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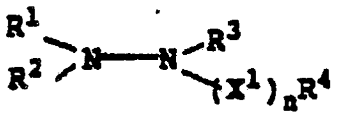
(54) Process of processing silver halide color photographic material.

(57) A process of processing a silver halide color photographic material is disclosed, which comprises, after imagewise exposure, processing a silver halide color photographic material with a color developer containing an aromatic primary amine color developing agent, at least one of hydrazines or hydrazides represented by following formula (I), and at least one selected from monoamines represented by formula (II) and condensed ring type amines represented by formula (III)



(I)

wherein R¹, R², and R³ each, independently, represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group; R⁴ represents a hydrogen atom, a hydroxyl group, a hydrazino group, an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, a carbamoyl group, or an amino group; X¹ represents a divalent group; n represents 0 or 1, provided that when n is 0, R⁴ represents an alkyl group, an aryl group, or a heterocyclic group; and R¹ and R² or R³ and R⁴ may form together a heterocyclic ring;

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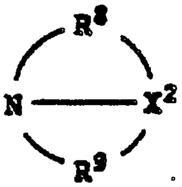
$$R^5-\overset{\displaystyle R^6 \atop |}{N}-R^7$$

(II)

wherein R^5, R^6, R^7 each represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an aralkyl group, or a heterocyclic group; and R^5 and R^6, R^5 and R^7, or R^6 and R^7 may combine with each other to form a nitrogen-containing heterocyclic ring; and



(III)

wherein X^2 represents a trivalent atomic group necessary for completing a condensed ring; and R^8 and R^9, which may be the same or different, each represents an alkylene group, an arylene group, an alkenylene group, or an aralkylene group.

PROCESS OF PROCESSING SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

This invention relates to a process of processing silver halide color photographic materials, and more particularly to a processing process for color photographic materials, wherein the stability and the coloring property of a color developer are improved and the increase of the formation of stains in continuous processing is greatly reduced.

BACKGROUND OF THE INVENTION

A color developer containing an aromatic primary amine color developing agent has hitherto been mainly used for the formation of color images but the aforesaid color developer is very liable to be oxidized by air or metal and it sometimes happens that the oxidation product thereof causes coupling with couplers in color photographic materials to form dyes or attaches to color photographic materials to cause undesirable stains.

It is well-known to add various kinds of antioxidants (preservatives) to color developers for preventing the occurrence of the oxidation of the color developing agent. However, hydroxylamines which are well-known preservatives and used for various kinds of color developers have such disadvantages that they reduce the coloring property of couplers and are liable to be decomposed by iron ions or copper ions to form the decomposition products thereof, which are liable to cause fog and give bad influences on the photographic properties. Thus, these preservatives are not always preferable.

Also sulfite ions are well-known as preservatives and have a function of preventing the formation of fog by decomposing dyes and causing reaction with the oxidation product of a color developing agent but have disadvantages of reducing the coloring property of couplers by acting as competing compounds to couplers and causing the reduction of color density by acting as a solvent for silver halide. Thus, sulfite ions are also not preferred preservatives.

For improving the stability of color developers, various investigations of various preservatives and chelating agents have been made. For example, as preservatives, there are proposed aromatic polyhydroxy compounds described in JP-A-52-49828, JP-A-59-160142, and JP-A-56-47038 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), and U.S. Patent 3,746,544, hydroxycarbonyl compounds described in U.S. Patent 3,615,503 and British Patent 1,306,176, α-aminocarbonyl compounds described in JP-A- 52-143020 and JP-A-53-89425, alkanolamines described in JP-A-54-3532, and metal salts described in JP-A-57-44148 and JP-A-57-53749. Also, as chelating agents, there are proposed aminopolycarboxylic acids described in JP-B-48-30496 and JP-B-44-30232 (the term "JP-B" as used herein means an "examined published Japanese patent application"), organic phosphonic acids described in JP-A-56-97347, JP-B-56-39359,and West German Patent 2,225,639, phosphonocarboxylic acids described in JP-A-52-102726, JP-A-53-42730, JP-A-54-121127, JP-A-55-126241 and JP-A-55-65956, and the compounds described in JP-A-58-195845 and JP-A-58-203440, and JP-B-53-40900.

However, by the use of these compounds, sufficient preservativity is not obtained and also the prevention of the occurrence of stains at continuous processing or after processing and the improvement of the stability of processing solutions, which are the objects of this invention, have not been sufficiently obtained.

Also, in processing of silver halide color photographic materials, shortening of the processing steps and processing time is becoming a very important technical theme since it greatly contributes to the promotion of mini processing laboratories for color photographic materials or shortening of the time for delivery of finished products as well as the reduction of the size of an automatic processor.

For silver halide color photographic materials, various kinds of dyes are used for the purposes of preventing irradiation at image exposure or at printing, or increasing the stability to so-called safelight without reducing the sensitivity, reducing the latent image storage stability, giving bad influences on the photographic properties, and reducing the quality of images by causing stains (color residue) after processing.

However, when in quick processing, washing is insufficient or these dyes are dissolved in a color developer, wash water, and/or a stabilization solution, the processing solutions are colored or even the processed color photographic materials are colored to form undesirable stains as the case may be. These phenomena are serious problems in, particularly, quick processing.

For preventing the occurrence of stains (stains at background portions) caused by such dyes, it is preferred to use dyes which become colorless dyes by being decomposed by alkali or reducing agent in a color developer but it frequently happens that the decomposition is insufficient to cause undesirable color stains and thus sufficiently satisfactory techniques of overcoming the aforesaid problems have not yet been found.

SUMMARY OF THE INVENTION

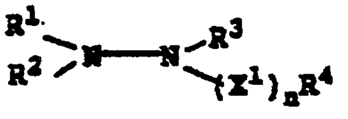
A first object of this invention is, therefore, to provide a process of processing silver halide color photographic materials excellent in the stability of the color developer being used.

A second object of this invention is to provide a process of processing silver halide color photographic materials giving greatly reduced formation of stains at continuous processing.

A third object of this invention is to provide a process of processing silver halide color photographic materials giving less stains after processing the color photographic materials even in quick processing.

It has now been discovered that the aforesaid objects can be effectively attained by the process of this invention as described herein below.

That is, according to this invention, there is provided a process of processing a silver halide color photographic material, which comprises processing, after imagewise exposure, a silver halide color photographic material with a color developer containing an aromatic primary amine color developing agent, at least one of hydrazines and hydrazides each represented by following formula (I), and at least one selected from monoamines represented by following formula (II) and condensed ring type amines represented by following formula (III)



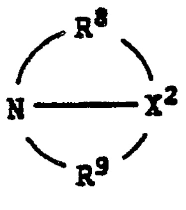
(I)

wherein R^1, R^2, and R^3 each represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group; R^4 represents a hydrogen atom, a hydroxyl group, a hydrazino group, an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, a carbamoyl group, or an amino group; X^1 represents a divalent group; n represents 0 or 1, provided that when n is 0, R^4 represents an alkyl group, an aryl group, or a heterocyclic group; and R^1 and R^2 or R^3 and R^4 may form together a heterocyclic ring;

$$R^5-\overset{\displaystyle R^6 \atop |}{N}-R^7$$

(II)

wherein R^5, R^6 and R^7 each represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an aralkyl group, or a heterocyclic group; and R^5 and R^6, R^5 and R^7, or R^6 and R^7 may combine with each other to form a nitrogen-containing heterocyclic ring; and



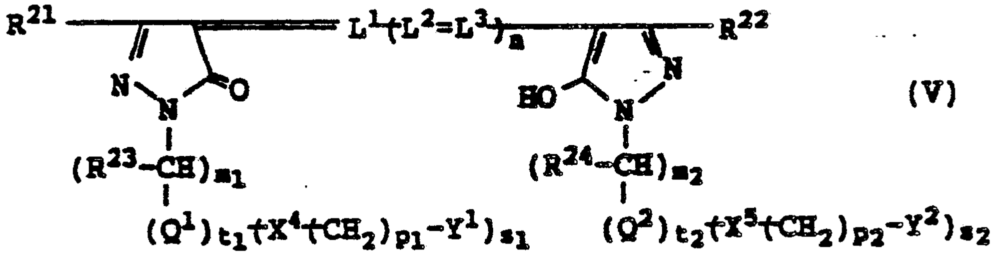
(III)

wherein X^2 represents a trivalent atomic group necessary for completing a condensed ring; and R^8 and R^9, which may be the same or different, each represents an alkylene group, an arylene group, an alkenylene group, or an aralkylene group.

Furthermore, in this invention, the formation of stains in quick processing or continuous processing with quick processing can be more effectively prevented by carrying out the aforesaid processing in the presence of at least one kind of compounds represented by following formula (IV) or by carrying out the aforesaid processing using a silver halide color photographic material containing at least one kind of compounds represented by following formula (V)

Z-S-M (IV)

wherein M represents a hydrogen atom, a cation, or -S-Z; and Z represents a heterocyclic residue containing at least one nitrogen atom; and



(V)

wherein R^{21} and R^{22} each represents $-COOR^{25}$,

$$-\underset{\displaystyle R^{26}}{\underset{|}{CON}}-R^{25},$$

$-COR^{25}$ (wherein R^{25} and R^{26} each represents a hydrogen atom, an alkyl group, or an aryl group), or -CN; R^{23} and R^{24} each represents a hydrogen atom or an alkyl group; Q^1 and Q^2 each represents an aryl group; X^4 and X^5 each represents a bond or a divalent linkage group; Y^1 and Y^2 each represents a sulfo group or a carboxyl group; L^1, L^2, and L^3 each represents a methine group; m_1 and m_2 each represents 0, 1, or 2; n represents 0, 1 or 2; p_1 and p_2 each represents 0, 1, 2, 3, or 4; s_1 and s_2 each represents 1 or 2; and t_1 and t_2 each represents 0 or 1, with, however, the exclusion of the cases that m_1, p_1, and t_1 are simultaneously 0 and that m_2, p_2, and t_2 are simultaneously 0.

DETAILED DESCRIPTION OF THE INVENTION

Then, the invention is explained in detail.

First, the compounds for use in this invention are described below in detail.

The compounds of formula (I) for use in this invention, that is, hydrazine analogues composed of hydrazines and hydrazides are explained.

In formula (I), R^1, R^2, and R^3 each, independently, represents a hydrogen atom, a substituted or unsubstituted alkyl group (preferably having from 1 to 20 carbon atoms, e.g., methyl, ethyl, sulfopropyl, carboxybutyl, hydroxyethyl, cyclohexyl, benzyl, phenethyl), a substituted or unsubstituted aryl group (preferably having from 6 to 20 carbon atoms, e.g., phenyl, 2,5-dimethoxyphenyl, 4-hydroxyphenyl, 2-carboxyphenyl), or a substituted or unsubstituted heterocyclic group (preferably having from 1 to 20 carbon atoms, more preferably a 5- or 6-membered ring having at least one of oxygen, nitrogen, sulfur, etc., as hetero atom, e.g., pyrydin-4-yl, N-acetylpiperidin-4-yl).

In formula (I), R^4 represents a hydrogen atom, a hydroxyl group, a substituted or unsubstituted hydrazino group (e.g., hydrazino, methylhydrazino, phenylhydrazino), a substituted or unsubstituted alkyl group (preferably having from 1 to 20 carbon atoms, e.g., methyl, ethyl, sulfopropyl, carboxybutyl, hydroxyethyl, n-octyl), a substituted or unsubstituted aryl group (preferably having from 6 to 20 carbon atoms, e.g., phenyl, 2,5-dimethoxyphenyl, 4-hydroxyphenyl, 2-carboxyphenyl, 4-sulfophenyl), a substituted or unsubstituted heterocyclic group (preferably having from 1 to 20 carbon atoms, more preferably a 5- or

6-membered ring having at least one of oxygen, nitrogen, and sulfur as hetero atom, e.g., pyridin-4-yl, imidazolyl), a substituted or unsubstituted alkoxy group (preferably having from 1 to 20 carbon atoms, e.g., methoxy, ethoxy, methoxyethoxy, benzyloxy, cyclohexyloxy, octyloxy), a substituted or unsubstituted aryloxy group (preferably having from 6 to 20 carbon atoms, e.g., phenoxy, p-methoxyphenoxy, p-carboxyphenyl, p-sulfophenoxy), a substituted or unsubstituted carbamoyl group (preferably having from 1 to 20 carbon atoms, e.g., unsubstituted carbamoyl, N,N-diethylcarbamoyl, phenylcarbamoyl), or a substituted or unsubstituted amino group (preferably having from 0 to 20 carbon atoms, e.g., amino, hydroxyamino, methylamino, hexylamino, methoxyethylamino, carboxyethylamino, sulfoethylamino, N-phenylamino, p-sulfophenylamino).

When the groups shown by R^1, R^2, R^3, and R^4 have a substituent, preferred examples of the substituent are halogen atoms (e.g., chlorine, bromine), a hydroxyl group, a carboxyl group, a sulfo group, an amino group, an alkoxy group, an amido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkyl group, an aryl group, an aryloxy group, an alkylthio group, an arylthio group, a nitro group, a cyano group, a sulfonyl group, and a sulfinyl group, and these groups each may further have a substituent.

Also, in formula (I), X^1 is preferably a divalent organic residue, such as -CO-, $-SO_2-$, and $-\overset{\overset{NH}{\|}}{C}-$; and n is 0 or 1. However, when n is 0, R^4 represents a group selected from a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, and a substituted or unsubstituted heterocyclic group. R^1 and R^2 or R^3 and R^4 may form together a heterocyclic group.

When n is 0, it is preferred that at least one of R^1 to R^4 is a substituted or unsubstituted alkyl group and it is more preferably that R^1, R^2, R^3, and R^4 are a hydrogen atom or a substituted or unsubstituted alkyl group (with, however, the exclusion of the case that R^1, R^2, R^3, and R^4 are simultaneously a hydrogen atom). In this case, it is particularly preferred that R^1, R^2, and R^3 are a hydrogen atom and R^4 is a substituted or unsubstituted alkyl group; R^1 and R^3 are a hydrogen atom and R^2 and R^4 are a substituted or unsubstituted alkyl group; or R^1 and R^2 are a hydrogen atom and R^3 and R^4 are a substituted or unsubstituted alkyl group (in this case R^3 and R^4 may form together a heterocyclic ring).

When n is 1, X^1 is preferably -CO-, R^4 is preferably a substituted or unsubstituted amino group, and R^1 to R^3 are a hydrogen atom or a substituted or unsubstituted alkyl group.

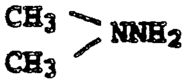
In formula (I), n is more preferably 0.

The alkyl group shown by R^1 to R^4 has preferably from 1 to 10 carbon atoms, more preferably from 1 to 7 carbon atoms. Also, preferred examples of the substituent for the substituted alkyl group are a hydroxyl group, a carboxylic acid group, a sulfo group, and a phosphonic acid group. When two or more substituents exist, they may be the same or different.

The compound shown by formula (I) may form a tris compound or a polymer bonded at R^1, R^2, R^3, or R^4.

Then, specific examples of the compound shown by formula (I) are illustrated below but the invention is not limited to them.

(I-1)

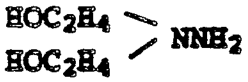


$$(CH_3)_2NNH_2$$

(I-2)

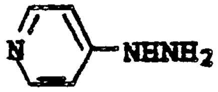
$CH_3NHNHCH_3$

(I-3)

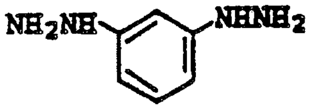


$$(HOC_2H_4)_2NNH_2$$

(I-4)

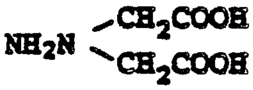


(I-5)



(I-6)

(I-7)



$NH_2N(CH_2COOH)_2$

(I-8)

$HOOCCH_2NHNHCH_2COOH$

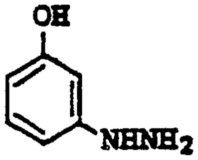
(I-9)

$NH_2NH{-}(CH_2)_3{-}NHNH_2$

(I-10)

$NH_2NHCH_2CH_2OH$

(I-11)



(I-12)

$NH_2NH{-}(CH_2)_3{-}SO_3H$

(I-13)

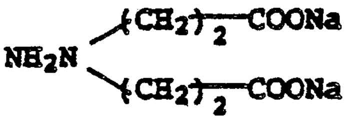
$NH_2NH{-}(CH_2)_4{-}SO_3H$

(I-14)

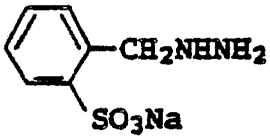
$NH_2NH-(CH_2)_3-COOH$

(I-15)

(I-16)



(I-17)



(I-18)

$NaOOCCH(CH_3)NHNHCH(CH_3)COONa$

(I-19)

$NH_2NHCH_2CH_2COONa$

(I-20)

NH_2NHCH_2COONa

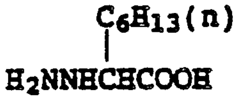
(I-21)

$H_2NNHCH_2CH_2SO_3Na$

(I-22)

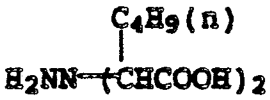
$$H_2NNH\overset{\overset{\displaystyle C_4H_9(n)}{|}}{C}HCOOH$$

(I-23)



$$H_2NNH\overset{\overset{\displaystyle C_6H_{13}(n)}{|}}{C}HCOOH$$

(I-24)



$H_2NN\text{-}(\overset{C_4H_9(n)}{\overset{|}{C}}HCOOH)_2$

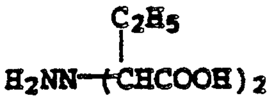
(I-25)

$H_2NN\text{-}(CH_2CH_2SO_3Na)_2$

(I-26)

$H_2NN\text{-}(CH_2CH_2CH_2SO_3Na)_2$

(I-27)

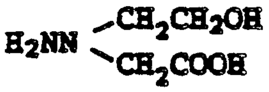


$H_2NN\text{-}(\overset{C_2H_5}{\overset{|}{C}}HCOOH)_2$

(I-28)

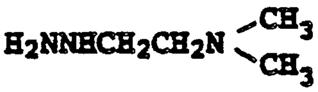
$H_2NNH\overset{CH_3}{\overset{|}{C}}HCOOH$

(I-29)



$$H_2NN{<}\begin{matrix}CH_2CH_2OH\\CH_2COOH\end{matrix}$$

(I-30)

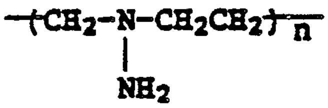


$$H_2NNHCH_2CH_2N{<}\begin{matrix}CH_3\\CH_3\end{matrix}$$

(I-31)

$$H_2NN\left(CH_2CH_2N{<}\begin{matrix}CH_3\\CH_3\end{matrix}\right)_2$$

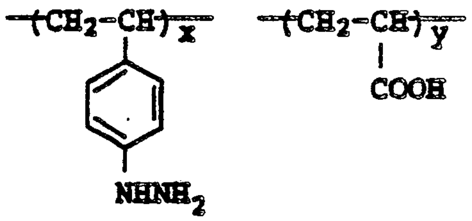
(I-32)



$$\left(CH_2-\underset{\displaystyle NH_2}{\underset{|}{N}}-CH_2CH_2\right)_n$$

(average molecular weight is about 4,000)

(I-33)



x:y=60:40

(average molecular weight is about 20,000)

(I-34)

$NH_2NHCONH_2$

(I-35)

$$\mathrm{NH_2NH}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{NH_2}$$

(I-36)

$NH_2NHCONHNH_2$

(I-37)

NH_2NHSO_3H

(I-38)

$NH_2NHSO_2NHNH_2$

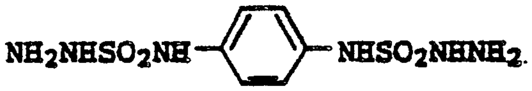
(I-39)

$CH_3NHNHSO_2NHNHCH_3$

(I-40)

$NH_2NHCONH-(CH_2)_3-NHCONHNH_2$

(I-41)



(I-42)

$NH_2NHCOCONHNH_2$

(I-43)

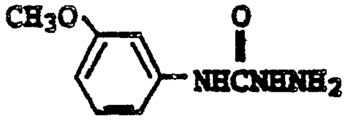
(I-44)

(I-45)

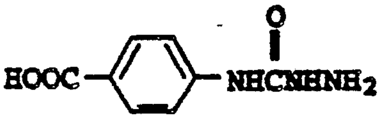
(I-46)

$NH_2COCONHNH_2$

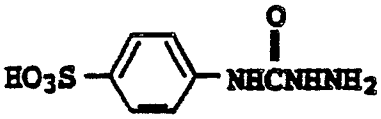
(I-47)



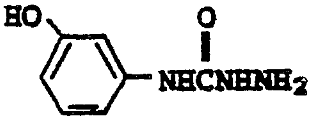
(I-48)



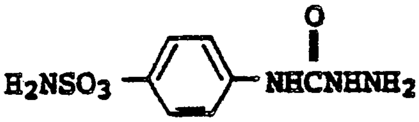
(I-49)



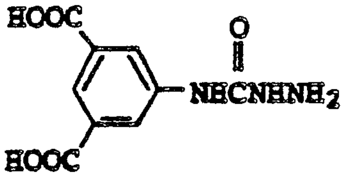
(I-50)



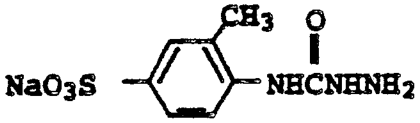
(I-51)



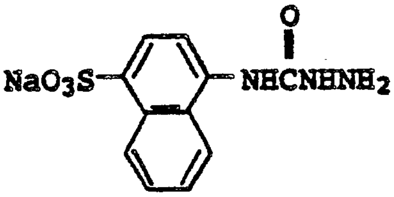
(I-52)



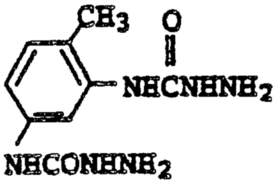
(I-53)



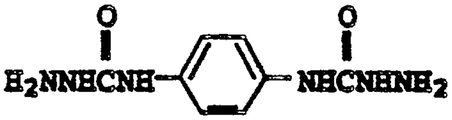
(I-54)



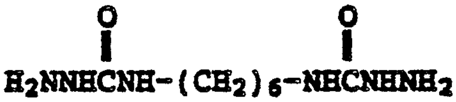
(I-55)



(I-56)

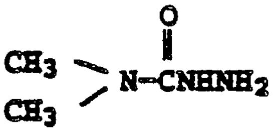


(I-57)

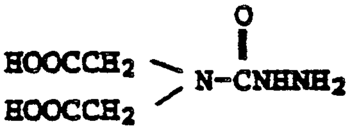


$H_2NNH\overset{O}{\overset{\|}{C}}NH-(CH_2)_6-NH\overset{O}{\overset{\|}{C}}NHNH_2$

(I-58)



(I-59)



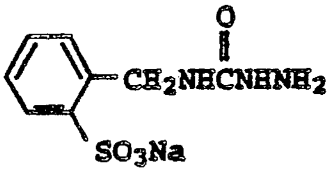
(I-60)

$NaO_3SCH_2CH_2NH\overset{O}{\overset{\|}{C}}NHNH_2$

(I-61)

$$HOOCCH_2CH_2NH\overset{O}{\overset{\|}{C}}NHNH_2$$

(I-62)



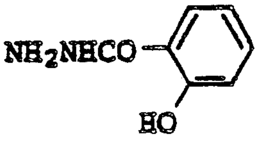
(I-63)

$NH_2NHCOOC_2H_5$

(I-64)

$NH_2NHCOCH_3$

(I-65)

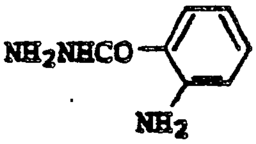


(I-66)

(I-67)

$NH_2NHCH_2PO_3H_2$

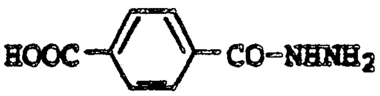
(I-68)



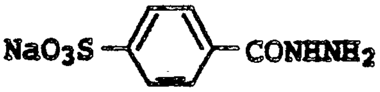
(I-69)

(I-70)

(I-71)



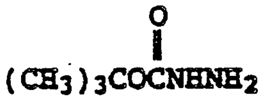
(I-72)



(I-73)

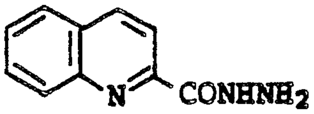
$(CH_3)_3CCONHNH_2$

(I-74)

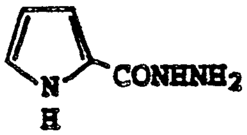


$(CH_3)_3CO\overset{O}{\overset{\|}{C}}NHNH_2$

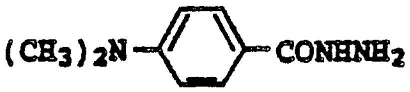
(I-75)



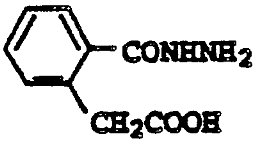
(I-76)



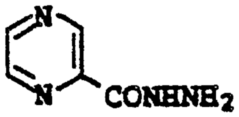
(I-77)



(I-78)



(I-79)



(I-80)

$HOCH_2CH_2SO_2NHNH_2$

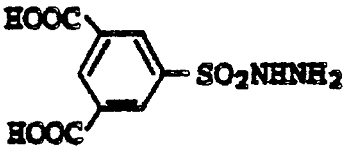
(I-81)

$NaO_3SCH_2CH_2CONHNH_2$

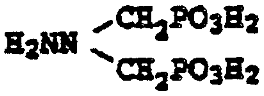
(I-82)

$H_2NCONHCH_2SO_2NHNH_2$

(I-83)



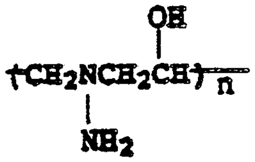
(I-84)



(I-85)

$H_2NNHCH_2CH_2PO_3H_2$

(I-86)



$$\left(CH_2\underset{NH_2}{N}CH_2\overset{OH}{CH}\right)_n \qquad (n=3 \text{ to } 100)$$

Other specific examples of the compounds shown by formula (I) are described in JP-A-63-146041, JP-A-63-170642, JP-A-63-146042, JP-A-63-170643, and JP-A-63-146043.

Many of the compounds shown by formula (I) are commercially available and also can be synthesized according to the methods described in Organic Syntheses, Coll., Vol. 2, pages 208 to 213, Journal of American Chemical Society, 36, 1747 (1914), Yukagaku (Oil Chemistry), 24, 31 (1975), Journal of Organic Chemistry, 25, 44 (1960), Yakugaku Zasshi (Journal of Pharmacology), 91, 1127 (1971), Organic Syntheses, Coll. Vol. 1, page 450, Shin Jikken Kagaku Kooza (New Experimental Chemistry Course), Vol. 14, III, pages 1621 to 1628 (published by Maruzen), Beil., 2, 559, ibid., 3, 117, E.B. Mohr et al, Inorganic Syntheses, 4, 32 (1953), F. J. Wilson and E.C. Pickering, Journal of Chemical Society, 123, 394 (1923), N.J. Leonard and J.H. Boyer, Journal of Organic Chemistry, 15, 42 (1950), Organic Syntheses, Coll., Vol. 5, page 1055, P.A.S. Smith, Derivatives of Hydrazine and Other Hydronitrogens Having n-n Bonds, pages 120 to 124 and pages 130 to 131 published by the Benjamin/Cummings Publishing Company, 1983, and Stanley R. Sandler and

Wolf Karo, Organic Functional Group Preparations, Vol. 1, 2nd Edition, 457 (1968).

The addition amount of the hydrazine or hydrazide shown by formula (I) is from 0.01 g to 50 g, preferably from 0.1 g to 30 g, and more preferably from 0.5 g to 10 g per liter of color developer.

The monoamines for use in this invention are the compounds shown by formula (II)

$$R^5-\overset{\displaystyle R^6 \atop |}{N}-R^7 \qquad \text{(II)}$$

wherein R^5, R^6, and R^7 each represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an aralkyl group, or a heterocyclic group; and R^5 and R^6, R^5 and R^7, or R^6 and R^7 may form together a nitrogen-containing heterocyclic ring.

The groups shown by R^5, R^6, and R^7 may have a substituent and as the substituent, there are a hydroxyl group, a sulfo group, a carboxyl group, a halogen atom, a nitro group, an amino group, etc. R^5, R^6, and R^7 are particularly preferably a hydrogen atom or an alkyl group.

Specific examples of the compounds shown by formula (II) are shown below but the invention is not limited to them.

II-1

$N(CH_2CH_2OH)_3$

II-2

$H_2NCH_2CH_2OH$

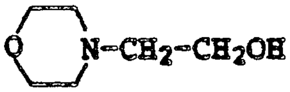
II-3

$HN(CH_2CH_2OH)_2$

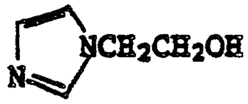
II-4

$C_7H_{15}N(CH_2CH(OH)CH_2OH)_2$

II-5

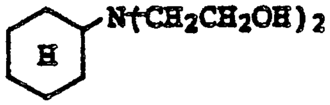


II-6

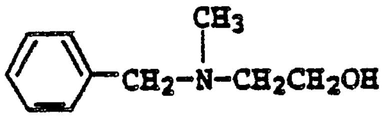


II-7

II-8



II-9



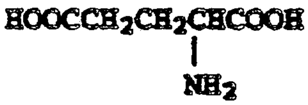
II-10

$(HOCH_2CH_2)_2NCH_2CH_2SO_2CH_3$

II-11

$HN(CH_2COOH)_2$

II-12



$HOOCCH_2CH_2CHCOOH$ with NH_2 on CH

II-13

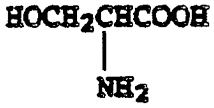
$H_2NCH_2CH_2SO_2HN_2$

II-14

II-15

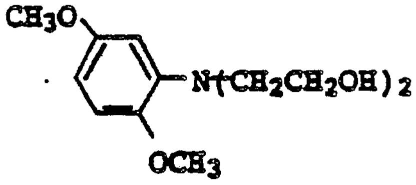
$H_2N-C(CH_2OH)_3$

II-16

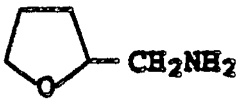


$HOCH_2CH(NH_2)COOH$

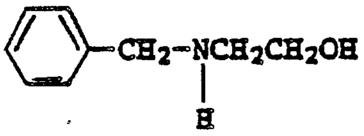
II-17



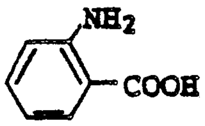
II-18



II-19

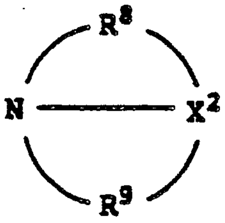


II-20



The aforesaid compounds of formula (II) are mostly commercially available.

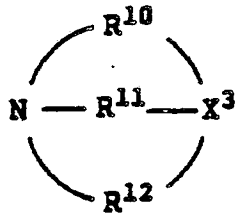
The condensed ring type amines for use in this invention are the compounds shown by formula (III)



(III)

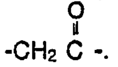
wherein X^2 represents a trivalent atomic group necessary for completing a condensed ring; and R^8 and R^9, which may be the same or different, each represents an alkylene group, an arylene group, an alkenylene group, or an aralkylene group.

In the amines shown by formula (III), the compounds shown by following formula (1-a) and (1-b) are particularly preferred.



(1-a)

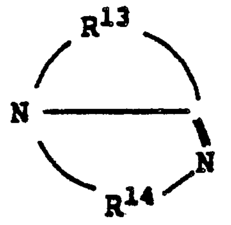
wherein X^3 represents $>N$ or $>CH$, R^{10} and R^{11} have the same meanings as R^8 and R^9 in the aforesaid formula (III) and R^{12} represents the group shown by R^{10} and R^{11} or



$-CH_2\overset{O}{\overset{\|}{C}}-$.

In formula (1-a), X^3 is preferably $>N$ and the carbon atom number of the group shown by R^{10}, R^{11}, or R^{12} is preferably 6 or less, more preferably 3 or less, and most preferably 2.

R^{10}, R^{11}, and R^{12} are preferably an alkylene group or an arylene group, and most preferably an alkylene group.



(1-b)

wherein R^{13} and R^{14} have the same meanings as R^8 and R^9 in the aforesaid dormula (III).

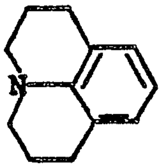
In the compounds shown by formulae (1-a) and (1-b), the compounds shown by formula (1-a) are particularly preferred.

Then, specific examples of the compounds shown by formula (III) described above are illustrated below but the invention is not limited to them.

