (Em C) calculated on silver	0.21
	Cyan coupler (C - 1)	0.17

	Cyan coupler (C - 2)	0.25
	Dye image stabilizer (ST-1)	0.20
	Antistain agent (HQ - 1)	0.01
	HBS - 1	0.20
	DOP	0.20
Fourth layer (UV ray absorbing layer)	Gelatin	0.94
	UV absorber (UV - 1)	0.28
	UV absorber (UV - 2)	0.09
	UV absorber (UV - 3)	0.38
	Antistain agent (HQ - 1)	0.03
	DNP	0.40
Third layer (Green-sensitive layer)	Gelatin	1.40
	Green-sensitive silver chloro-bromide emulsion (Em B) calculated on silver	0.17
	Magenta coupler (M - 1)	0.35
	Dye image stabilizer (ST-3)	0.15
	Dye image stabilizer (ST-4)	0.15
	Dye image stabilizer (ST-5)	0.15
	DNP	0.20
	Irradiation preventive dye (AI - 1)	0.01
Second layer (Intermediate layer)	Gelatin	1.20
	Antistain agent (HQ - 2)	0.12
	DIDP	0.15
First layer (Blue-sensitive layer)	Gelatin	1.20
	Blue-sensitive silver chloro-bromide emulsion (Em A) calculated on silver	0.26
	Yellow coupler (Y - 1)	0.80
	Dye image stabilizer (ST-1)	0.30
	Dye image stabilizer (ST-2)	0.20
	Antistain agent (HQ - 1)	0.02
	Irradiation preventive dye (AI - 3)	0.01
	DNP	0.20
Support	Polyethylene laminated paper	

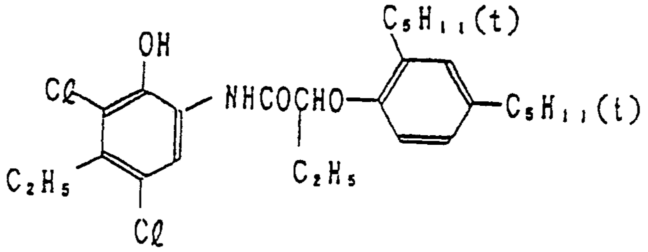
Y－1



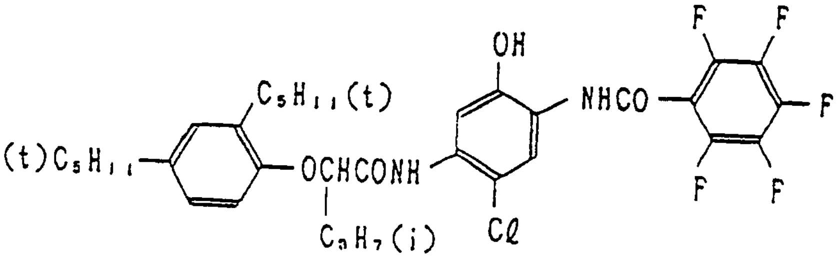
M－1



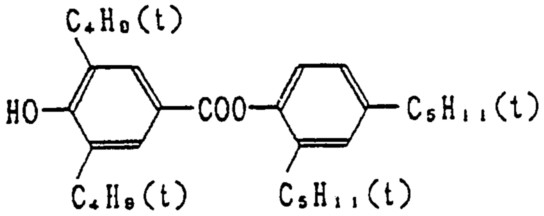
C－1



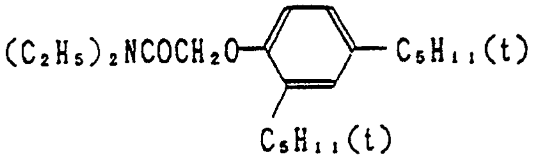
C－2



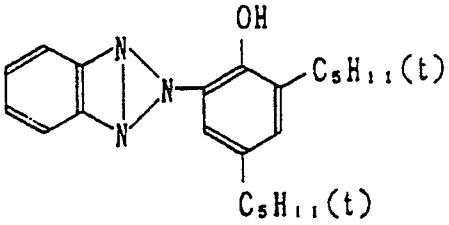
ST－1



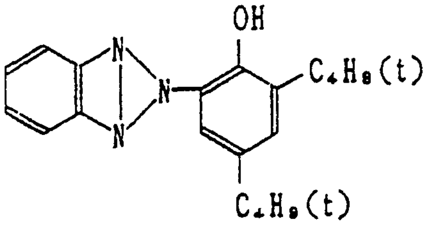
ST－2



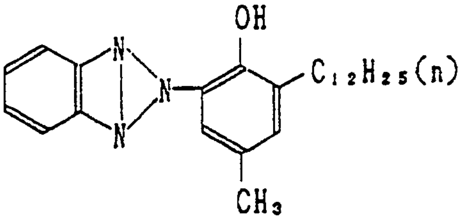
UV－1



UV－2

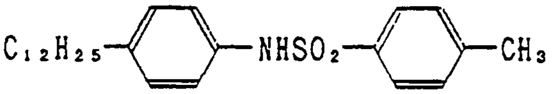


UV－3

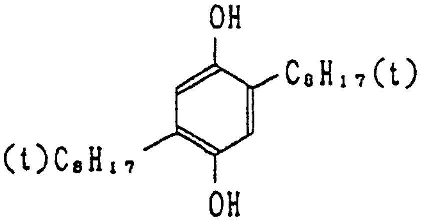


DOP	Dioctylphthalate	DNP	Dinonylphthalate
DIDP	Diisodecylphthalate	PVP	Polyvinylpyrrolidone

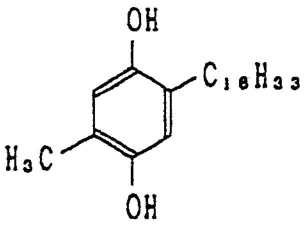
HBS－1



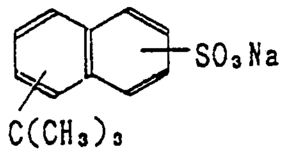
HQ－1



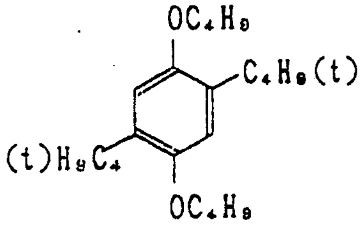
HQ－2



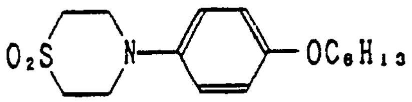
SU-1



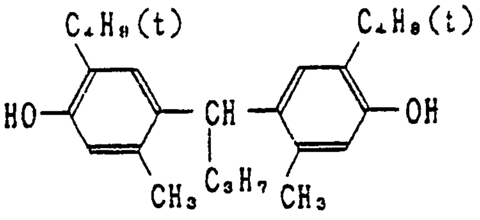
ST-3



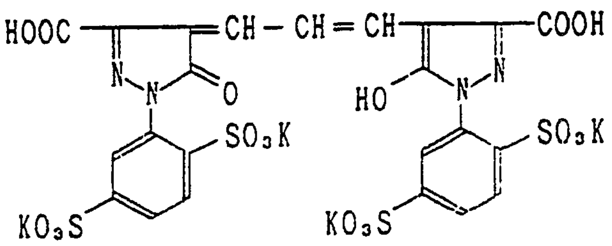
ST-4



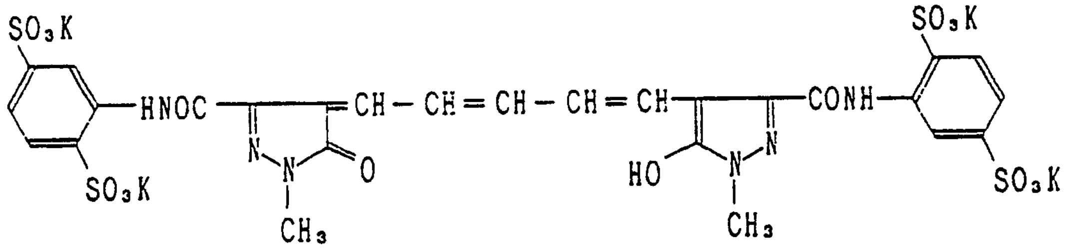
ST-5



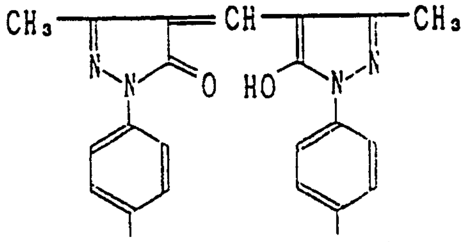
AI-1



AI-2

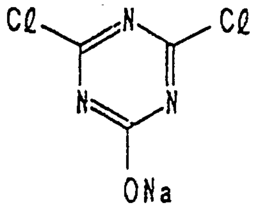


AI-3



As the hardener, the following H - 1 was used.

H - 1



(Preparation method of blue-sensitive silver halide emulsion)

In 1000 ml of a 2 % gelatin aqueous solution maintained at 40 °C were added simultaneously the following (Solution A) and (Solution B) while controlling a pAg = 6.5 and a pH = 3.0 over 30 minutes and further added simultaneously the following (Solution C) and (Solution D) while controlling a pAg = 7.3 and a pH = 5.5 over 180 minutes.

At this time, control of the pAg was carried out according to the method described in Japanese Provisional Patent Publication No. 45437/1984, and control of the pH was carried out by using an aqueous solution of sulfuric acid and sodium hydroxide.

(Solution A)

Sodium chloride	3.42 g
Potassium bromide	0.03 g

Made up to 200 ml with addition of water.

(Solution B)

Silver nitrate	10 g

Made up to 200 ml with addition of water.

(Solution C)

Sodium chloride	102.7 g
Potassium bromide	1.0 g

Made up to 600 ml with addition of water.

(Solution D)

Silver nitrate	300 g

Made up to 600 ml with addition of water.

After completion of addition, desalting was carried out by using a 5 % aqueous solution of Demol N (trade name, available from Kao Atlas Co.) and a 20 % aqueous magnesium sulfate solution, and then the mixture was mixed with a gelatin aqueous solution to prepare a monodispersed cubic emulsion EMP - 1 having an average diameter of 0.85 µm, a variation coefficient (σ/r) = 0.07 and a silver chloride content of 99.5 mole %.

To the above emulsion EMP - 1 was subjected chemical ripenning at 50 °C for 90 minutes by using the following compounds to obtain a blue-sensitive silver halide emulsion (Em A).

Sodium thiosulfate	0.8 mg/mole AgX
Chloroauric acid	0.5 mg/mole AgX
Stabilizer SB - 5	6×10^{-4} mole/mole AgX
Sensitizing dye D - 1	4.3×10^{-4} mole/mole AgX
" D - 4	0.7×10^{-4} mole/mole AgX

(Preparation method of green-sensitive silver halide emulsion)

In the same manner as in preparation of EMP - 1 except for changing an addition time of (Solution A) and (Solution B) and an addition time of (Solution C) and (Solution D), a monodispersed cubic emulsion EPM - 2 having an average diameter of 0.43 µm, a variation coefficient (σ/r) = 0.08 and a silver chloride content of 99.5 mole % was obtained.

To the above emulsion EMP - 2 was subjected chemical ripenning at 55 °C for 120 minutes by using the following compounds to obtain a blue-sensitive silver halide emulsion (Em B).

Sodium thiosulfate	1.5 mg/mole AgX
Chloroauric acid	1.0 mg/mole AgX
Stabilizer SB - 5	6×10^{-4} mole/mole AgX
Sensitizing dye D - 2	4×10^{-4} mole/mole AgX

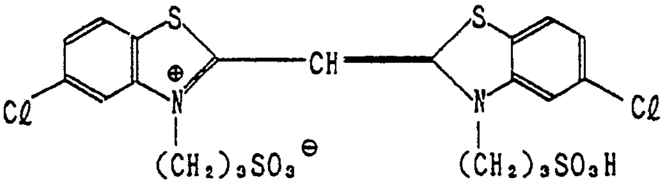
(Preparation method of red-sensitive silver halide emulsion)

In the same manner as in preparation of EMP - 1 except for changing an addition time of (Solution A) and (Solution B) and an addition time of (Solution C) and (Solution D), a monodispersed cubic emulsion EPM - 3 having an average diameter of 0.50 µm, a variation coefficient (σ/r) = 0.08 and a silver chloride content of 99.5 mole % was obtained.

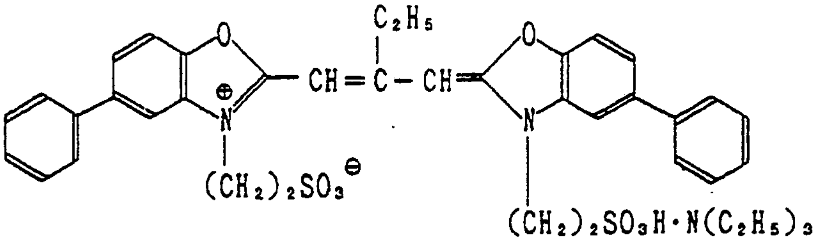
To the above emulsion EMP - 3 was subjected chemical ripenning at 60 °C for 90 minutes by using the following compounds to obtain a red-sensitive silver halide emulsion (Em C).

Sodium thiosulfate	1.8 mg/mole AgX
Chloroauric acid	2.0 mg/mole AgX
Stabilizer SB - 5	6×10^{-4} mole/mole AgX
Sensitizing dye D - 3	1.0×10^{-4} mole/mole AgX

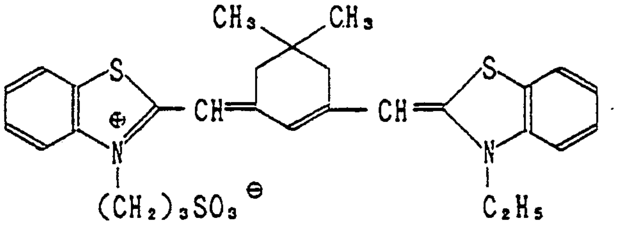
D－1



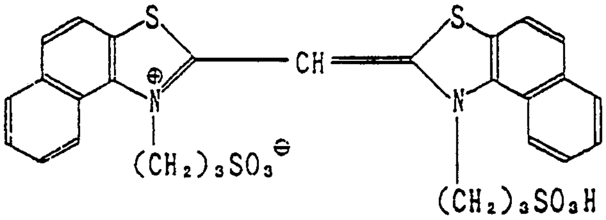
D－2



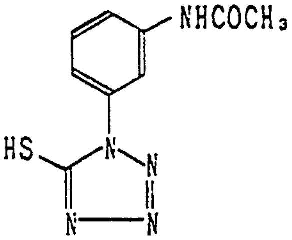
D－3



D－4



SB－5



This sample was exposed according to the conventional manner, and then, processings were carried out by using the following processing steps and processing solutions.

