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(71) Applicant: **FUJI PHOTO FILM CO., LTD.**
**210 Nakanuma Minami Ashigara-shi**
**Kanagawa(JP)**

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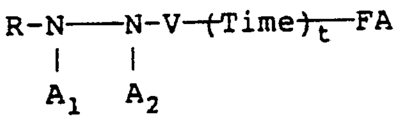
(72) Inventor: **Hirano, Shigeo, c/o Fuji Photo Film Co., Ltd.**
**No. 210 Nakanuma**
**Minami Ashigara-shi, Kanagawa(JP)**

(74) Representative: **Patentanwälte Grünecker, Kinkeldey, Stockmair & Partner**
**Maximilianstrasse 58**
**D-8000 München 22(DE)**

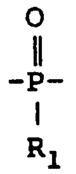
# (54) Silver halide photograpic material.

(57) A silver halide photographic material comprising a support having thereon at least one light-sensitive silver halide emulsion layer, wherein the silver halide photographic material contains at least one compound represented by the following general formula (I):



$$\underset{A_1}{\underset{|}{R-N}}-\underset{A_2}{\underset{|}{N}}-V\!-\!(\mathrm{Time})_t\!-\!FA \qquad (I)$$

wherein $A_1$ and $A_2$ each represents a hydrogen atom or one of them represents a hydrogen atom and the other represents a sulfonyl group or $-(\underset{\underset{O}{\|}}{C})_{\ell}-R_0$ (wherein $R_0$ represents an alkyl group, an alkenyl group, an aryl group, an alkoxy group or an aryloxy group; and $\ell$ represents 1 or 2); Time represents a divalent linking group; t represents 0 or 1; FA represents a moiety of a nucleating agent or a development accelerating agent; V represents a carbonyl group, $-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-$, a sulfonyl group, a sulfoxy group,



$$-\overset{\overset{O}{\|}}{\underset{\underset{R_1}{|}}{P}}-$$

(wherein $R_1$ represents an alkoxy group or an aryloxy group), an iminomethylene group or a thiocarbonyl group; and R represents an aliphatic group, an aromatic group or a heterocyclic group.

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# SILVER HALIDE PHOTOGRAPHIC MATERIAL

## FIELD OF THE INVENTION

The present invention relates to a photographic light-sensitive material, and more particularly, to a silver halide photographic material having at least one layer containing a compound which is capable of releasing imagewise a fogging agent or a development accelerating agent.

## BACKGROUND OF THE INVENTION

It has been hitherto known that a development accelerating agent or a fogging agent is released from certain kinds of couplers during color development processing of silver halide color photographic material. For example, in JP-A-57-150845, JP-A-59-50439 and JP-A-59-170840 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), couplers which release a fogging agent upon a reaction with an oxidation product of a color developing agent are disclosed. It is further disclosed that the imagewise release of the fogging agents provides high contrast and accelerated development.

Further, compounds which release imagewise a fogging agent upon an oxidation-reduction reaction with an oxidation product of a black and white developing agent, for example, hydroquinone, Metol or 3-pyrazolidone during black and white development are described in JP-A-60-107029, and their effectiveness on increasing sensitivity and contrast of negative emulsions is also disclosed. However, their effects are not yet sufficient.

In direct positive image formation using a light fogging method or a chemical fogging method, the developing speed is low and a long processing time is required as compared with processing of conventional negative type photographic materials. Therefore, to shorten the processing time for direct positive type photographic materials, developing solutions having high pH and/or high temperature have been employed. However, it is known that the minimum image density of direct positive images increase when the image is developed at high pH. Further, under high pH conditions, degradation of developing agents due to air oxidation is apt to occur, and thus development activity is seriously decreased.

Other methods for increasing developing speed in direct positive image formation are known. One such method employs a hydroquinone derivative as described in U.S. Patent 3,227,552; another employs a mercapto compound having a carboxylic acid group or a sulfonic acid group, as described in JP-A-60-170843. However, use of these compounds results in only small increases in developing speed, and a technique for effectively increasing the maximum density of direct positive images using these compounds has not been found. Therefore, it has been desired to develop a technique which provides a sufficiently high maximum image density even when processing is carried out in a developing solution having a low pH.

Further, upon imagewise exposure of direct positive photographic materials, when the width of an unexposed area is narrow, the maximum image density obtained is reduced remarkably as compared with the maximum image density of a wide unexposed area. As a result, the resolving power of direct positive photographic materials tends to be less than that of comparable negative type photographic materials. Therefore, it has been desired to solve this problem also.

To increase the maximum density of direct positive images, a surface chemical sensitization treatment is often conducted, particularly in core shell type silver halide emulsions. However, the surface chemical sensitization is ordinarily required to stop in an appropriate degree for the purpose of preventing increases in the minimum density, decreases in sensi tivity, occurrence of pseudo images in highly exposed areas, and other problems caused by superfluous chemical sensitization. The surface chemical sensitizing nuclei formed are weak as compared with those formed in conventional negative type photographic materials and their stability over time is extremely poor.

To solve these problems, addition of conventionally well known stabilizers such as 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene or 1-phenyl-5-mercaptotetrazole has been studied. However, to prevent changes in performance over time, a large amount of stabilizer is required, which results in various adverse affects on photographic characteristics. In particular, these adverse affects include: decreases in the maximum density of positive images: increases in re-reversal image sensitivity due to the development inhibiting function of stabilizers; and degradation of sensitivity in spectrally sensitized regions because stabilizer interfere with the adsorption of the typical sensitizing dyes used to spectrally sensitize silver halide emulsions. Therefore, it has been desired to develop a technique for eliminating these adverse affects and improving stability over time.