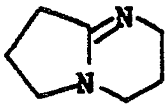
III-1

III-2

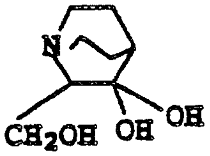
III-3



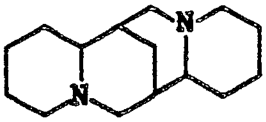
III-4



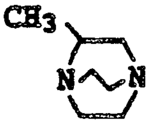
III-5



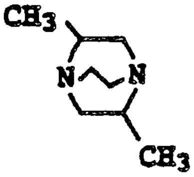
III-6



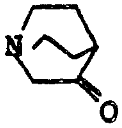
III-7



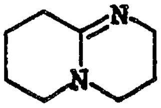
III-8



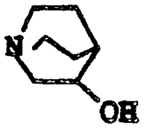
III-9



III-10



III-11

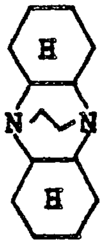


III-12

III-13

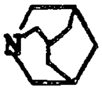
III-14

III-15

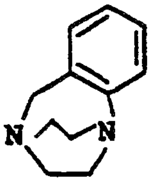


III-16

III-17



III-18



The compounds of formula (III) are mostly easily commercially available and also can be synthesized according to the methods described in Khim. Geterotsikl. Soedin., (2), 272-275 (1976), ibid., (8), 1123-1126 (1976), U.S. Patents 3,297,701, 3,375,252, and 4,092,316.

The addition amount of the compounds shown by formulae (II) and (III) is from 0.1 g to 50 g, preferably from 0.5 g to 20 g per liter of color developer.

Then, the compounds shown by formula (IV) described above are explained in detail.

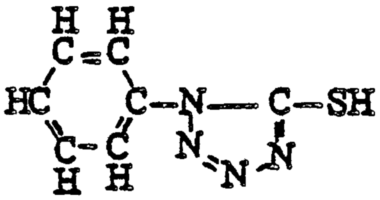
The heterocyclic residue shown by Z in formula (IV) may be condensed and specific examples of the preferred compound are imidazole, triazole tetrazole, thiazole, oxazole, selenazole, benzimidazole, benzoxazole, benzthiazole, thiadiazole, oxadiazole, benzselenazole, pyrazole, pyrimidine, triazine, pyridine, naphthothiazole, naphthimidazole, naphthoxazole, azabenzimidazole, purine, and azaindenes (e.g., triazaindene, tetraazaindene, pentaazaindene).

The heterocyclic residue and the condensed ring thereof may be substituted by a proper substituent. Examples of the substituent are an alkyl group (e.g., methyl, ethyl, hydroxyethyl, trifluoromethyl, sulfopropyl, dipropylaminoethyl, adamantane), an alkenyl group (e.g., allyl), an aralkyl group (e.g., benzyl, p-chlorophenethyl), an aryl group (e.g., phenyl, naphthyl, p-carboxyphenyl, 3,5-di-carboxyphenyl, m-sulfophenyl, p-acetamidophenyl, 3-capramidophenyl, p-sulfamoylphenyl, m-hydroxyphenyl, p-nitrophenyl, 3,5-dichlorophenyl, 2-methoxyphenyl), a heterocyclic residue (e.g., pyridine, furan, thiphene), a halogen atom (e.g., chlorine, bromine), a mercapto group, a cyano group, a carboxyl group, a sulfo group, a hydroxyl group, a carbamoyl group, a sulfamoyl group, an amino group, a nitro group, an alkoxy group (e.g., methoxy), an aryloxy group (e.g., phenoxy), an acyl group (e.g., acetyl), an acylamino group (e.g., acetylamino, capramido, methylsulfonylamino), a substituted amino group (e.g., diethylamino, hydroxyamino), an alkylthio or arylthio group (e.g., methylthio, carboxyethylthio, sulfobutylthio), an alkoxycarbonyl group (e.g., methoxycarbonyl), and an aryloxycarbonyl group (e.g., phenoxycarbonyl).

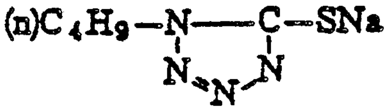
It is necessary that the heterocyclic residue shown by Z in formula (IV) contains at least one nitrogen atom but the heterocyclic residue contains preferably at least 2 nitrogen atoms, more preferably at least 3 carbon atoms, and particularly preferably at least 4 carbon atoms.

Specific examples of the preferred mercapto type compounds shown by formula (IV) are illustrated below but the invention is not limited to these compounds.

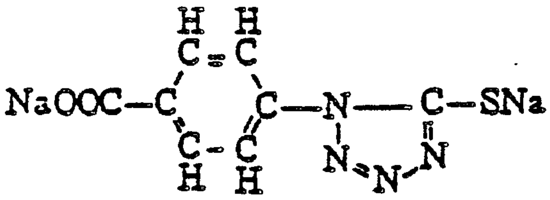
(IV - 1)



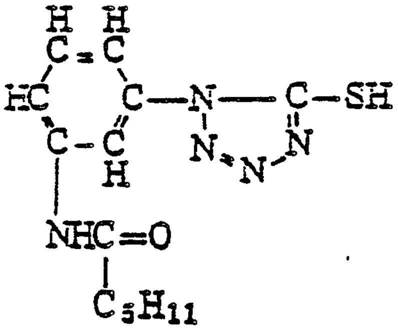
(IV - 2)



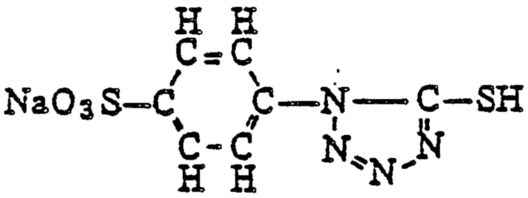
(IV - 3)



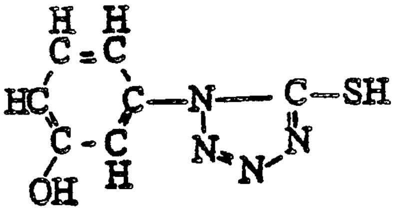
(IV - 4)



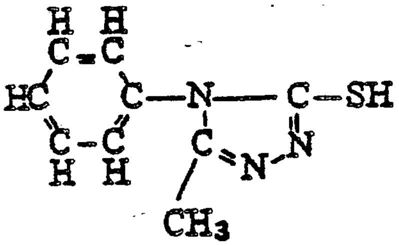
(IV - 5)



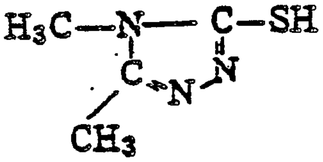
(IV-6)



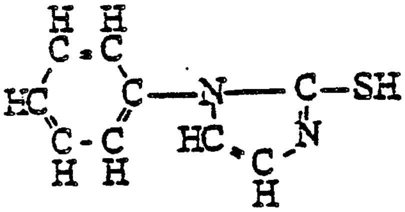
(IV-7)



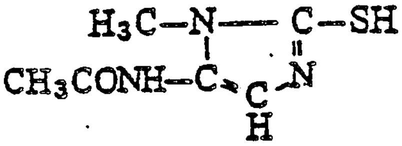
(IV-8)



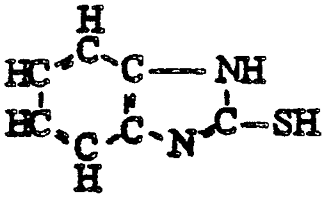
(IV-9)



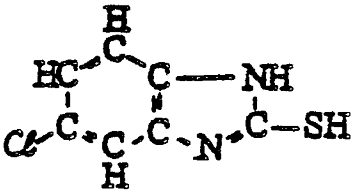
(IV-10)



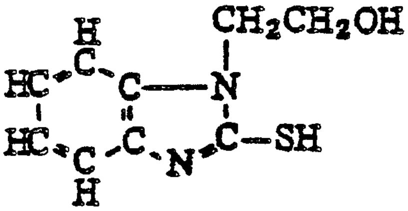
(IV – 11)



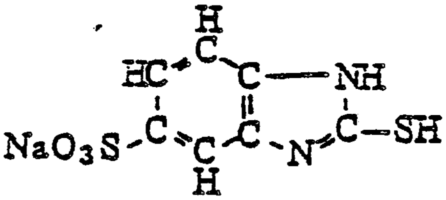
(IV – 12)



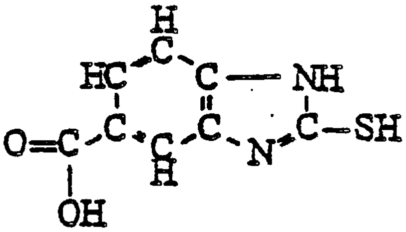
(IV – 13)



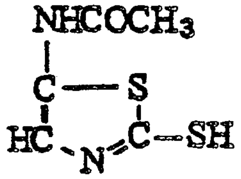
(IV – 14)



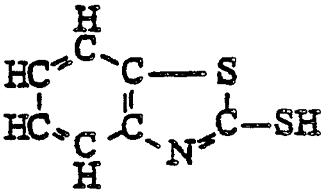
(IV – 15)



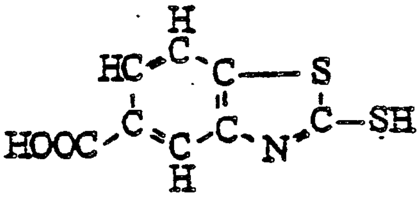
(IV-16)



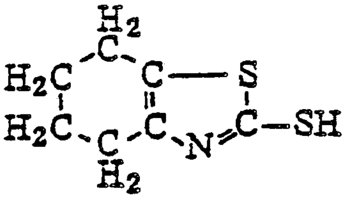
(IV-17)



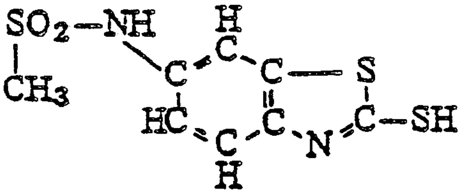
(IV-18)



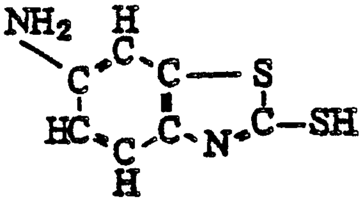
(IV-19)



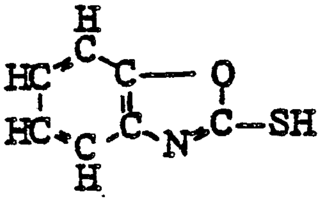
(IV-20)



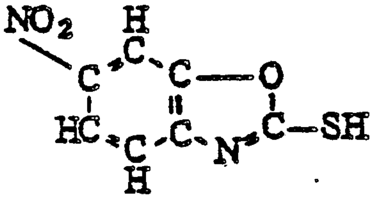
(IV − 21)



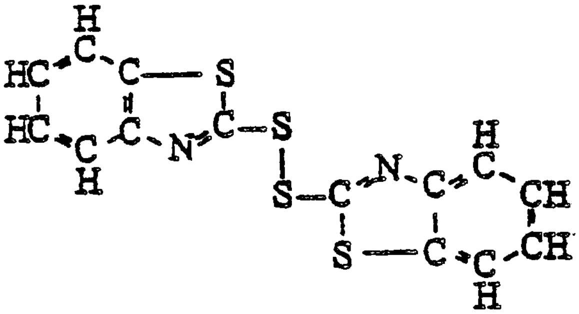
(IV − 22)



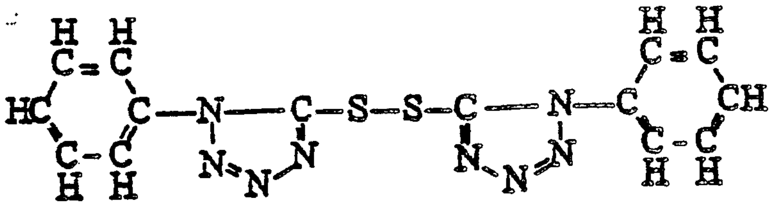
(IV − 23)



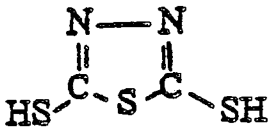
(IV − 24)



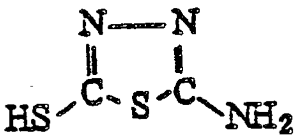
(IV－25)



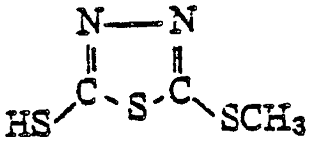
(IV－26)



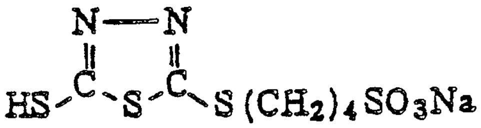
(IV－27)



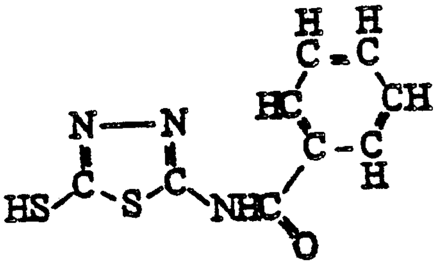
(IV－28)



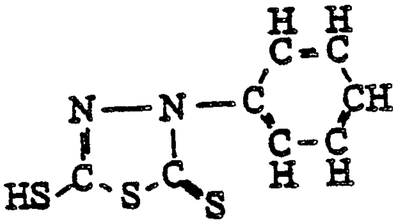
(IV－29)



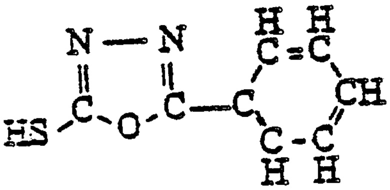
(IV－30)



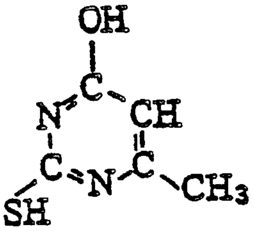
(IV－31)



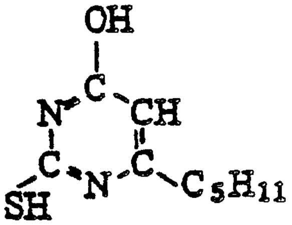
(IV－32)



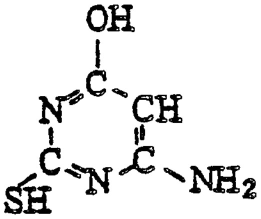
(IV－33)



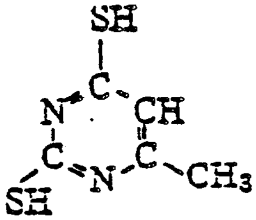
(IV − 34)



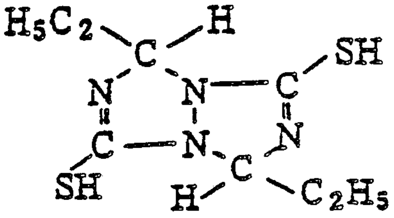
(IV − 35)



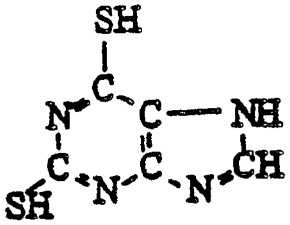
(IV − 36)



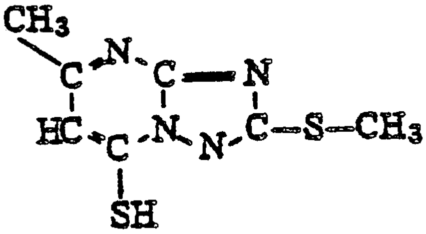
(IV − 37)



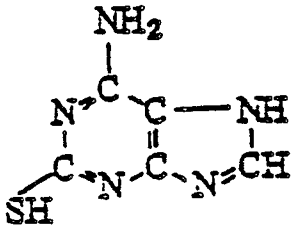
(IV－3 8)



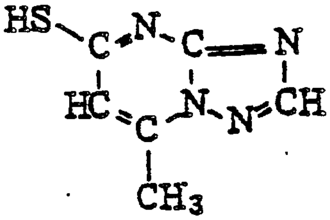
(IV－3 9)



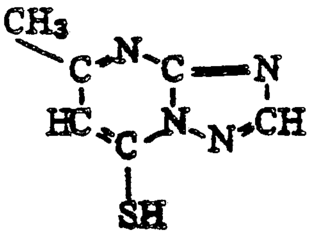
(IV－4 0)



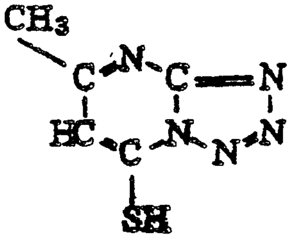
(IV－4 1)



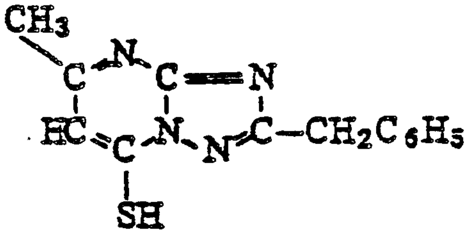
(IV-42)



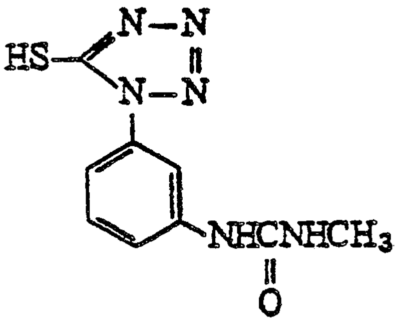
(IV-43)



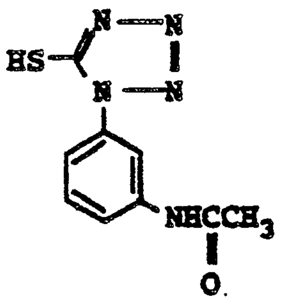
(IV-44)



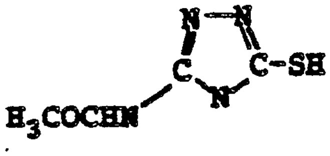
(IV-45)



(IV-46)



(IV-47)



In the compounds shown by formula (IV), particularly preferred compounds are compounds IV-27, IV-45, IV-46, and IV-47.

The compound shown by formula (IV) for use in this invention may exist in a silver halide color photographic material and/or a color developer and particularly preferably exists in a silver halide color photographic material.

Also, the compounds shown by formula (IV) may be used singly or as a mixture thereof.

When the compound shown by formula (IV) exists in a silver halide color photographic material, the compound may exist in any layer of the photographic material and further may exist in two or more layers. Also, the amount of the compound shown by formula (IV) is in the range of preferably from 10^{-7} mol to 10^{-1} mol, more preferably from 10^{-5} mol to 10^{-2} mol per mol of the silver halide in the layer containing the compound.

When the compound shown by formula (IV) exists in a color developer, the amount of the compound is preferably from 10^{-10} mol to 10^{-3} mol, more preferably from 10^{-10} mol to 10^{-4} mol per liter of the color developer.

The processing process of this invention, which is carried out in the presence of the compound shown by formula (IV), is particularly effectively applied to a silver halide color photographic material having at least one silver halide emulsion layer containing a silver halide substantially composed of silver chloride. The term "substantially composed of silver chloride" means that 80% or more, preferably 95% or more, and more preferably 98% or more of the silver halide is silver chloride. From the standpoint of prevention of the reduction of sensitivity, it is preferred that no more than 99.8% of the silver halide is silver chloride.

Then, the compounds shown by formula (V) are explained in detail.

In formula (V), R^{21} and R^{22} each, independently, represents $-COOR^{25}$,

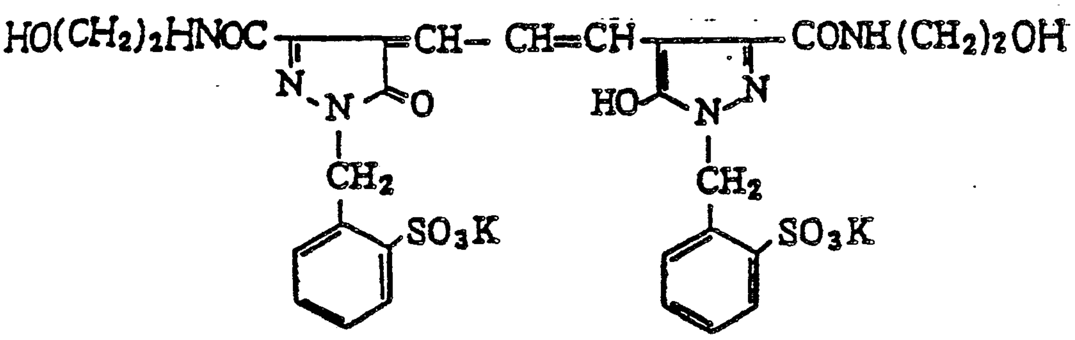
$$-\underset{\displaystyle R^{26}}{\underset{|}{CON}}-R^{25},$$

$-COR^{25}$ or $-CN$ [wherein R^{25} and R^{26} each represents a hydrogen atom, an alkyl group or substituted alkyl group (e.g., methyl, ethyl, butyl, hydroxyethyl, phenethyl), or an aryl group or substituted aryl group (e.g., phenyl, hydroxyphenyl)]; and R^{23} and R^{24} each represents a hydrogen atom or an alkyl group or substituted alkyl group (e.g., methyl, ethyl, butyl, hydroxyethyl).

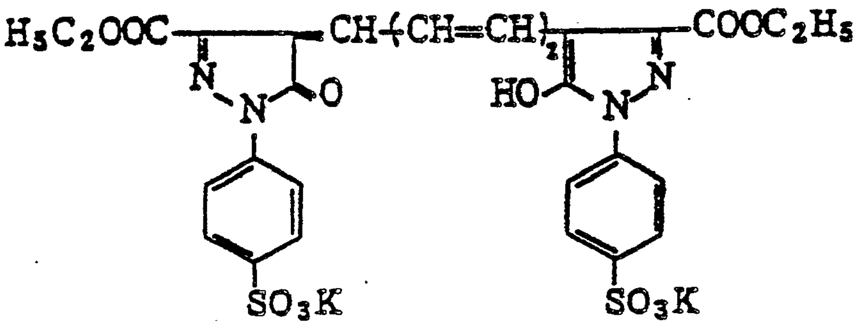
In formula (V), Q^1 and Q^2 each represents an aryl group (e.g., phenyl, naphthyl); X^4 and X^5 each represents a bond or a divalent linkage group; Y^1 and Y^2 each represents a sulfo group or a carboxyl group; L^1, L^2, and L^3 each represents a methine group; m_1 and m_2 each represents 0, 1 or 2; n represents 0, 1 or 2; p_1 and p_2 each represents 0, 1, 2, 3 or 4; s_1 and s_2 each represents 1 or 2; and t_1 and t_2 each represents 0 or 1, with the exclusion of the cases that m_1, p_1, and t_1 are simultaneously 0 and that m_2, p_2, and t_2 are simultaneously 0.

Then, specific examples of the compounds shown by formula (V) described above are illustrated below but the invention is not limited to these compounds.

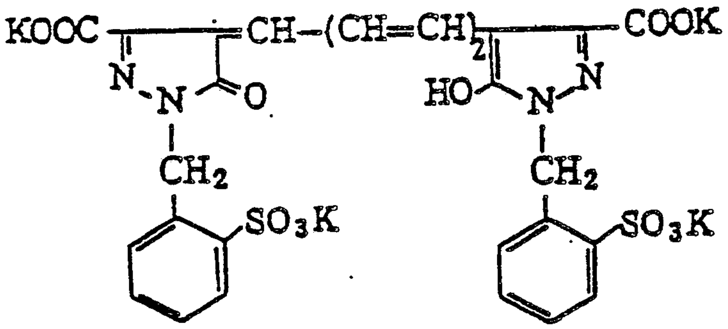
(V-1)



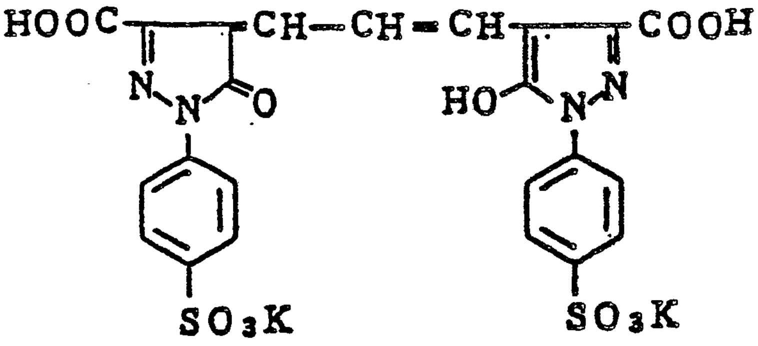
(V-2)



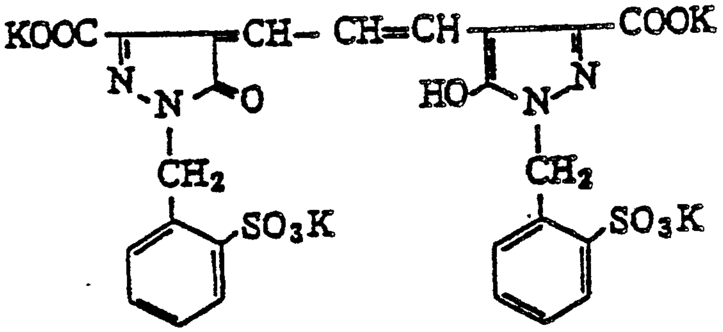
(V-3)



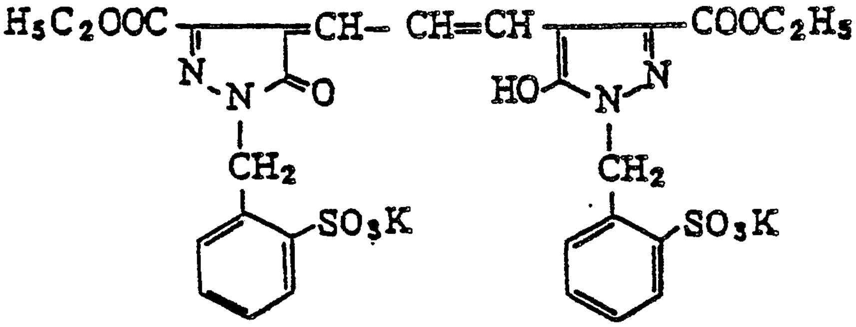
(V-4)



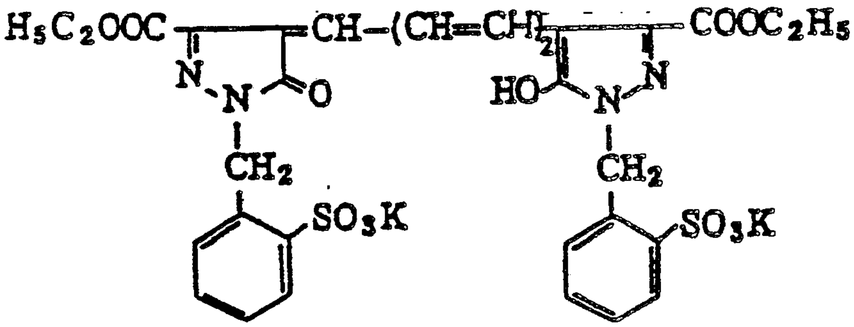
(V-5)



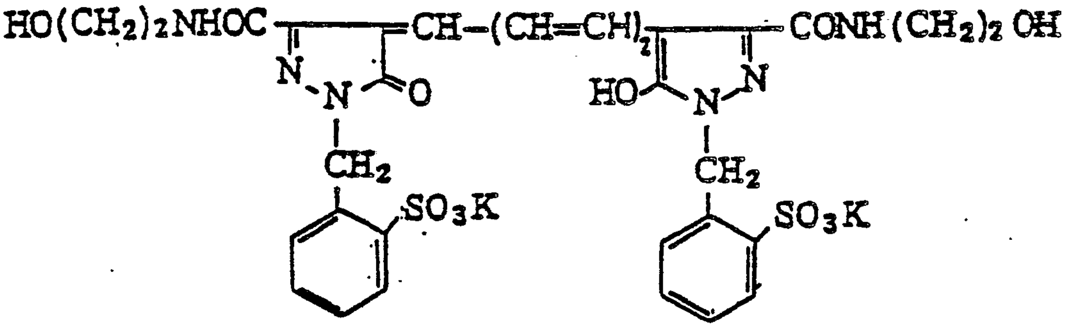
(V-6)



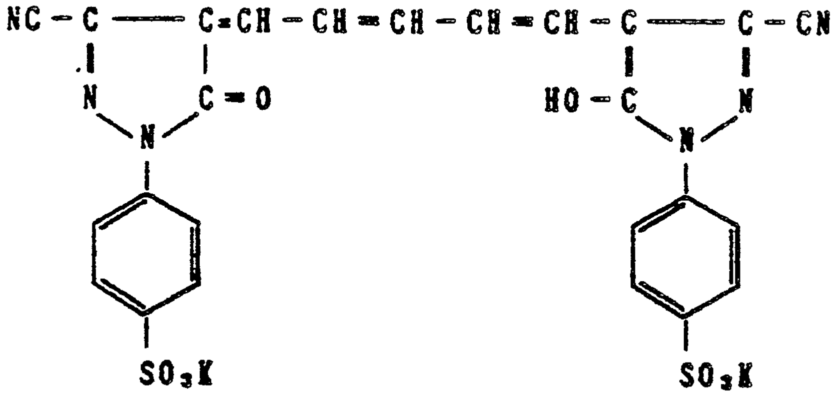
(V-7)



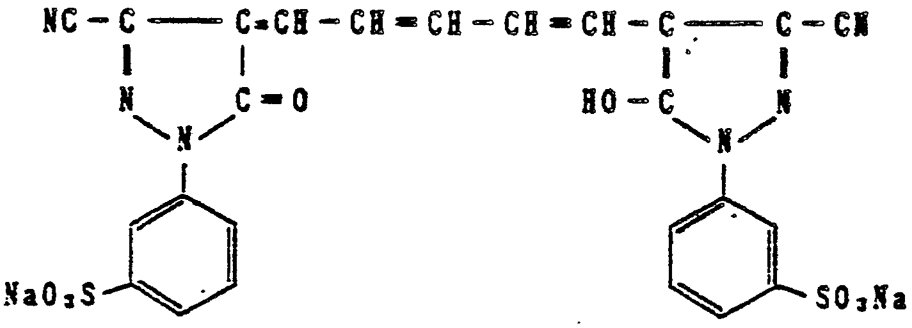
(V-8)



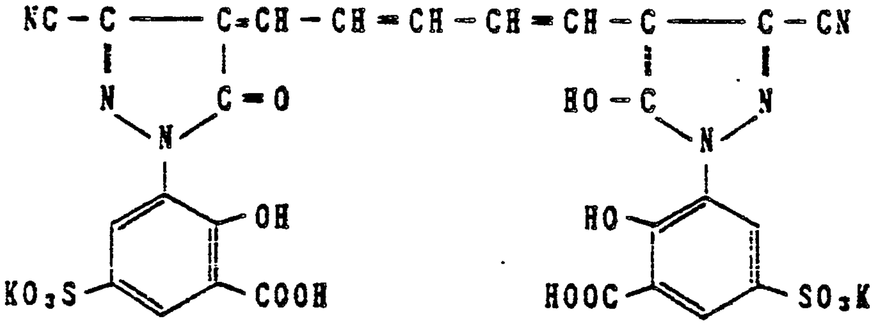
(V - 9)



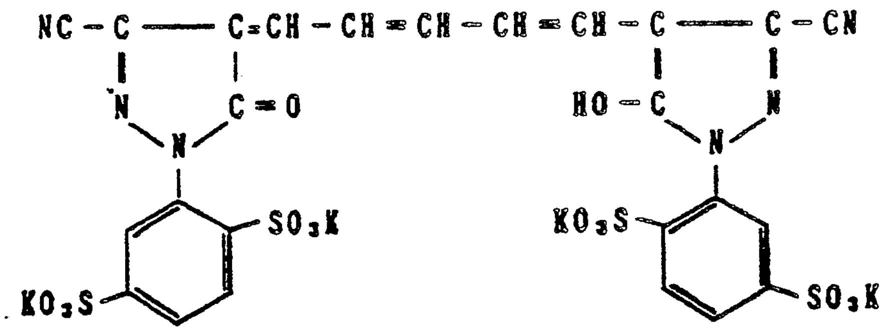
(V - 10)



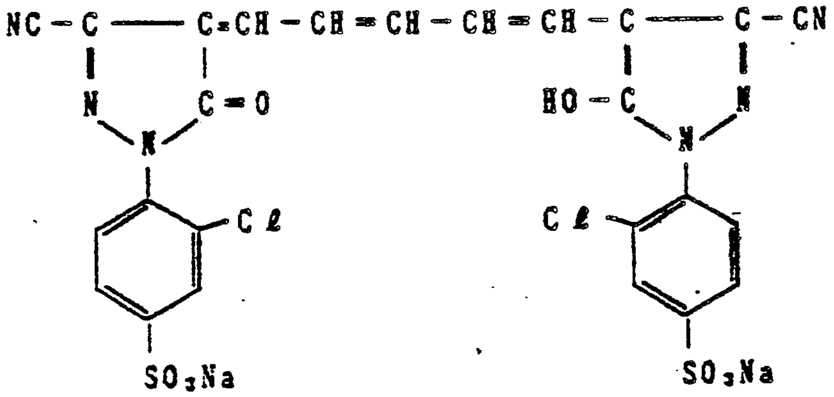
(V - 11)