Processing steps

(1)	Color development	35.0 ± 0.3 °C	45 sec
(2)	Bleach-fixing	35.0 ± 0.5 °C	45 sec
(3)	Stabilizing (3 tanks cascade)	30 to 34 °C	90 sec
(4)	Drying	60 to 80 °C	30 sec

(Color developing tank solution)

Triethanolamine	10 g
Ethylene glycol	1 g
N,N-Diethylhydroxylamine	3.6 g
Hydrazinodiacetic acid	5.0 g
Potassium bromide	20 mg
Potassium chloride	2.5 g
Diethylenetriaminepentaacetic acid	5 g
Potassium sulfite	5.0×10^{-4} mole
Color developing agent (3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate)	5.5 g
Potassium carbonate	25 g
Potassium hydrogen carbonate	2.5 g

Made up to 1 liter in total with addition of water, and adjusted to pH = 10.10 with potassium hydroxide or sulfuric acid.

(Color developing replenishing solution)

Triethanolamine	14.0 g
Ethylene glycol	8.0 g
N,N-Diethylhydroxylamine	5 g
Hydrazinodiacetic acid	7.5 g
Potassium bromide	8 mg
Potassium chloride	0.3 g
Diethylenetriaminepentaacetic acid	7.5 g

Potassium sulfite	7.0×10^{-4} mole
Color developing agent (3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate)	8 g
Potassium carbonate	30 g
Potassium hydrogen carbonate	1 g

Made up to 1 liter in total with addition of water, and adjusted to pH = 10.40 with potassium hydroxide or sulfuric acid.

(Bleach-fixing tank solution and replenishing solution)

Ferric ethylenediaminetetraacetate ammonium salt	53.0 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (70 % solution)	123.0 g
Ammonium sulfite (40 % solution)	51.0 g

Made up to 1 liter in total with addition of water as well as adjusted to pH to 5.4 with aqueous ammonia or glacial acetic acid.

(Stabilizing tank solution and replenishing solution)

Orthophenylphenol	0.1 g
Ubitex (trade name, available from Ciba Geigy AG)	1.0 g
$ZnSO_4 \cdot 7H_2O$	0.1 g
Ammonium sulfite (40 % solution)	5.0 ml
1-Hydroxyethylidene-1,1-diphosphonic acid (60 % solution)	3.0 g
Ethylenediaminetetraacetic acid	1.5 g

Made up to 1 liter in total with addition of wateras well as adjusted to pH to 7.8 with aqueous ammonia or sulfuric acid.

Using the color paper and processing solutions thus prepared, running processing was carried out.

The running processing was carried out by filling the above color developing solution in an automatic processor and also filling the bleach-fixing tank solution and the stabilizing solution, and while processing the above color paper sample and supplementing the above color developing replenishing solution, the bleach-fixing replenishing solution and the stabilizing replenishing solution through a quantitative pump every 3 minutes interval.

As a replenishing amount in the color developing tank, 100 ml thereof was replenished per 1 m2 of the color paper, as a replenishing amount in the bleach-fixing tank, 220 ml of the bleach-fixing replenishing solution and as a replenishing amount in the stabilizing tank, 250 ml of the stabilizing replenishing solution, respectively.

The running processing was carried out until an amount of the color developing solution replenished in the color developing tank solution becomes 3-times of the volume of the color developing tank solution with a continuous processing of 0.05R per day. 1R herein mentioned means that the color developing replenishing solution was replenished with the same amount as the color developing tank volume.

After continuous processing, the tank solution was divided and 2.5 g of the water-soluble surfactant shown in Table 1 was added per liter of the solution and stain at the unexposed portion and crystallization property were evaluated.

The stain at the unexposed portion was obtained by measuring spectral reflective densities at 440 nm and 640 nm to determine difference in densities before and after addition of the surfactant. It shows that the larger density difference is, the more marked in improved effect of stain is. As for crystallization property, the solution was placed in a narrow-mouthed bottle (with ground glass) having an opening area of 10 cm^2 and stored at normal temperature for 10 days while effecting evaporation correction every day whereby crystallization property was evaluated. Provided that the evaluation of the crystallization property was carried out as shown below.

◎ : No deposited crystals on the ground glass surface.
○ : Deposited crystals are minutely admitted on the ground glass surface.
Δ : A little amount of deposited crystals is found on the ground glass surface.
× : Large amount of deposited crystals are found on the ground glass surface.
×× : Large amount of deposited crystals are found on the ground glass surface and precipitated at the bottom of the beaker.

The above results are shown in Table 1.

Table 1

Experiment No.	Water-soluble surfactant (2.5 g/l)	Cryatalization property	Stain at unexposed portion (440 nm) Density difference of (without addition - after addition	Stain at unexposed portion (640 nm) Density difference of (without addition - after addition
	—	XX	0.0	0.0
1 - 2	II - 5	◎	0.075	0.013
1 - 3	II - 16	◎	0.060	0.012
1 - 4	II - 22	◎	0.063	0.011
1 - 5	II - 24	◎	0.065	0.012
1 - 6	II - 27	◎	0.080	0.015
1 - 7	II - 32	◎	0.083	0.015
1 - 8	II - 33	◎	0.075	0.014
1 - 9	II - 34	◎	0.080	0.015
1 - 10	II - 36	◎	0.087	0.016
1 - 11	II - 37	◎	0.053	0.010
1 - 12	II - 54	◎	0.047	0.009
1 - 13	II - 59	◎	0.047	0.009
1 - 14	II - 72	◎	0.050	0.009
1 - 15	I - 2	◎	0.045	0.012
1 - 16	I - 4	◎	0.043	0.013
1 - 17	I - 9	◎	0.080	0.028
1 - 18	I - 11	◎	0.082	0.028
1 - 19	I - 12	◎	0.087	0.030

Table 1 (Contd)

Experiment No.	Water-soluble surfactant (2.5 g/l)	Cryatallization property	Stain at unexposed portion (440 nm) Density difference of (without addition - after addition	Stain at unexposed portion (640 nm) Density difference of (without addition - after addition
1 - 20	I - 14	◎	0.089	0.031
1 - 21	I - 18	◎	0.083	0.030
1 - 22	I - 23	◎	0.085	0.029
1 - 23	III - 5	◎	0.050	0.009
1 - 24	IV - 6	◎	0.049	0.009
1 - 25	V - 1	◎	0.043	0.008
1 - 26	V - 3	◎	0.048	0.009
1 - 27	VI - 1	○	0.033	0.007
1 - 28	VI - 5	○	0.030	0.007
1 - 29	VII - 1	○	0.030	0.007
1 - 30	VIII - 1	△	0.023	0.005
1 - 31	VIII - 4	△	0.027	0.006
1 - 32	VIII - 24	△	0.027	0.006
1 - 33	IX - 1	○	0.035	0.007
1 - 34	IX - 12	○	0.038	0.007
1 - 35	X - 1	○	0.041	0.008
1 - 36	XI - 1	○	0.035	0.007
1 - 37	XI - 4	○	0.032	0.007

As clearly seen from Table 1, it can be understood that when the water-soluble surfactant of the present invention is used, the crystallization property and the stain at the unexposed portion are remarkably improved. Particularly, it can be understood that the effects of the nonionic surfactants represented by the formulae (I) and (II) are remarkable, and the effects of the surfactant represented by the formula (I) are further remarkable.

When samples which are prepared by replacing the water-soluble surfactant of the present invention with the exemplary compound I - 1, 13, 17, 19, 24, 25, II - 1, 2, 12, 14, 21, 26, 29, 40, 51, III - 6, IV - 2, 7, V - 7, VI - 2, VII - 2, VIII - 2, 7, 14, IX - 2, 7, 14 or XI - 6 were evaluated in the same manner as in Example 1, substantially the same effects as in Example 1 can be obtained.

Example 2

The same processings as in Example 1 were carried out except that the color developing tank solution and color developing replenishing solution in Example 1 were changed to those as shown below, respectively, and the surfactants shown in Table 2 were added thereto, and contamination at a rack or roller and stain at the unexposed portion were evaluated in the same methods as in Example 1.

The results are shown in Table 2.

(Color developing tank solution)

Triethanolamine	10 g
Ethyleneglycol	6 g
Chinopal SFP (trade name, available from Ciba Geigy AG)	1 g
Ubitex MST (trade name, available from Ciba Geigy AG)	1 g
N,N-Diethylhydroxylamine	3.6 g

Potassium bromide	20 mg
Potassium chloride	2.5 g
Diethylenetriaminepentaacetic acid	5 g
Potassium sulfite	5.0 x 10^{-4} mole
Color developing agent (3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate)	5.5 g
Exemplary compound	(shown in Table 2)
Potassium carbonate	25 g
Potassium hydrogen carbonate	5 g

Made up to 1 liter in total with addition of water and adjusted to pH to 10.10 with potassium hydroxide or sulfuric acid.

(Color developing replenishing solution)

Triethanolamine	14.0 g
Ethyleneglycol	8.0 g
Chinopal SFP (trade name, available from Ciba Geigy AG)	1.2 g
Ubitex MST (trade name, available from Ciba Geigy AG)	1.5 g
N,N-Diethylhydroxylamine	5 g
Potassium bromide	8 mg
Potassium chloride	0.3 g
Diethylenetriaminepentaacetic acid	7.5 g
Potassium sulfite	7.0 x 10^{-4} mole
Color developing agent (3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate)	8 g
Exemplary compound	(shown in Table 2)
Potassium carbonate	30 g
Potassium hydrogen carbonate	1 g

Made up to 1 liter in total with addition of water and adjusted to pH to 10.40 with potassium hydroxide or sulfuric acid.

Table 2

Experiment No.	Surfactant to be added to color developing tank solution and replenishing solution		Contamination at rack and roller portions	Stain at unexposed portion Density difference of (without addition - after addition)	
	Kind	Amount added (g/l)		(440 nm)	(640 nm)
2 - 1	—	0	XX	0.0	0.0
2 - 2	II - 5	0.1	XX	0.005	0.001
2 - 3		0.4	X	0.012	0.002
2 - 4		0.5	○	0.035	0.007
2 - 5		1.0	◎	0.056	0.015
2 - 6		10	◎	0.062	0.017
2 - 7		20	◎	0.064	0.017
2 - 8		25	◎	0.064	0.017
2 - 9	II - 27	0.1	XX	0.006	0.001
2 - 10		0.4	X	0.015	0.002
2 - 11		0.5	○	0.038	0.007
2 - 12		1.0	◎	0.063	0.013
2 - 13		10	◎	0.069	0.015
2 - 14		20	◎	0.070	0.015
2 - 15		25	◎	0.070	0.015
2 - 16	II - 36	0.1	XX	0.009	0.002
2 - 17		0.4	X	0.019	0.002
2 - 18		0.5	○	0.043	0.008
2 - 19		1.0	◎	0.069	0.015
2 - 20		10	◎	0.072	0.016
2 - 21		20	◎	0.073	0.016
2 - 22		25	◎	0.073	0.016

Table 2 (Contd)

Experiment No.	Surfactant to be added to color developing tank solution and replenishing solution		Contamination at rack and roller portions	Stain at unexposed portion Density difference of (without addition - after addition)	
	Kind	Amount added (g/l)		(440 nm)	(640 nm)
2 - 22	IV - 5	0.1	XX	0.004	0.001
2 - 24		0.4	X	0.010	0.002
2 - 25		0.5	○	0.029	0.006
2 - 26		1.0	◎	0.041	0.010
2 - 27		10	◎	0.045	0.011
2 - 28		20	◎	0.046	0.011
2 - 29		25	◎	0.046	0.011
2 - 30	V - 3	0.1	XX	0.004	0.001
2 - 31		0.4	X	0.012	0.002
2 - 32		0.5	○	0.027	0.006
2 - 33		1.0	◎	0.042	0.009
2 - 34		10	◎	0.045	0.010
2 - 35		20	◎	0.045	0.010
2 - 36		25	◎	0.045	0.010
2 - 37	VI - 1	0.1	XX	0.003	0.001
2 - 38		0.4	X	0.009	0.001
2 - 39		0.5	△	0.020	0.004
2 - 40		1.0	○	0.027	0.006
2 - 41		10	◎	0.032	0.007
2 - 42		20	◎	0.032	0.008
2 - 43		25	◎	0.032	0.008

Table 2 (Contd)

Experiment No.	Surfactant to be added to color developing tank solution and replenishing solution		Contamination at rack and roller portions	Stain at unexposed portion Density difference of (without addition - after addition)	
	Kind	Amount added (g/l)		(440 nm)	(640 nm)
2 - 44	I - 12	0.1	XX	0.010	0.002
2 - 45		0.4	X	0.021	0.004
2 - 46		0.5	○	0.047	0.014
2 - 47		1.0	◎	0.072	0.027
2 - 48		10	◎	0.075	0.027
2 - 49		20	◎	0.075	0.028
2 - 50		25	◎	0.075	0.029
2 - 51	I - 14	0.1	XX	0.011	0.002
2 - 52		0.4	X	0.023	0.003
2 - 53		0.5	○	0.052	0.015
2 - 54		1.0	◎	0.078	0.029
2 - 55		10	◎	0.080	0.030
2 - 56		20	◎	0.082	0.031
2 - 57		25	◎	0.082	0.031
2 - 58	I - 18	0.1	XX	0.009	0.002
2 - 59		0.4	X	0.021	0.003
2 - 60		0.5	○	0.046	0.015
2 - 61		1.0	◎	0.070	0.028
2 - 62		10	◎	0.074	0.028
2 - 63		20	◎	0.074	0.029
2 - 64		25	◎	0.074	0.029

As clearly seen from Table 2, it can be understood that the water-soluble surfactant of the present invention clearly has an amount dependency to the effects of the present invention, and when it is added with an amount of 0.5 g or more, preferably 1.0 g or more, marked effects can be obtained. Particularly, the effects are remarkable when the water-soluble surfactant represented by the formula (I) is added.