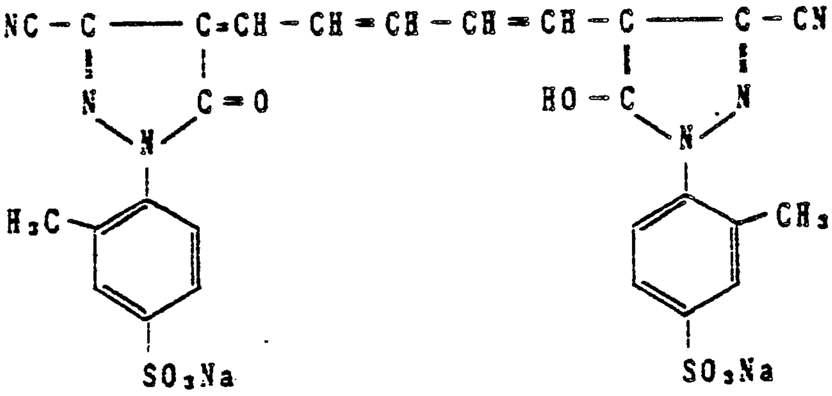
(V- 12)



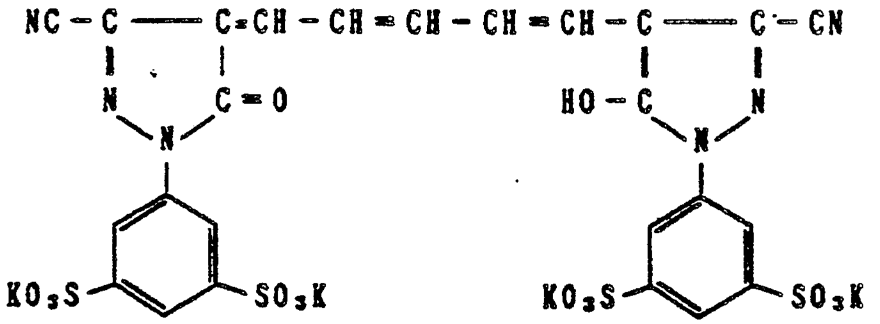
(V - 13)



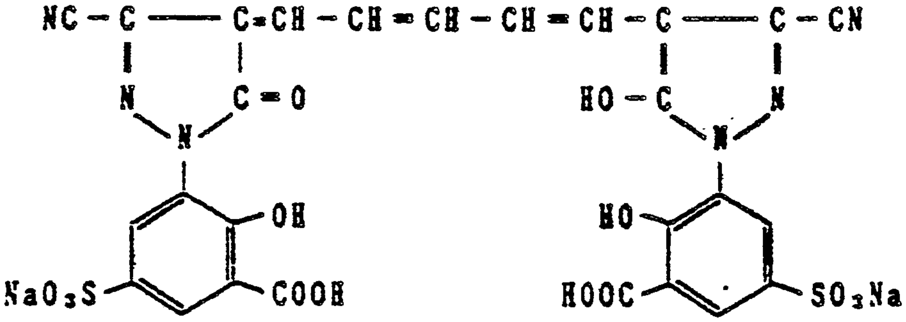
(V - 14)



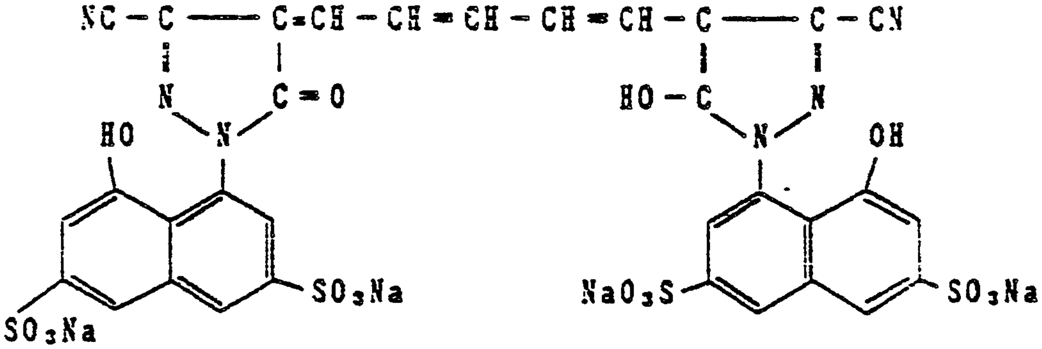
(V-15)


NC
CN
HO
KO₃S
SO₃K
KO₃S
SO₃K

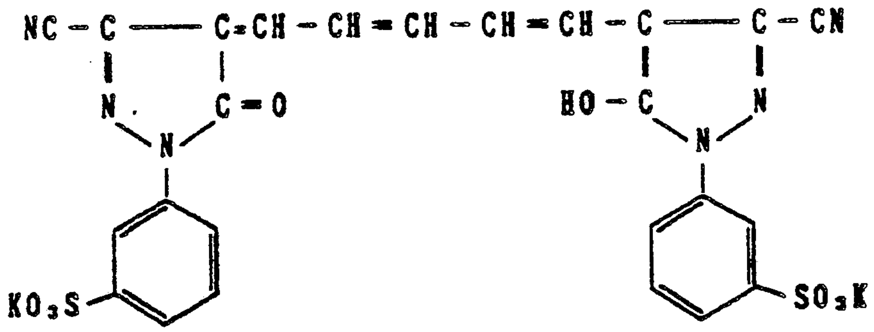
(V-16)


NC
CN
HO
OH
HO
NaO₃S
COOH
HOOC
SO₃Na

(V-17)


NC
CN
HO
HO
OH
SO₃Na
SO₃Na
NaO₃S
SO₃Na

(V - 18)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C=O
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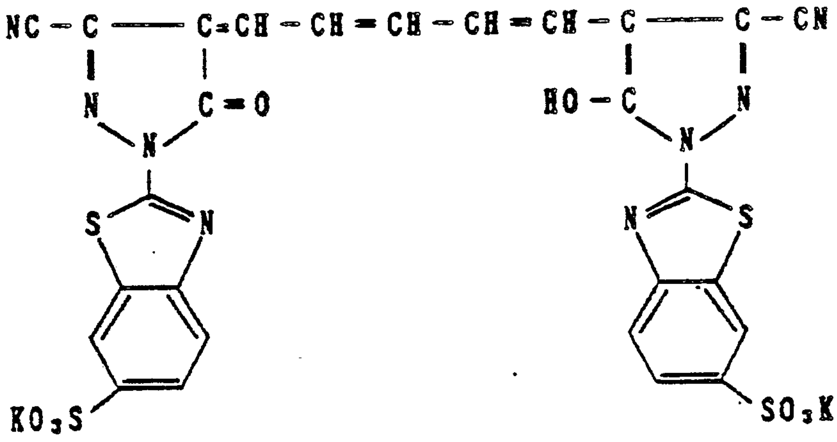
HO
N
N
KO3S
SO3K

(V - 19)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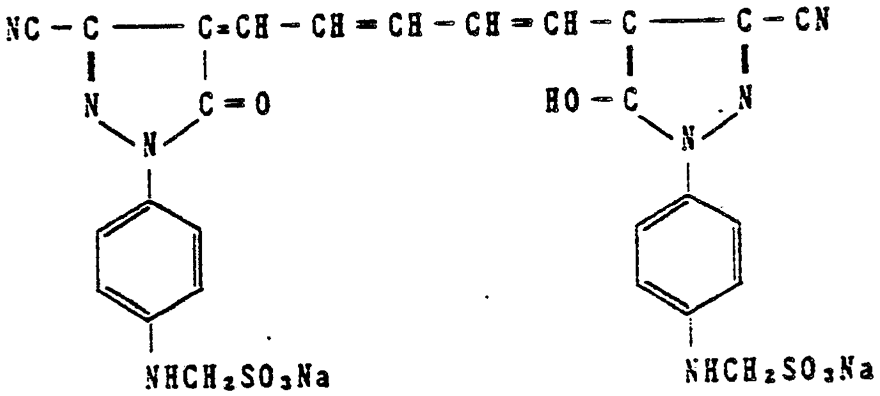
(V - 20)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HO
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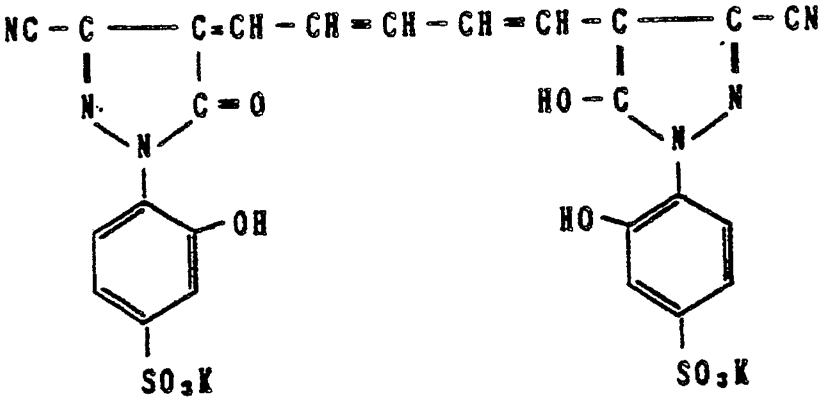
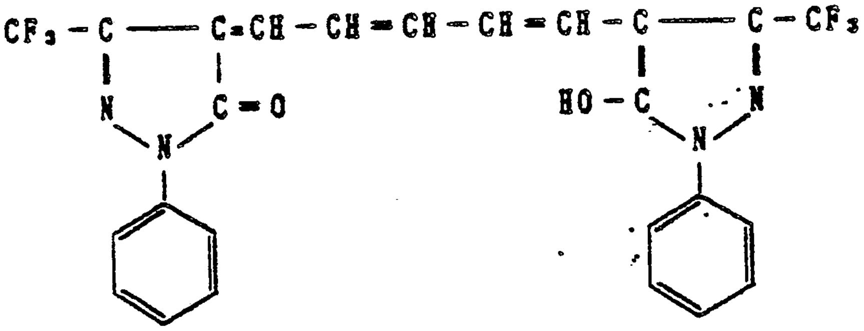
NHCH2SO3Na

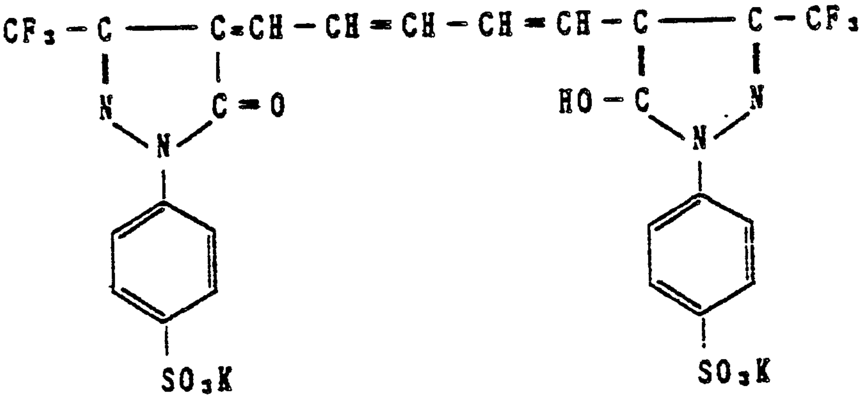
(V -21)



(V-22)



(V-23)



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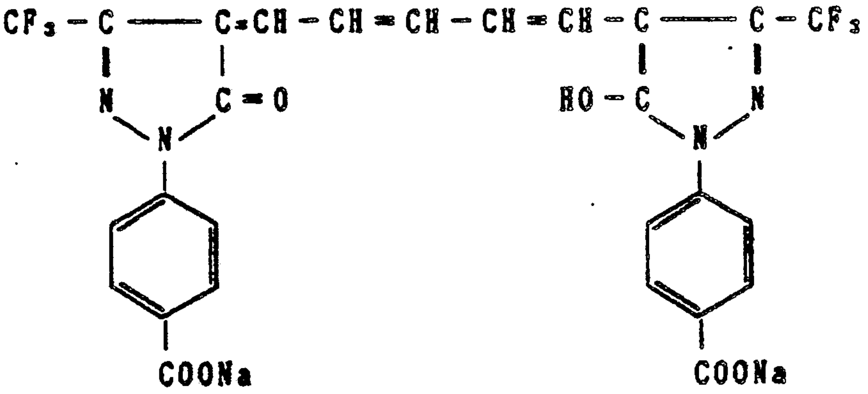

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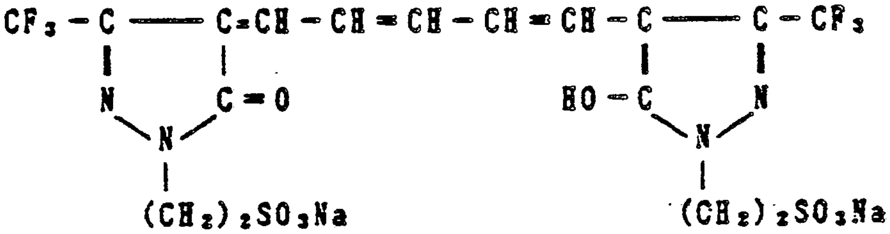

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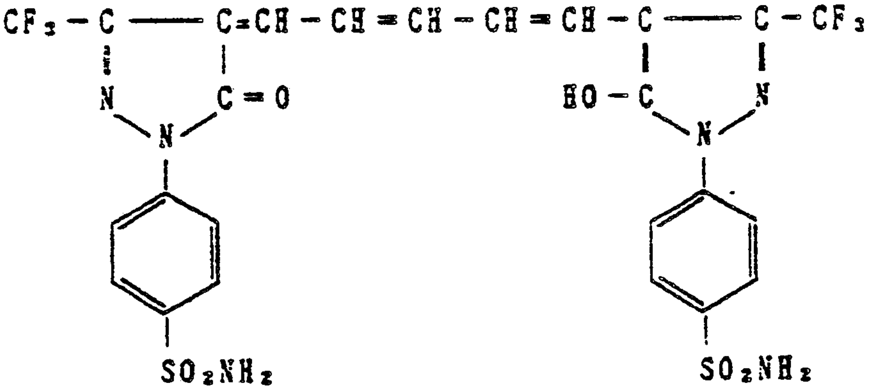

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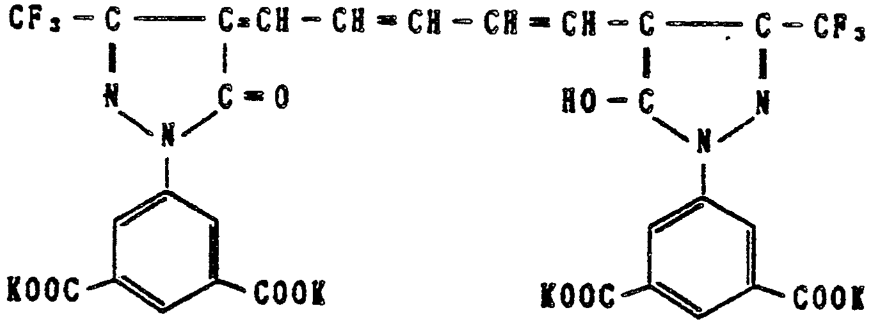

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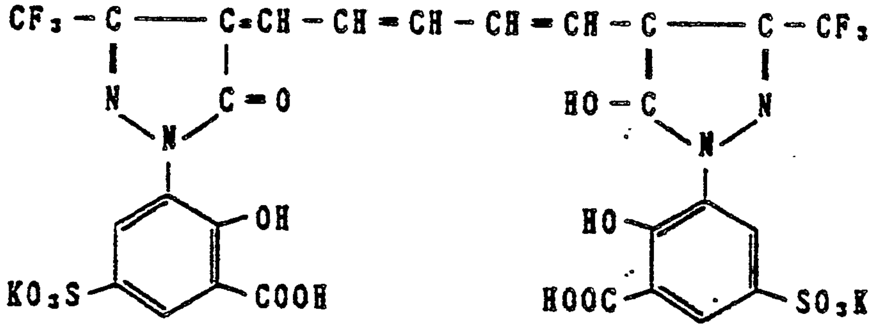

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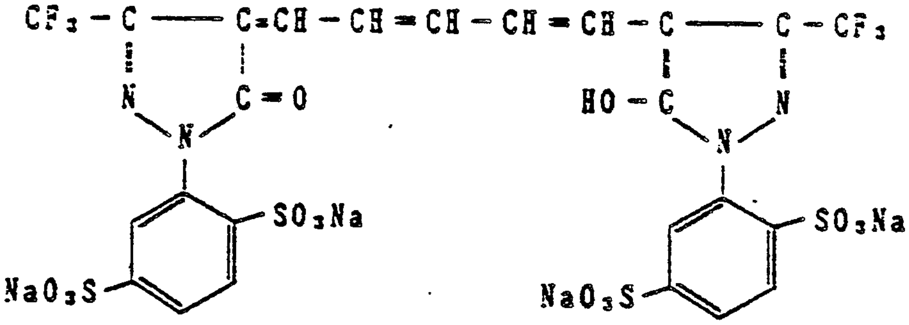

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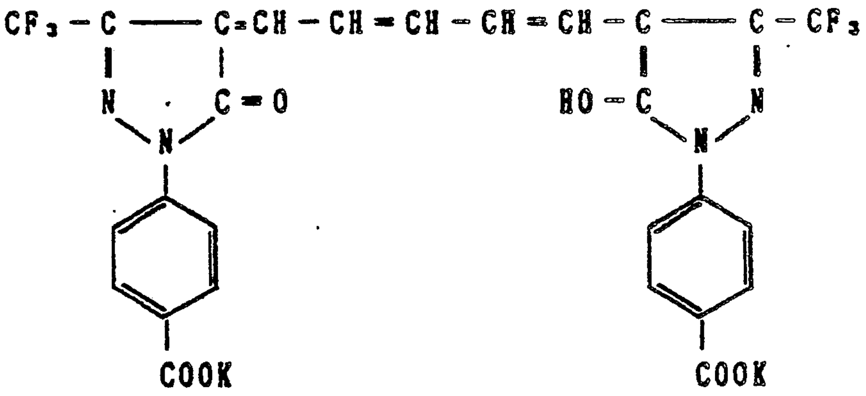

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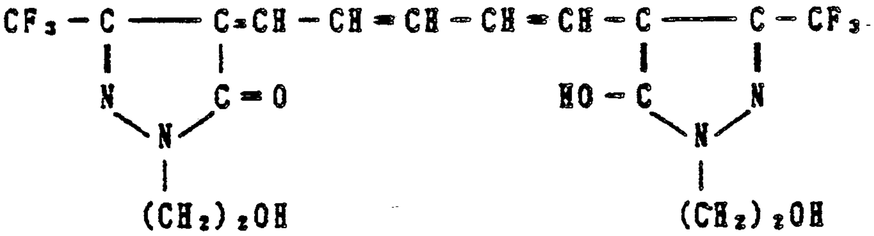
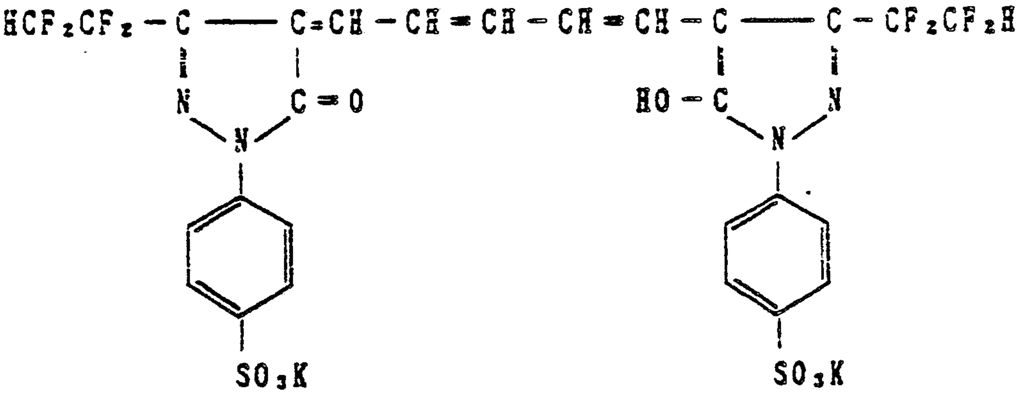
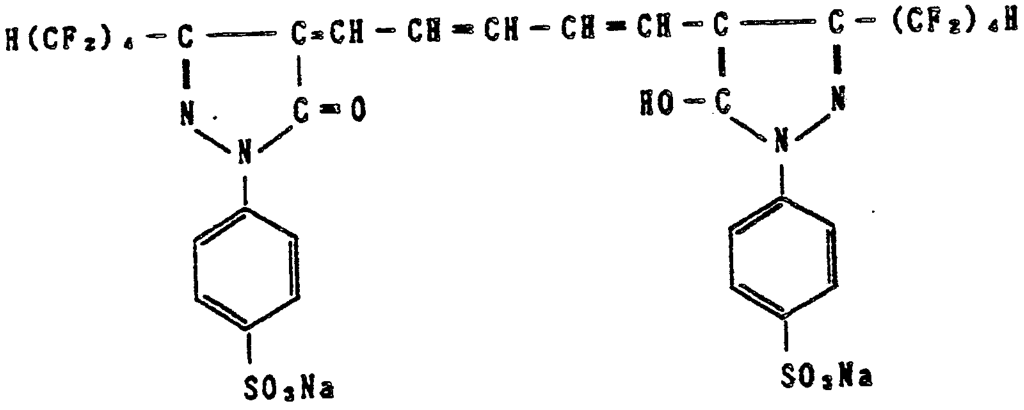


(V-32)



(V-33)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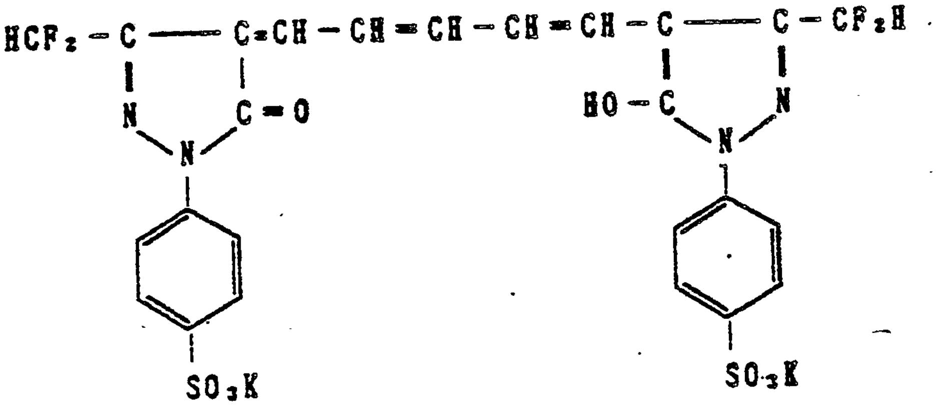
C=O
HO-C
N
SO₃Na
SO₃Na

(V-34)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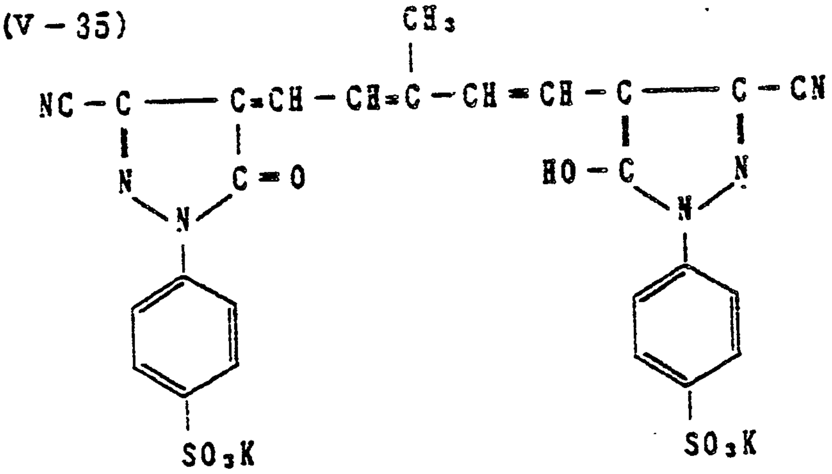
CF₂H
C=O
HO-C
N
SO₃K
SO₃K

(V-35)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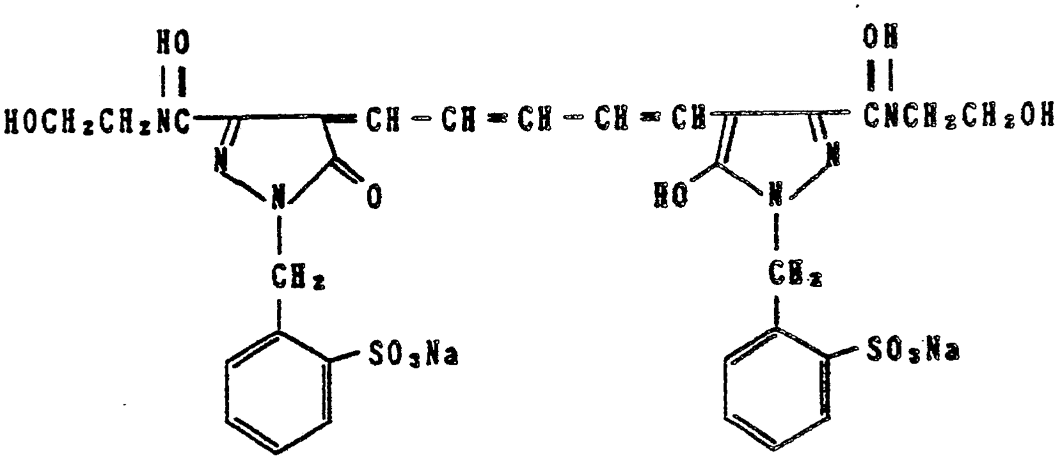
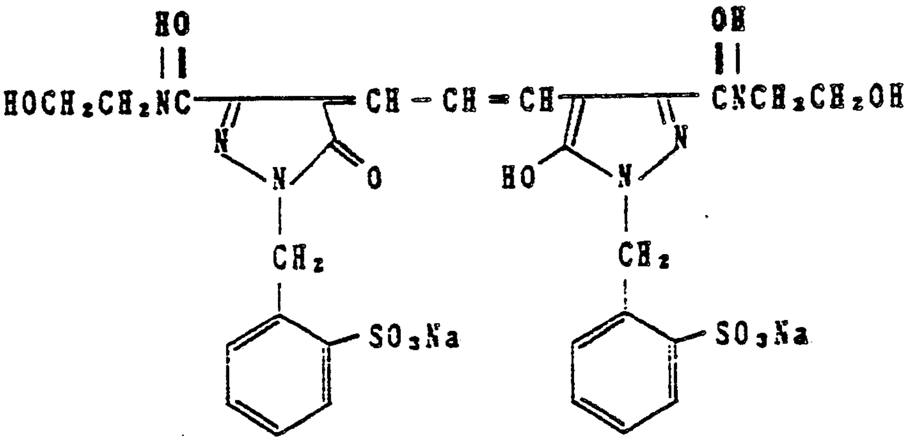
CN
C=O
HO-C
N
SO₃K
SO₃K

(V-36)



(V-37)



The amount of the compound shown by formula (V) is preferably from 0.0001 g to 1 g, more preferably from 0.0005 g to 0.1 g per square meter of the color photographic material containing the compound.

The dye shown by formula (V) is usually used as an irradiation inhibiting dye. The dye is usually used for silver halide emulsion layer(s), and is particularly preferably used for a green-sensitive emulsion layer or a red-sensitive emulsion layer.

The color developer for use in this invention contains an aromatic amine color developing agent. Preferred examples thereof are p-phenylenediamine derivatives and specific examples thereof are illustrated below although the invention is not limited to them.

D-1: N,N-Diethyl-p-phenylenediamine
D-2: 2-Amino-5-diethylaminotoluene
D-3: 2-Amino-5-(N-ethyl-N-laurylamino)toluene
D-4: 4-[N-Ethyl-N-(β-hydroxyethyl)amino]aniline
D-5: 2-Methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline
D-6: 4-Amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]aniline
D-7: N-(2-Amino-5-diethylaminophenylethyl)methanesulfonamide
D-8: N,N-Dimethyl-p-phenylenediamine
D-9: 4-Amino-3-methyl-N-ethyl-N-methoxyethylaniline
D-10: 4-Amino-3-methyl-N-ethyl-N-β-ethoxylethylaniline

D-11: 4-Amino-3-methyl-N-ethyl-N-β-butoxyethylaniline.

In the aforesaid p-phenylenediamine derivatives, 4-amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)-ethyl]aniline (Compound D-6) is particularly preferred.

Also, these p-phenylenediamine derivaties may be in the form of salts such as sulfates, hydrochlorides, sulfites, p-toluenesulfonates, etc.

The addition amount of the aromatic primary amine color developing agent is preferably from about 0.1 g to about 20 g, more preferably from about 0.5 g to about 10 g per liter of the color developer.

The color developer for use in this invention can, if necessary, contain an optional development accelerator. However, from the viewpoints of the inhibition of the occurrence of environmental pollution, the easiness of the preparation of solution, the inhibition of the occurrence of magenta, cyan, and yellow fogs, and the inhibition of the deviation of gradation, it is preferred that the color developer contains substantially no benzyl alcohol. The term "contains substantially no benzyl alcohol" means that contains benzyl alcohol in an amount of not higher than 2 ml per liter of the color developer. It is preferred that the color developer contains no benzyl alcohol.

Also, the color developer may contain, if necessary, other preservative such as sulfites (e.g., sodium sulfite, potassium sulfite, sodium hydrogensulfite, potassium hydrogensulfite, sodium metalsulfite, potassium metalsulfite) and carbonyl-sulfurous acid addition products. The addition amount of the preservative is from 0 g/liter to 20 g/liter, more preferably from 0 g/liter to 5 g/liter. If the preservativity of the color developer is kept, the amount of the preservative is as small as possible from the viewpoints of fog and gradation in the case of, in particular, using the cyan couplers described hereinafter for the color photographic materials being developed.

Other preservatives are hydroxyacetones described in U.S. Patent 3,615,503 and British Patent 1,306,176, α-aminocarbonyl compounds described in JP-A-52-143020 and JP-A-53-89425, various kinds of metals described in JP-A-57-44148 and JP-A-57-53749, various kinds of saccharides described in JP-A-52-102727, α-α′-dicarbonyl compounds described in JP-A-59-160141, salicyclic acids described in JP-A-59-180588, and gluconic acid derivatives described in JP-A-56-75647.

These preservatives may be used singly or as a mixture thereof. In particular, the aromatic polyhydroxy compounds are preferred.

The pH of the color developer for use in this invention is preferably from 9 to 12, more preferably from 9 to 11.0. The color developer may further contain other compounds known as components for color developer.

For keeping the aforesaid pH of the color developer, it is preferred to use various kinds of buffers such as carbonates, phosphates, borates, tetraborates, hydroxybenzoates, glycine salts, N,N-dimethylglycine salts, leucine salts, norleucine salts, guanine salts, 3,4-dihydroxyphenylalanine salts, alanine salts, aminobutyrates, 2-amino-2-methyl-1,3-propanediol salts, valine salts, proline salts, trihydroxyaminomethane salts, lysine salts, etc. In particular, carbonates, phosphates, tetraborates, and hydroxybenzoates have such advantages that they are excellent in solubility and also in buffer function in a high pH range of 9.0 or higher, they give no bad influences (fog formation, etc.) on photographic performance when they are added to the color developer, and they are available at low cost, and hence the use of such buffers is preferred.

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

The addition amount of the buffer to a color developer is preferably at least 0.1 mol/liter, more preferably from 0.1 mol/liter to 0.4 mol/liter.

Moreover, for the color developer for use in this invention can be used various chelating agents as a precipitation inhibitor for calcium and magnesium or for improving the stability of the color developer.

As the chelating agent, organic acid compounds are preferred and examples thereof are aminopolycarboxylic acids described in JP-B-48-30496 and JP-B-44-30232, organic phosphonic acids described in JP-A-56-973347, JP-B-56-39359, and West German Patent 2,227,639, phosphonocarboxylic acids described in JP-A-52-102726, JP-A-53-42730, JP-A-54-121127, JP-A-55-126241, and JP-A-55-659506, and the compounds described in JP-A-58-195845, JP-A-58-203440, and JP-B-53-40900.

Specific but non-limitative examples of these chelating agents are nitrilotriacetic acid, diethylenetriaminepentaacetic acid, ethylenediaminetetraacetic acid, N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N′,N′-tetramethylenephosphonic acid, transcyclohexanediaminetetraacetic acid, 1,2-

diaminopropanetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediamine o-hydroxyphenylacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, and N,N′-bis(2-hydroxybenzyl)ethylenediamine-N,N′-diacetic acid.

These chelating agents may be used singly or as a mixture thereof.

The addition amount of the chelating agent may be one sufficient for blocking the metal ions in the color developer and, for example, from about 0.1 g to about 10 g per liter of the color developer.

The color developer may, if necessary, contain an optional development accelerator. However, the color developer for use in this invention contains substantially no benzyl alcohol from the viewpoints of the inhibition of the occurrence of environmental polution and the formation of fog, and the easiness of the preparation of the solution as described above.

The compounds of aforesaid formula (I) and the compounds of aforesaid formula (II) or (III) give the remarkable effects in the stability of the color developer containing substantially no benzyl alcohol.

As other development accelerators, there are thio ether series compounds described in JP-B-37-16088, JP-B-37-5987, JP-B-38-7826, JP-B-44-12380, and JP-B-45-9019, and U.S. Patent 3,913,247, p-phenylenediamine series compounds described in JP-A-52-49829 and JP-A-50-15554, quaternary ammonium salts described in JP-A-50-137726, JP-A-56-156826, JP-A-52-43429, and JP-B-44-30074, amine series compounds described in JP-B-41-11431 and U.S. Patents 2,494,903, 3,128,182, 4,230,796, 3,253,919, 2,482,546, 2,596,926, and 3,582,346, polyalkylene oxides described in JP-B-37-16088, JP-B-42-25201, JP-B-41-11431, JP-B-42-23883, and U.S. Patents 3,128,183 and 3,532,501, and also 1-phenyl-3-pyrazolidones and imidazoles.

In this invention, the color developer can, if necessary, contain an optional antifoggant. As the antifoggant, there are alkali metal halides such as sodium chloride, potassium bromide, and potassium iodide and organic antifoggants. Examples of the organic antifoggant are nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitro isoindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 2-thiazolyl-benzimidazole, 2-thiazolylmethyl-benzimidazole, indazole, hydroxyazaindolidine, and adenine.

It is preferred that the color developer for use in this invention contains a fluorescent whitening agent. As the fluorescent whitening agent, 4,4′-diamino-2,2′-disulfostilbene series compounds are preferred. The addition amount thereof is from 0 to 5 g/liter, preferably from 0.1 g/liter to 4 g/liter.

Also, if necessary, the color developer for use in this invention may further contain various kinds of surface active agents such as alkylsulfonic acids, arylphosphonic acids, aliphatic carboxylic acids, aromatic carboxylic acids, etc.

The processing temperature for the color developer in this invention is from 20° C to 50° C, more preferably from 30° C to 40° C and the processing time is from 20 seconds to 5 minutes, preferably from 30 seccnds to 2 minutes. The replenishing amount is preferably less but is usually from 20 ml to 600 ml, preferably from 50 ml to 300 ml, and more preferably from 100 ml to 200 ml per square meter of the color photographic material being processed.

Then, a bleaching solution, a bleach-fix (blix) solution, and a fix solution for use in this invention are explained.

As the fixing agent for the bleach solution or blix solution, any conventional bleaching agents can be used. In particular, organic complex salts of iron(III) (e.g., iron(III) complex salts of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, etc., aminophosphonic acids, phosphonocarboxylic acids, and organic phosphonic acids); organic acids such as citric acid, tartaric acid, malic acid, etc.; persulfates; hydrogen peroxide, etc.

In these bleaching agents, the organic complex salts of iron(III) are particularly preferred from the viewpoints of quick processing and the prevention of the occurrence of environmental polution.

Useful aminopolycarboxylic acids, aminopolyphosphonic acids, and organic phosphonic acids for forming the organic complex salts of iron(III) are, for example, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, 1,3-diaminopropanetetraacetic acid, propylenediaminetetraacetic acid, nitrolotriacetic acid, cyclohexanediaminetetraacetic acid, methylimino diacetic acid, iminodiacetic acid, and glycol ether diaminetetraacetic acid.

These compounds may be in the form of sodium salts, potassium salts, lithium salts, or ammonium salts. In these compounds, the iron(III) complex satls of ethylelendiaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, 1,3-diaminopropanetetraacetic acid, and methyliminodiacetic acid are preferred from the viewpoint of showing high bleaching power.

The ferric ion complex salt may be used in the form of the complex salt or may be formed in an aqueous solution by using a ferric salt such as ferric sulfate, ferric chloride, ferric nitrate, ferric ammonium sulfate, ferric phosphate, etc., and a chelating agent such as amonopolycarboxylic acid, aminopolyphosphonic acid, phosphonocarboxylic acid, etc. In this case, the chelating agent may be used in an excessive amount to the formation of the ferric complex salt. In the ferric complex salts, the ferric complex salt of aminopolycarboxylic acid is preferred and the addition amount thereof is from 0.01 mol/liter to 1.0 mol/liter, more preferably from 0.05 mol/liter to 0.50 mol/liter.

For bleach solution, a blix solution and/or a pre-bath therefor can be used various compounds as a bleach accelerator. Examples thereof are the compounds having a mercapto group or a disulfide bond described in U.S. Patent, 3,893,858, German Patent 1,290,812, JP-A-53-95630, and Research Disclosure, No. 17129 (July, 1978), thiourea compounds described in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735, and U.S. Patent 3,706,561, and halides such as iodine ions, bromine ions, etc. They are excellent in bleaching power.

The bleach solution or blix solution for use in this invention may further contain a rehalogenating agent such as bromides (e.g., potassium bromide, sodium bromide, ammonium bromide), chlorides (e.g., potassium chloride, sodium chloride, ammonium chloride), and iodides (e.g., ammonium iodide). Furthermore, if necessary, the bleach solution or the blix solution may contain a corrosion inhibitor such as inorganic or organic acids having a pH buffer faculty or the alkali metal salts and ammonium salts of these acids (e.g., boric acid, borax, sodium metaborate, acetic acid, sodium acetate, sodium carbonate, potassium carbonate, phosphorous acid, phosphoric acid, sodium phosphate, citric acid, sodium citrate, tartaric acid), ammonium nitrate, guanidine, etc.

As a fixing agent for the blix solution or the fix solution being used in this invention, there are conventional fixing agents such as thiosulfates (e.g., sodium thiosulfate, ammonium thiosulfate), thiocyanates (e.g., sodium thiocyanate, ammonium thiocyanate), thioether compounds (e.g., ethylenebisthioglycolic acid, 3,6-dithia-1,8-octanediol), and thioureas known as water-soluble silver halide solvents. They can be used singly or as a mixture thereof. Also, specific blix solutions composed of a combination of a fixing agent and a large amount of halides such as potassium iodide described in JP-A-55-155354 can be used. In this invention, the use of thiosulfates, in particular ammonium thiosulfate is preferred.

The amount of the fixing agent is preferably from 0.3 mol to 2 mols, more preferably from 0.5 mol to 1.0 mol per liter of the blix solution or the fix solution. The pH range of the blix solution or the fix solution is preferably from 3 to 10, more preferably from 5 to 9.

Also, the blix solution can further contain various kinds of fluorescent whitening agents, defoaming agents or surface active agents, polyvinylpyrrolidone, and organic solvents such as methanol, etc.

The blix solution or the fix solution further contains a sulfite ion releasing compound such as sulfites (e.g., sodium sulfite, potassium sulfite, ammonium sulfite), hydrogensulfites (e.g., ammonium hydrogensulfite, sodium hydrogensulfite, potassium hydrogensulfite), and metahydrogensulfites (e.g., potassium metahydrogensulfite, sodium metahydrogensulfite, ammonium metahydrogensulfite) as a preservative.

The content of the compound is preferably from 0.02 mol/liter to 0.50 mol/liter, more preferably from 0.04 mol/liter to 0.40 mol/liter.

As the preservative, sulfites are generally added but, ascorbic acid, a carbonyl-hydrogensulfurous acid addition product, or a carbonyl compound may be used.

Furthermore, the blix solution or the fix solution may, if necessary, contain a buffer, a fluorescent whitening agent, a chelating agent, a defoaming agent, a fungicidal agent, etc.

In this invention, after desilvering processing such as blixing or fixing, the silver halide color photographic material is generally washed and/or stabilized.

The amount of wash water in the wash step is selected in a wide range according to various conditions such as the characteristics (by the materials being used, such as couplers, etc.) and uses of the color photographic materials, the temperature of wash water, the replenishing system such as countercurrent system and concurrent system. The relation of the number of wash tanks and the amount of wash water can be determined by the method described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, 248-253 (1955). The stage number of the tanks in a multistage countercurrent system is preferably from 2 to 6, particularly from 2 to 4.

By a multistage countercurrent system, the amount of wash water can be greatly reduced, for example, 0.5 liter to 1 liter per square meter of the color photographic material being processed but in this case, the increase of the residence time of water in the tanks is accompanied with a problem of growing bacteria and attaching floats formed onto the color photographic materials.

For solving the aforesaid problem, a method of reducing calcium and magnesium described in JP-A-62-288838 can be very effectively used. Also, isothiazolone compounds and thiabendazoles described in JP-A-57-8542, chlorine series sterilizers such as chlorinated sodium isocyanurates described in JP-A-61-120145, benzotriazoles described in JP-A-61-267761, copper ions, and the sterilizers described in Hiroshi Horiguchi, Bokin Bobaizai no Kaqaku (Chemistry of Antibacterial and Antifungal Agents), Biseibutsu no Mekkin, Sakkin, Bobai Gijutsu (Antibacterial and Antifungal Technique of Microorganisms), edited by Eisei Gijutsu Kai, and Bokin Bobaizai Jiten (Handbook of Antibacterial and Antifungal Agents) can be used.

Furthermore, for wash water can be used a surface active agent as a wetting agent and a chelating agent such as ethylenediaminetetraacetic acid (EDTA) as a water softener.

The pH of the wash water in the processing process of this invention is from 4 to 9, preferably from 5 to 8. The temperature and time for the wash step can be selected properly according to the properties and the use of the color photographic materials being processed but are generally from 20 seconds and 10 minutes at from 15° C to 45° C and preferably from 30 seconds to 5 minutes at from 25° C to 40° C.

After the aforesaid wash step or without employing the wash step, the color photographic materials can be processed by a stabilization solution. The stabilization solution contains a compound having a function of stabilizing images formed, such as an aldehyde compound (e.g., formalin), a buffer for controlling the pH of layers, and an ammonium compound. Also, for preventing the growth of bacteria in the solution and imparting an antifungal property to the photographic material after processing, the various kinds of sterilizers or antifungal agents described above can be used.

Furthermore, the stabilization solution may contain a surface active agent, a fluorescent whitening agent, a hardening agent, etc. When the stabilization is directly performed without employing wash step, the processes described in JP-A-57-8543, JP-A-58-14834, JP-A-59-184343, JP-A-60-220345, JP-A-60-238832, JP-A-60-239784, JP-A-60-239749, JP-A-61-4054, and JP-A-61-118749 can be used.

Furthermore, in a preferred embodiment of this invention, a chelating agent such as 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetramethylenephosphonic acid, etc., or a magnesium or bismuth compound can be used for the stabilization solution.

The solution used for the wash step and/or the stabilization step can be used for the pre-step. As an example thereof, there is a process wherein the overflow of wash water, the amount of which is reduced by a multistage countercurrent system, is supplied to a blix bath which is the pre-bath of the wash step and a concentrated solution is applied to the blix bath to reduce the amount of the waste solution.

The process of this invention can be applied to any processing processes using a color developer. For example, the invention can be applied to processing of color photographic papers, color reversal photographic papers, direct positive color photographic materials, color positive photographic films, color negative photographic films, color reversal photographic films, etc., but the invention is particularly preferably applied to processing of color photographic papers and color reversal photographic papers.

The silver halide emulsion for the color photographic materials being processed by the process of this invention is composed of silver iodobromide, silver bromide, silver chlorobromide, silver chloride, etc. For example, in the case of performing quick processing or low-replenishing process of color photographic papers, etc., a silver chlorobromide emulsion or silver chloride emulsion containing at least 60 mol% silver chloride is preferred and further the case that the content of silver chloride is from 80 mol% to 100 mol% is particularly preferred. Also, when a high speed is required and also the formation of fog at the production, storage, and/or processing the color photographic materials is kept at particularly low, a silver chlorobromide emulsion or silver bromide emulsion containing at least 50 mol% silver bromide (the emulsion may contain not higher than 3 mol% silver iodide) is preferred and the aforesaid emulsion containing at least 70 mol% silver bromide is more preferred.

For color photographic materials for camera use, a silver iodobromide emulsion or a silver chloroiodobromide emulsion is preferred and in this case, the content of silver iodide is preferably from 3 to 15 mol%.

The silver halide grains for use in this invention may have different phases between the inside and the surface layer thereof, may have a multiphase structure having a junction structure, or may be composed of a uniform phase throughout the whole grain. Also, the silver halide grains may be composed of a mixture thereof.

The mean grain size (shown by the diameter of the grains when the grain is spherical or similar to spherical, and shown by the mean value based on the projected area using, in the case of cubic grains, the long side length as the grain size, or further shown by the mean value calculated as circle in the case of tabular grains) of the silver halide grains for use in this invention is preferably in the range of from 0.1 µm to 2 µm, particularly preferably from 0.15 µm to 1.5 µm. The grain size distribution of the silver halide grains may be narrow or broad but the use of a so-called monodispersed silver halide emulsion, wherein the value (coefficient of variation) obtained by dividing the standard deviation in the grain size distribution curve of the silver halide emulsion by the mean grain size of the silver halide grains in the emulsion is within 20% (preferably within 15%), is preferred. Also, for satisfying the desired gradation for the color photographic materials, two or more kinds of monodispersed silver halide emulsions (preferably having the above-described coefficient of variation) each having different grain sizes can be used as a mixture thereof for one emulsion layer or as separate emulsion layers each having substantially the same color sensitivity. Furthermore, two or more kinds of polydispersed silver halide emulsions or a combination of the monodispersed silver halide emulsion and a polydispersed silver halide emulsion can be used as a mixture thereof for one emulsion layer or as separate emulsion layers.

The silver halide grains for use in this invention may have a regular crystal form such as cubic, octahedral, dodecahedral, tetradecahedral, etc., a mixture thereof, an irregular crystal form such as spherical, etc., or a composite form of these crystal forms. Also, the silver halide grains may be tabular grains and in this case, a tabular grain silver halide emulsion wherein grains having an aspect ratio (length/thickness) of from 5 to 8 or 8 or more account for at least 50% of the total projected area of the silver halide grains can be used in this invention. A mixture of these silver halide emulsions each containing silver halide grains having different crystal forms may be also used. The silver halide emulsion may be of a surface latent image type of forming latent images mainly on the surface thereof or of an internal latent image type of forming latent images mainly in the inside of the grains.

The silver halide emulsions for use in this invention can be prepared by the methods described in Research Disclosure (RD), Vol. 176, No. 17643, I, II, and III (December, 1978).

The emulsion for use in this invention is usually chemically ripened and spectrally sensitized after physical ripening. The additives being used in such steps are described in Research Disclosure, Vol. 176, No. 17643 (December, 1978), and ibid., Vol. 187, No. 18716 (November, 1979) and the corresponding portions thereof are shown in the following table together with other photographic additives for use in this invention.

Additive		RD 17643	RD 18716
1.	Chemical sensitizer	Page 23	Page 648, right column
2.	Sensitivity increasing agent		"
3.	Spectral sensitizer	Pages 23-24	Page 648, right column to page 649, right column
4.	Supersensitizer		Page 649, right column
5.	Whitening agent	Page 24	
6.	Antifoggant and stabilizer	Pages 24-25	Page 649, right column
7.	Coupler	Page 25	
8.	Organic solvent	Page 25	
9.	Ligh absorbent, filter dye, ultraviolet absorbent	Pages 25-26	Page 649, right column to page 650, left column
10.	Stain inhibitor	Page 25, right column	Page 650, left to right columns
11.	Dye image stabilizer	Page 25	
12.	Hardening agent	Page 26	Page 651, left column
13.	Binder	Page 26	"
14.	Plasticizer, lubricant	Page 27	Page 650, right column
15.	Coating aid and surface active agent	Pages 26-27	"
16.	Static inhibitor	Page 27	"

In this invention, various color couplers can be used for color photographic materials being processed. The term "color coupler" means a compound capable of forming a dye by causing coupling reaction with the oxidation product of an aromatic primary amine color developing agent. Typical examples of the useful coupler are naphtholic or phenolic couplers, pyrazolone or pyrazoloazole series compounds, and open chain or heterocyclic ketomethylene compounds. Specific examples of the cyan magenta and yellow couplers for use in this invention are described in the patents cited in Research Disclosure, No. 17643, VII-D (December, 1978) and ibid., No. 18717 (November, 1979).

It is preferred that the color couplers contained in the color photographic materials are rendered non-diffusible by a ballast group or by being polymerized. Furthermore, the use of 2-equivalent color couplers, the coupling active site of which is substituted by a releasing group, is more effective for reducing the amount of silver than the case of using 4-equivalent color couplers having a hydrogen atom at the coupling active site thereof. Couplers providing colored dyes having a proper diffusibility, non-coloring couplers, DIR couplers releasing a development inhibitor with the coupling reaction, and couplers releasing a development accelerator with the coupling reaction can be also used.

Typical examples of the yellow couplers for use in this invention are oil-protect type acylacetamide series couplers. Specific examples thereof are described in U.S. Patents 2,407,210, 2,875,057, and 3,265,506.

In this invention, 2-equivalent yellow couplers are preferably used and typical examples thereof are oxygen atom-releasing type yellow couplers described in U.S. Patents 3,408,194, 3,447,928, 3,933,501, and 4,022,620 and nitrogen atom-releasing type yellow couplers described in JP-B-55-10739, U.S. Patents 4,401,752 and 4,326,024, British Patent 1,425,020, West German Patent Application (OLS) Nos. 2,219,917, 2,261,361, 2,329,587, and 2,433,812, and Research Disclosure, No. 18053 (April, 1979). In these couplers, α-pivaloylacetanilide series couplers are excellent in fastness, in particular, light fastness of the colored dyes formed, while α-benzoylacetanilide series yellow couplers give high coloring density.

As the magenta couplers for use in this invention, there are oil-protect type inadazolone series and cyanoacetyl series couplers, preferably 5-pyrazolone series couplers and pyrazoloazole series couplers such as pyrazolotriazole series couplers.

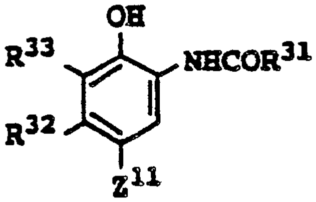
The 5-pyrazolone series couplers having an arylamino group or an acylamino group at the 3-position thereof are preferred from the viewpoint of the hue of the colored dyes and typical examples are described in U.S. Patents 2,311,082, 2,343,703, 2,600,788, 2,908,573, 3,062,653, 3,152,896, and 3,936,015.

Preferred releasing groups for the 2-equivalent 5-pyrazolone series magenta couplers include nitrogen atom-releasing groups described in U.S. Patent 4,310,619 and arylthio groups described in U.S. Patent 4,351,897. Also, 5-pyrazolone series magenta couplers having a ballast group described in European Patent 73,636 give high coloring density.

Pyrazoloazole series magenta couplers include pyrazolobenzimidazoles described in U.S. Patent 3,369,879, preferably pyrazolo[5,1-c][1,2,4]triazoles described in U.S. Patent 3,725,067, pyrazolotetrazoles described in Research Disclosure, No. 24220, (June, 1981), and pyrazolopyrazoles described in Research Disclosure, No. 24230 (June, 1984). From the viewpoint of less yellow side absorption of colored dyes and high light fastness of colored dyes, imidazo[1,2-b]pyrazoles described in European Patent 119,741 are preferred and pyrazolo[1,5-b][1,2,4]triazoles described in European Patent 119,860 are particularly preferred.

Cyan couplers for use in this invention include oil-protect type naphtholic and phenolic couplers, and typical examples are naphtholic couplers described in U.S. Patent 2,474,293, preferably oxygen atom-releasing type 2-equivalent naphtholic couplers described in U.S. Patents 4,052,212, 4,146,396, 4,228,233, and 4,296,200. Also, specific examples of the phenolic cyan couplers are described in U.S. Patents 2,369,929, 2,801,171, 2,772,162, and 2,895,826. Cyan couplers having high fastness to moisture and heat are preferably used in this invention, and typical examples thereof are the phenolic cyan couplers having an alkyl group of two or more carbon atoms at the meta-position of the phenol nucleus described in U.S. Patent 3,772,002, 2,5-diacylamino-substituted phenolic cyan couplers described in U.S. Patents 2,772,162, 3,758,308, 4,126,396, 4,334,011 and 4,327,173, West German Patent Application (OLS) No. 3,329,729, and JP-A-59-166956, and phenolic cyan couplers having a phenylureido group at the 2-position and an acylamino group at the 5-position thereof described in U.S. Patents 3,446,622, 4,333,999, 4,451,559, and 4,427,767.

In particular, the processing process of this invention, good photographic properties with less formation of fog can be obtained by using at least one kind of cyan couplers shown by following formula (C-1), which is also a specific effect.



wherein R^{31} represents an alkyl group, a cycloalkyl group, an aryl group, an amino group, or a heterocyclic group; R^{32} represents an acylamino group or an alkyl group having 2 or more carbon atoms, R^{33} represents a hydrogen atom, a halogen atom, an alkyl group, or an alkoxy group; R^{32} and R^{33} may combine with each other to form a ring; and Z^{11} represents a hydrogen atom, a halogen atom or a group capable of being released at the reaction with the oxidation product of an aromatic primary amine color developing agent.

The alkyl group shown by R^{31} is formula (C-1) is preferably an alkyl group having from 1 to 32 carbon atoms (e.g., methyl, butyl, tridecyl, cyclohexyl, allyl), examples of the aryl group shown by R^{31} are phenyl and naphthyl, and examples of the heterocyclic group are 2-pyridyl and 2-furyl.

When R^{31} in formula (C-1) is an amino group, a phenyl-substituted amino group which may be further substituted is preferred.

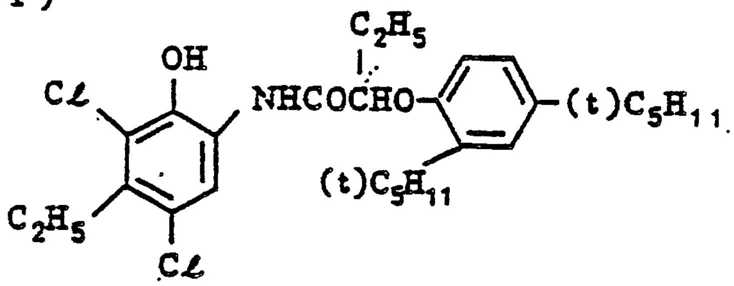
The groups shown by R^{31} may be substituted by an alkyl group, an aryl group, an alkyloxy or aryloxy group (e.g., methoxy, dodecyloxy, methoxyethoxy, phenyloxy, 2,4-di-tert-amylphenoxy, 3-tert-butyl-4-hydroxyphenyloxy, naphthyloxy), a carboxy group, an alkylcarbonyl or arylcarbonyl group (e.g., acetyl, tetradecanoyl, benzoyl), an alkyloxycarbonyl or aryloxycarbon group (e.g., methoxycarbonyl, phenoxycarbonyl), an acyloxy group (e.g., acetoxy, benzoyloxy), a sulfamoyl group (e.g., N-ethylsulfamoyl, N-octadecylsulfamoyl), a carbamoyl group (e.g., N-ethylcarbamoyl, N-methyldodecylcarbamoyl), a sulfonamido group (e.g., methanesulfonamido, benzenesulfonamido), an acylamino group (e.g., acetylamino, benzamido, ethoxycarbonylamino, phenylaminocarbonylamino), an imido group (e.g., succinimido, hydantoinyl), a sulfonyl group (e.g., methanesulfonyl), a hydroxyl group, a cyano group, a nitro group, or a halogen atom.

In formula (C-1), Z^{11} represents a hydrogen atom or a coupling releasing group such as, for example, a halogen atom (e.g., fluorine, chlorine, bromine), an alkoxy group (e.g., dodecyloxy, methoxycarbamoylmethoxy, carboxypropyloxy, methylsulfonylmethoxy), an aryloxy group (e.g., 4-chlorophenoxy, 4-methoxyphenoxy), an acyloxy group (e.g., acetoxy, tetradecanoyloxy, benzoyloxy), a sulfonyloxy group (e.g., methanesulfonyloxy, toluenesulfonyloxy), an amido group (e.g., dichloroacetylamino, methanesulfonylamino, toluenesulfonylamino), an alkoxycarbonyloxy group (e.g., ethoxycarbonyloxy, benzyloxycarbonyloxy), an aryloxycarbonyloxy group (e.g., phenoxycarbonyloxy), an aliphatic or aromatic thio group (e.g., phenylthio, tetrazolylthio), an imido group (e.g., succinimido, hydantoinyl), an N-heterocyclic group (e.g., 1-pyrazolyl, 1-benztriazole), or an aromatic azo group (e.g., phenylazo). These releasing groups may contain a photographically useful group.

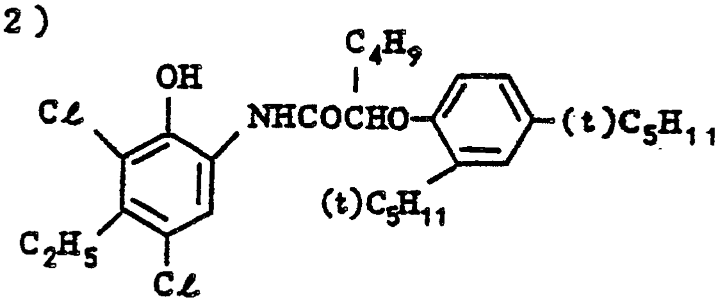
The compounds shown by formula (C-1) may form a dimer or a more polymer at R^{31} or R^{32}.

Then, specific examples of the cyan couplers shown by formula (C-1) are illustrated below but the invention is not limited to them.

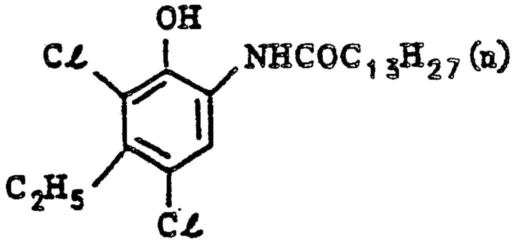
(C-1)



(C-2)



(C-3)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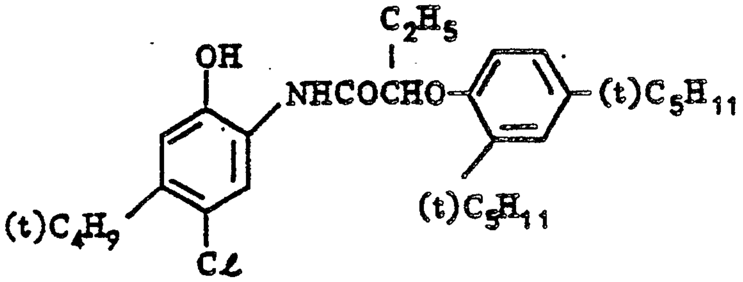
Cℓ
NHCOC13H27(n)
C2H5
Cℓ

(C-4)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OH
NHCOCHO
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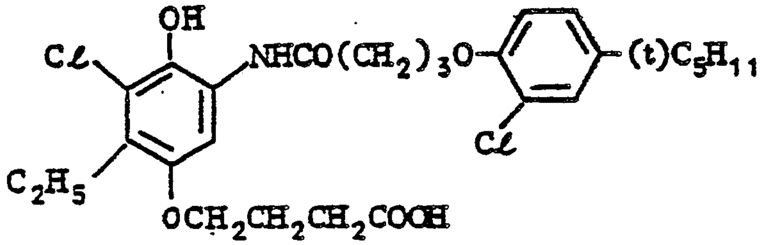
(t)C5H11
(t)C4H9
Cℓ

(C-5)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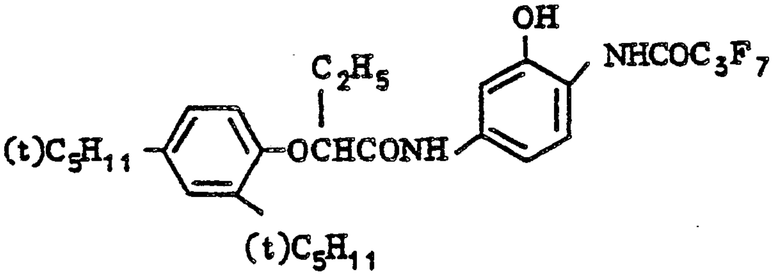
Cℓ
NHCO(CH2)3O
(t)C5H11
Cℓ
C2H5
OCH2CH2CH2COOH

(C-6)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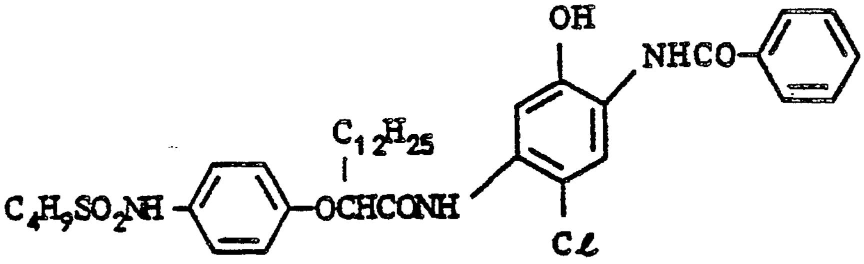
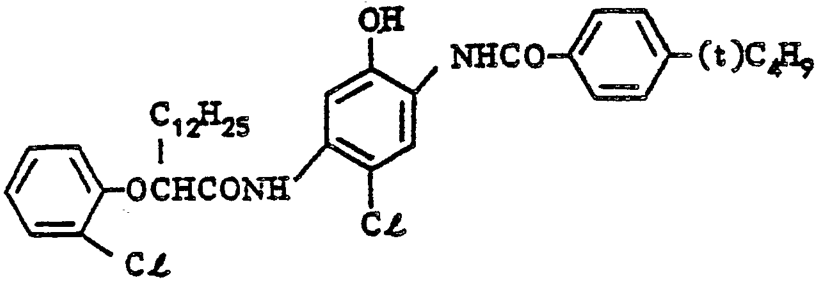
C2H5
(t)C5H11
OCHCONH
(t)C5H11

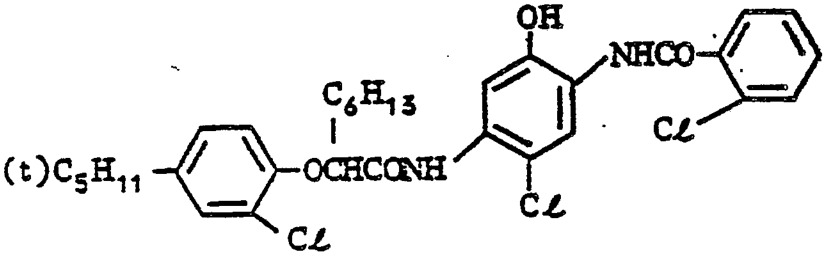
(C-7)



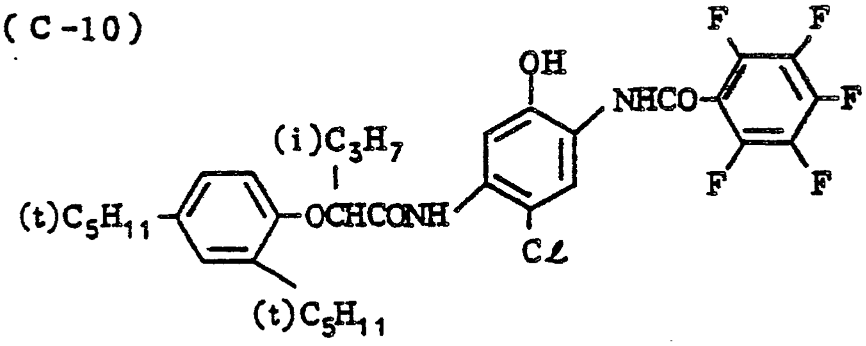
(C-8)



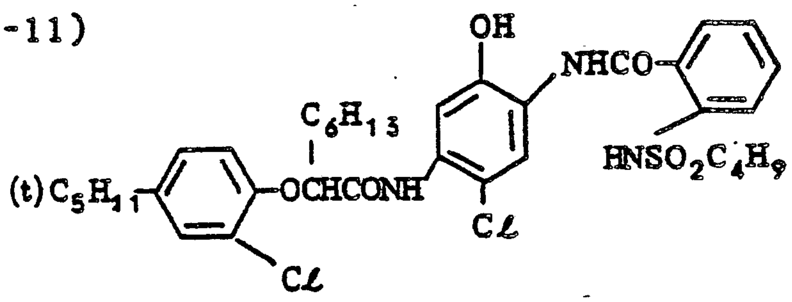
(C-9)