Also, when it is added with an amount of 25 g, no change in effects can be observed but foaming property becomes potent so that it is not preferred since foaming is found during processing.

Example 3

By using the same color paper as in Example 1 and the same processing solutions as in Example 2, the running processing was carried out in the same manner as in Example 1 except for using the compounds shown in Table 3 as the water-soluble surfactant to be added in the color developing tank solution and the replenishing solution therefor, and changing the sulfite concentration of the color developing tank solution and the replenishing solution therefor as shown in Table 3, contamination at a rack or roller in the color developing tank of the automatic developer, stain at the unexposed portion and developability after termination of said running processing were evaluated.

As for the developability, the maximum spectral reflective density of blue at the sulfite concentration of 0 was measured as 100, and the stain at the unexposed portion was measured from the density difference from the reflective density at no surfactant and the sulfite concentration of 0. The results are shown in Table 3.

Table 3

Experiment No.	Surfactant (3.0 g/l)	Sulfite concentration (mole/l)	Contamination at rack and roller portions	Stain at unexposed portion Density difference of (without addition - after addition) (440 nm)	(640 nm)	Developability
3 - 1	II - 5	1×10^{-2}	◎	0.066	0.015	64
3 - 2		2×10^{-3}	◎	0.063	0.012	83
3 - 3		1×10^{-3}	◎	0.061	0.012	96
3 - 4		1×10^{-4}	◎	0.060	0.012	99
3 - 5		0	◎	0.060	0.011	100
3 - 6	II - 27	1×10^{-2}	◎	0.068	0.011	65
3 - 7		2×10^{-3}	◎	0.066	0.011	85
3 - 8		1×10^{-3}	◎	0.065	0.011	97
3 - 9		1×10^{-4}	◎	0.065	0.010	99
3 - 10		0	◎	0.065	0.010	100
3 - 11	II - 36	1×10^{-2}	◎	0.074	0.017	68
3 - 12		2×10^{-3}	◎	0.072	0.014	86
3 - 13		1×10^{-3}	◎	0.070	0.013	97
3 - 14		1×10^{-4}	◎	0.069	0.012	100
3 - 15		0	◎	0.069	0.012	100
3 - 16	III - 5	1×10^{-2}	◎	0.056	0.011	59
3 - 17		2×10^{-3}	◎	0.050	0.008	81
3 - 18		1×10^{-3}	◎	0.047	0.007	93
3 - 19		1×10^{-4}	◎	0.045	0.007	96
3 - 20		0	◎	0.045	0.006	100

Table 3 (Contd)

Experiment No.	Surfactant (3.0 g/l)	Sulfite concentration (mole/l)	Contamination at rack and roller portions	Stain at unexposed portion Density difference of (without addition - after addition) (440 nm)	(640 nm)	Developability
3 - 21	None	1×10^{-2}	△	0.021	0.008	65
3 - 22		2×10^{-3}	X	0.010	0.002	85
3 - 23		1×10^{-3}	XX	0.004	0.002	96
3 - 24		1×10^{-4}	XX	0.002	0.001	99
3 - 25		0	XX	0	0	100
3 - 26	I - 12	1×10^{-2}	◎	0.078	0.030	67
3 - 27		2×10^{-3}	◎	0.076	0.028	85
3 - 28		1×10^{-3}	◎	0.075	0.027	97
3 - 29		1×10^{-4}	◎	0.075	0.026	100
3 - 30		0	◎	0.075	0.026	100
3 - 31	I - 14	1×10^{-2}	◎	0.084	0.032	67
3 - 32		2×10^{-3}	◎	0.082	0.030	86
3 - 33		1×10^{-3}	◎	0.081	0.030	98
3 - 34		1×10^{-4}	◎	0.081	0.029	100
3 - 35		0	◎	0.081	0.029	100
3 - 36	I - 18	1×10^{-2}	◎	0.077	0.029	66
3 - 37		2×10^{-3}	◎	0.075	0.028	85
3 - 38		1×10^{-3}	◎	0.075	0.027	96
3 - 39		1×10^{-4}	◎	0.074	0.027	100
3 - 40		0	◎	0.074	0.027	100

As clearly seen from Table 3, when the emulsion composed mainly of silver chloride, accompanying with increase of the sulfite concentration, the developability becomes worse whereby it cannot be used practically. Also, when no surfactant is added and when the sulfite concentration is low, deposition is remarkable and stain is bad so that it cannot be used practically.

Accordingly, contamination and stain can be prevented without impairing rapid processing only by the constitution of the present invention, and it can also be understood that the surfactant represented by the formula (I) is particularly effective.

Example 4

In Example 3, the surfactants described in Example 1 were also investigated and substantially the effects could be obtained.

Example 5

A light-sensitive material (2) was prepared in the same manner as in Example 1 except that the silver bromide contents of the red-sensitive, green-sensitive and blue-sensitive silver bromide emulsions of the light-sensitive color photographic material (light-sensitive material (1)) composed mainly of silver chloride in Example 1 were made 70, 80 and 90 mole %, respectively, with the same average grain size and variation coefficient, as the sensitizing method, chemical sensitization was carried out by using sodium thiosulfate, and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (2.5 g per one mole of silver halide) as a stabilizer, bis-(vinylsulfonylmethyl)ether (15 mg per 1 g of gelatin) as a hardener and saponin as a coating aid were contained, respectively.

Other additives, an amount of silver and the like than the above are the same as those of the light-sensitive material (light-sensitive material (1)) used in Example 1.

By using the following color developing processing conditions and the processing solutions, samples were evaluated in the same methods as in Example 2 except for using the surfactant as shown in Table 4.

As for the developability, it was obtained by making the maximum spectral reflective density of blue of the sample containing no surfactant as 100.

(Color developing processing conditions)

Processing temperature: 33 °C

Processing time: 3 min 30 sec

(Color developing tank solution)

Benzyl alcohol	15 ml
Ethylene glycol	15 ml
Potassium sulfite	2.0 g
Potassium bromide	0.7 g
Sodium chloride	0.2 g
Potassium carbonate	30.0 g
Hydroxylamine sulfate	3.0 g
Polyphosphoric acid (TPPS)	2.5 g
Color developing agent (3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate)	5.5 g
Optical brightening agent (4,4'-diaminostylbene disulfonic acid derivative)	1.0 g
Potassium hydroxide	2.0 g

Made up to 1 liter in total with addition of water and adjusted to pH to 10.10 with potassium hydroxide or sulfuric acid.

(Color developing replenishing solution)

Benzyl alcohol	20 ml
Ethylene glycol	20 ml
Potassium sulfite	3.0 g
Potassium carbonate	30.0 g
Hydroxylamine sulfate	4.0 g
Polyphosphoric acid (TPPS)	3.0 g
Color developing agent (3-Methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)aniline sulfate)	7.0 g
Optical brightening agent (4,4'-diamino-stylbene disulfonic acid derivative)	1.5 g
Potassium hydroxide	3.0 g

Made up to 1 liter in total with addition of water and adjusted to pH to 10.40 with potassium hydroxide or sulfuric acid.

(Amount of the color developing replenishing solution)

320 ml/m^2

The results are shown in Table 4.

Table 4

Experiment No.	Light-sensitive material	Surfactant	Amount of surfactant added (g/l)	Contamination at rack and roller portions	Stain at unexposed portion: Density difference of (without addition - after addition) (440 nm)	Stain at unexposed portion: Density difference of (without addition - after addition) (640 nm)	Developability
4 - 1	(1)	None	—	XX	0.0	0.0	100
4 - 2		II - 5	0.2	XX	0.005	0.001	100
4 - 3			0.5	○	0.035	0.007	101
4 - 4			2.0	◎	0.059	0.015	102
4 - 5			25.0	◎	0.060	0.017	112
4 - 6		II - 32	0.2	XX	0.007	0.001	100
4 - 7			0.5	○	0.040	0.007	100
4 - 8			2.0	◎	0.072	0.014	102
4 - 9			25.0	◎	0.073	0.016	110
4 - 10		III - 5	0.2	XX	0.003	0.001	100
4 - 11			0.5	○	0.028	0.005	103
4 - 12			2.0	◎	0.043	0.007	105
4 - 13			25.0	◎	0.044	0.008	115

Table 4 (Contd)

Experiment No.	Light-sensitive material	Surfactant	Amount of surfactant added (g/l)	Contamination at rack and roller portions	Stain at unexposed portion Density difference of (without addition - after addition) (440 nm)	Stain at unexposed portion Density difference of (without addition - after addition) (640 nm)	Developability
4 - 14	(2)	None	—	△	0.0	0.0	100
4 - 15		II - 5	0.2	◎	0.002	0.001	105
4 - 16			0.5	◎	0.010	0.004	117
4 - 17			2.0	◎	0.018	0.008	123
4 - 18			25.0	◎	0.019	0.008	135
4 - 19		II - 32	0.2	◎	0.004	0.001	106
4 - 20			0.5	◎	0.012	0.004	119
4 - 21			2.0	◎	0.021	0.008	130
4 - 22			25.0	◎	0.022	0.009	142
4 - 23		III - 5	0.2	◎	0.002	0.001	104
4 - 24			0.5	◎	0.010	0.003	113
4 - 25			2.0	◎	0.015	0.005	121
4 - 26			25.0	◎	0.016	0.006	133

Table 4 (Contd)

Experiment No.	Light-sensitive material	Surfactant	Amount of surfactant added (g/l)	Contamination at rack and roller portions	Stain at unexposed portion: Density difference of (without addition - after addition) (440 nm)	Stain at unexposed portion: Density difference of (without addition - after addition) (640 nm)	Developability
4 - 27	(1)	I - 12	0.2	XX	0.006	0.003	100
4 - 28			0.5	○	0.045	0.014	100
4 - 29			2.0	◎	0.076	0.027	100
4 - 30			25.0	◎	0.076	0.028	108
4 - 31		I - 14	0.2	XX	0.007	0.003	100
4 - 32			0.5	○	0.048	0.015	100
4 - 33			2.0	◎	0.081	0.029	100
4 - 34			25.0	◎	0.082	0.031	109
4 - 35	(2)	I - 12	0.2	◎	0.002	0.001	102
4 - 36			0.5	◎	0.015	0.008	111
4 - 37			2.0	◎	0.028	0.013	120
4 - 38			25.0	◎	0.029	0.014	128
4 - 39		I - 14	0.2	◎	0.002	0.001	102
4 - 40			0.5	◎	0.017	0.008	110
4 - 41			2.0	◎	0.030	0.014	118
4 - 42			25.0	◎	0.032	0.015	125

As clearly seen from Table 4, in the light-sensitive material (1) composed mainly of silver chloride, stain at the unexposed portion or contamination at the rack or roller could be removed without affecting substantially no effect in developability even when the surfactant had been added. To the contrary, in the light-sensitive material (2) composed mainly of silver bromide, it can be admitted that improving effect against stain at the unexposed portion is not remarkable the reason of which could be considered due to a high sulfite concentration, whereas an amount of the surfactant added is markedly affect to the developability. Also, it is clear that when the surfactant of the present invention is added with an amount of 25 g, such an addition affects to the developability.

Example 6

By using the same color paper as in Example 1 and the same processing solutions as in Example 2, the running processing was carried out in the same manner as in Example 1 except for fixedly using the water-soluble surfactant to be added in the color developing tank solution and replenishing solution therefor to the exemplary compound II - 36 and changing a replenishing amount to the color developing tank to those shown in Table 5, contamination at a rack or roller portion in the color developing tank of the automatic developer, and stain at the unexposed portion were evaluated in the same manner as in Example 2.

Provided that as for the stain at the unexposed portion, it was measured by using a sample without adding the surfactant at each replenishing amount as the standard.

Table 5

Experiment No.	Replenishing amount to color developing tank	Concentration of surfactant (II-36) to be added to color developing tank solution and replenishing solution (mole/l)	Contamination at rack and roller portions	Stain at unexposed portion Density difference of (without addition - after addition)	
				(440 nm)	(640 nm)
5 - 1	20	0	XX	0.0	0.0
5 - 2		0.2	XX	0.013	0.002
5 - 3		0.4	XX	0.023	0.004
5 - 4		0.5	△	0.051	0.009
5 - 5		1.0	○	0.079	0.014
5 - 6		10	○	0.082	0.016
5 - 7		20	○	0.083	0.016
5 - 8	80	0	XX	0.0	0.0
5 - 9		0.2	XX	0.011	0.002
5 - 10		0.4	XX	0.011	0.003
5 - 11		0.5	○	0.047	0.010
5 - 12		1.0	◎	0.075	0.014
5 - 13		10	◎	0.078	0.015
5 - 14		20	◎	0.080	0.015
5 - 15	120	0	XX	0.0	0.0
5 - 16		0.2	X	0.008	0.002
5 - 17		0.4	X	0.017	0.003
5 - 18		0.5	◎	0.039	0.008

Table 5 (Contd)

Experiment No.	Replenishing amount to color developing tank	Concentration of surfactant (II-36) to be added to color developing tank solution and replenishing solution (mole/l)	Contamination at rack and roller portions	Stain at unexposed portion Density difference of (without addition - after addition) (440 nm)	(640 nm)
5 - 19	120	1.0	◎	0.062	0.012
5 - 20		10	◎	0.068	0.013
5 - 21		20	◎	0.070	0.014
5 - 22	200	0	X	0.0	0.0
5 - 23		0.2	X	0.005	0.001
5 - 24		0.4	△	0.012	0.002
5 - 25		0.5	◎	0.027	0.008
5 - 26		1.0	◎	0.049	0.010
5 - 27		10	◎	0.054	0.012
5 - 28		20	◎	0.055	0.012
5 - 29	320	0	X	0.0	0.0
5 - 30		0.2	△	0.004	0.001
5 - 31		0.4	○	0.009	0.002
5 - 32		0.5	◎	0.020	0.007
5 - 33		1.0	◎	0.037	0.009
5 - 34		10	◎	0.044	0.009
5 - 35		20	◎	0.045	0.009

As clearly seen from Table 5, it can be understood that when the water-soluble surfactant is added with an amount within the range of the present invention, contamination at a rack or roller portion and stain at the unexposed portion could be removed markedly even in the system wherein the replenishing amount to the color developing tank was small.