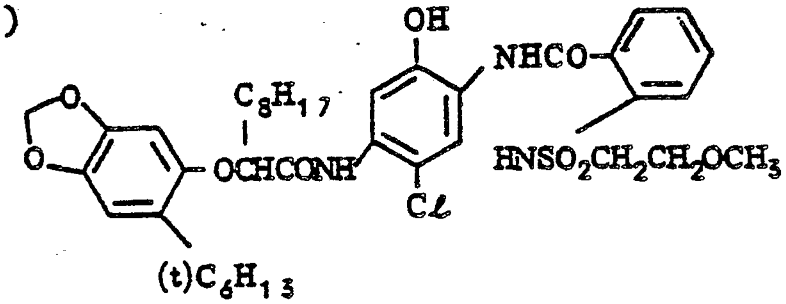
(C-10)



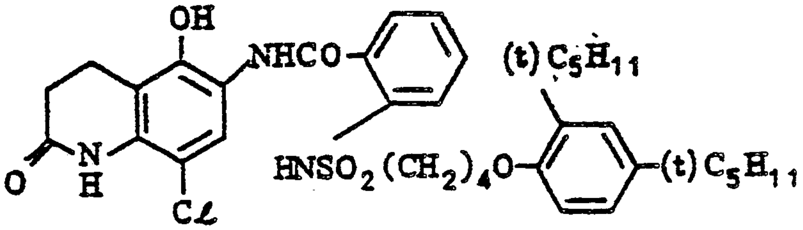
(C-11)



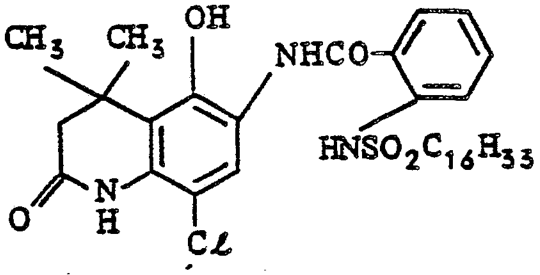
(C-12)



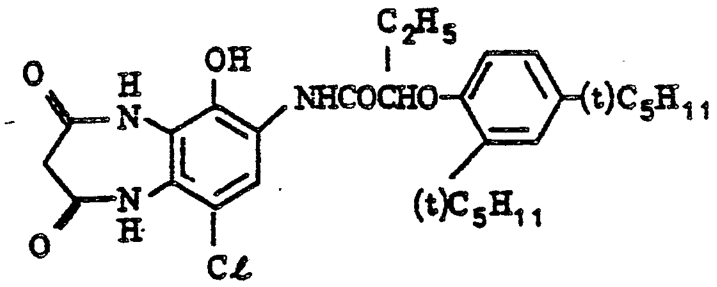
(C-13)



(C-14)



(C-15)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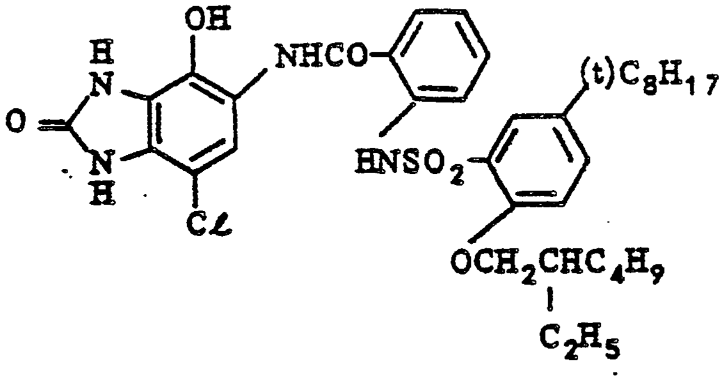
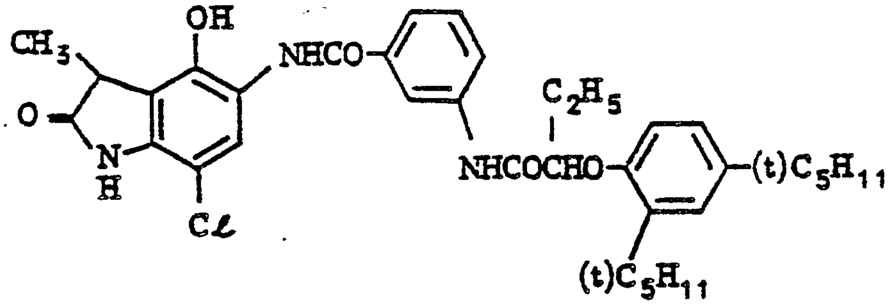
O
H
N
NHCOCHO
(t)C5H11
N
H
O
Cℓ
(t)C5H11

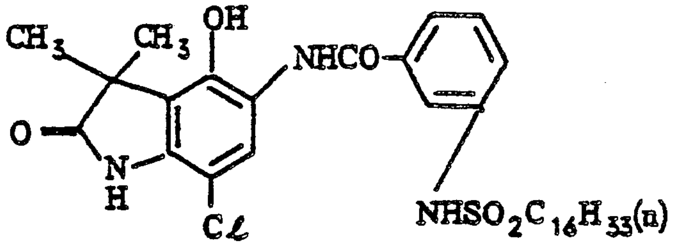
(C-16)


OH
H
N
NHCO
(t)C8H17
O
N
H
HNSO2
Cℓ
OCH2CHC4H9
C2H5

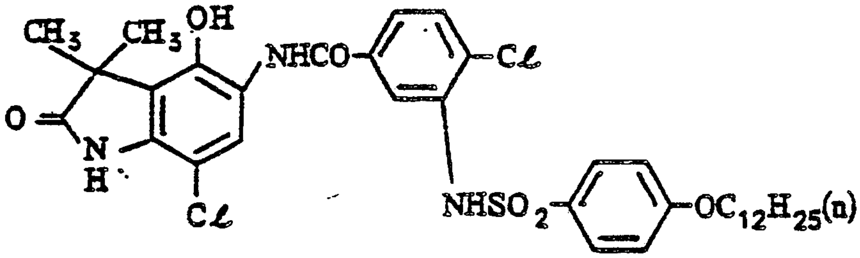
(C-17)


OH
CH3
NHCO
C2H5
O
N
H
NHCOCHO
(t)C5H11
Cℓ
(t)C5H11

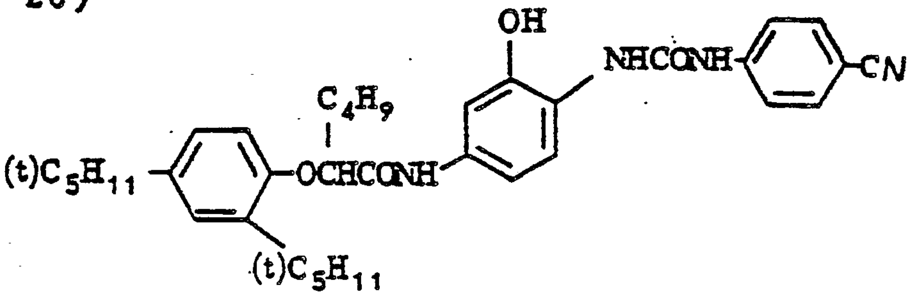
(C-18)



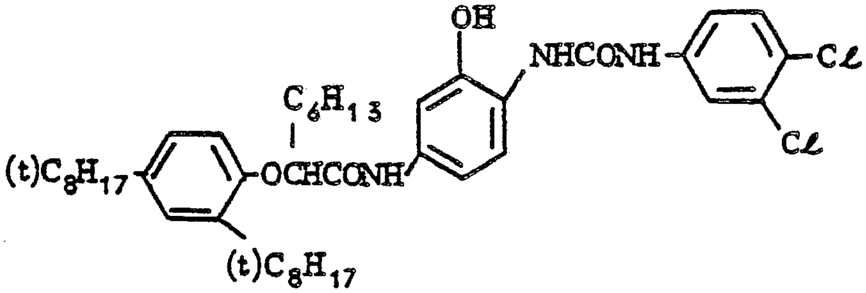
(C-19)



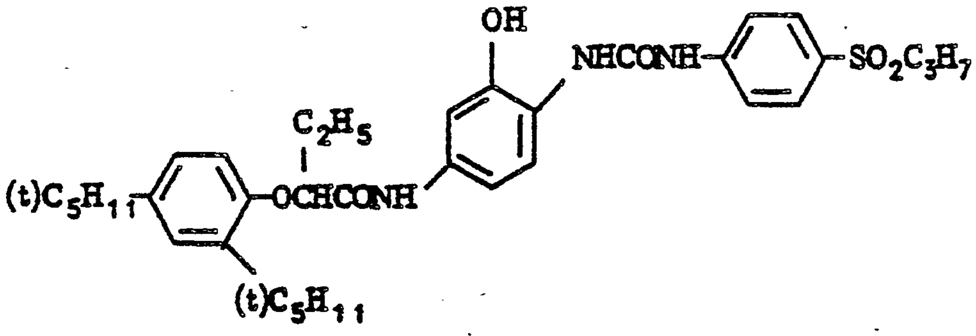
(C-20)



(C-21)



(C-22)


OH
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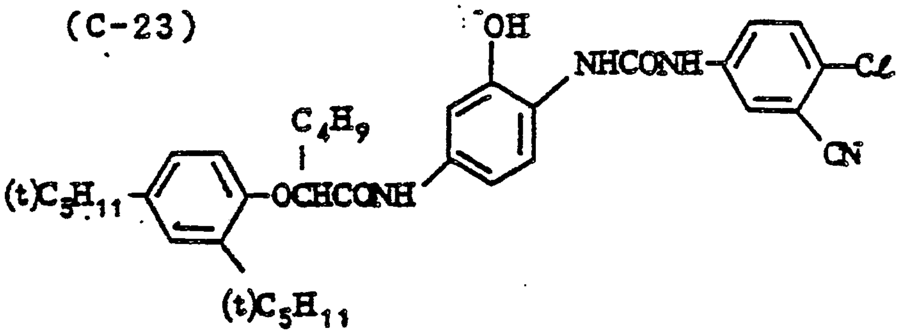
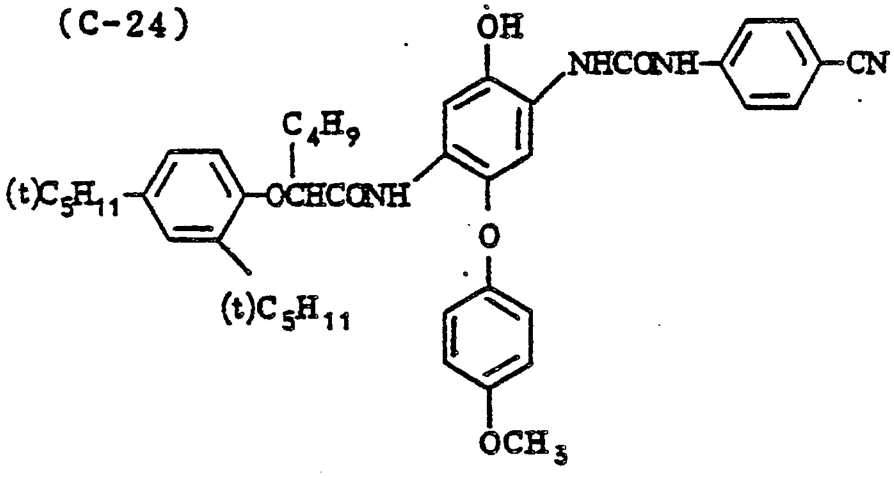
$SO_2C_3H_7$
C_2H_5
$(t)C_5H_{11}$
OCHCONH
$(t)C_5H_{11}$

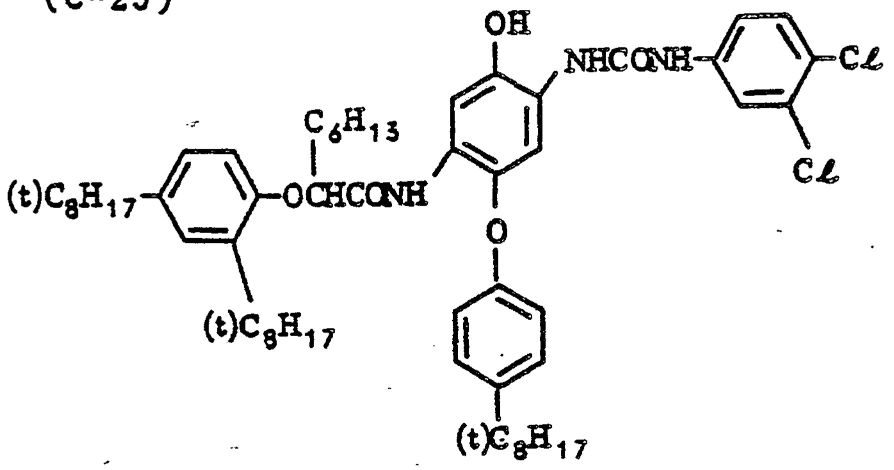
(C-23)


OH
NHCONH
Cℓ
CN
C_4H_9
$(t)C_5H_{11}$
OCHCONH
$(t)C_5H_{11}$

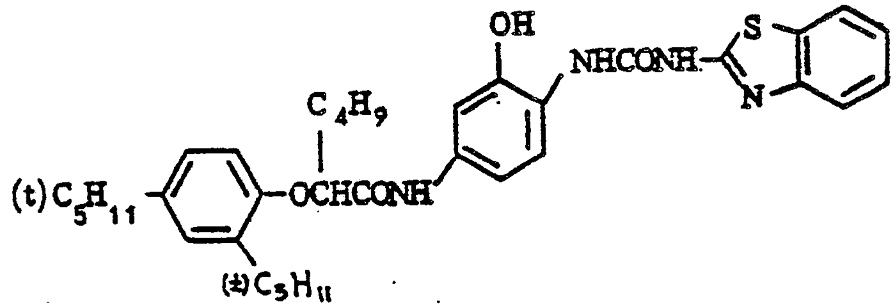
(C-24)


OH
NHCONH
CN
C_4H_9
$(t)C_5H_{11}$
OCHCONH
$(t)C_5H_{11}$
O
OCH_3

(C-25)



(C-26)



The cyan couplers shown by formula (C-1) can be synthesized based on the descriptions in JP-A-59-166956 and JP-B-49-11572.

In this invention, the graininess of the color images formed can be improved by using a coupler giving colored dye having a proper diffusibility together with the aforesaid coupler(s). About such couplers giving diffusible dyes, specific examples of the magenta couplers are described in U.S. Patent 4,366,237 and British Patent 2,125,570 and specific examples of the yellow, magenta and cyan couplers are described in European Patent 96,570 and West German Patent Application (OLS) No. 3,234,533.

The dye-forming couplers and the specific couplers described above may form a dimer or polymer. Typical examples of the polymerized dye-forming couplers are described in U.S. Patents 3,451,820 and 4,080,211. Also, specific examples of the polymerized magenta couplers are described in British Patent 2,102,173 and U.S. Patent 4,367,282.

The couplers for use in this invention can be used for one light-sensitive emulsion layer as a mixture of two or more for meeting the properties required for the color photographic material or the same kind of coupler may be incorporated in two or more photographic layers.

The coupler for use in this invention can be introduced into silver halide emulsions by an oil drop-in-water dispersion method. Examples of a high-boiling organic solvent being used for the oil drop-in-water dispersion method are described in U.S. Patent 2,322,027. Also, the coupler can be introduced into the silver halide emulsions by a latex dispersion method and specific examples of the step and the effect of the latex dispersion method and the latex for the impregnation are described in U.S. Patent 4,199,363 and West German Application (OLS) Nos. 2,541,274 and 2,541,230.

A standard amount of the color coupler is in the range of from 0.001 mol to 1 mol per mol of the light-sensitive silver halide in the silver halide emulsion, with from 0.01 mol to 0.5 mol of a yellow coupler, from 0.003 mol to 0.3 mol of a magenta coupler, and from 0.002 mol to 0.3 mol of a cyan coupler, per mol of the light-sensitive silver halide being preferred.

The color photographic materials being processed by the process of this invention is prepared by coating the aforesaid emulsions, etc., on a flexible support such as plastic films (films of cellulose nitrate, cellulose acetate, polyethylene terephthalate, etc.), papers, etc., or a solid support such as glass plates, etc.

Detailed of such supports and the coating methods are described in Research Disclosure, Vol. 176, No. 17643, XV (page 27) and XVII (page 28) (December, 1978).

The process of this invention is preferably applied to color photographic materials using reflective supports. The "reflective support" is a support having high reflectivity for clearly viewing color images forming in silver halide emulsion layer(s) and includes a support coated with a hydrophobic resin having dispersed therein a light reflective material such as titanium oxide, zinc oxide, calcium carbonate, calcium sulfate, etc., and a support composed of a hydrophobic resin containing the light reflective material described above.

The invention is now illustrated in detail with reference to the following examples but the invention is not limited thereto.

EXAMPLE 1

A color Developer having the following composition was prepared.

Color Developer	
Compound (A) (Compounds of formulae (II) and (III)	Shown in Table 1 below
Compound (B) (Compound of formula (I))	Shown in Table 1
Sodium Sulfite	0.2 g
Potassium Carbonate	30 g
Disodium Ethylenediaminetetraacetate	1 g
4-Amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]aniline Sulfate	5.0 g
Whitening Agent (4,4′-diaminostilbene series, UVITEX-CK®, made by Chiba-Geigy AG)	3.0 g
Water to make 1 liter	
pH	10.05

Thus, Samples No. 1 to No. 17 of color developer were prepared. Each of the samples was placed in a test tube so that the opening ratio (opening area/sample area) became 0.02 cm^{-1} and stirred for 4 weeks while controlling to 35° C. After 4 weeks, the volume of water reduced by evaporation was supplemented by distilled water and the residual rate of the aromatic primary amine color developing agent in the developer was measured by liquid chromatography. The results obtained are shown in Table 1.

Table 1

Sample No.	Compound (A)*1 (0.03 mol/ℓ)	Compound (B)*2 (0.4 mol/ℓ)	Residual Rate*3 (%)	Note
1	-	I-7	58	Comparison
2	-	I-12	61	"
3	Triethanolamine (II-1)	N,N-diethylhydroxylamine	60	"
4	Polyethyleneimine*4	"	50	"
5	III-7	"	62	"
6	II-1	I-7	95	Invention
7	II-3	"	90	"
8	III-1	"	91	"
9	III-7	"	91	"
10	II-1	I-12	98	"
11	II-3	"	92	"
12	III-1	"	93	"
13	III-7	"	94	"
14	II-1	I-22	93	"
15	"	I-25	93	"
16	"	I-48	92	"
17	"	I-49	90	"

*1: The compounds are shown by the number of compounds shown above.

*2: The compounds are shown by the number of compounds shown above.

***3: Residual rate(%) of color developing agent =** $\frac{(A)}{5.0g/\ell} \times 100$

***4:** $-\!\!(CH_2CH_2NH)\!\!-_n$ **n=500 to 2,000**

As is clear from the results shown in Table 1, it can be seen that the residual rate is insufficient in the case of using the compound of formula (I) alone (Sample Nos. 1 and 2) and the residual rate is not sufficient even in the case of using the polyethyleneimine such as triethanolamine or the compound such as Compound III-7 together with N,N-diethylhydroxylamine (Sample Nos. 3, 4, and 5). However, as is clear from the results of Sample Nos. 6 to 17 of this invention, it can be seen that by the use of the compound shown by formula (II) or (III) together with the compound of formula (I), the residual rate of the color developing agent is greatly improved, which shows the preservativity of the color developer being improved.

EXAMPLE 2

By following the same procedure as Example 1 except that Compound I-28, I-44, I-58 or I-60 was used in place of Compound I-7 in Sample Nos. 6 and 7, almost same preferred results were obtained.

EXAMPLE 3

By following the same procedure as Example 1 except that Compound II-4, II-5, II-10 or II-15 and Compound III-2, III-5, III-8 or III-11 were used in place of Compound II-3 and Compound III-1 in Sample Nos. 7 and 8, almost the same results were obtained.

EXAMPLE 4

A multilayer color photographic paper having the following layers on a paper support having polyethylene coating on both surfaces thereof was prepared.

The coating compositions for the layer were prepared as follows.

Preparation of Coating Compositions

In 27.2 ml of ethyl acetate and 7.7 ml (8.0 g) of a high-boiling solvent (Solv-1) were dissolved 19.1 g of a yellow coupler (ExY-1) and 4.4 g of a color image stabilizer (Cpd-1) and the solution was dispersed by emulsification in 185 ml of an aqueous 10% gelatin solution containing 8 ml of a solution of 10% sodium dodecylbenzenesulfonate. The emulsified dispersion was mixed with silver halide emulsions EM 7 and EM 8 and the gelatin concentration was adjusted as shown below to provide the coating composition for Layer 1. The coating compositions for Layers 2 to 7 were prepared by the similar manner as above. For each layer was used 1- oxy-3,5-dichloro-s-triazine sodium salt as a gelatin hardening agent. Also, for each layer was used Compound (Cpd-1) as a thickener.

Layer Structure

The composition of each layer was shown below. The numeral shows the coating amount (g/m^2), wherein a silver halide emulsion is shown by the coating amount calculated as silver.

In addition, the polyethylene coating at the emulsion side contained a white pigment (TiO_2) and a bluish dye.

Layer 1 Blue-sensitive Emulsion Layer	
Monodispersed silver chlorobromide emulsion (EM 7) spectrally sensitized by sensitizing dye (ExS-1)	0.15
Monodispersed silver chlorobromide emulsion (EM 8) spectrally sensitized by sensitizing dye (ExS-1)	0.15
Gelatin	1.86
Yellow coupler (ExY-1)	0.82
Color image stabilizer (Cpd-2)	0.19
Solvent (Solv-1)	0.35

Layer 2 Color Mixing Inhibiting Layer	
Gelatin	0.99
Color mixing inhibitor (Cpd-3)	0.08

Layer 3 Green-sensitive Emulsion Layer	
Monodispersed silver chlorobromide emulsion (EM 9) spectrally sensitized by sensitizing dyes (ExS-2 and 3)	0.12
Monodispersed silver chlorobromide emulsion (EM 10) spectrally sensitized by sensitizing dyes (ExS-2 and 3)	0.24
Gelatin	1.24
Magenta coupler (ExM-1)	0.39
Color image stabilizer (Cpd-4)	0.25
Color image stabilizer (Cpd-5)	0.12
Solvent (Solv-2)	0.25

Layer 4 Ultraviolet Absorption Layer	
Gelatin	1.60
Ultraviolet absorbents (Cpd-6/Cpd-7/Cpd-8 = 3/2/6 by weight ratio)	0.70
Color mixing inhibitor (Cpd-9)	0.05
Solvent (Solv-3)	0.42

Layer 5 Red-sensitive Emulsion Layer	
Monodispersed silver chlorobromide emulsion (EM 11) spectrally sensitized by sensitizing dyes (ExS-4 and 5)	0.07
Monodispersed silver chlorobromide emulsion (EM 12) spectrally sensitized by sensitizing dyes (ExS-4 and 5)	0.16
Gelatin	0.92
Cyan coupler (ExC-1)	1.46
Cyan coupler (ExC-2)	1.84
Color image stabilizers (Cpd-7/Cpd-8/Cpd-10 = 3/4/2 by weight ratio)	0.17
Dispersing polymer (Cpd-11)	0.14
Solvent (Solv-1)	0.20

Layer 6 Ultraviolet Absorption Layer	
Gelatin	0.54
Ultraviolet absorbents (Cpd-6/Cpd-8/Cpd-10 = 1/5/3 by weight ratio)	0.21
Solvent (Solv-4)	0.08

Layer 7 Protective Layer	
Gelatin	1.33
Acryl-modified copolymer of polyvinyl alcohol (modification degree 17%)	0.17
Liquid paraffin	0.03

Also, in this case, Compounds (Cpd-12 and Cpd-13) were used as irradiation inhibiting dyes. Furthermore, for each layer Alkanol XC® (trade name, made by DuPont), sodium alkylbenzenesulfonate, and Magefacx® F-120 (trade name, made by Dainippon Ink and Chemicals, Inc.) were used as emulsion-dispersing agent and coating aid. Further, Compounds (Cpd-14 and Cpd-15) were used as stabilizers of the silver halides.

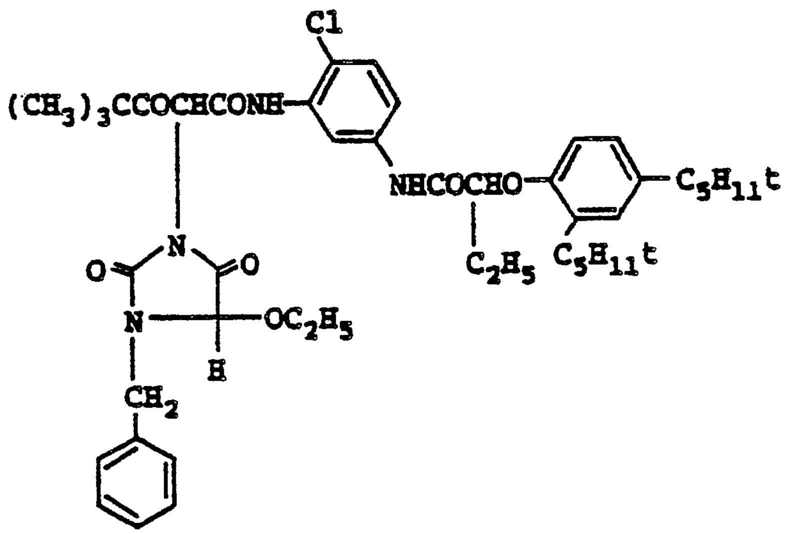
The details of the silver halide emulsions used were as follows.

Emulsion	Form	Grain Size (μm)	Br-Content (mol%)	Coefficient of variation*
EM 7	Cubic	1.1	1.0	0.10
EM 8	Cubic	0.8	1.0	0.10
EM 9	Cubic	0.45	1.5	0.09
EM 10	Cubic	0.34	1.5	0.09
EM 11	Cubic	0.45	1.5	0.09
EM 12	Cubic	0.34	1.6	0.10

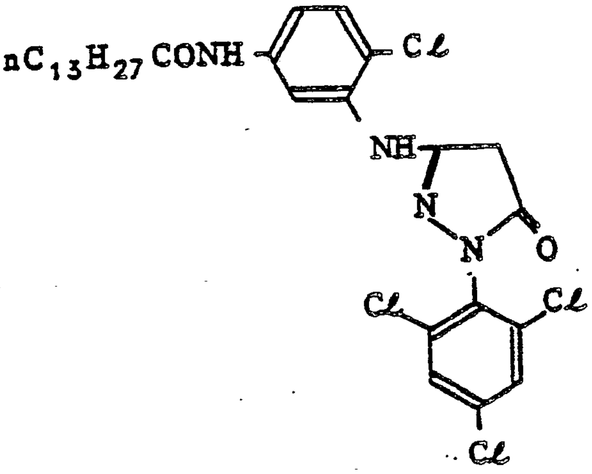
(*): Standard deviation/mean grain size, which shows the distribution of grains

The compounds used are as follows.

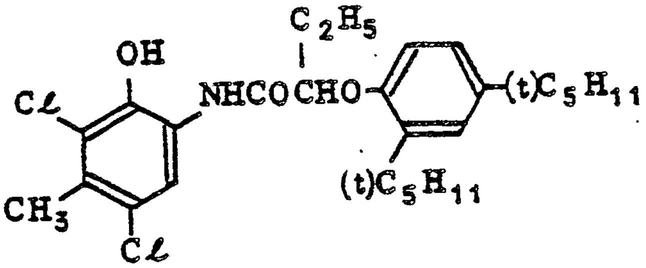
ExY-1



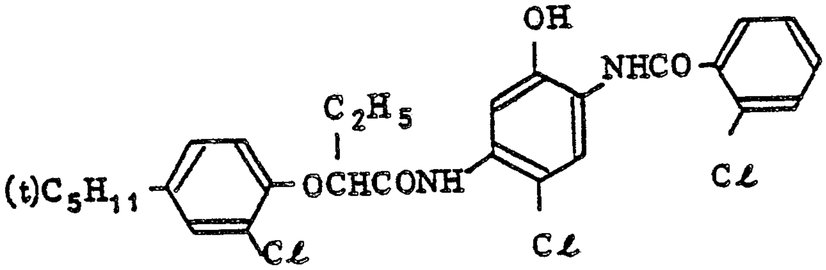
ExM-1



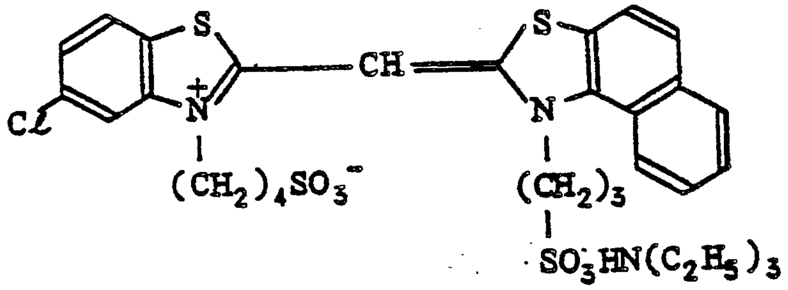
ExC-1



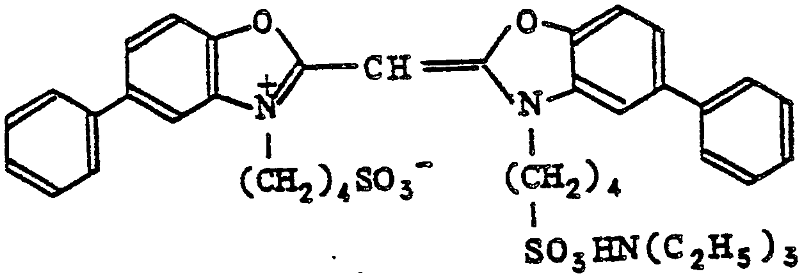
ExC-2



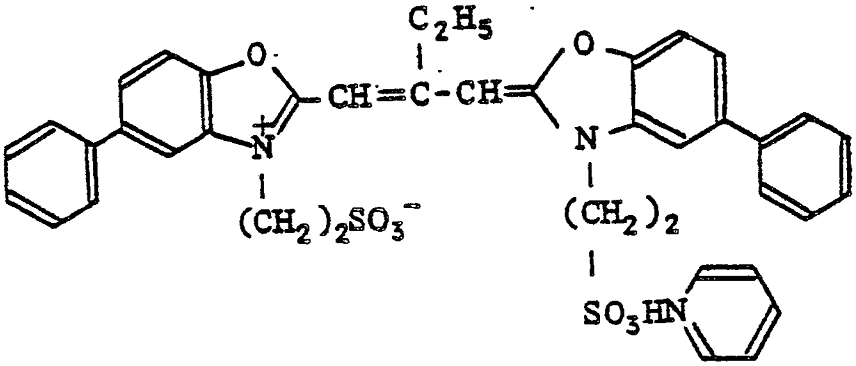
ExS-1



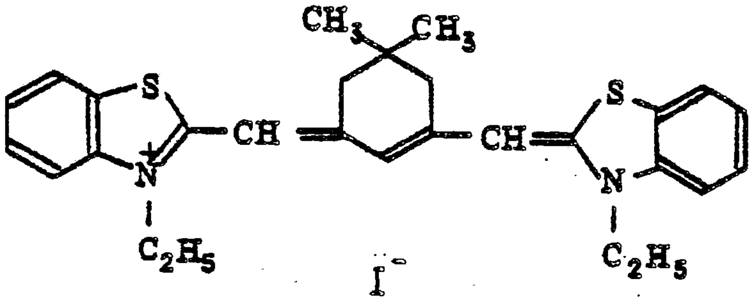
ExS-2



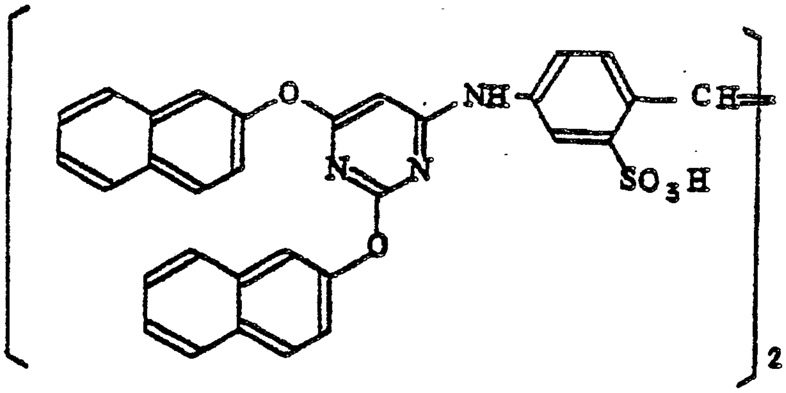
ExS-3



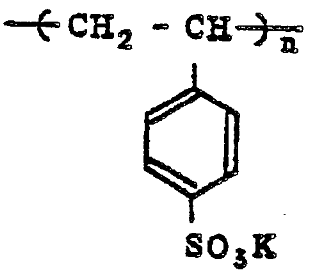
ExS-4



ExS-5

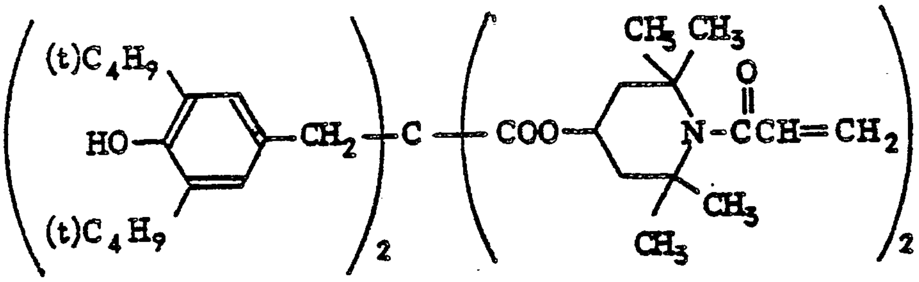


Cpd-1

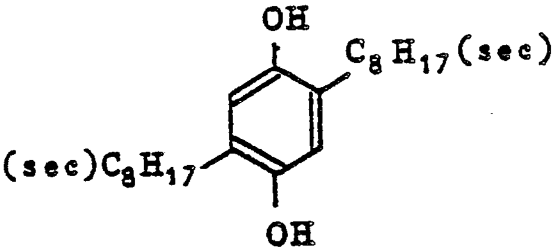


$-\!\!(CH_2 - CH)_n-$ (n=500 to 1,000)

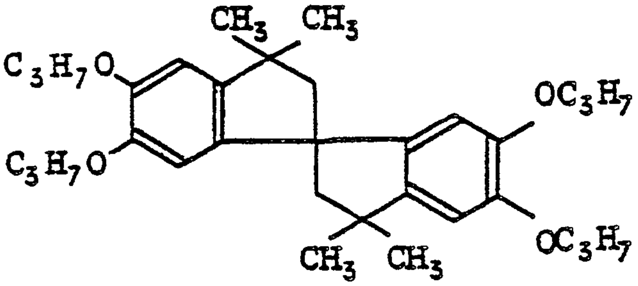
Cpd-2



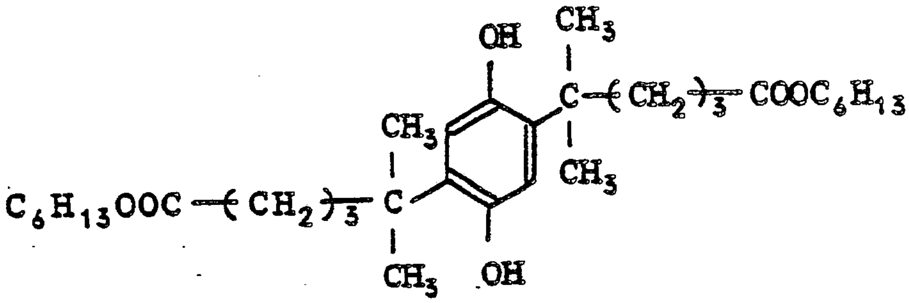
Cpd-3



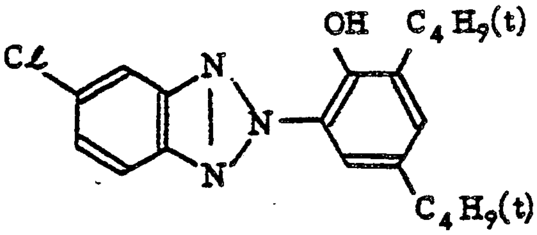
Cpd-4



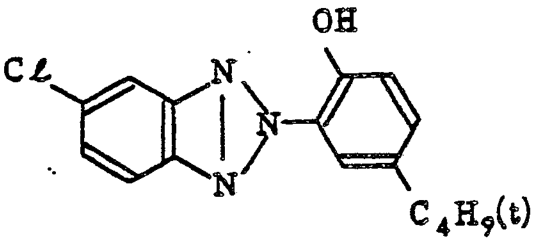
Cpd-5



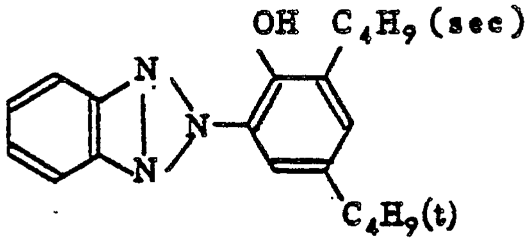
Cpd-6



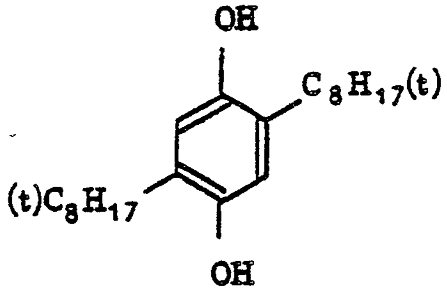
Cpd-7



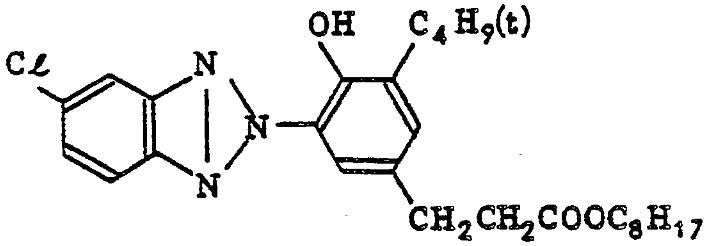
Cpd-8



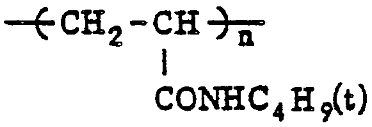
Cpd-9



Cpd-10



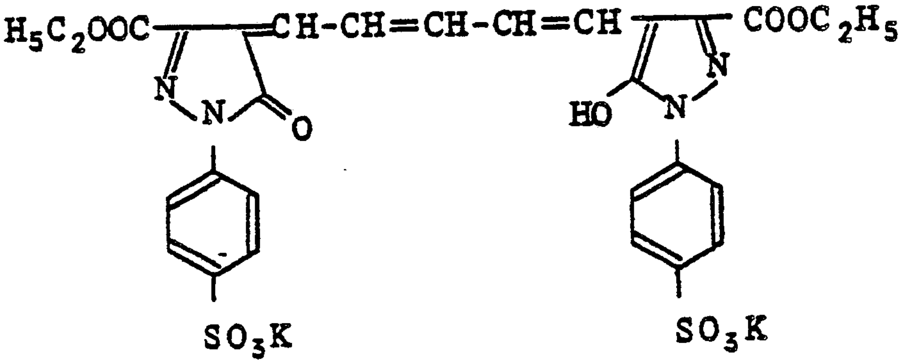
Cpd-11



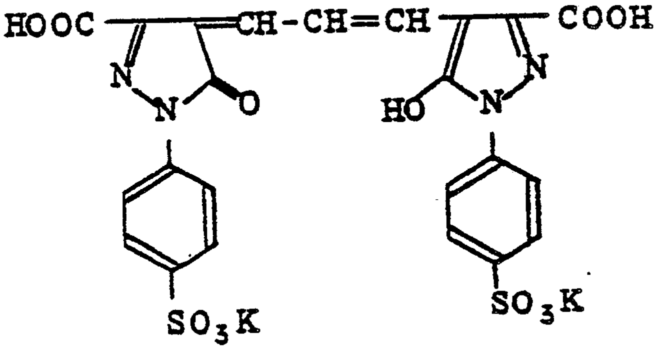
$$\underset{\displaystyle CONHC_4H_9(t)}{-\!\!\left(CH_2-\underset{|}{CH}\right)_n}$$

(n = 100~1000)

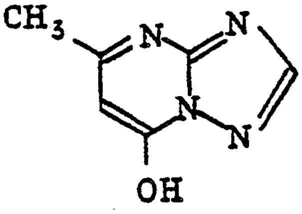
Cpd-12



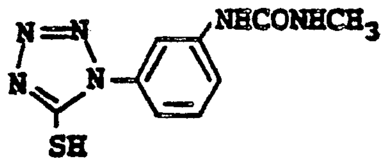
Cpd-13



Cpd-14



Cpd-15



Solv-1 Dibutyl phthalate

Solv-2 Trioctyl phosphate

Solv-3 Trinonyl phosphate

Solv-4 Tricresyl phosphate

Each of the color photographic papers obtained was wedge-exposed and process in the following processing steps, wherein a running processing test (continuous processing test) was performed on various color developers until the amount of the replenisher for the color developer became 3 times the volume of the tank.

Processing Step	Temperature	Time	Replenisher Amount
Color Development	35° C	45 sec.	160 ml/m²
Blix	35° C	45 sec.	100 ml/m²
Rinse (1)	30° C	20 sec.	-
Rinse (2)	30° C	20 sec.	-
Rinse (3)	30° C	20 sec.	200 ml/m²
Drying	60-70° C	30 sec.	-

The rinse was performed by a countercurrent system of from Rinse (3) to Rinse (1).

The composition of each processing solution used was as follows.

Color Developer		
	Tank	Replenisher
Additives C and D	Shown in Table 2	
Fluorescent Whitening Agent (4,4-diaminostilbene series)	3.0 g	4.0 g
Ethylenediaminetetraacetic Acid	1.0 g	1.5 g
Potassium Carbonate	30.0 g	30.0 g
Sodium Chloride	1.4 g	0.1 g
4-Amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]-aniline Sulfate	5.0 g	7.0 g
Benzyl Alcohol	Shown in Table 2	
Diethylene Glycol	Shown in Table 2	
1,2-Dihydroxybenzene-3,4,6-trisulfonic Acid	300 mg	300 mg
Water to make	1 liter	1 liter
pH	10.10	10.50

Blix Solution (The composition of the tank solution was same as that of the replenisher.)	
EDTA Fe(III)NH_4•$2H_2O$	60 g
EDTA•2Na•$2H_2O$	4 g
Ammonium Thiosulfate (70%)	120 ml
Sodium Sulfite	16 g
Glacial Acetic Acid	7 g
Water to make	1 liter
pH	5.5

Rinse Solutions (1), (2), and (3)	
(The composition of the tank solution was same as that of the replenisher.)	
Ethylenediamine-N,N,N′,N′-tetramethylenephosphonic Acid	0.3 g
Benzotriazole	1.0 g
Water to make	1 liter
pH adjusted by KOH to	7.50

The aforesaid processing steps were carried out using the aforesaid processing solutions and the B-(blue), G(green), and R(red) densities (stains) at the unexposed portions of each sample at the start of the running processing and at the end of the running processing were measured using a self densitometer, made by Fuji Photo Film Co., Ltd. Furthermore, after allowing to stand each sample at the end of the running processing for 2 months at 80° C (5 to 10 RH), the B, G, and R densities were measured again.

The changes of the photographic properties obtained are shown in Table 2 below.

Table 2

Test No.	Tank Liquid Benzyl Alcohol (ml)	Tank Liquid Diethylene Glycol (ml)	Replenisher Benzyl Alcohol (ml)	Replenisher Diethylene Glycol (ml)	Additive C (0.04 mol)	Additive D (0.03 mol)	Dmin Increase* (at the end of Running) B	G	R	Dmin Increase* (After 2 months at 80°C) B	G	R	Note
1	-	-	-	-	N,N-Diethylhydroxylamine	Triethanolamine (II-1)	+0.05	+0.04	+0.01	+0.25	+0.18	+0.05	Comparison
2	15	10	20	10	I-7	-	+0.07	+0.04	+0.01	+0.27	+0.20	+0.07	"
3	-	-	-	-	I-7	-	+0.05	+0.03	0	+0.21	+0.12	+0.06	"
4	-	-	-	-	I-12	-	+0.05	+0.02	0	+0.22	+0.10	+0.05	"
5	15	10	20	10	I-7	II-1	+0.03	+0.01	0	+0.17	+0.09	+0.05	Invention
6	-	-	-	-	"	"	+0.01	0	0	+0.15	+0.08	+0.04	"
7	-	-	-	-	"	III-1	0	0	0	+0.15	+0.07	+0.03	"
8	-	-	-	-	"	III-7	0	0	0	+0.15	+0.08	+0.04	"
9	-	-	-	-	I-12	II-1	+0.01	0	0	+0.14	+0.07	+0.03	"

Table 2 (cont'd)

Test No.	Tank Liquid		Replenisher		Additive C (0.04 mol)	Additive D (0.03 mol)	Dmin Increase* (at the end of Running)			Dmin Increase* (After 2 months at 80°C)			Note
	Benzyl Alcohol (ml)	Diethylene Glycol (ml)	Benzyl Alcohol (ml)	Diethylene Glycol (ml)			B	G	R	B	G	R	
10	-	-	-	-	I-12	III-7	0	0	0	+0.13	+0.07	+0.03	Invention
11	-	-	-	-	I-22	II-1	+0.01	0	0	+0.16	+0.08	+0.05	"
12	-	-	-	-	I-25	II-1	+0.01	0	0	+0.15	+0.08	+0.04	"
13	-	-	-	-	I-48	II-1	+0.02	0	0	+0.17	+0.08	+0.05	"

(*) Increased Dmin to the Dmin at the start of running processing.

From the results shown in Table 2 above, it can be seen that in Test Nos. 1 to 4, the formation of stains is greatly increased as the result of the running processing, whereas in Test Nos. 5 to 13, the increase of stains is very few. Also, it can be seen that in the change of the photographic properties with the passage of time after processing is very less in Test Nos. 5 to 13 as compared with Test Nos. 1 to 4.

EXAMPLE 5

A multilayer color photographic paper having the following layers on a paper support having polyethylene coating on both surfaces was prepared.

Preparation of the coating compositions for layers

In 27.2 ml of ethyl acetate and 7.7 ml (8.0 g) of a high-boiling solvent (Solv-1) were dissolved 19.1 g of a yellow coupler (ExY-1) and 4.4 g of a color image stabilizer (Cpd-1) and the solution was dispersed by emulsification in 185 ml of an aqueous 10% gelatin solution containing a solution of 10% sodium dodecylbenzenesulfonate. The emulsified emulsion was mixed with silver halide emulsions EM 7 and EM 8 and the gelatin concentration was adjusted as shown below to provide the coating composition for Layer 1. The coating compositions for Layer 2 to Layer 7 were also prepared by the similar manner to above.

Layer Structure

The composition of each layer was shown below, wherein the numeral shows the coating amount (g/m^2), in which the amount of the silver halide emulsion is shown by the coating amount of silver calculated.

In this case, the polyethylene coating at the emulsion side contains a white pigment (TiO_2) and a bluish dye.

Layer 1 Blue-sensitive Emulsion Layer	
Monodispersed silver chlorobromide emulsion (EM 7) spectrally sensitized by sensitizing dye (shown in Table 3)	0.15
Monodispersed silver chlorobromide emulsion (EM 8) spectrally sensitized by sensitizing dye (shown in Table 3)	0.15
Gelatin	1.86
Yellow coupler (ExY-1)	0.82
Color image stabilizer (Cpd-2)	0.19
Solvent (Solv-1)	0.35

Layer 2 Color Mixing Inhibiting Layer	
Gelatin	0.99
Color mixing inhibitor (Cpd-3)	0.08

Layer 3 Green-sensitive Emulsion Layer	
Monodispersed silver chlorobromide emulsion (EM 9) spectrally sensitized by sensitizing dye(s) (shown in Table 3)	0.12
Monodispersed silver chlorobromide emulsion (EM 10) spectrally sensitized by sensitizing dye(s) (shown in Table 3)	0.24
Gelatin	1.24
Magenta coupler (ExM-1)	0.39
Color image stabilizer (Cpd-4)	0.25
Color image stabilizer (Cpd-5)	0.12
Solvent (Solv-2)	0.25

Layer 4 Ultraviolet Absorption Layer	
Gelatin	1.60
Ultraviolet absorbents (Cpd-6/Cpd-7/Cpd-8 = 3/2/6 by weight ratio)	0.70
Color mixing inhibitor (Cpd-9)	0.05
Solvent (Solv-3)	0.42

Layer 5 Red-sensitive Emulsion Layer	
Monodispersed silver chlorobromide emulsion (EM 11) spectrally sensitized by sensitizing dyes (shown in Table 3 and ExS-5)	0.07
Monodispersed silver chlorobromide emulsion (EM 12) spectrally sensitized by sensitizing dyes (shown in Table 3 and ExS-5)	0.16
Gelatin	0.92
Cyan coupler (ExC-1)	1.46
Cyan Coupler (ExC-2)	1.84
Color image stabilizers (Cpd-7/Cpd-8/Cpd-10 = 3/4/2 by weight ratio)	0.17
Dispersing polymer (Cpd-11)	0.14
Solvent (Solv-1)	0.20

Layer 6 Ultraviolet Absorption Layer	
Gelatin	0.54
Ultraviolet absorbents (Cpd-6/Cpd-8/Cpd-10 = 1/5/3 by weight ratio)	0.21
Solvent (Solv-4)	0.08

Layer 7 Protective Layer	
Gelatin	1.33
Acryl-modified copolymer of polyvinyl alcohol (modification degree 17%)	0.17
Liquid paraffin	0.03

For each layer were used Alkanol XC® (trade name, made by DuPont), sodium alkylbenzenesulfonate, a succinic acid ester, and Magefacx® F-120 (trade name, made by Dainippon Ink and Chemicals, Inc.) as emulsification dispersing agent and coating aids. Also, for each layer were used Compounds Cpd-14 and 15 as stabilizers of the silver halides.

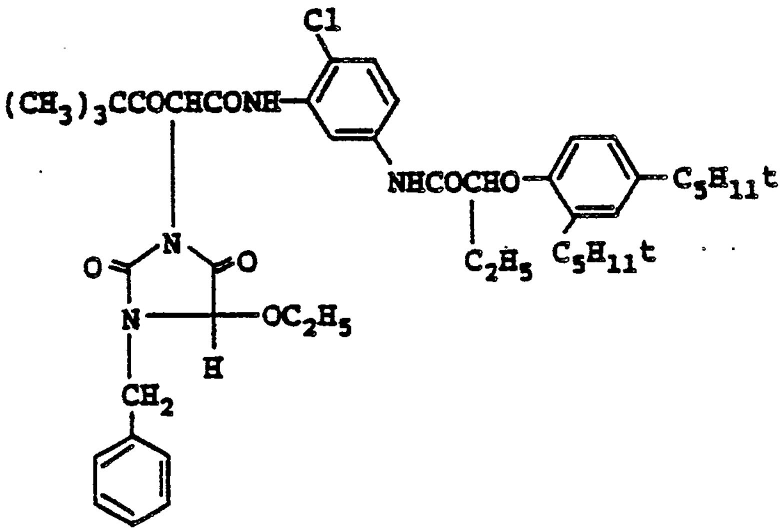
The details of the silver halide emulsions used are as follows.

Emulsion	Form	Grain Size (µm)	Br-Content (mol%)	Coefficient of variation*
EM 7	Cubic	1.1	1.0	0.10
EM 8	Cubic	0.8	1.0	0.10
EM 9	Cubic	0.45	1.5	0.09
EM 10	Cubic	0.34	1.5	0.09
EM 11	Cubic	0.45	1.5	0.09
EM 12	Cubic	0.34	1.6	0.10

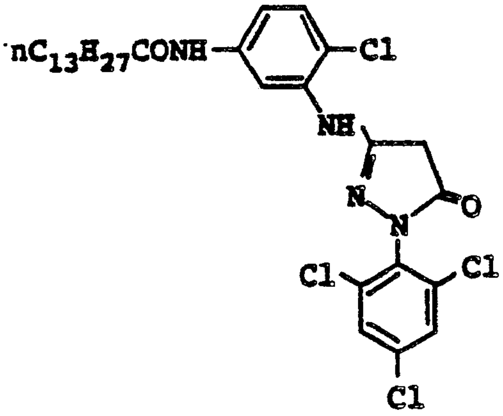
*: Same as above

The compounds used above are as follows.

ExY-1



ExM-1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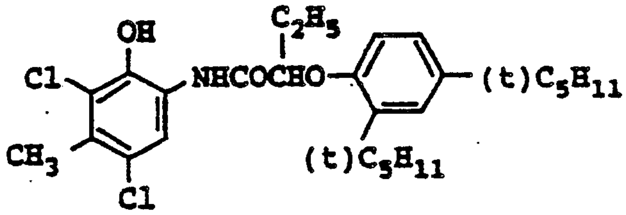
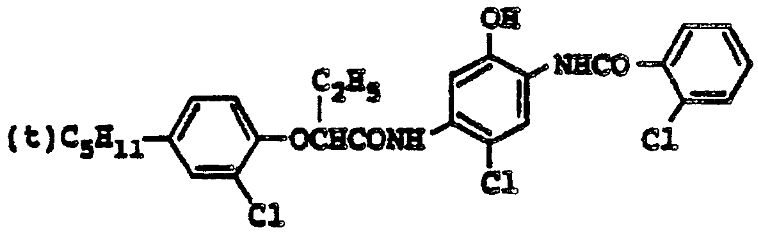
Cl
NH
N
N
O
Cl
Cl
Cl

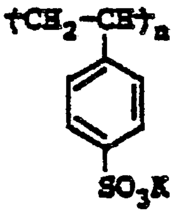
ExC-1


OH
Cl
CH3
Cl
NHCOCHO
C2H5
(t)C5H11
(t)C5H11

ExC-2

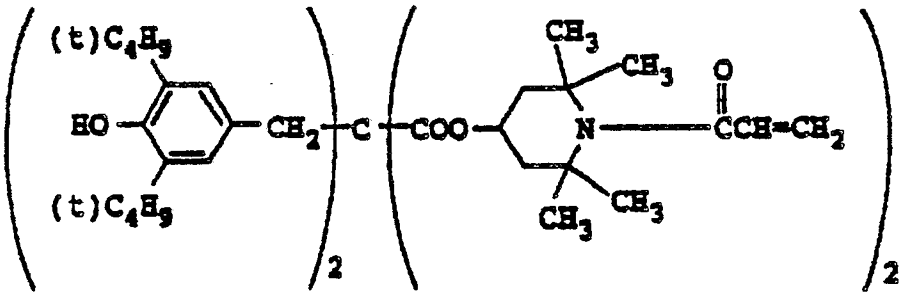


Cpd-1

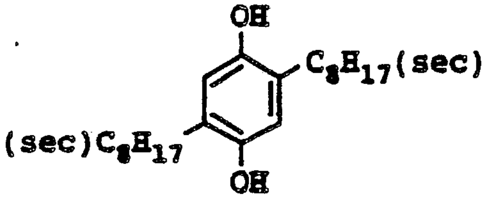


(n=500 to 1,000)

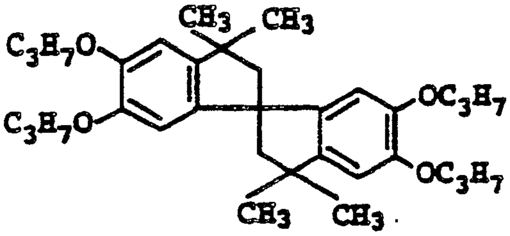
Cpd-2



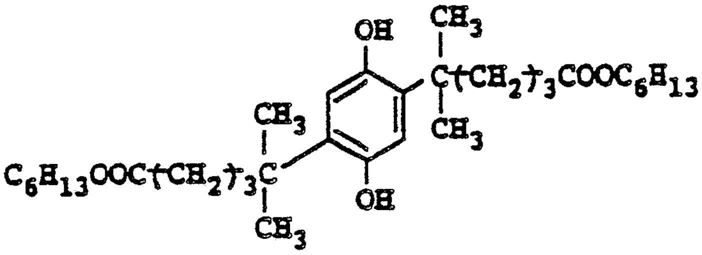
Cpd-3



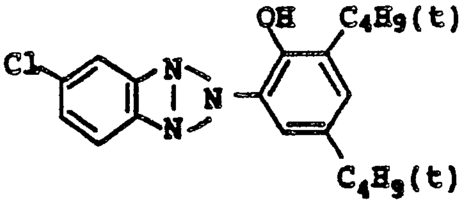
Cpd-4



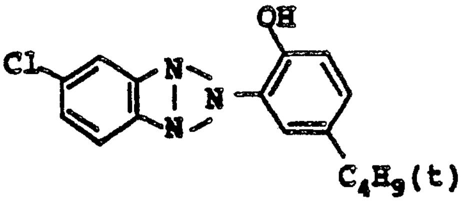
Cpd-5



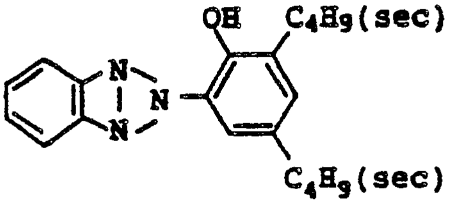
Cpd-6



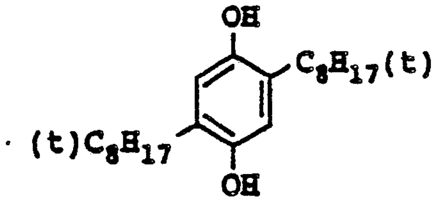
Cpd-7



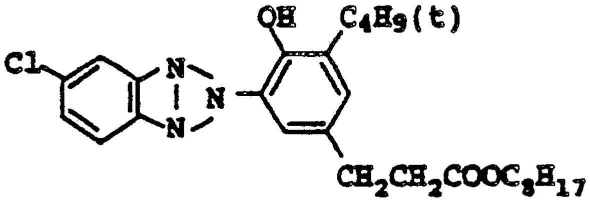
Cpd-8



Cpd-9



Cpd-10

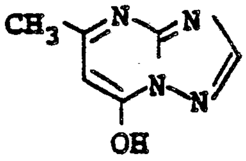


Cpd-11

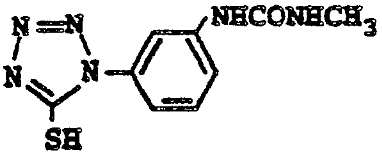
$$-\!\!\left(CH_2-\underset{\displaystyle CONHC_4H_9(t)}{\underset{|}{CH}}\right)_n$$

(n=100~1000)

Cpd-14



Cpd-15



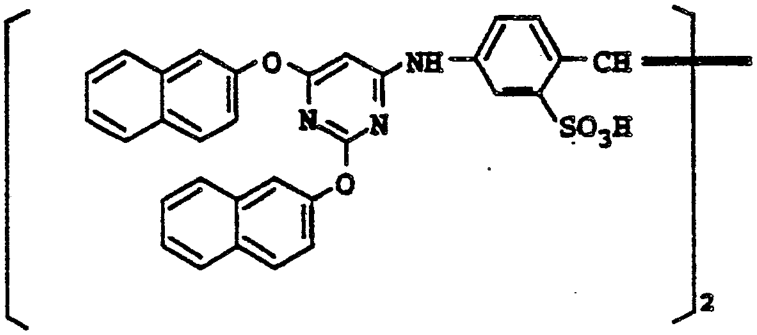
Solv-1 Dibutyl phthalate

Solv-2 Trioctyl phosphate

Solv-3 Trinonyl phosphate

Solv-4 Tricresyl phosphate

ExS-5



Each of Samples 2-F, 2-G, 2-H, 2-I, 2-J, and 2-K were prepared by changing the sensitizing dyes and the irradiation inhibiting dyes as shown in Table 3 below.

Table 3

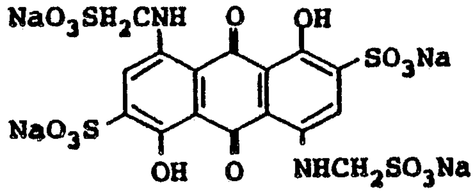
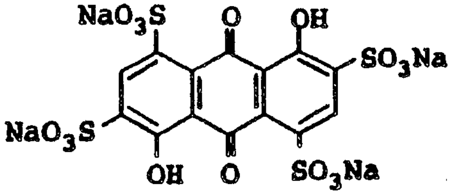
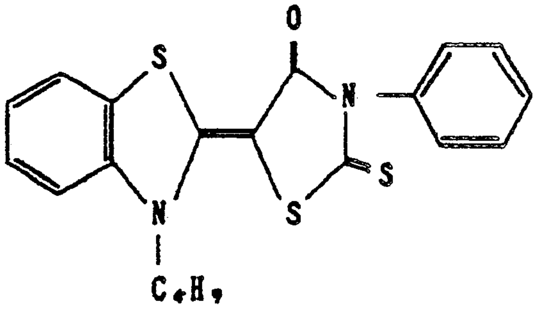
			Sensitizing Dye		
Sample	Irradiation Inhibiting Dye (amount mg/m^2)		Blue-Sensitive Layer	Green-sensitive Layer	Red-sensitive Layer
2-F		(8)	IIIa-41	IIIb-35 IIIb-36	IIIa-42
2-G		(8)	IIIa-41	IIIb-35 IIIb-36	IIIa-42
2-H	V-2 V-4	(4) (4)	S-A	S-B	S-C
2-I	V-36 V-37	(4) (4)	S-A	S-B	S-C

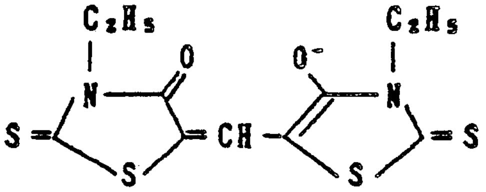
Table 3

Sample	Irradiation Inhibiting Dye (amount mg/m^2)	Sensitizing Dye		
		Blue-Sensitive Layer	Green-sensitive Layer	Red-sensitive Layer
2-J	V-2 (4)	IIIa-41	IIIb-35	IIIa-42
	V-4 (4)		IIIb-35	
2-K	V-36 (4)	IIIa-41	IIIb-35	IIIa-42
	V-37 (4)		IIIb-35	

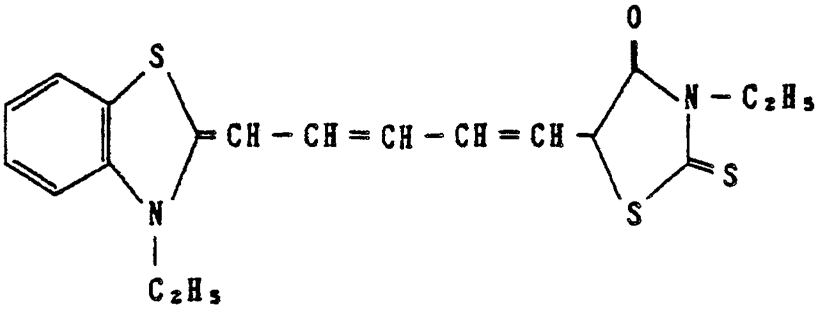
S – A


S
O
N
S
S
N
C₄H₉

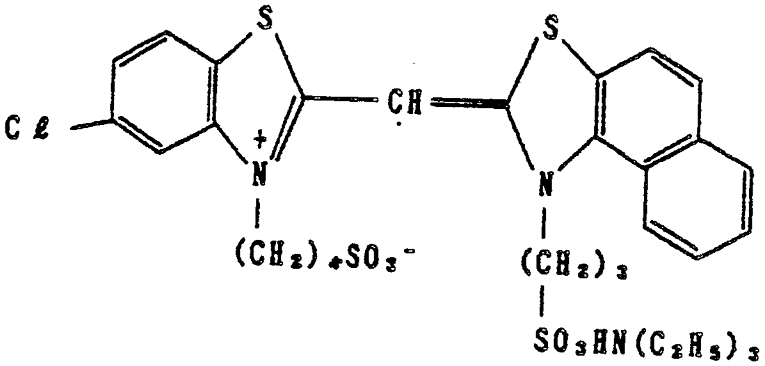
S – B


C₂H₅
O
N
S
S
CH
O⁻
C₂H₅
N
S
S

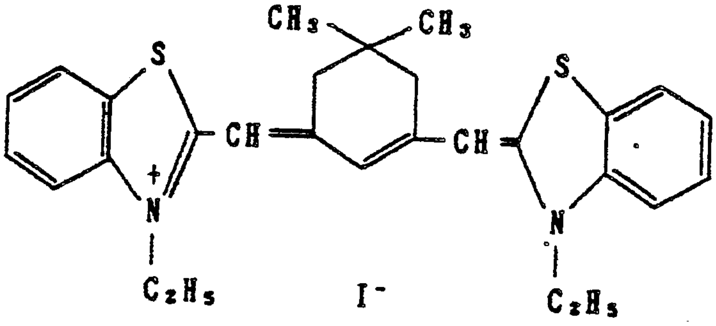
S – C


S
N
C₂H₅
CH – CH = CH – CH = CH
O
N – C₂H₅
S
S

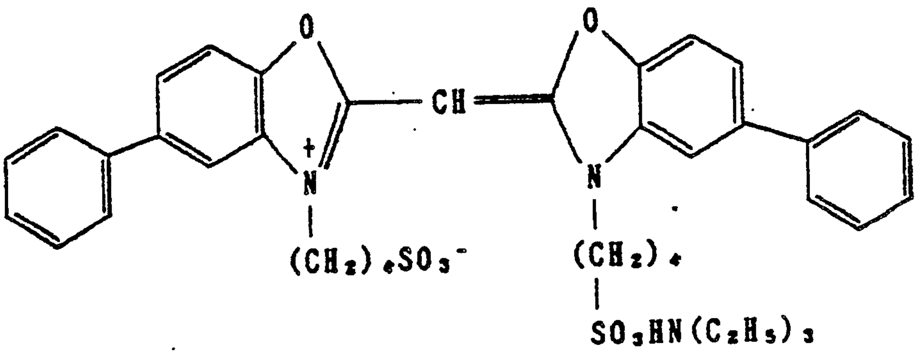
(Ⅲ a －41)


S
S
Cℓ
CH
N
N
+
(CH₂)₄SO₃⁻
(CH₂)₃
SO₃HN(C₂H₅)₃

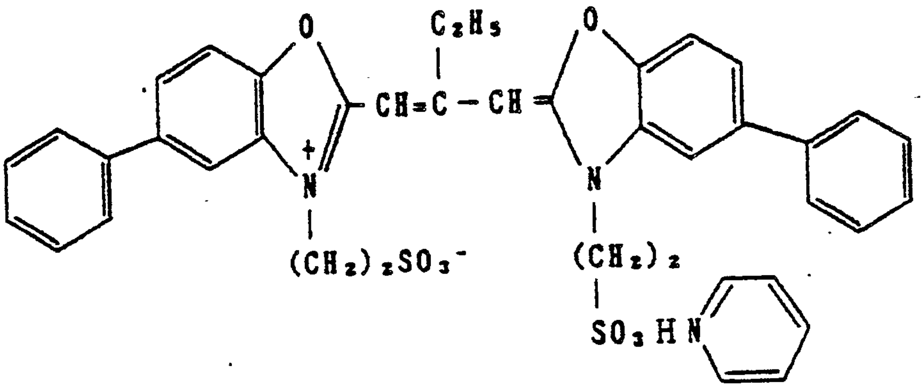
(Ⅲ a －42)


CH₃
CH₃
S
S
CH
CH
N
N
+
C₂H₅
I⁻
C₂H₅

(Ⅲ b -35)



(Ⅲ b -36)



Each of the color photographic papers thus obtained was subjected to a wedge-exposure and running processing (continuous processing) as in Example 4.