It can be also understood that the effects of the present invention, particularly improved effect in stain at the unexposed portion becomes large as the replenishing amount becomes little.

Also, by using I - 2, 9, 11, 12, 14, 18, 23, II - 4, 27, 32, 33, 36, 37, 72, III - 5, V - 1, VI - 1, VII - 1 or X - 1 instead of the exemplary compound II - 36, the same experiment was carried out to obtain good results.

Particularly, when the compound represented by the formula (I) is used, remarkable effects to cyan stain at the unexposed portion can be obtained.

Example 7

When a concentration of the color developing agent in Example 6 was increased to 6.5, 8.0 and 10.0 g, respectively, stain at the unexposed portion becomes large. However, when the surfactant of the present invention was used, improved effect in stain at the unexposed portion becomes remarkable. This tendency is the same as in the surfactant used in Example 1.

Example 8

By using the same color paper as in Example 1 and the same processing solutions as in Example 2, the running processing was carried out in the same manner as in Example 1 except for fixedly using the water-soluble surfactant to be added in the color developing tank solution and replenishing solution therefor to the exemplary compound I - 23 and changing color developing processing conditions to those shown in Table 6, contamination at a rack or roller portion in the color developing tank of the automatic developer, and stain at the unexposed portion were evaluated in the same manner as in Example 2.

(Color developing processing solution)

Processing steps	Color developing processing time	Color developing temperature
(1)	3 min	33 °C
(2)	1 min	35 °C
(3)	45 sec	35 °C
(4)	20 sec	39 °C

Table 6

Experiment No.	Processing step	Amount of surfactant added (g/l)	Contamination at rack and roller portions	Stain at unexposed portion	
				(440 nm)	(640 nm)
6 - 1	(1)	0.2	XX	0.004	0.001
6 - 2		0.5	◎	0.040	0.005
6 - 3		2.0	◎	0.057	0.008
6 - 4	(2)	0.2	XX	0.005	0.002
6 - 5		0.5	◎	0.050	0.007
6 - 6		2.0	◎	0.070	0.010
6 - 7	(3)	0.2	XX	0.006	0.003
6 - 8		0.5	◎	0.053	0.010
6 - 9		2.0	◎	0.072	0.013
6 - 10	(4)	0.2	XX	0.009	0.005
6 - 11		0.5	○	0.069	0.012
6 - 12		2.0	◎	0.077	0.015

As clearly seen from Table 6, it can be understood that as the processing becomes more rapid, the effect of the present invention, particularly against stain at the unexposed portion becomes more marked.

This tendency was the same in the surfactants used in Example 1 and the exemplary compound I - 9, 11, 12, 14, 18, 23, II - 10, 25, 36, 39, 40, 58, III - 4 or V - 5.

Example 9

On a paper support laminated with a polyethylene on the both surfaces thereof were provided the following layers to prepare a multi-layer color printing paper having the following layer constitution. The coating solutions were prepared as shown below.

Preparation of the first layer coating solution

To 20.1 g of yellow coupler (Y - 2), 4.5 g of a color image stabilizer (ST - 6) and 0.8 g of a color image stabilizer (ST - 7) were added 28.0 cc of ethyl acetate and 8.0 g of a solvent (Sol - 4) to dissolve them, and the solution was emulsifed and dispersed in 200 cc of a 10 % of gelatin aqueous solution containing 10 cc of a 10 % sodium dodecylbenzenesulfonate solution.

On the other hand, an emulsion was prepared by effecting sulfur sensitization and gold sensitization after adding two kinds of the blue-sensitive sensitizing dyes (D - 5 and D - 6) shown below to silver bromide emulsion (cubic with grain size of 0.83 μm and variation coefficient of 0.05, which contains 1 mole % of silver bromide based on the whole grain at part of the grain surface localized).

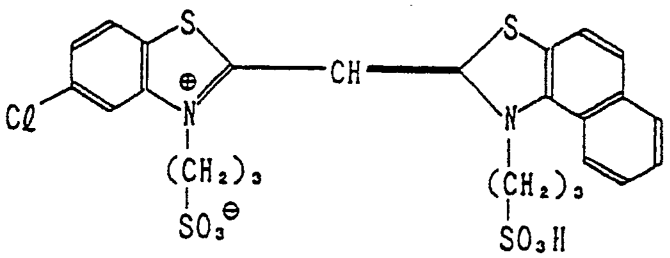
The above emulsified dispersion and the emulsion were mixed and dissolved, and the first layer coating solution was prepared so as to have a composition as shown below. Coating solutions for the second to the seventh layers were also prepared in the same manner as in the preparation of the first layer coating solution.

As the gelatin hardener for the respective layers, 1-oxy-3,5-dichloro-s-triazine sodium salt was used.

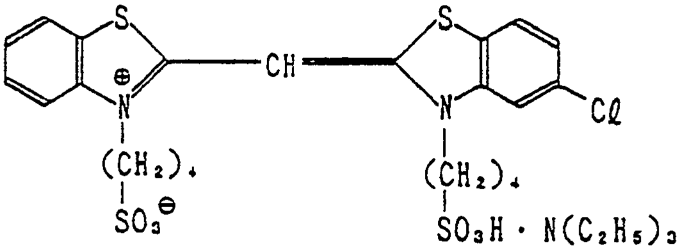
As the spectral sensitizing dye for each layer, the following were used.

(Blue-sensitive emulsion layer)

D - 5



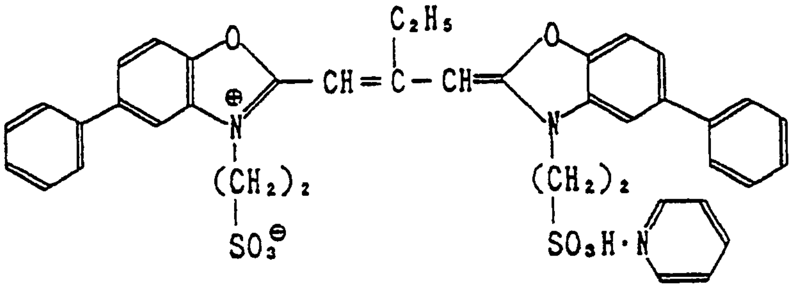
D - 6



(the above two kinds were added each 2.5 x 10^{-4} mole per mole of silver halide)

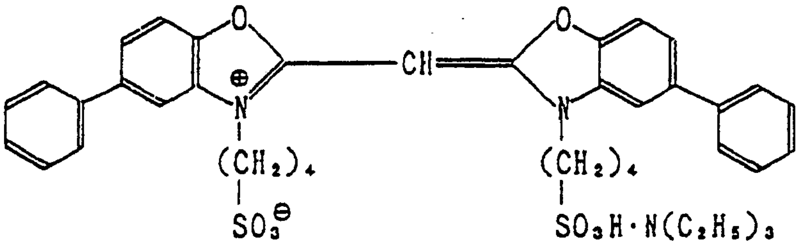
(Green-sensitive emulsion layer)

D - 7



(added with an amount of 3.5 x 10^{-4} mole per mole of silver halide)

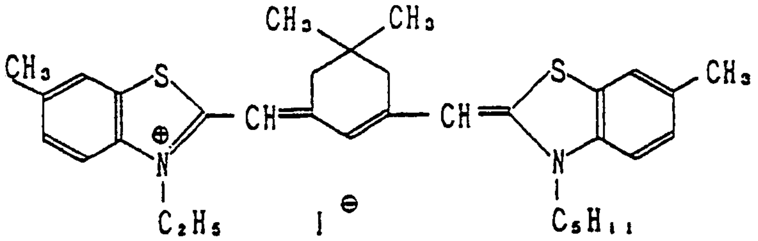
D - 8



(added with an amount of 7.0 x 10^{-5} mole per mole of silver halide)

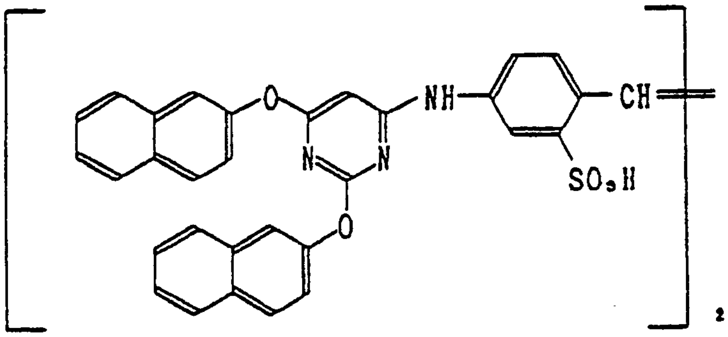
(Red-sensitive emulsion layer)

D - 9



(added with an amount of 0.9 x 10^{-4} mole per mole of silver halide)

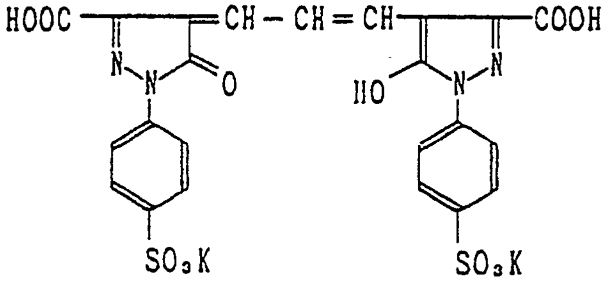
With respect to the red-sensitive emulsion layer, the following compound was added with an amount of 2.5 x 10-3 mole per mole of silver halide.



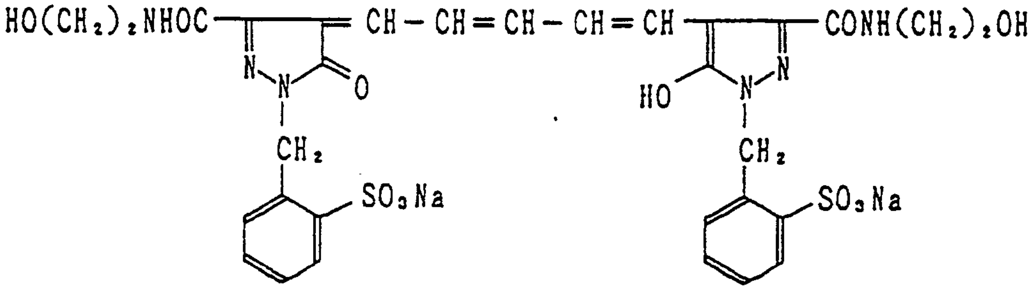
Also, to the blue-sensitive emulsion layer, the green-sensitive emulsion layer and the red-sensitive emulsion layer, 1-(5-methylureidophenyl)-5-mercaptotetrazole with amounts of 8.0 x 10^{-5} mole, 8.0 x 10^{-4} mole and 2.0 x 10^{-4} mole, per mole of silver halide, respectively.

As the irradiation preventive dye, the following were used.

A I - 4



A I - 5



In the following, compositions of each layer were shown. The numeral shows a coating amount (g/m^2). An amount of the silver halide emulsion is shown with a coated amount calculated in terms of silver.

Support

Polyethylene laminated paper

(Polyethylene at the side of the first layer contains white pigment (TiO_2) and bluish dye (ultramarine))

First layer (blue-sensitive layer)

Silver bromide emulsion mentioned above	0.35
Gelatin	1.85
Yellow coupler (Y - 2)	0.80
ST - 6	0.20
ST - 7	0.05
Solvent (Sol - 4)	0.35

Second layer

Gelatin	1.00
HQ - 1	0.09
Solvent (Sol - 5)	0.20
Solvent (Sol - 6)	0.05

Third layer

Silver bromide emulsion	0.25
(cubic with grain size of 0.45 μm and variation coefficient of 0.10, which contains 1 mole % of silver bromide based on the whole grain at part of the grain surface localized)	
Gelatin	1.25
M - 2	0.30
ST - 8	0.10
ST - 9	0.05
Solvent (Sol - 7)	0.30
Solvent (Sol - 8)	0.15

Fourth layer

Gelatin	1.50
UV - 3	0.50
HQ - 1	0.05
Solvent (Sol - 9)	0.25

Fifth layer (red-sensitive layer)

Silver bromide emulsion (cubic with grain size of 0.35 µm and variation coefficient of 0.09, which contains 1.4 mole % of silver bromide based on the whole grain at part of the grain surface localized)	0.19
Gelatin	1.30
C - 3	0.30
ST - 10	0.18
ST - 7	0.30
ST - 9	0.05
Solvent (Sol - 6)	0.40