In this case, however, the color developer only having the following composition was used.

Color Developer		
	Tank	Replenisher
Additives A and B	Shown in Table 4	
Fluorescent Whitening Agent (4,4-diaminostilbene series)	3.0 g	4.0 g
Ethylenediaminetetraacetic Acid	1.0 g	1.5 g
Potassium Carbonate	30.0 g	30.0 g
Sodium Chloride	1.4 g	0.1 g
4-Amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]-aniline Sulfate	5.0 g	7.0 g
1,2-Dihydroxybenzene-3,4,5-trisulfonic acid	300 mg	300 mg
Water to make	1 liter	1 liter
pH	10.10	10.50

After processing as in Example 4, the change (ΔDmin) of the minimum densities at the start of the running test and at the end thereof was measured. The results are shown in Table 4.

Table 4

Test No.	Additive A (0.04 mol)	Additive B (0.03 mol)	Sample*1	ΔDmin B	ΔDmin G	ΔDmin R	Note
1	N,N-Dimethylhydroxylamine	-	2-F	+0.05	+0.04	+0.05	Comparison
2	"	-	2-G	+0.07	+0.04	+0.06	"
3	"	-	2-(H)	+0.06	+0.04	+0.06	"
4	"	-	2-(I)	+0.05	+0.04	+0.06	"
5	I-7	-	2-F	+0.07	+0.04	+0.06	"
6	"	-	2-G	+0.06	+0.04	+0.05	"
7	"	II-1	2-F	+0.01	+0.01	+0.02	Invention
8	"	"	2-G	+0.02	+0.01	+0.01	"
9	"	"	2-(H)	0	0	0	"
10	"	"	2-(I)	0	0	0	"
11	"	"	2-(J)	+0.01	0	0	"

Table 4 (cont'd)

Test No.	Additive A (0.04 mol)	Additive B (0.03 mol)	Sample*1	ΔDmin			Note
				B	G	R	
12	I-7	II-1	2-(K)	0	0	0	Invention
13	I-7	III-1	2-F	+0.01	+0.01	+0.01	"
14	"	"	2-G	+0.01	0	+0.01	"
15	"	"	2-(H)	0	0	0	"
16	"	"	2-(I)	0	0	0	"
17	I-12	II-1	2-G	+0.02	0	+0.01	"
18	"	"	2-(H)	0	0	0	"

*1: The samples containing the compound of formula (V) are parenthesized.

As is clear from the results shown in Table 4, it can be seen that the cases of using the compound of formula (I) together with the compound of formula (II) or (III) (including the cases of using the samples containing or not containing the compound of formula (V)) (Test Nos. 7 to 18) according to this invention show less change of stain as compared to the cases of using N,N-dimethylhydroxylamine (Test Nos. 1 to 4) and the cases of using the compound of formula (I) alone (Test Nos. 5 and 6). In particular, it can be also seen that the aforesaid effect is more remarkable in the cases of using the compound of formula (I) together with the compound of formula (II) or (III) and processing the samples containing the compound of formula (V) (Test Nos. 9 to 12, 15, 16, and 18) as compared to even the cases of using the compound of formula (I) together with the compound of formula (II) or (III) and processing the samples containing no compound of formula (V) (Test Nos. 7, 8, 13, 14, and 17).

EXAMPLE 6

A multilayer color photographic paper having the layer structure shown below on a paper support having polyethylene coating on both surfaces thereof was prepared. The coating compositions for the layers were prepared by mixing each silver halide emulsion, various chemicals, and each emulsified dispersion of coupler(s) as follows.

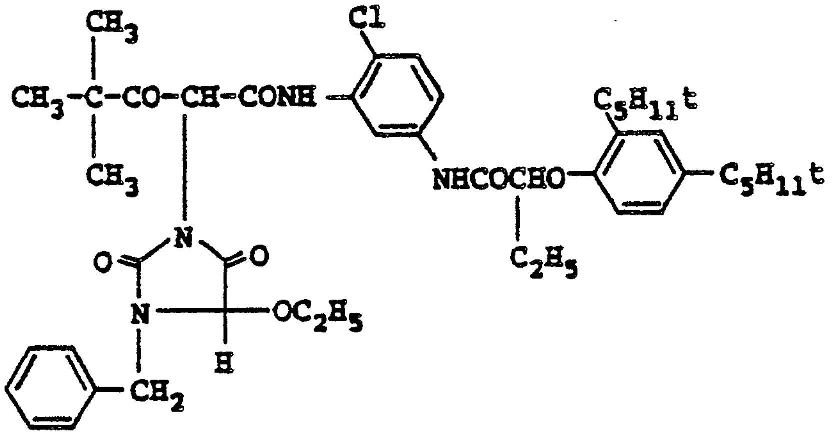
Preparation of coupler emulsion:

In 27.2 ml of ethyl acetate and 7.7 ml of a solvent (Solv-1) were dissolved 19.1 g of a yellow coupler (ExY) and 4.4 g of a color image stabilizer (Cpd-1) and the solution was dispersed by emulsification in 185 ml of an aqueous 10% gelatin solution of 8 ml of a solution of 10% sodium dodecylbenzenesulfonate.

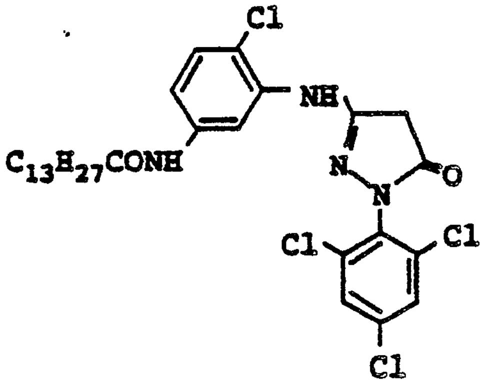
Also, by the similar manner to above, a magenta emulsion, a cyan emulsion, and each emulsion for each interlayer were prepared.

The compounds used for the emulsions are shown below.

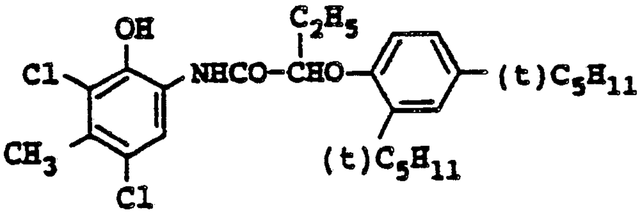
(ExY) Yellow coupler



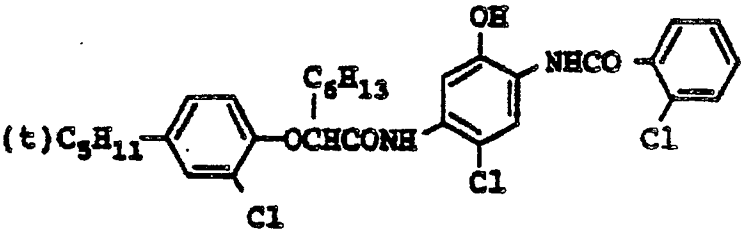
(ExM-1) Magenta coupler



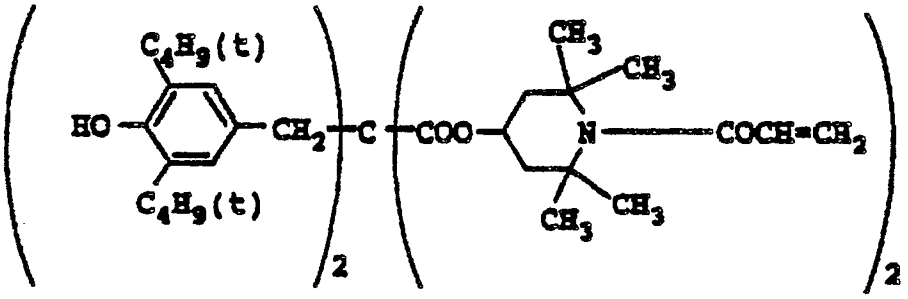
(ExC-1) Cyan coupler



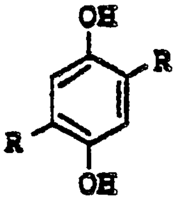
(ExC-2) Cyan coupler



(Cpd-1) Color image stabilizer

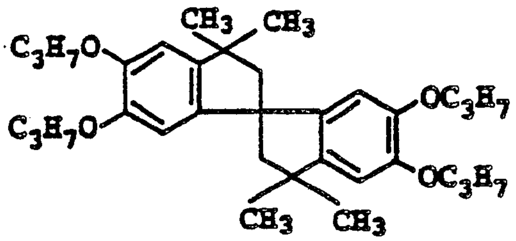


(Cpd-2) Color mixing inhibitor

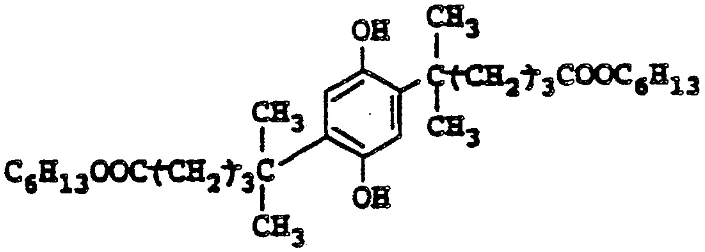


$R = C_8H_{17}(sec)$

(Cpd-3)



(Cpd-4)



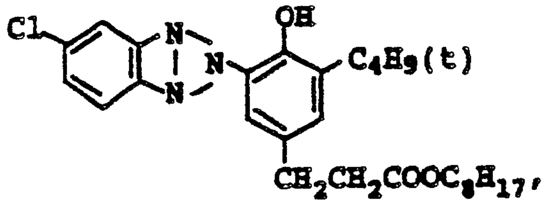
(Cpd-5) Color mixing inhibitor

Same as Cpd-2; $R=C_8H_{17}(t)$

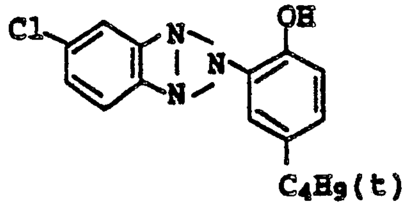
(Cpd-6) Color image stabilizer

A 5:8:9 (by weight) mixture of 6a, 6b and 6c.

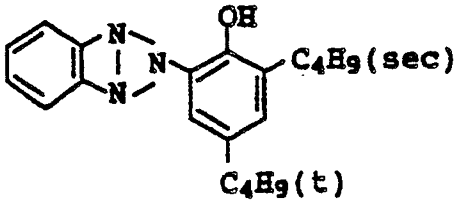
6a



6b



6c



(Cpd-7) Polymer

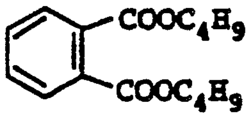
$$\left(CH_2-\underset{CONHC_4H_9(t)}{\underset{|}{CH}} \right)_n$$

Average molecular weight: 80,000

(UV-1) Ultraviolet absorbent

A 2:9:8 (by weight) mixture of Cpd-6a, 6b and 6c.

(Solv-1) Solvent



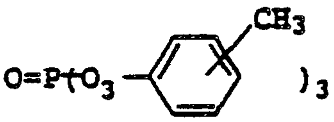
(Solv-2) Solvent

$O=P(O-C_8H_{17}(iso))_3$

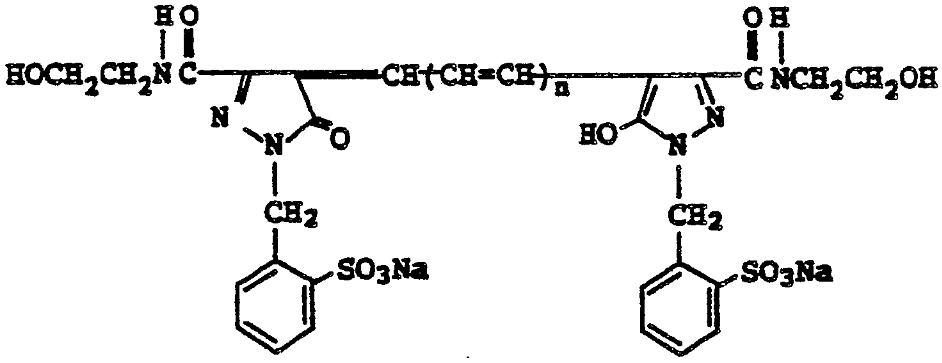
(Solv-3) Solvent

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

(Solv-4) Solvent



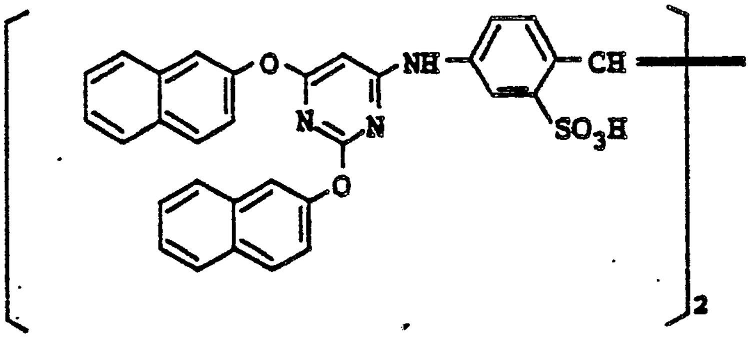
Also, for irradiation inhibition, the following dyes are used for the silver halide emulsion layers.
For Red-Sensitive Layer: Dye-R



wherein n = 2

For Green Sensitive Layer: Same as Dye-R
(wherein, however, n is 1)

Also, for the red-sensitive emulsion layer was used the following compound in an amount of 2.6x10^{-3} mol per mol of the silver halide.



The silver halide emulsions for use in the examples were prepared as follows.

Blue-Sensitive Emulsion:

A monodispersed cubic silver chloride emulsion (containing K_2IrCl_6 and 1,3-dimethylimidazolin-5-thione) having a mean grain size of 1.1 µm and a coefficient of variation of 0.10 was prepared by a conventional method. To 10 kg of the emulsion was added 26 ml of a 0.6% solution of a spectral blue-sensitizing dye (S-1), a fine grain silver bromide emulsion having a mean grain size of 0.05 µm was added to the host silver chloride emulsion in an amount of 0.5 mol% to the host emulsion followed by performing ripening, sodium thiosulfate was added to perform the optimum chemical sensitization, and then a stabilizer (shown in Table A below) was added thereto in an amount of 10^{-4} mol per mol of silver to provide the blue-sensitive emulsion.

Green-Sensitive Emulsion:

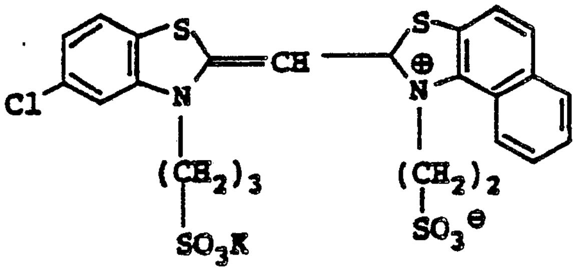
After preparing silver chloride grains containing K_2IrCl_6 and 1,3-dimethylimidazolin-2-thione by a conventional manner, 4x10^{-4} mol/mol-Ag of a sensitizing dye (S-2) and KBr were added to the emulsion followed by ripening, and after adding thereto sodium thiosulfate to perform the optimum chemical sensitization, 5x10^{-4} mol/mol-Ag of a stabilizer (shown in Table A below) was added thereto to provide a mono-dispersed cubic silver chloride emulsion having a mean grain size of 0.48 µm and a coefficient of variation of 0.10.

Red-Sensitive Emulsion:

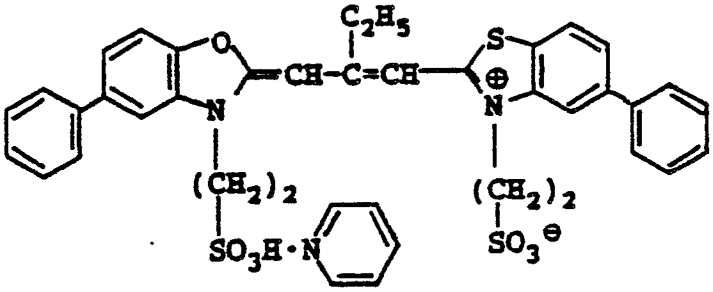
By following the same manner as the case of preparing the green-sensitive emulsion while using 1.5×10^{-4} mol/mol-Ag of a sensitizing dye (S-3) was used in place of the sensitizing dye (S-2), a red-sensitive emulsion was prepared.

The sensitizing dyes used are shown below.

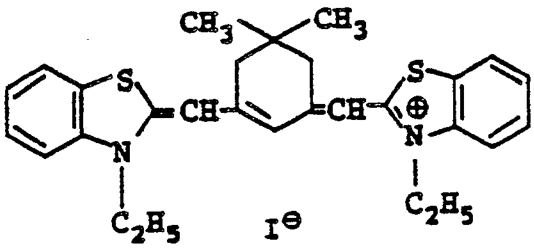
(S-1) Sensitizing Dye



(S-2) Sensitizing Dye



(S-3) Sensitizing dye



Layer Structure

The composition of the layers are shown below, wherein the numeral is the coating amount (g/m^2), in which the amount of a silver halide emulsion is shown by the amount of silver calculated.

In addition, the polyethylene coating on the emulsion side contained a white pigment (TiO_2) and a bluish dye (ultramarine blue).

Layer 1 Blue-sensitive Emulsion Layer	
Silver Halide Emulsion	0.25
Gelatin	1.86
Yellow coupler (ExY)	0.82
Color image stabilizer (Cpd-1)	0.19
Solvent (Solv-1)	0.35

Layer 2 Color Mixing Inhibiting Layer	
Gelatin	0.99
Color mixing inhibitor (Cpd-2)	0.08

Layer 3 Green-sensitive Emulsion Layer	
Silver Halide Emulsion	0.31
Gelatin	1.24
Magenta coupler (ExM-1)	0.31
Color image stabilizer (Cpd-3)	0.25
Color image stabilizer (Cpd-4)	0.12
Solvent (Solv-2)	0.42

Layer 4 Ultraviolet Absorption Layer	
Gelatin	1.58
Ultraviolet absorbents (UV-1)	0.62
Color mixing inhibitor (Cpd-5)	0.05
Solvent (Solv-3)	0.24

Layer 5 Red-sensitive Emulsion Layer	
Silver Halide Emulsion	0.21
Gelatin	1.34
Cyan coupler (a blend of ExC-1 and C-2 at 1:1)	0.34
Color image stabilizer (Cpd-6)	0.17
Polymer (Cpd-7)	0.40
Solvent (Solv-4)	0.23

Layer 6 Ultraviolet Absorption Layer	
Gelatin	0.53
Ultraviolet absorbents (UV-1)	0.21
Solvent (Solv-3)	0.08

Layer 7 Protective Layer	
Gelatin	1.33
Acryl-modified copolymer of polyvinyl alcohol (modification degree 17%)	0.17
Liquid paraffin	0.03

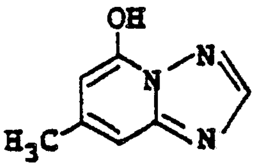
For each layer was used 1-oxy-3,5-dichloro-s-triazine sodium salt as a hardening agent.

Thus, Sample A was prepared. Furthermore, by following the same procedure as above while changing the stabilizer as shown in Table A below, Samples B, C, D, E, F, and G were also prepared.

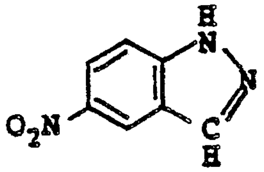
Table A

Sample	Stabilizer	Amount (mol/mol-Ag)
A	-	-
B	a-1	10^{-4}
C	a-2	"
D	a-3	"
E	IV-27	"
F	IV-45	"
G	IV-46	"

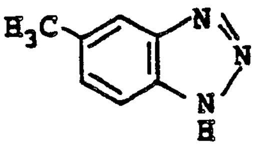
(a-1)



(a-2)



(a-3)



Each of the samples thus prepared was imagewise exposed and then subjected to continuous processing (running test) by the following processing steps and the processing compositions until the amount of the replenisher for the color developer supplied became twice the volume of the tank for the color developer. In this case, however, the composition of the color developer was changed as shown in Table 5 below for each running test.

Also, the processed amount per day was, in average, 2.5 m^2 of the color photographic paper.

The processing step employed was as follows.

Processing Step	Temp.	Time	Replenisher Amount	Tank Volume
Color Development	38°C	45 sec.	100 ml	8 liters
Blix	35°C	45 sec.	161 ml	8 liters
Rinse (1)	35°C	20 sec.	-	4 liters
Rinse (2)	35°C	20 sec.	-	4 liters
Rinse (3)	35°C	20 sec.	-	4 liters
Rinse (4)	35°C	30 sec.	200 ml	4 liters
Drying	80°C	60 sec.		4 liters

The replenisher amount was per m^2 of the color photographic paper.
Also, the rinse was performed by a 4 tank countercurrent system of from Rinse (4) to Rinse (1).
The compositions of the processing solutions were as follows.

Color Developer		
	Tank	Replenisher
Water	800 ml	800 ml
Methyltriethylenediamine (1,4-diazabicyclo[2,2,2]octane)	5.0 g	5.0 g
Compound (I) (shown in Table 5)	50 mmols	58 mmols
Ethylenediamine-N,N,N′,N′-tetramethylenephosphonic Acid	3.0 g	4.0 g
Sodium Chloride	1.9 g	0 g
Potassium Carbonate	30.0 g	30.0 g
4-Amino-3-methyl-N-ethyl(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline Sulfate	5.4 g	7.2 g
Water to make	1 liter	1 liter
pH(25 °C)	10.10	10.50

Blix Solution (The composition of the tank solution was same as that of the replenisher.)	
EDTA Fe(III)$NH_4 \cdot 2H_2O$	60 g
EDTA$\cdot$2Na$\cdot 2H_2O$	4 g
Sodium Thiosulfate (70%)	120 ml
Sodium Sulfite	16 g
Glacial Acetic Acid	7 g
Water to make	1 liter
pH (25° C)	5.5

Rinse Solution	
(The composition of the tank solution was same as that of the replenisher.)	
Ion-exchanged water (no more than 3 ppm of each of Ca and Mg)	
Water to make	1 liter
pH	7.0

Then, each of the samples prepared was subjected to gradation exposure of photographic paper for sensitometry using a sensitometer (Type FWH, made by Fuji Photo Film Co., Ltd., color temperature of light source: 3200° K). In this case, the exposure was performed so that the exposure amount became 250 CMS at an exposure time of 1/10 second.

At the end of the running test, the aforesaid sensitometry was performed and the minimum densities (Dmin) of yellow, magenta, and cyan and the maximum density (Dmax) of yellow were measured using a Macbeth densitometer. The results obtained are shown in Table 5.

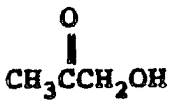
Table 5

Test No.	Sample	Compound (IV)	Compound (I)	Dmin Yellow	Dmin Magenta	Dmin Cyan	Dmax Yellow	
1	A	–	Diethylhydroxylamine	0.41	0.45	0.45	2.40	Comparison
2	B	–	"	0.20	0.21	0.20	2.38	"
3	F	IV-45	"	0.19	0.19	0.17	2.37	"
4	G	IV-46	"	0.17	0.18	0.18	2.37	"
5	A	–	α-Hydroxyketone (a)*	0.40	0.43	0.43	2.56	"
6	B	–	"	0.20	0.20	0.21	2.51	"
7	F	IV-45	"	0.13	0.14	0.13	2.52	"
8	G	IV-46	"	0.13	0.13	0.13	2.51	"
9	B	–	Hydroxylamine	0.18	0.19	0.19	1.48	"
10	G	IV-46	"	0.16	0.17	0.17	1.45	"
11	A	–	I-7	0.41	0.40	0.41	2.55	"
12	B	–	"	0.19	0.19	0.19	2.50	"
13	C	–	"	0.21	0.19	0.18	2.51	"
14	D	–	"	0.19	0.18	0.20	2.51	"

Table 5 (cont'd)

Test No.	Sample	Compound (IV)	Compound (I)	Dmin Yellow	Dmin Magenta	Dmin Cyan	Dmax Yellow	
15	E	IV-27	I-7	0.10	0.09	0.10	2.50	Invention
16	F	IV-45	"	0.09	0.10	0.11	2.50	"
17	G	IV-46	"	0.09	0.11	0.12	2.52	"
18	"	"	I-12	0.10	0.10	0.11	2.51	"
19	"	"	I-22	0.08	0.09	0.09	2.52	"
20	"	"	I-25	0.09	0.11	0.11	2.53	"
21	"	"	I-28	0.10	0.12	0.09	2.51	"
22	"	"	I-44	0.09	0.09	0.10	2.51	"
23	F	IV-45	I-48	0.08	0.08	0.10	2.53	"
24	"	"	I-49	0.09	0.09	0.09	2.49	"
25	"	"	I-58	0.10	0.11	0.10	2.52	"
26	E	IV-27	I-60	0.10	0.10	0.11	2.53	"
27	"	"	I-8	0.11	0.09	0.09	2.59	"

(*) Hydroxyketone (a) is the compound shown by the formula



$CH_3C(=O)CH_2OH$

As is clear from Table 5, it can be seen that in the cases of using the compound of formula (I) together with the compound of formula (IV) (Test Nos. 15 to 27), Dmin is greatly improved as compared to the cases of using the compound of formula (I) or (IV) solely (Test Nos. 3, 4, 11, 12, 13, and 14). Also, it can be seen that when a hydroxylamine which is conventionally used for color developer is used in place of the compound of formula (I), a sufficient effect is not obtained in the system of using together the compound of formula (IV) and, in particular, in the case of using hydroxylamine, Dmax is greatly reduced (Test Nos. 9 to 10).

EXAMPLE 7

When the same procedure as Example 6 was followed while using each of Compounds IV-10, IV-11, IV-14, IV-22, IV-28, and IV-47 in place of Compound IV-45 in Sample F in Test No. 16, similar preferred results were obtained.

EXAMPLE 8

A multilayer color photographic paper having the following layer structure on a paper support having polyethylene coating on both surfaces thereof was prepared. The coating compositions for the layer were prepared as follows.

Preparation of Coating Compositions

In 27.2 ml of ethyl acetate and 7.7 ml of a high-boiling solvent (Solv-1) were dissolved 10.2 g of a yellow coupler (ExY-1), 9.1 g of a yellow coupler (ExY-2), and 4.4 g of a color image stabilizer (Cpd-1) and the solution was dispersed by emulsification in 185 ml of an aqueous 10% gelatin solution containing 8 ml of a solution of 10% sodium dodecylbenzenesulfonate. The emulsification dispersion was mixed with Emulsions EM 1 and EM 2 and the gelatin concentration was adjusted as shown below to provide the coating composition for Layer 1.

The coating compositions for Layer 2 to Layer 7 were also prepared by the similar manner to above.

For each layer was used 1-oxy-3,5-dichloro-s-triazine sodium salt as a gelatin hardening agent. Also, Compound (Cpd-2) was used as a thickener.

Layer Structure

The composition of each layer was shown below. The numeral shows the coating amount (g/m^2), wherein the amount of silver halide emulsion is shown by the amount of silver calculated.

In addition, the polyethylene coating at the emulsion side contained a white pigment (TiO_2) and a bluish dye.

Layer 1 Blue-sensitive Emulsion Layer	
Monodispersed silver chlorobromide emulsion (EM 1) spectrally sensitized by sensitizing dye (ExS-1)	0.13
Monodispersed silver chlorobromide emulsion (EM 2) spectrally sensitized by sensitizing dye (ExS-1)	0.13
Gelatin	1.86
Yellow coupler (ExY-1)	0.44
Yellow coupler (ExY-2)	0.39
Color image stabilizer (Cpd-1)	0.19
Solvent (Solv-1)	0.35

Layer 2 Color Mixing Inhibition Layer	
Gelatin	0.99
Color mixing inhibitor (Cpd-3)	0.08

Layer 3 Green-sensitive Emulsion Layer	
Monodispersed silver chlorobromide emulsion (EM 3) spectrally sensitized by sensitizing dyes (ExS-2 and 3)	0.05
Monodispersed silver chlorobromide emulsion (EM 4) spectrally sensitized by sensitizing dyes (ExS-2 and 3)	0.11
Gelatin	1.80
Magenta coupler (ExM-1)	0.39
Color image stabilizer (Cpd-4)	0.20
Color image stabilizer (Cpd-5)	0.02
Color image stabilizer (Cpd-6)	0.03
Solvent (Solv-2)	0.12
Solvent (Solv-3)	0.25

Layer 4 Ultraviolet Absorption Layer	
Gelatin	1.60
Ultraviolet absorbents (Cpd-7/Cpd-8/Cpd-9 = 3/2/6 by weight ratio)	0.70
Color image inhibitor (Cpd-10)	0.05
Solvent (Solv-4)	0.27

Layer 5 Red-sensitive Emulsion Layer	
Monodispersed silver chlorobromide emulsion (EM 5) spectrally sensitized by sensitizing dyes (ExS-4 and 5)	0.07
Monodispersed silver chlorobromide emulsion (EM 6) spectrally sensitized by sensitizing dyes (ExS-4 and 5)	0.16
Gelatin	0.92
Cyan coupler (ExC-1)	0.32
Color image stabilizers (Cpd-8/Cpd-9/Cpd-12 = 3/4/2 by weight)	0.17
Dispersing polymer (Cpd-11)	0.28
Solvent (Solv-2)	0.20

Layer 6 Ultraviolet Absorption Layer	
Gelatin	0.54
Ultraviolet absorbents (Cpd-7/Cpd-9/Cpd-12 = 1/5/3 by weight ratio)	0.21
Solvent (Solv-2)	0.08

Layer 7 Protective Layer	
Gelatin	1.33
Acryl-modified copolymer of polyvinyl alcohol (modification degree 17%)	0.17
Liquid paraffin	0.03

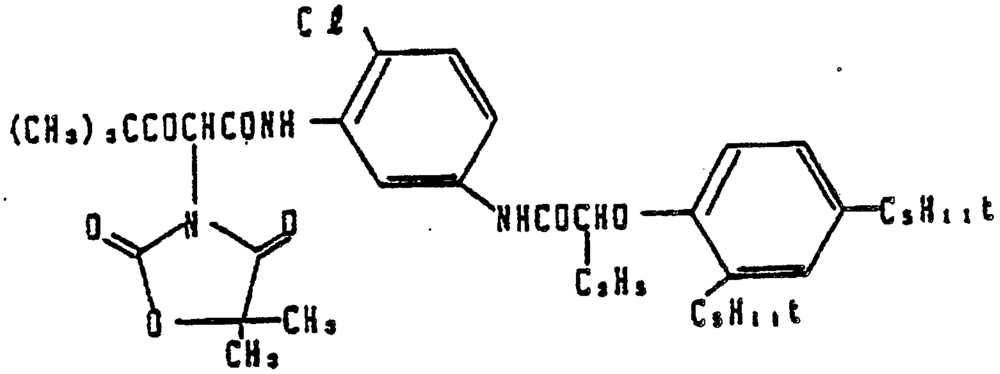
For each layer were used Compounds Cpd-14 and 15 as irradiation preventing dyes. Also, for each layer were used Alkanol B® (trade name, made by DuPont), sodium alkylbenzenesulfonate, a succinic acid ester, and Magefacx® F-120 (trade name, made by Dainippon Ink and Chemicals, Inc.) as emulsification dispersion agent and coating aids. Further, for each layer was used each of the compounds shown in Table B as a stabilizer of the silver halides.