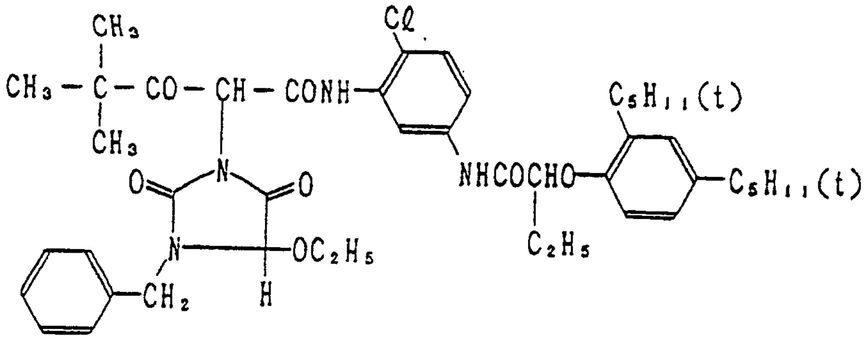
Sixth layer

Gelatin	0.50
UV - 1	0.15
HQ - 1	0.20
Solvent (Sol - 9)	0.07

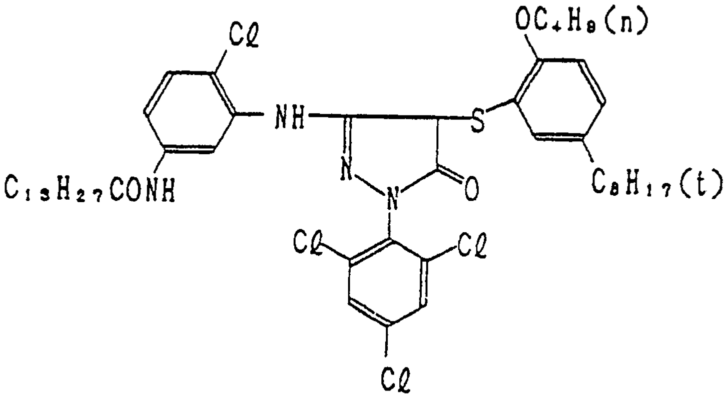
Seventh layer

Gelatin	1.40
Acryl-modified copolymer (modified degree of 17 %) of polyvinyl alcohol	0.15
Liquid paraffin	0.02

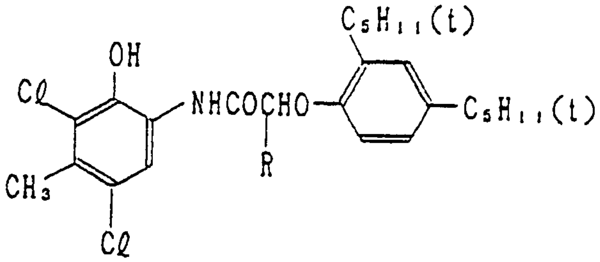
Y – 2



M – 2

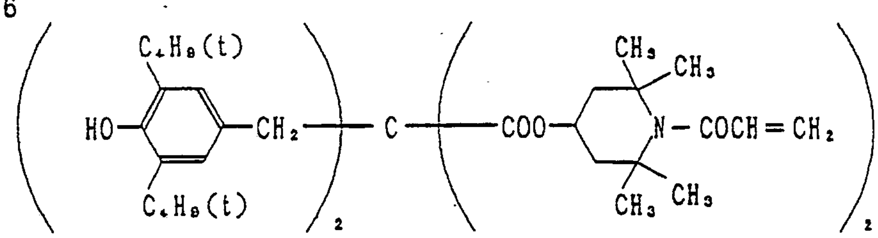


C – 3

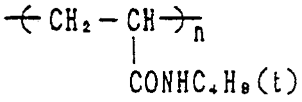


Mixture (weight ratio) of R = H, C_2H_5 and C_4H_9 of 1 : 3 : 6

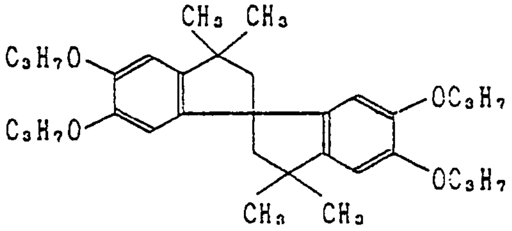
ST－6



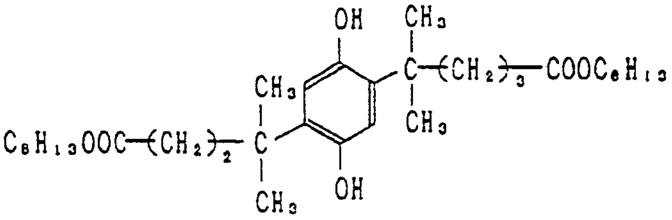
ST－7



ST－8

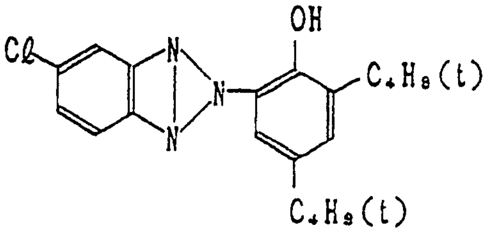


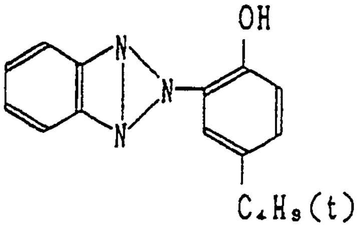
ST－9

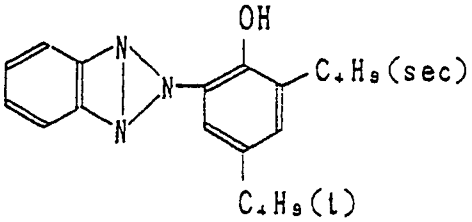


ST-10

Mixture (weight ratio) of



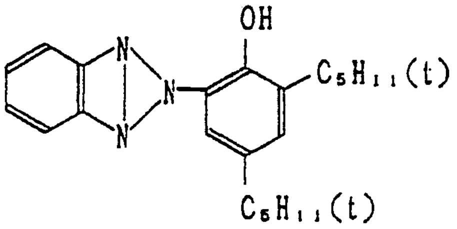


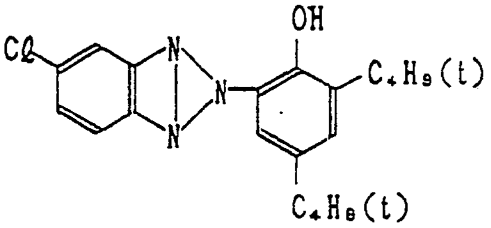


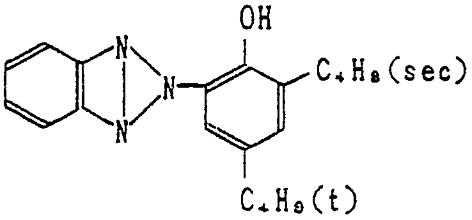
with the ratio of 4 : 2 : 4

UV－3

Mixture (weight ratio) of





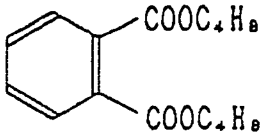


with the ratio of 4 : 2 : 4

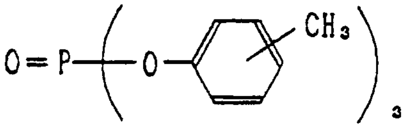
Sol-4

$$O=P\text{-}(O-C_9H_{19}(iso))_3$$

Sol-5



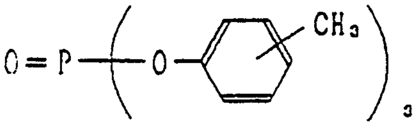
Sol-6



Sol-7

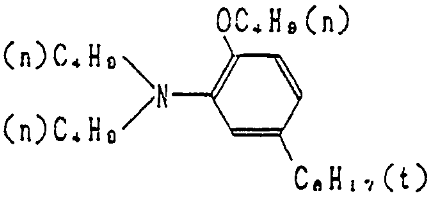
Mixture (volume ratio) of

$$O=P\text{-}(OCH_2CH(C_2H_5)C_4H_9)_3$$

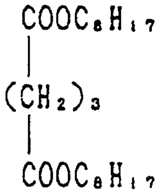


with the ratio of 3 : 7

Sol-8



Sol-9



$$COOC_8H_{17}-(CH_2)_3-COOC_8H_{17}$$

When the light-sensitive silver halide material prepared as mentioned above was subjected to the same evaluations as in Example 6, substantially the same results could be obtained.

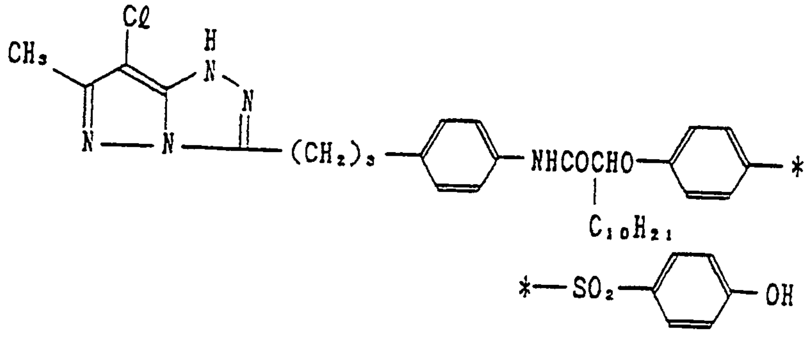
Example 10

The same evaluations were carried out in the same manner as in Example 6 except for changing the magenta coupler M - 1 used in Example 1 to the magenta couplers M - 2 to M - 11 and Comparative magenta couplers MR - 1 and MR - 2 mentioned below, respectively, or changing the cyan couplers C - 1 and C - 2 to C - 58, C - 76, C - 83 in the exemplary compounds mentioned at pages 76 to 124 of Japanese

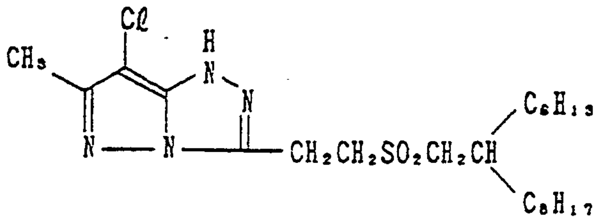
Patent Application No. 92655/1986, or CC - 9 and Comparative cyan couplers CCR - 1 and CCR - 2 in the exemplary compounds mentioned at pages 81 to 85 of the same, respectively.

As the results, as compared with Comparative magenta couplers and Comparative cyan couplers, samples of the present invention showed values 20 to 30 % lower in each of magenta stain and cyan stain than the comparative ones.

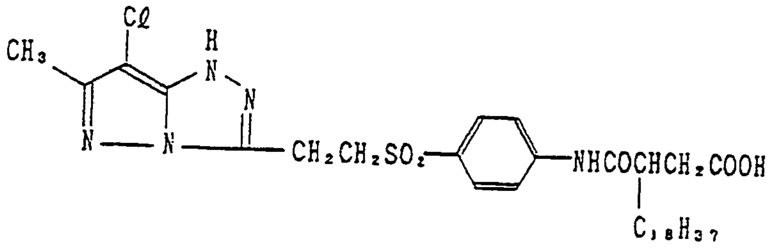
[M-2]



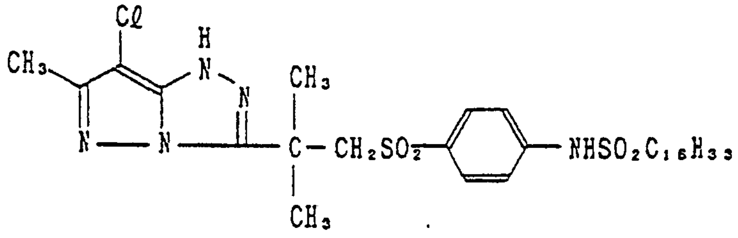
[M-3]



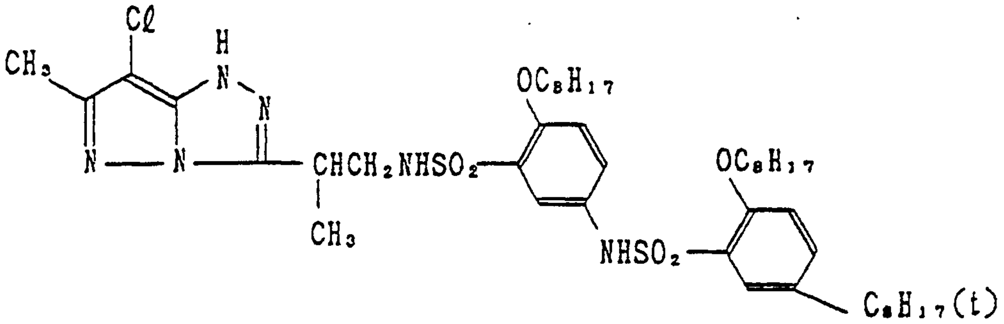
[M-4]



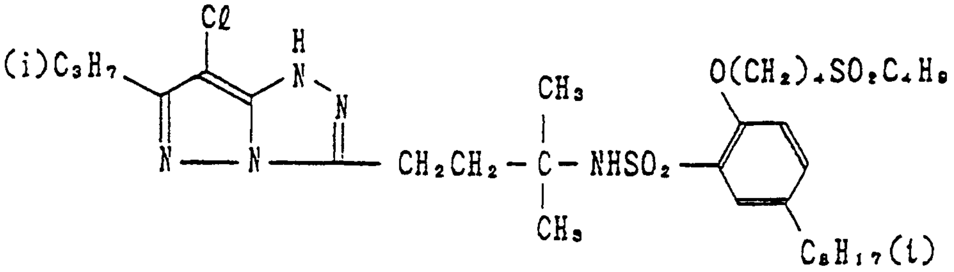
[M-5]



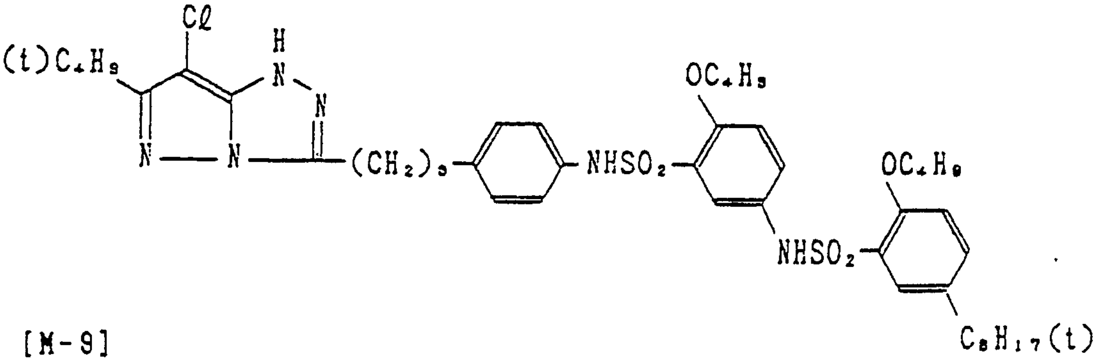
[M-6]


Cℓ
H
CH₃
N
N
N
N
OC₈H₁₇
CHCH₂NHSO₂
CH₃
OC₈H₁₇
NHSO₂
C₈H₁₇(t)

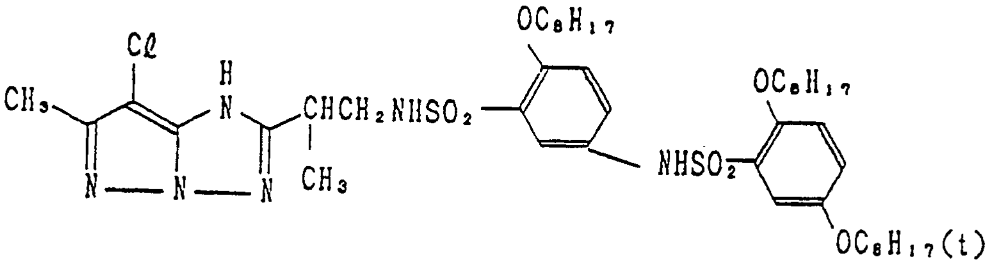
[M-7]


Cℓ
H
(i)C₃H₇
N
N
N
N
CH₃
O(CH₂)₄SO₂C₄H₉
CH₂CH₂
C
NHSO₂
CH₃
C₈H₁₇(t)

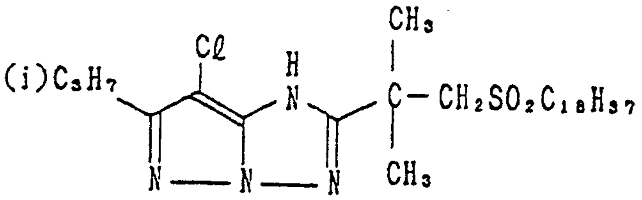
[M-8]


Cℓ
H
(t)C₄H₉
N
N
N
N
OC₄H₉
(CH₂)₃
NHSO₂
OC₄H₉
NHSO₂
C₈H₁₇(t)

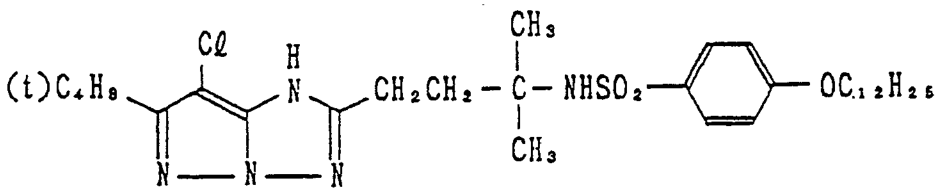
[M-9]


OC₈H₁₇
Cℓ
H
CH₃
N
CHCH₂NHSO₂
CH₃
N
N
N
OC₈H₁₇
NHSO₂
OC₈H₁₇(t)

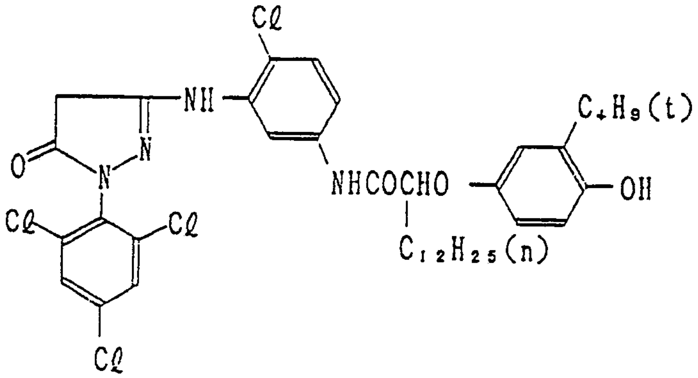
[M-10]



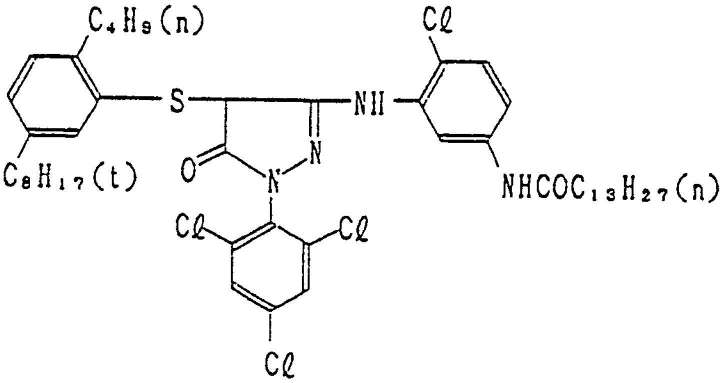
[M-11]



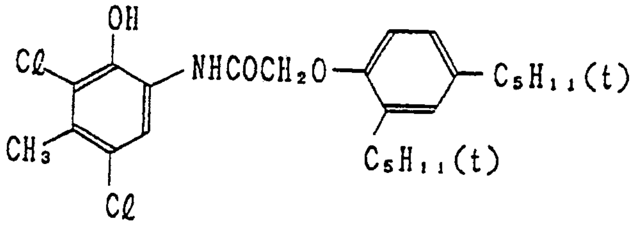
(MR-1)



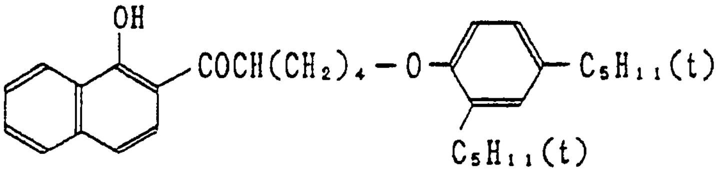
(MR-2)



(CCR-1)



(CCR-2)



Example 11

In the same manner as in Example 1 except for using the compounds shown in Table 7 instead of N,N-diethylhydroxylamine in the color developing tank solution and the replenishing solution in Example 1, processing was carried out to evaluate the contamination at the rack and roller portions and stain at the unexposed portion in the same manner as in Example 1. As for the stain at the unexposed portion, evaluation was carried out by measuring spectral reflective densities at 440 nm and 640 nm. The results are shown in Table 7.

Table 7

Experiment No.	Compound to be added instead of N,N-diethyl hydroxylamine (5 g/l)	Surfactant (2.5 g/l)	Contamination at rack and roller portions	Stain at unexposed portion	
				440 nm	660 nm
7 - 1	None	None	XX	0.180	0.125
7 - 2	Hydroxylamine sulfate		XX	0.174	0.122
7 - 3	A - 1		XX	0.145	0.108
7 - 4	A - 2		XX	0.147	0.107
7 - 5	A - 18		XX	0.148	0.109
7 - 6	A - 21		XX	0.146	0.108
7 - 7	None	I - 14	△	0.102	0.103
7 - 8	Hydroxylamine sulfate		○	0.097	0.095
7 - 9	A - 1		◎	0.062	0.080
7 - 10	A - 2		◎	0.064	0.081
7 - 11	A - 18		◎	0.063	0.082
7 - 12	A - 21		◎	0.063	0.081

As clearly seen from Table 7, by adding the water-soluble surfactant of the present invention to the color developing solution and adding the compound (A) described in the specification thereto, it can be understood that contamination at the roller and rack portions as well as stain at the unexposed portion can further be improved.

Example 12

In the same manner as in Example 1 except for adding the compounds shown in Table 8 to the color developing tank solution and the replenishing solution, processing was carried out as in Example 1 to evaluate the contamination at the rack and roller portions and stain at the unexposed portion in the same manner as in Example 1. As for the stain at the unexposed portion, evaluation was carried out by measuring spectral reflective densities at 440 nm and 640 nm. The results are shown in Table 8.

Table 8

Experiment No.	Compound to be added (2 g/l)	Surfactane (2.5 g/l)	Contamination at rack and roller portions	Stain at unexposed portion	
				440 nm	640 nm
8 - 1	None	None	XX	0.145	0.108
8 - 2	E - 36		XX	0.138	0.107
8 - 3	E - 39		XX	0.139	0.107
8 - 4	E - 40		XX	0.137	0.107
8 - 5	E - 45		XX	0.138	0.108
8 - 6	None	I - 14	◎	0.062	0.080
8 - 7	E - 36		◎	0.052	0.077
8 - 8	E - 39		◎	0.053	0.078
8 - 9	E - 40		◎	0.050	0.077
8 - 10	E - 45		◎	0.053	0.078

As clearly seen from Table 8, it can be understood that by adding the water-soluble surfactant of the present invention to the color developing solution and adding the compounds shown in Table 8 to the same, contaminations of the roller and rack portions as well as stain at the unexposed portion, particularly the stain at the unexposed portion can be further improved.

Claims

1. A color developing solution for a light-sensitive silver halide color photographic material which comprises a sulfite concentration of 1.0×10^{-3} mole or lower per liter of the color developing solution and containing 0.5 to 20 g/ℓ of a water-soluble surfactant.

2. The solution of Claim 1 wherein said water-soluble surfactant is at least one of a nonionic surfactant and an anionic surfactant.

3. The solution of Claim 1 wherein an amount of said water-soluble surfactant is 1.0 to 10 g per liter of the color developing solution.

4. The solution of Claim 2 wherein said water-soluble surfactant is a compound represented by the following formula (I):

   $R^1X(E^1)_{\ell 1}\text{-}(E^2)_{m1}\text{-}(E^3)_{n1}\text{-}R^2$ (I)

   wherein R^1 represents a hydrogen atom, an aliphatic group or an acyl group, R^2 represents a hydrogen atom or an aliphatic group, E^1 represents ethylene oxide, E^2 represents propylene oxide, E^3 represents ethylene oxide, X represents an oxygen atom or a -R^3N- group where R^3 represents an aliphatic group, a hydrogen atom or $(E^1)_{\ell 2}\text{-}(E^2)_{m2}\text{-}(E^3)_{n2}\text{-}R^4$, where R4 represents a hydrogen atom or an aliphatic group, and ℓ1, ℓ2, ml, m2, n1 and n2 each represent a value of 0 to 300.

5. The solution of Claim 4 wherein said compound is selected from the group consisting of I - 1

$C_{12}H_{25}COO{(C_2H_4O)}_{10}\text{-}H$

I - 2

$C_9H_{19}COO{-}(C_2H_4O)_4{-}H$

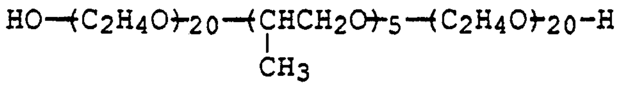
I - 3

$C_{12}H_{25}NH{-}(C_2H_4O)_{10}{-}H$

I - 4

$C_{12}H_{25}NH{-}(C_2H_4O)_{15}{-}H$

I - 5

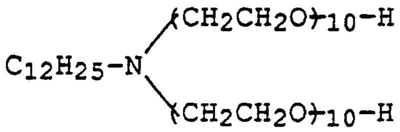


$HO{-}(C_2H_4O)_{20}{-}(\underset{\displaystyle CH_3}{CH}CH_2O)_5{-}(C_2H_4O)_{20}{-}H$

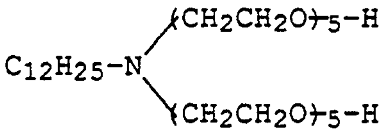
I - 6

$C_{12}H_{25}NHCH_2CH_2OH$

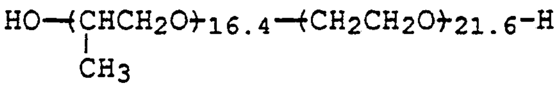
I - 7



I - 8

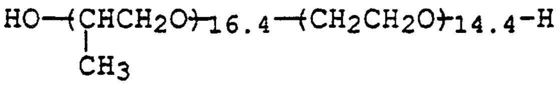


I - 9



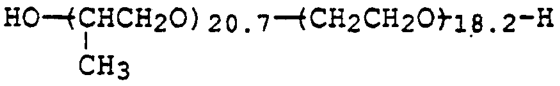
$HO{-}(\underset{\displaystyle CH_3}{CH}CH_2O)_{16.4}{-}(CH_2CH_2O)_{21.6}{-}H$

I - 10



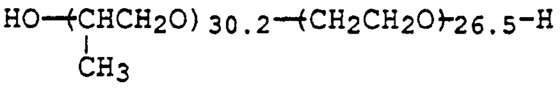
$HO{-}(\underset{\displaystyle CH_3}{CH}CH_2O)_{16.4}{-}(CH_2CH_2O)_{14.4}{-}H$

I - 11



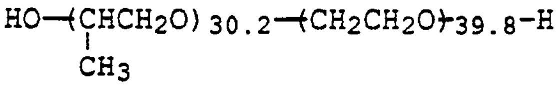
$HO{-}(\underset{\displaystyle CH_3}{CH}CH_2O)_{20.7}{-}(CH_2CH_2O)_{18.2}{-}H$

I - 12



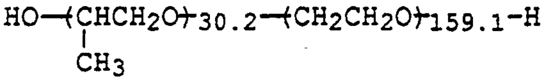
$HO{-}(\underset{\displaystyle CH_3}{CH}CH_2O)_{30.2}{-}(CH_2CH_2O)_{26.5}{-}H$

I - 13



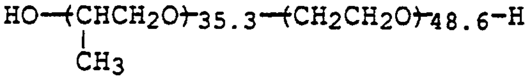
$HO{-}(\underset{\displaystyle CH_3}{CH}CH_2O)_{30.2}{-}(CH_2CH_2O)_{39.8}{-}H$

I - 14



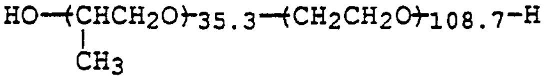
$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{30.2}-(CH_2CH_2O)_{159.1}-H$$