Emulsion	Form	Grain Size (μm)	Br-Content (mol%)	Coefficient of variation*
EM 1	Cubic	1.0	80	0.08
EM 2	Cubic	0.75	80	0.07
EM 3	Cubic	0.5	83	0.09
EM 4	Cubic	0.4	83	0.10
EM 5	Cubic	0.5	73	0.09
EM 6	Cubic	0.4	73	0.10

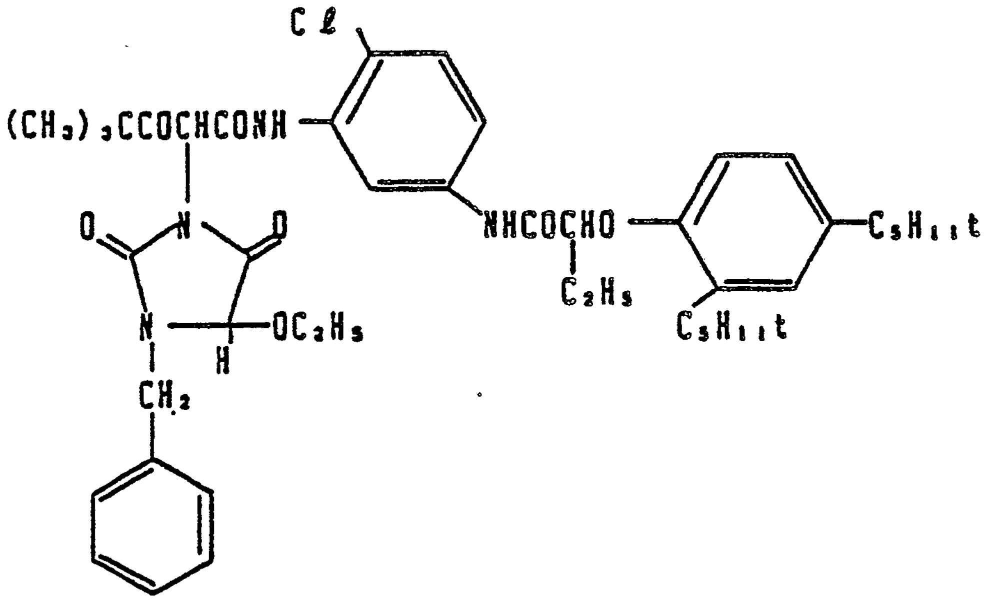
*: Same as above

The compounds used are as follows.

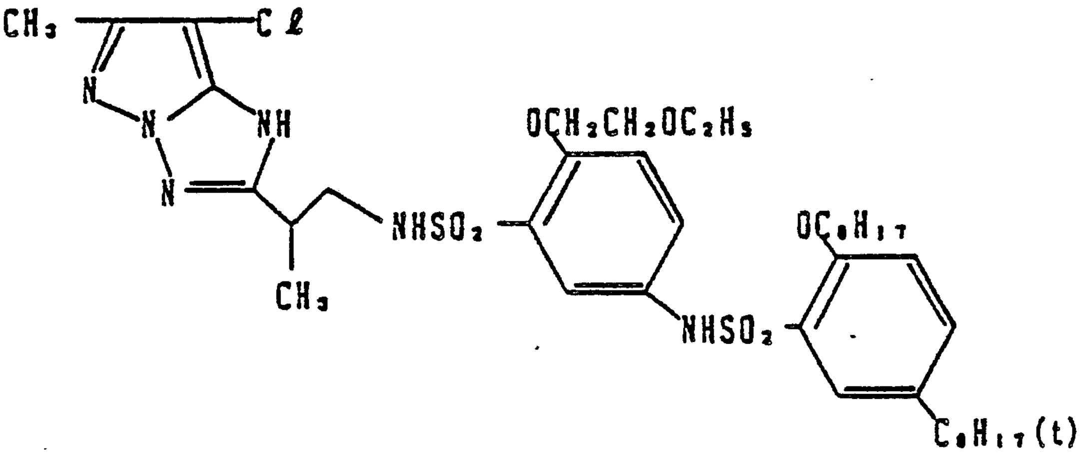
ExY-1



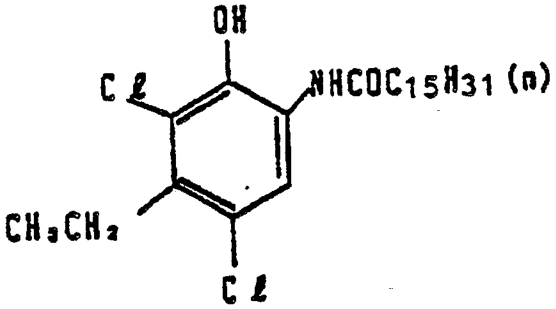
ExY-2



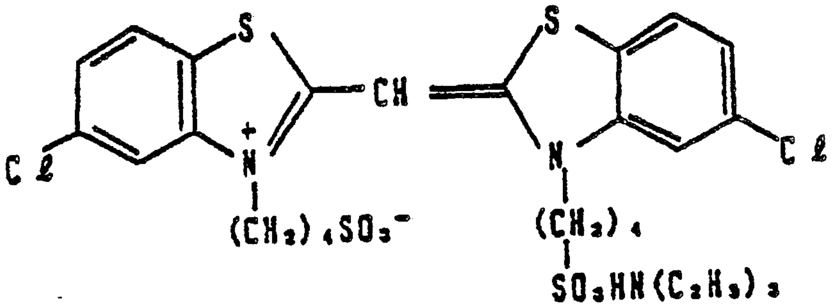
ExM-1



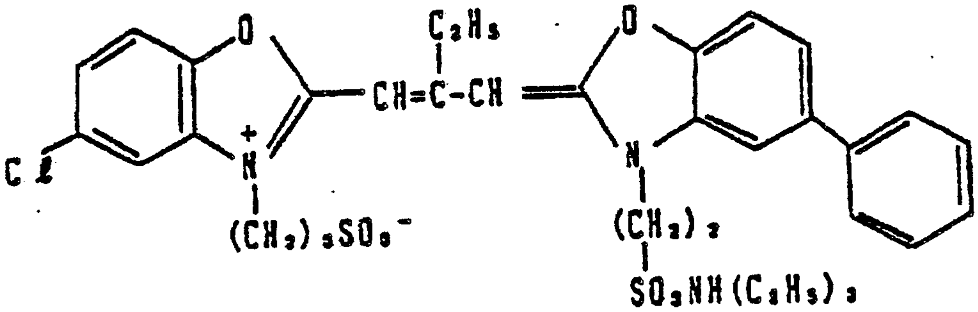
ExC−1



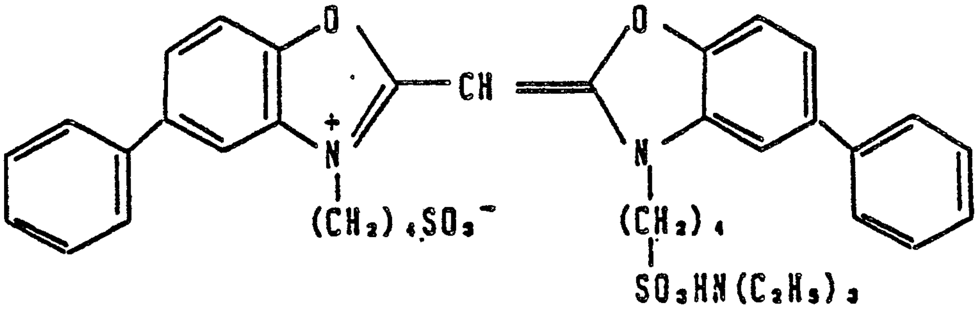
ExS−1



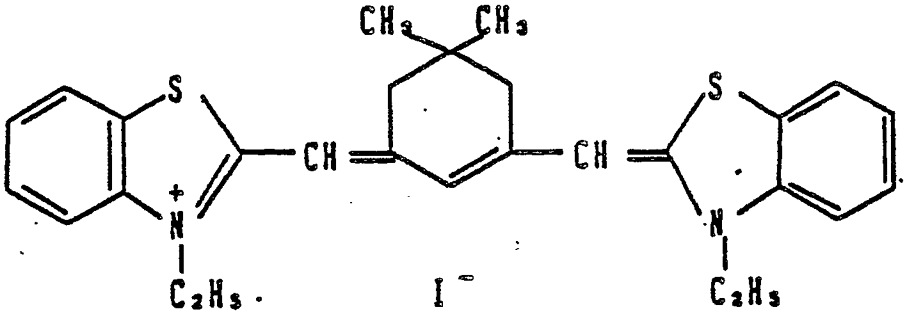
ExS−2



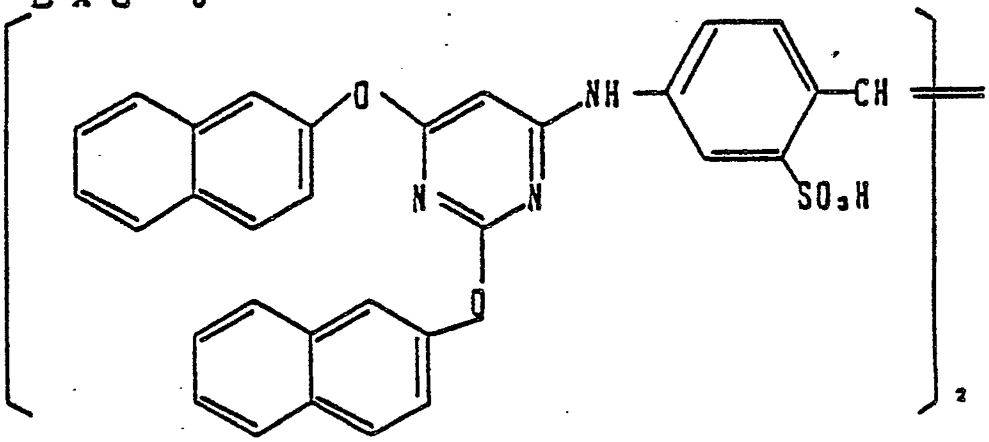
ExS-3



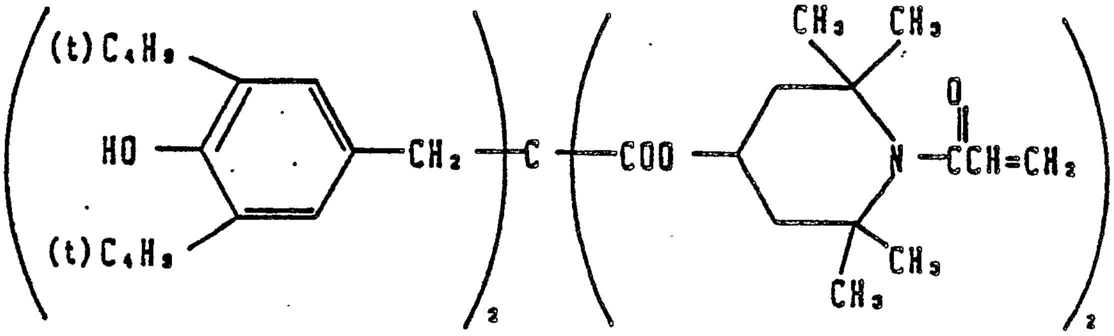
ExS-4



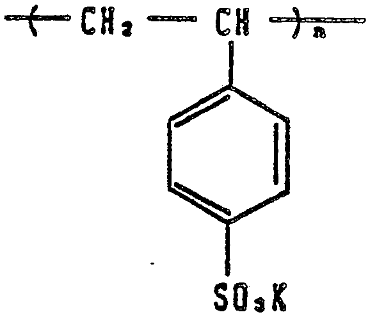
ExS-5



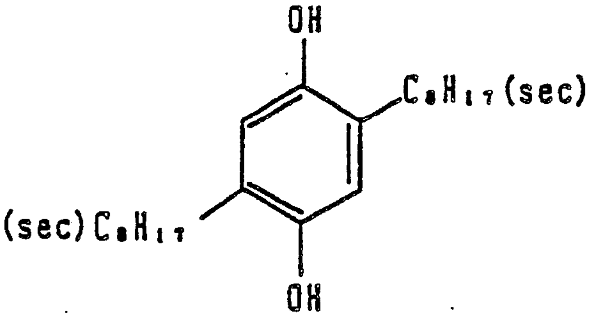
Cpd-1



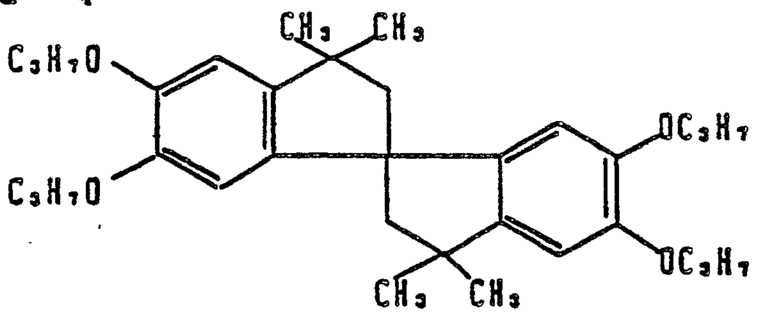
Cpd-2



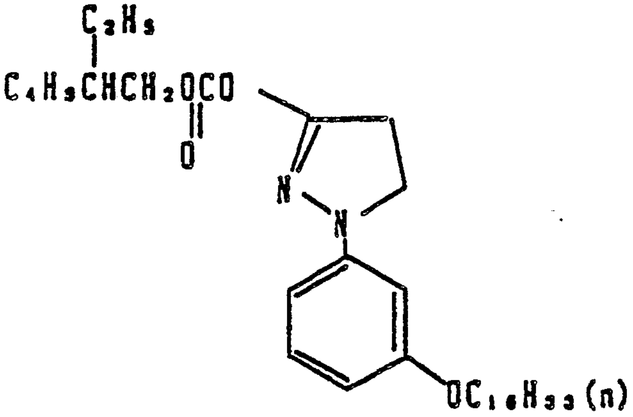
Cpd-3



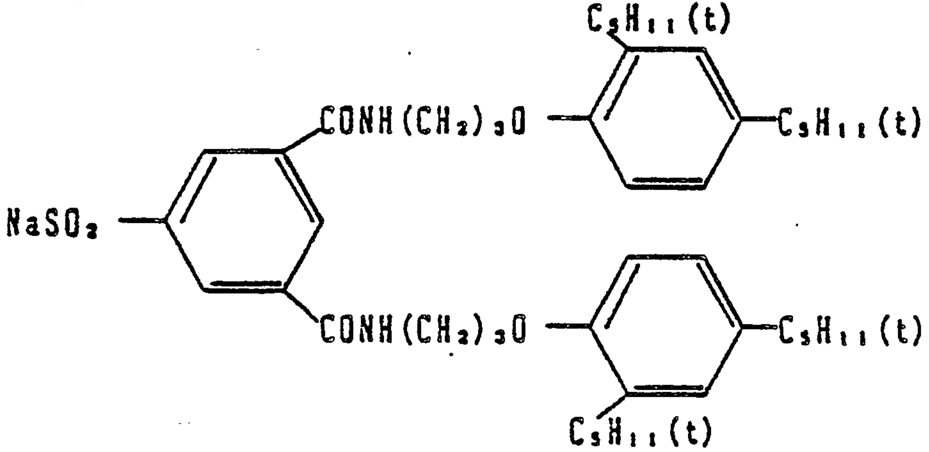
Cpd－4



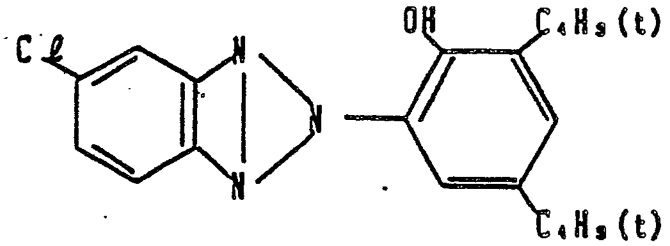
Cpd－5



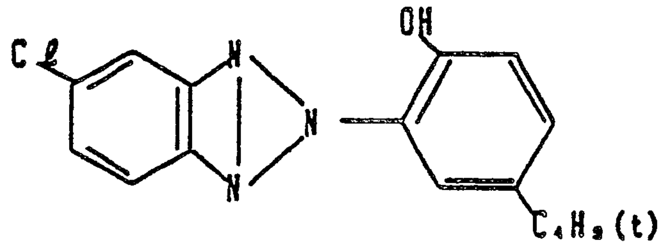
Cpd－6



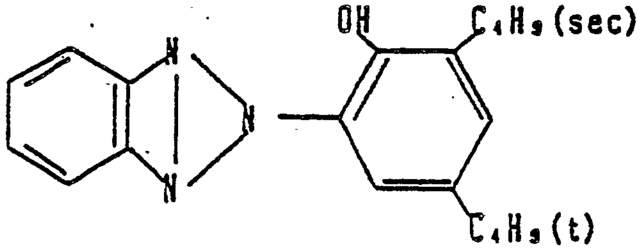
Cpd－7



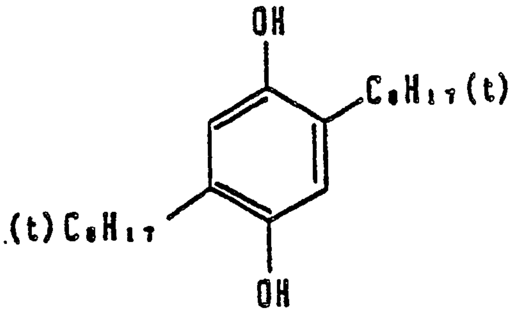
Cpd－8



Cpd－9



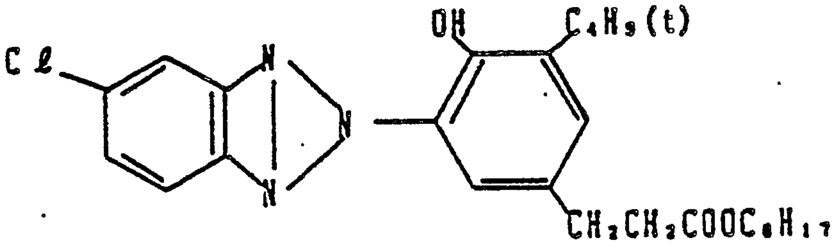
Cpd-10



Cpd-11

$$-\!\!\left(CH_2-\underset{CONHC_4H_9(t)}{\underset{|}{CH}}\right)_{\!n}\!\!- \qquad (n=100\sim1000)$$

Cpd-12



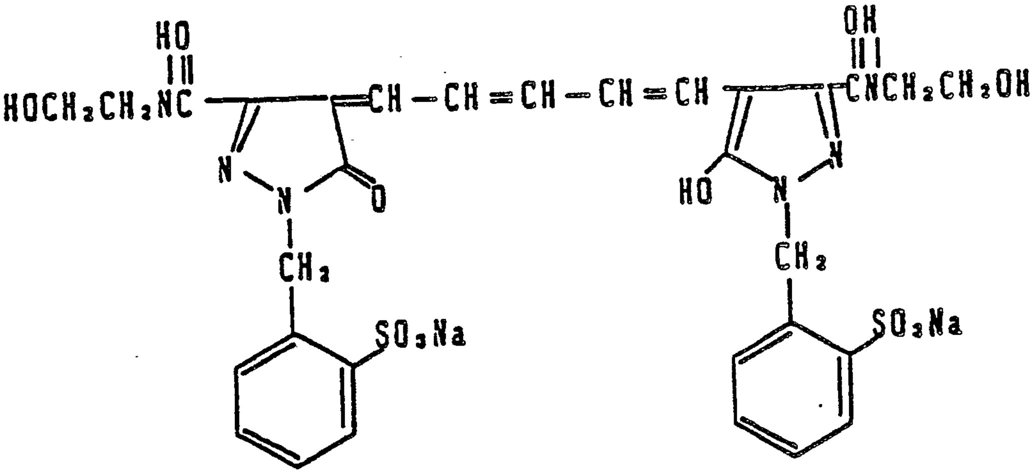
Solv-1 Dibutyl Phthalate

Solv-2 Tricresyl Phosphate

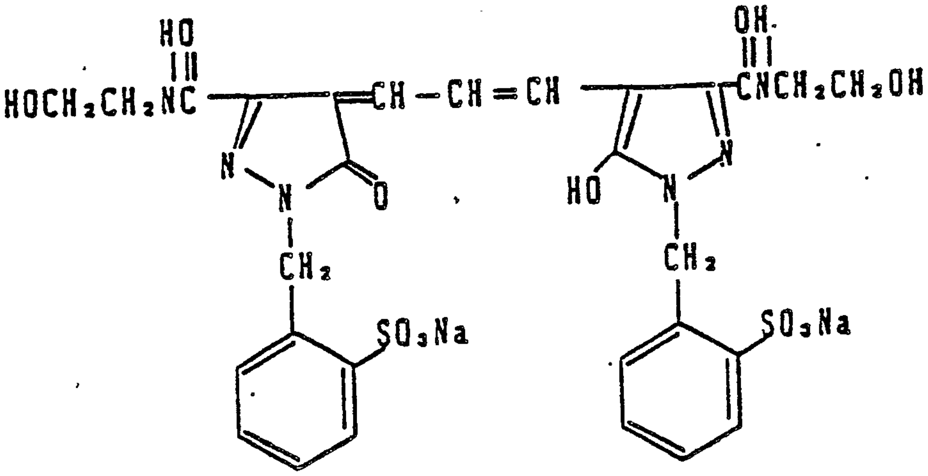
Solv-3 Trioctyl Phosphate

Solv-4 Trinonyl Phosphate

Cpd-13



Cpd-14



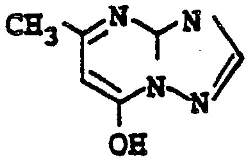
Thus, Sample A′ was prepared. Furthermore, by following the same procedure as above while changing the stabilizer as shown in Table B below, Samples B′, C′, D′, E′, F′, and G′ were also prepared.

Table B

Sample	A'	B'	C'	D'	E'	F'	G'
Stabilizer	-	a-4	a-1	IV-27	IV-45	IV-46	IV-47

The addition amount of each stabilizer was 10^{-4} mol/mol-Ag.

(a-4)



(a-1)

Same as a-1 in Example 6

Also, by changing the Br content of the emulsions EM 5 and EM 6 for Layer 5 of sample E' (IV-45), other samples were prepared.

A color developer having the composition shown below was placed in a beaker and allowed to stand for 15 days at an opening rate of 0.08 cm^{-1} and at room temperature

Each of the color photographic papers (samples) was exposed through an optical wedge and processed as follows. The processed amount per day was 2.2 m^2.

Processing Step	Temp.	Time	Replenisher Amount	Tank Volume
Color Development	38 °C	100 sec.	190 ml	17 liters
Blix	33 °C	60 sec.	100 ml	9 liters
Rinse (1)	33 °C	15 sec.	-	4 liters
Rinse (2)	33 °C	15 sec.	-	4 liters
Rinse (3)	33 °C	15 sec.	200 ml	4 liters
Drying	80 °C	50 sec.		

The amount of replenisher is m^2 of the sample.
In addition, the rinse was performed by a 3 tank countercurrent system of from Rinse (3) to Rinse (1).
The compositions of the processing solutions were as follows.

Color Developer		
	Tank	Replenisher
Water	800 ml	800 ml
Diethylenetriaminepentaacetic Acid	1.0 g	1.0 g
Nitrilotriacetic Acid	2.0 g	2.0 g
1-Hydroxyethylidene-1,1-diphosphonic Acid	2.0 g	2.0 g
Benzyl Alcohol	16 ml	22 ml
Diethylene Glycol	10 ml	10 ml
Sodium Sulfite	2.0 g	2.8 g
Potassium Bromide	0.7 g	-
Potassium Carbonate	30 g	30 g
Compound (I) (Table 6)	53 mmols	60 mmols
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.9 g	8.0 g
Fluorescent Whitening Agent (Whitex® 4, made by Sumitomo Chemical Company, Ltd.)	1.5 g	2.0 g
Triethylenediamine (1,4-diazabicyclo[2,2,2]octane)	5.0 g	5.0 g
Water to make	1 liter	1 liter
pH(25 °C)	10.20	10.06

Blix Solution		
	Tank	Replenisher
Water	400 ml	400 ml
Ammonium Thiosulfate (70%)	80 ml	95 ml
Ammonium Sulfite	24 g	32 g
Ethylenediaminetetraacetic Acid Iron(III) Ammonium	30 g	40 g
Disodium ethylenediaminetetraacetate	5 g	10 g
Water to make	1 liter	1 liter
pH (25 °C)	6.50	6.00

Rinse Water

Ion-exchanged water (content of calcium and magnesium each being less than 3 ppm) was used.

After processing, the minimum density (Dmin) of cyan was measured. The results obtained are shown in Table 6.

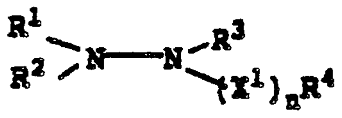
Sample No.	Br Content (mol%)	Compound (I) 53 mmols/liter	Compound (IV)	Dmin Cyan	
1	30	-	IV-45	0.20	Comparison
2	10	-	"	0.23	"
3	2	-	"	0.28	"
4	1	-	"	0.29	"
5	30	I-7	"	0.11	Invention
6	10	"	"	0.11	"
7	2	"	"	0.09	"
8	1	"	"	0.08	"
9	1	I-28	"	0.08	"
10	1	I-44	"	0.09	"
11	30	Diethylhydroxylamine	"	0.18	Comparison
12	2	"	"	0.21	"
13	1	"	"	0.21	"

As is clear from the results shown in Table 6, it can be seen that according to this invention, good results are obtained and the effect by the using the compound of formula (I) and the compound of formula (IV) is larger as the Br content is lower (Test Nos. 5 to 10).

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

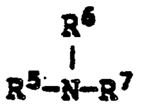
Claims

1. A process of processing a silver halide color photographic material, which comprises, after imagewise exposure, processing a silver halide color photographic material with a color developer containing an aromatic primary amine color developing agent, at least one of hydrazines or hydrazides represented by following formula (I), and at least one selected from monoamines represented by formula (II) and condensed ring type amines represented by formula (III)



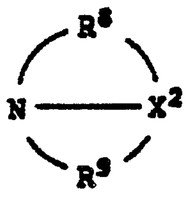
(I)

wherein R^1, R^2, and R^3 each, independently, represents a hydrogen atom, an alkyl group, an aryl group, or a heterocyclic group; R^4 represents a hydrogen atom, a hydroxyl group, a hydrazino group, an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, a carbamoyl group, or an amino group; X^1 represents a divalent group; n represents 0 or 1, provided that when n is 0, R^4 represents an alkyl group, an aryl group, or a heterocyclic group; and R^1 and R^2 or R^3 and R^4 may form together a heterocyclic ring;



$$R^5-\overset{\displaystyle R^6 \atop |}{N}-R^7 \qquad \text{(II)}$$

wherein R^5, R^6, R^7 each represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an aralkyl group, or a heterocyclic group; and R^5 and R^6, R^5 and R^7, or R^6 and R^7 may combine with each other to form a nitrogen-containing heterocyclic ring; and



(III)

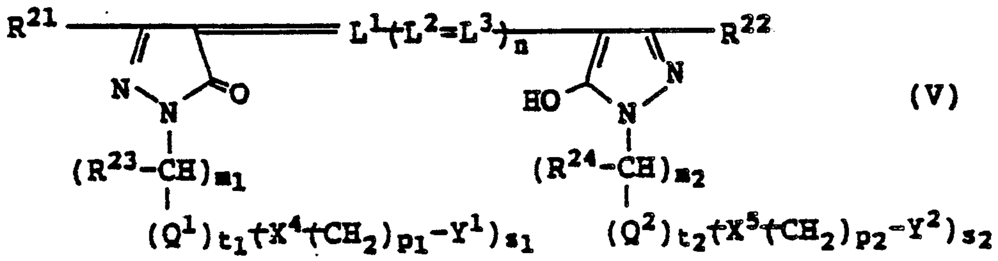
wherein X^2 represents a trivalent atomic group necessary for completing a condensed ring; and R^8 and R^9, which may be the same or different, each represents an alkylene group, an arylene group, an alkenylene group, or an aralkylene group.

2. The process of processing a silver halide color photographic material as claimed in claim 1, wherein the processing is performed in the presence of at least one of the compounds represented by formula (IV)

Z-S-M (IV)

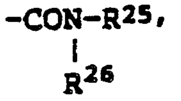
wherein M represent a hydrogen atom, a cation, or -S-Z; and Z represents a heterocyclic residue containing at least one nitrogen atom.

3. The process of processing silver halide color photographic material as claimed in claim 1, wherein the silver halide color photographic material contains at least one of the compounds represented by formula (V)



(V)

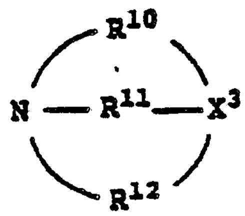
wherein R^{21} and R^{22} each represents $-COOR^{25}$,



$$-\underset{\substack{|\\R^{26}}}{CON}-R^{25},$$

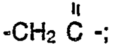
$-COR^{25}$, wherein R^{25} and R^{26} each represents a hydrogen atom, an alkyl group or an aryl group, or -CN; R^{23} and R^{24} each represents a hydrogen atom or an alkyl group; Q^1 and Q^2 each represents an aryl group; X^4 and X^5 each represents a bond or a divalent linkage group; Y^1 and Y^2 each represents a sulfo group or a carboxyl group; L^1, L^2, and L^3 each represents a methine group; m_1 and m_2 each represents 0, 1, or 2; n represents 0, 1, or 2, p_1 and p_2 each represents 0, 1, 2, 3, or 4; s_1 and s_2 each represents 1 or 2; and t_1 and t_2 represents 0 or 1, with the exclusion of the cases that m_1, p_1 and t_1 are simultaneously 0 and that m_2, p_2 and t_2 are simultaneously 0.

4. The process of processing a silver halide color photographic material as claimed in claim 1, wherein the condensed ring type amine is a compound shown by following formula (1-a) or (1-b)

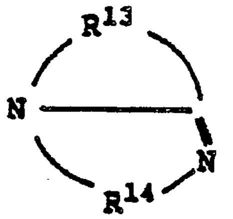


(1-a)

wherein X^3 represents $\gt N$ or $\gt CH$, R^{10} and R^{11} have the same meanings as R^8 and R^9 in the formula (III) as claimed in claim 1 and R^{12} represents the group shown by R^{10} and R^{11} or



$-CH_2\overset{\overset{\displaystyle O}{\|}}{C}-$;



(1-b)

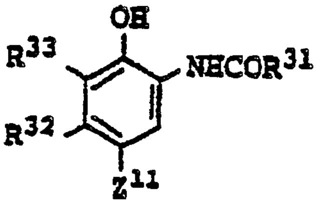
wherein R^{13} and R^{14} have the same meanings as R^8 and R^9 in the formula (III) as claimed in claim 1.

5. The process of processing a silver halide color photographic material as claimed in claim 1, wherein the hydrazine or hydrazide represented by the formula (I) is used in an amount of from 0.01 g to 50 g per liter of the color developer.

6. The process of processing a silver halide color photographic material as claimed in claim 1, wherein the monoamine represented by the formula (II) and the condensed ring type amine represented by the formula (III) are used in an amount of from 0.1 g to 50 g per liter of color developer.

7. The process of processing a silver halide color photographic material as claimed in claim 1, wherein the silver halide is substantially composed of silver chloride.

8. The process of processing a silver halide color photographic material as claimed in claim 1, wherein at least one kind of cyan couplers shown by following formula (C-1)



wherein R^{31} represents an alkyl group, a cycloalkyl group, an aryl group, an amino group, or a heterocyclic group; R^{32} represetns an acylamino group or an alkyl group having 2 or more carbon atoms; R^{33} represents a hydrogen atom, a halogen atom, an alkyl group, or an alkoxy group; R^{32} and R^{33} may combine with each other to form a ring; and Z^{11} represents a hydrogen atom, a halogen atom or a group capable of being released at the reaction with the oxidation product of an aromatic primary amine color developing agent, is used.