I - 15



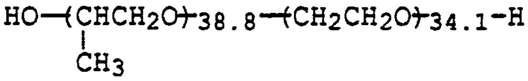
$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{35.3}-(CH_2CH_2O)_{48.6}-H$$

I - 16



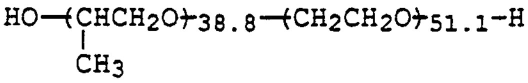
$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{35.3}-(CH_2CH_2O)_{108.7}-H$$

I - 17



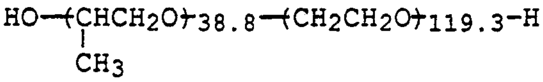
$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{38.8}-(CH_2CH_2O)_{34.1}-H$$

I - 18



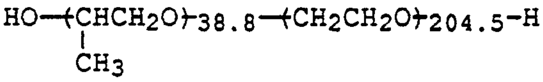
$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{38.8}-(CH_2CH_2O)_{51.1}-H$$

I - 19



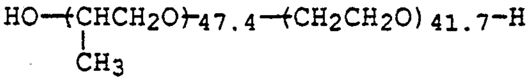
$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{38.8}-(CH_2CH_2O)_{119.3}-H$$

I - 20



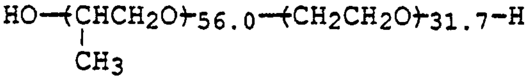
$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{38.8}-(CH_2CH_2O)_{204.5}-H$$

I - 21



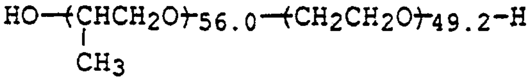
$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{47.4}-(CH_2CH_2O)_{41.7}-H$$

I - 22



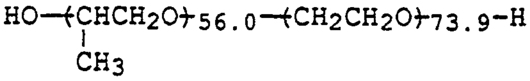
$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{56.0}-(CH_2CH_2O)_{31.7}-H$$

I - 23



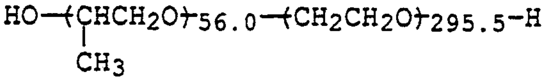
$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{56.0}-(CH_2CH_2O)_{49.2}-H$$

I - 24



$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{56.0}-(CH_2CH_2O)_{73.9}-H$$

I - 25

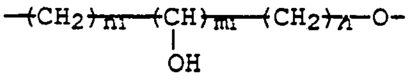


$$HO-(\underset{\underset{CH_3}{|}}{C}HCH_2O)_{56.0}-(CH_2CH_2O)_{295.5}-H$$

6. The solution of Claim 2 wherein said water-soluble surfactant is a compound selected from the group consisting of:

$$A_2\text{-O-}(B)_m\text{-}(C)_n\text{-}X_1 \qquad \text{(II)}$$

wherein A_2 represents a monovalent organic group such as an alkyl group having 6 to 50, preferably 6 to 35 carbon atoms and an aryl group substituted by an alkyl group having 3 to 35 carbon atoms or by an alkenyl group having 2 to 35 carbon atoms; B or C represents ethylene oxide or propylene oxide, or

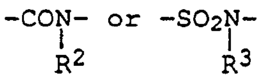


$$\text{-}(CH_2)_{n_1}\text{-}(\underset{OH}{CH})_{m_1}\text{-}(CH_2)_{\ell_1}\text{-O-}$$

where n_1, m_1 and ℓ_1 each represent 0, 1, 2 or 3; m and n each represent an integer of 0 to 100; X_1 represents a hydrogen atom, an alkyl group, an aralkyl group or an aryl group,

$$R^1\text{-}(X\text{-}L)_\ell\text{-}COOM \qquad \text{(III)}$$

wherein R^1 represents an aliphatic group; X represents

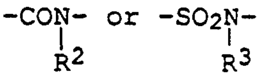


$$\text{-}\underset{R^2}{CON}\text{- or -}SO_2\underset{R^3}{N}\text{-}$$

where R^2 and R^3 each represent a hydrogen atom or the groups defined in R^1; ℓ is 0 or 1, M represents a hydrogen atom, an alkali metal, an ammonium ion or an organic ammonium ion; and L represents an alkylene group,

$$R^1\text{-}(X\text{-}L)_\ell\text{-}(Y)_{m'}SO_3M \qquad \text{(IV)}$$

wherein R^1 represents an aliphatic group; X represents

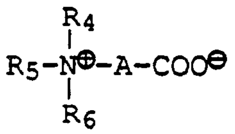


$$\text{-}\underset{R^2}{CON}\text{- or -}SO_2\underset{R^3}{N}\text{-}$$

where R^2 and R^3 each represent a hydrogen atom or the groups defined in R^1; and m' are each 0 or 1; L represents an alkylene group; Y represents an oxygen atom and M represents a hydrogen atom, an alkali metal or a monovalent cation,

$$A_2\text{-O-}(CH_2CH_2O)_n\text{-}SO_3M \qquad \text{(V)}$$

wherein M represents a hydrogen atom, an alkali metal or a monovalent cation; n is 1 to 100; and A_2 represents a monovalent organic group or an aryl group substituted by an alkyl group having 3 to 20 carbon atoms,



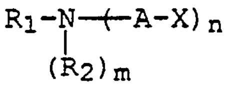
(VI)

$$R_5\text{-}\overset{R_4}{\underset{R_6}{N^{\oplus}}}\text{-A-COO}^{\ominus}$$

wherein R_4, R_5 and R_6 each represent a substituted or unsubstituted alkyl group, and R_4 and R_5, or R_5 and R_6 may form a ring, respectively; and A represents

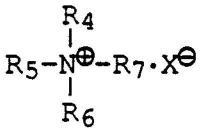
$$-(CH)_n-$$

where n is an integer of 1, 2 or 3,



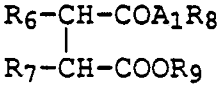
$$R_1-\underset{(R_2)_m}{\underset{|}{N}}-(-A-X)_n \qquad \text{(VII)}$$

wherein R_1 has the same meaning as A_2 in the formula (II); R_2 represents a hydrogen atom or an alkyl group; m and n are each 0, 1 or 2; A represents an alkyl group or a substituted or unsubstituted aryl group; and X is -COOM or -SO_3H where M is a hydrogen atom, an alkali metal or a monovalent cation,



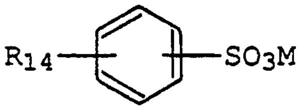
$$R_5-\overset{\overset{R_4}{|}}{\underset{\underset{R_6}{|}}{N^{\oplus}}}-R_7\cdot X^{\ominus} \qquad \text{(VIII)}$$

wherein R_4, R_5, R_6 and R_7 each represent a hydrogen atom, a substituted or unsubstituted alkyl group or a phenyl group; and $X^{\ominus}$ represents an anion of a halogen atom, a hydroxyl group, a sulfate group, a carbonate group, a nitrate group, an acetate group or a p-toluenesulfonate group,

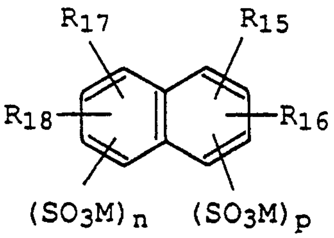


$$\begin{array}{l} R_6-CH-COA_1R_8 \\ \qquad | \\ R_7-CH-COOR_9 \end{array} \qquad \text{(IX)}$$

wherein one of R_6 and R_7 represents a hydrogen atom or an alkyl group and the other represents a group represented by the formula: -SO_3M where M represents a hydrogen atom, an alkali metal or a monovalent cation; A_1 represents an oxygen atom or a group represented by the formula: -NR_{10}- where R_{10} represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms; and R_8 and R_9 each represent an alkyl group having 4 to 30 carbon atoms, provided that the alkyl group represented by R_8, R_9 or R_{10} may be substituted by a fluorine atom,



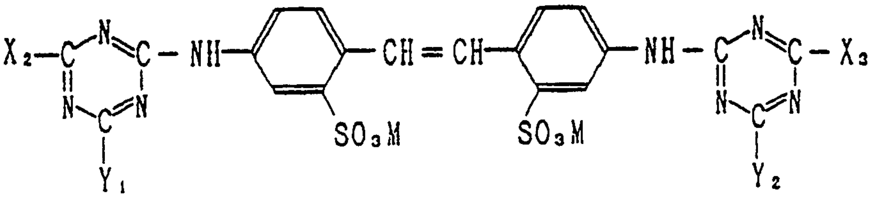
(X)



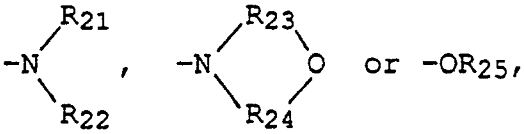
(XI)

wherein R_{14}, R_{15}, R_{16}, R_{17} and R_{18} each represent a hydrogen atom or an alkyl group, M has the same meaning with M as defined in the formula (III), and n and p are each 0 or an integer of 1 to 4 and numbers satisfying $1 \leqq n + p \leqq 8$.

7. The solution of Claim 1 wherein said solution further contains a triazinylstylbene type optical brightening agent represented by the following formula:



wherein X_2, X_3, Y_1 and Y_2 each represent a hydroxyl group, a halogen atom such as chlorine and bromine, an alkyl group, an aryl group,



where R_{21} and R_{22} each represent a hydrogen atom, an alkyl group which may have a substituent(s), or a substituted or unsubstituted aryl group, R_{23} and R_{24} each represent a substituted or unsubstituted alkylene group, R_{25} represents a hydrogen atom, a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group, and M represents a cation.

8. A processing method of a light-sensitive silver halide color photographic material which comprises processing the light-sensitive silver halide color photographic material with a color developing solution after imagewise exposure, the improvement wherein said color developing solution contains 1.0×10^{-3} mole or less of a sulfite per liter of the color developing solution and contains 0.5 to 20 g/ℓ of a water-soluble surfactant.

9. The method of Claim 8 wherein an amount of said water-soluble surfactant is 1.0 g to 10 g per liter of the color developing solution.

10. The method of Claim 8 wherein a replenishing amount of said color developing solution is 120 ml or less per 1 m^2 of the light-sensitive silver halide color photographic material.

11. The method of Claim 8 wherein said water-soluble surfactant is at least one of a nonionic surfactant and an anionic surfactant.

12. The method of Claim 11, wherein said water-soluble surfactant is a compound represented by the following formula (I):

$$R^1X(E^1)_{\ell 1}\text{-}(E^2)_{m1}\text{-}(E^3)_{n1}\text{-}R^2 \qquad \text{(I)}$$

wherein R^1 represents a hydrogen atom, an aliphatic group or an acyl group, R^2 represents a hydrogen atom or an aliphatic group, E^1 represents ethylene oxide, E^2 represents propylene oxide, E^3 represents ethylene oxide, X represents an oxygen atom or a $-R^3N-$ group where R^3 represents an aliphatic group, a hydrogen atom or $(E^1)_{\eta}\text{-}(E^2)_{m2}\text{-}(E^3)_{n2}\text{-}R^4$, where R4 represents a hydrogen atom or an aliphatic group, and ℓ1, ℓ2, ml, m2, n1 and n2 each represent a value of 0 to 300.

13. The method of Claim 12, wherein said compound is selected from the group consisting of

I - 1

$C_{12}H_{25}COO-(C_2H_4O)_{10}-H$

I - 2

$C_9H_{19}COO-(C_2H_4O)_4-H$

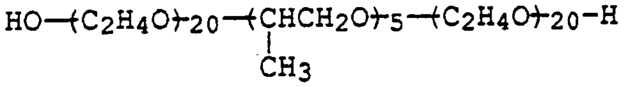
I - 3

$C_{12}H_{25}NH-(C_2H_4O)_{10}-H$

I - 4

$C_{12}H_{25}NH-(C_2H_4O)_{15}-H$

I - 5

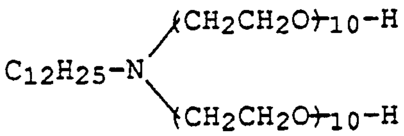


$HO{-}(C_2H_4O)_{20}{-}(\underset{CH_3}{\underset{|}{C}}HCH_2O)_5{-}(C_2H_4O)_{20}{-}H$

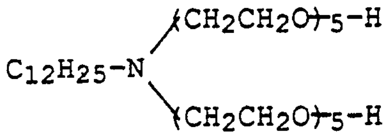
I - 6

$C_{12}H_{25}NHCH_2CH_2OH$

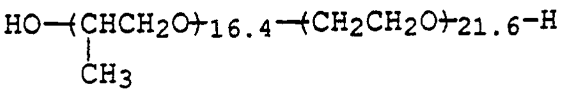
I - 7



I - 8

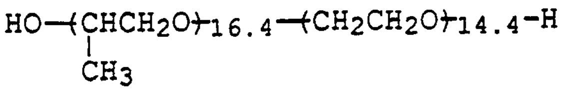


I - 9



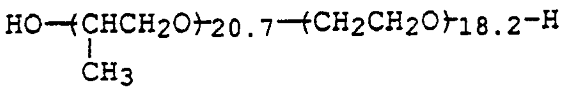
$HO{-}(\underset{CH_3}{\underset{|}{C}}HCH_2O)_{16.4}{-}(CH_2CH_2O)_{21.6}{-}H$

I - 10



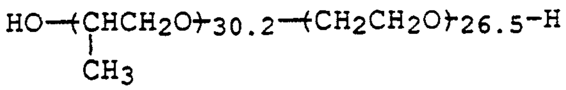
$HO{-}(\underset{CH_3}{\underset{|}{C}}HCH_2O)_{16.4}{-}(CH_2CH_2O)_{14.4}{-}H$

I - 11



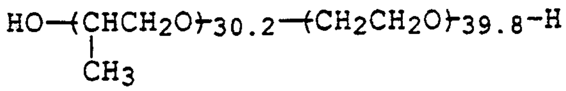
$HO{-}(\underset{CH_3}{\underset{|}{C}}HCH_2O)_{20.7}{-}(CH_2CH_2O)_{18.2}{-}H$

I - 12



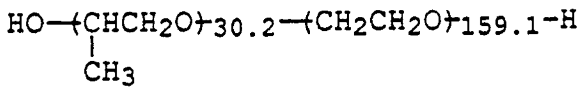
$HO{-}(\underset{CH_3}{\underset{|}{C}}HCH_2O)_{30.2}{-}(CH_2CH_2O)_{26.5}{-}H$

I - 13



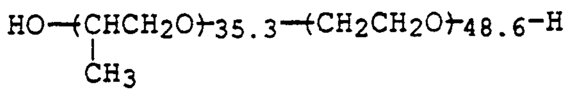
$HO{-}(\underset{CH_3}{\underset{|}{C}}HCH_2O)_{30.2}{-}(CH_2CH_2O)_{39.8}{-}H$

I - 14



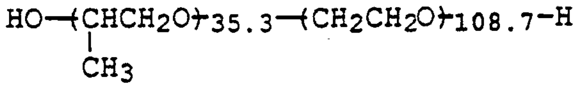
$HO{-}(\underset{CH_3}{\underset{|}{C}}HCH_2O)_{30.2}{-}(CH_2CH_2O)_{159.1}{-}H$

I - 15



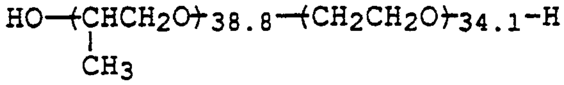
$HO{-}(\underset{CH_3}{\underset{|}{C}}HCH_2O)_{35.3}{-}(CH_2CH_2O)_{48.6}{-}H$

I - 16



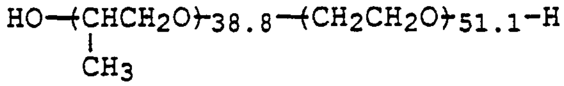
$HO-(\underset{CH_3}{CH}CH_2O)_{35.3}-(CH_2CH_2O)_{108.7}-H$

I - 17



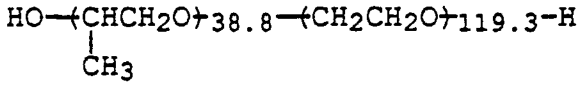
$HO-(\underset{CH_3}{CH}CH_2O)_{38.8}-(CH_2CH_2O)_{34.1}-H$

I - 18



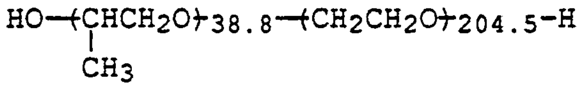
$HO-(\underset{CH_3}{CH}CH_2O)_{38.8}-(CH_2CH_2O)_{51.1}-H$

I - 19



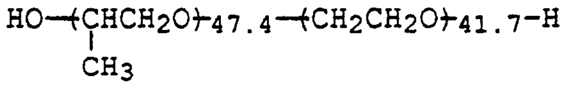
$HO-(\underset{CH_3}{CH}CH_2O)_{38.8}-(CH_2CH_2O)_{119.3}-H$

I - 20



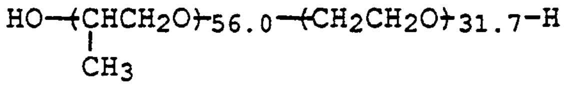
$HO-(\underset{CH_3}{CH}CH_2O)_{38.8}-(CH_2CH_2O)_{204.5}-H$

I - 21



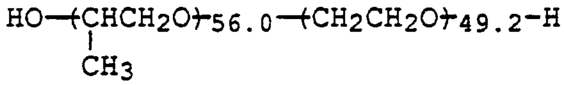
$HO-(\underset{CH_3}{CH}CH_2O)_{47.4}-(CH_2CH_2O)_{41.7}-H$

I - 22



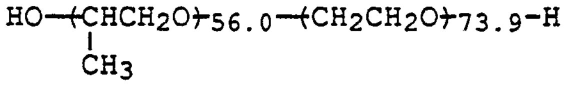
$HO-(\underset{CH_3}{CH}CH_2O)_{56.0}-(CH_2CH_2O)_{31.7}-H$

I - 23



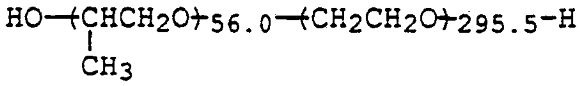
$HO-(\underset{CH_3}{CH}CH_2O)_{56.0}-(CH_2CH_2O)_{49.2}-H$

I - 24



$HO-(\underset{CH_3}{CH}CH_2O)_{56.0}-(CH_2CH_2O)_{73.9}-H$

I - 25

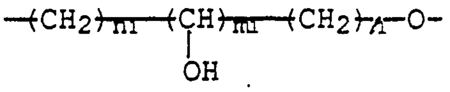


$HO-(\underset{CH_3}{CH}CH_2O)_{56.0}-(CH_2CH_2O)_{295.5}-H$

14. The method of Claim 11 wherein said water-soluble surfactant is a compound selected from the group consisting of:

$A_2\text{-O-}(B)_m\text{-}(C)_n\text{-}X_1$ (II)

wherein A_2 represents a monovalent organic group such as an alkyl group having 6 to 50, preferably 6 to 35 carbon atoms and an aryl group substituted by an alkyl group having 3 to 35 carbon atoms or by an alkenyl group having 2 to 35 carbon atoms; B or C represents ethylene oxide or propylene oxide, or

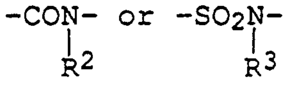


$$-(CH_2)_{n_1}-(\underset{\displaystyle OH}{\underset{|}{CH}})_{m_1}-(CH_2)_{\ell_1}-O-$$

where n_1, m_1 and ℓ_1 each represent 0, 1, 2 or 3; m and n each represent an integer of 0 to 100; X_1 represents a hydrogen atom, an alkyl group, an aralkyl group or an aryl group,

$$R^1-(X-L)_{\ell}-COOM \qquad (III)$$

wherein R^1 represents an aliphatic group; X represents

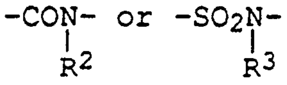


$$-CO\underset{\displaystyle R^2}{\underset{|}{N}}- \text{ or } -SO_2\underset{\displaystyle R^3}{\underset{|}{N}}-$$

where R^2 and R^3 each represent a hydrogen atom or the groups defined in R^1; ℓ is 0 or 1, M represents a hydrogen atom, an alkali metal, an ammonium ion or an organic ammonium ion; and L represents an alkylene group,

$$R^1-(X-L)_{\ell}-(Y)_{m'}SO_3M \qquad (IV)$$

wherein R^1 represents an aliphatic group; X represents

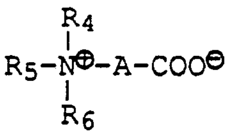


$$-CO\underset{\displaystyle R^2}{\underset{|}{N}}- \text{ or } -SO_2\underset{\displaystyle R^3}{\underset{|}{N}}-$$

where R^2 and R^3 each represent a hydrogen atom or the groups defined in R^1; ℓ and m' are each 0 or 1; L represents an alkylene group; Y represents an oxygen atom and M represents a hydrogen atom, an alkali metal or a monovalent cation,

$$A_2-O-(CH_2CH_2O)_n-SO_3M \qquad (V)$$

wherein M represents a hydrogen atom, an alkali metal or a monovalent cation; n is 1 to 100; and A_2 represents a monovalent organic group or an aryl group substituted by an alkyl group having 3 to 20 carbon atoms,



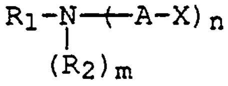
(VI)

$$R_5-\overset{\displaystyle R_4}{\overset{|}{\underset{\displaystyle R_6}{\underset{|}{N^{\oplus}}}}}-A-COO^{\ominus} \qquad (VI)$$

wherein R_4, R_5 and R_6 each represent a substituted or unsubstituted alkyl group, and R_4 and R_5, or R_5 and R_6 may form a ring, respectively; and A represents

$$-(CH)_n-$$

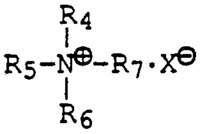
where n is an integer of 1, 2 or 3,



$$R_1-\underset{(R_2)_m}{\underset{|}{N}}-\!\!\!(-A-X)_n$$

(VII)

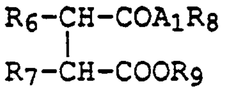
wherein R_1 has the same meaning as A_2 in the formula (II); R_2 represents a hydrogen atom or an alkyl group; m and n are each 0, 1 or 2; A represents an alkyl group or a substituted or unsubstituted aryl group; and X is -COOM or $-SO_3H$ where M is a hydrogen atom, an alkali metal or a monovalent cation,



$$R_5-\overset{R_4}{\underset{R_6}{N^{\oplus}}}-R_7\cdot X^{\ominus}$$

(VIII)

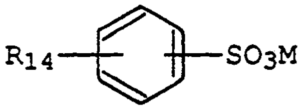
wherein R_4, R_5, R_6 and R_7 each represent a hydrogen atom, a substituted or unsubstituted alkyl group or a phenyl group; and $X^{\ominus}$ represents an anion of a halogen atom, a hydroxyl group, a sulfate group, a carbonate group, a nitrate group, an acetate group or a p-toluenesulfonate group,



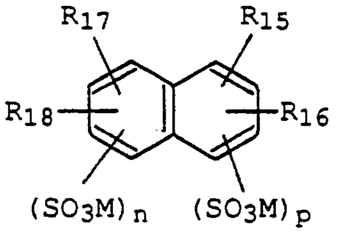
$$\begin{array}{l} R_6-CH-COA_1R_8 \\ \qquad\ | \\ R_7-CH-COOR_9 \end{array}$$

(IX)

wherein one of R_6 and R_7 represents a hydrogen atom or an alkyl group and the other represents a group represented by the formula: $-SO_3M$ where M represents a hydrogen atom, an alkali metal or a monovalent cation; A_1 represents an oxygen atom or a group represented by the formula: $-NR_{10}-$ where R_{10} represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms; and R_8 and R_9 each represent an alkyl group having 4 to 30 carbon atoms, provided that the alkyl group represented by R_8, R_9 or R_{10} may be substituted by a fluorine atom,



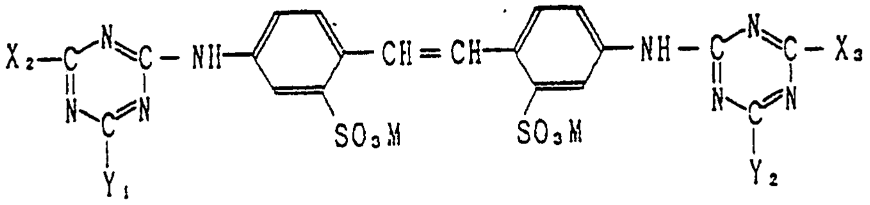
(X)



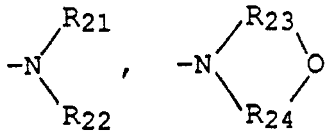
(XI)

wherein R_{14}, R_{15}, R_{16}, R_{17} and R_{18} each represent a hydrogen atom or an alkyl group, M has the same meaning with M as defined in the formula (III), and n and p are each 0 or an integer of 1 to 4 and numbers satisfying $1 \leqq n + p \leqq 8$.

15. The method of Claim 8 wherein said solution further contains a triazinylstylbene type optical brightening agent represented by the following formula:



wherein X_2, X_3, Y_1 and Y_2 each represent a hydroxyl group, a halogen atom such as chlorine and bromine, an alkyl group, an aryl group,



or $-OR_{25}$,

where R_{21} and R_{22} each represent a hydrogen atom, an alkyl group which may have a substituent(s), or a substituted or unsubstituted aryl group, R_{23} and R_{24} each represent a substituted or unsubstituted alkylene group, R_{25} represents a hydrogen atom, a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group, and M represents a cation.

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 12 5712

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	PATENT ABSTRACTS OF JAPAN vol. 4, no. 47 (P-6)(529) 11 April 1980, & JP-A-55 18675 (CHIYUUGAI SHIYASHIN YAKUHIN KK) 08 February 1980, * the whole document *	1-15	G 03 C 7/413
Y	RESEARCH DISCLOSURE. no. 287, March 1988, HAVANT GB page 120 ANONYMOUS: "Tarring inhibitor for photographic colour developing solutions"	1-15	
Y	US-A-4 232 112 (S.KUSE) * column 2, line 20 - column 2, line 64 *	1-3,6-11, 14,15	
Y	PATENT ABSTRACTS OF JAPAN vol. 11, no. 252 (P-605)(2699) 15 August 1987, & JP-A-62 56961 (FUJI PHOTO FILM CO.LTD.) 12 March 1987, * the whole document *	1-5,12-13	
Y	EP-A-0 312 984 (FUJI PHOTO FILM CO.LTD.) * page 4, line 52 - page 4, line 10 * * page 35, line 15 - page 36, line 50 * * page 47, lines 13 - 15 *	1-5,12,13	
Y	EP-A-0 273 986 (KONISHIROKU PHOTO INDUSTRY CO LTD) * claim 52 * * page 165, line 15 - page 166, line 8 * * page 123, lines 2 - 9 * * page 123, lines 5 - 8 @page 125,General formula A-III *	1-5,12,13	
A	GB-A-6 695 05 (KODAK LIMITED) * page 2, lines 60 - 70 * * claims 1, 2 *	1	

-/-

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	26 April 91	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
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Application Number

EP 90 12 5712

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	FR-A-1 080 765 (AGFA-GEVAERT AG) * page 2, column 2, lines 16 - 24 * – – –	1	
A	US-A-3 996 054 (H.J.SANTEMMA) * column 5, lines 1 - 15 * – – –	1	
A	GB-A-1 094 826 (FUJI SHASHIN FILM KK) * page 2, column 2, lines 21 - 28 * – – – – –	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	26 April 91	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
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