Using the above-described known techniques individually or in combination, it is difficult to obtain a direct positive color photographic material which has excellent image sharpness and stability, together with a satisfactory maximum image density.

According to the present invention a high contrast negative photographic material which is sufficiently high contrast and has a high maximum density with reduced amounts of black spots can be obtained.

## SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a silver halide photographic material which has a high contrast.

Another object of the present invention is to provide a silver halide photographic material which may be developed quickly and may be processed rapidly.

Still another object of the present invention is to provide a silver halide photographic material which has a high sensitivity.

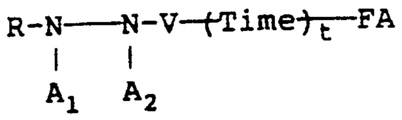
A further object of the present invention is to provide a direct positive color light-sensitive material which provides a direct positive image having a high maximum image density and a high resolving power.

A still further object of the present invention is to provide a direct positive color light-sensitive material which has excellent preservability, particularly under high temperature and high humidity conditions.

A still further object of the present invention is to provide a direct positive color light-sensitive material which can form a direct positive image having a sufficiently high color density even when it is processed with a stable developing solution having a low pH.

Other objects of the present invention will become apparent from the following description and examples.

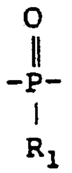
These objects of the present invention are accomplished by a silver halide photographic material comprising a support having thereon at least one light-sensitive silver halide emulsion layer, wherein the silver halide photographic material contains at least one compound represented by the following general formula (I):



$$R-\underset{A_1}{\underset{|}{N}}-\underset{A_2}{\underset{|}{N}}-V-(Time)_t-FA \qquad (I)$$

wherein $A_1$ and $A_2$ each represents a hydrogen atom or one of them represents a hydrogen atom and the other represents a sulfonyl group or $\left(\underset{\underset{O}{\|}}{C}\right)_{\ell}R_0$

wherein $R_0$ represents an alkyl group, an alkenyl group, an aryl group, an alkoxy group or an aryloxy group; and $\ell$ represents 1 or 2); Time represents a divalent linking group; t represents 0 or 1; FA represents a moiety of a nucleating agent or a development accelerating agent; V represents a carbonyl group, $-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-$, a sulfonyl group, a sulfoxy group,

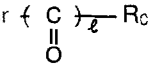


$$-\overset{\overset{O}{\|}}{\underset{\underset{R_1}{|}}{P}}-$$

(wherein $R_1$ represents an alkoxy group or an aryloxy group), an iminomethylene group or a thiocarbonyl group; and R represents an aliphatic group, an aromatic group or a heterocyclic group.

## DETAILED DESCRIPTION OF THE INVENTION

The compounds represented by general formula (I) will be described in greater detail below.

In general formula (I) described above, A1 and $A_2$ each represents a hydrogen atom, an alkylsulfonyl or arylsulfonyl group having at most 20 carbon atoms (preferably a phenylsulfonyl group or a phenylsulfonyl group substituted such that the sum of the Hammett's substituent constants is at least -0.5), or  $\left( \underset{\underset{O}{\|}}{C} \right)_{\ell} R_c$ (wherein $R_c$ represents a straight chain, branched chain or cyclic alkyl group or alkenyl group preferably having at most 30 carbon atoms, an aryl group (preferably a phenyl group or a phenyl group substituted such that the sum of the Hammett's substituent constants is at least -0.5), an alkoxy group (for example, ethoxy), or an aryloxy group (preferably a monocyclic aryloxy group); and $\ell$ represents 1 or 2. The above $A_1$ and $A_2$ groups may be substituted with one or more substituents selected from an alkyl group, an aralkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an aryl group, a substituted amino group, an acylamino group, a sulfonylamino group, a ureido group, a urethane group, an aryloxy group, a sulfamoyl group, a carbamoyl group, an alkylthio group, an arylthio group, a sulfonyl group, a sulfinyl group, a hydroxyl group, a halogen atom, a cyano group, a sulfo group, a carboxyl group, an aryloxycarbonyl group, an acyl group, an alkoxycarbonyl group, an acyloxy group, and a nitro group, and these substituents may be further substituted.

The sulfonyl group represented by $A_1$ or $A_2$ preferably represents one which is specifically described in U.S. Patent 4,478,928.

$A_1$ or $A_2$ may be connected with Time, R or V which is defined hereinafter to form a ring, if desired.

$A_1$ and $A_2$ are most preferably hydrogen atoms.

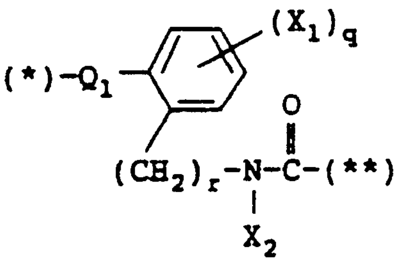
In the general formula (I), Time represents a divalent linking group and may have a timing control function, and t represents 0 or 1. When t is 0, FA is directly connected to V.

In a case wherein the divalent linking group represented by Time has a timing control function, Time represents a group which releases FA through one or more reaction stages from Time-FA which has been released from an oxidation product of the oxidation-reduction mother nucleus.

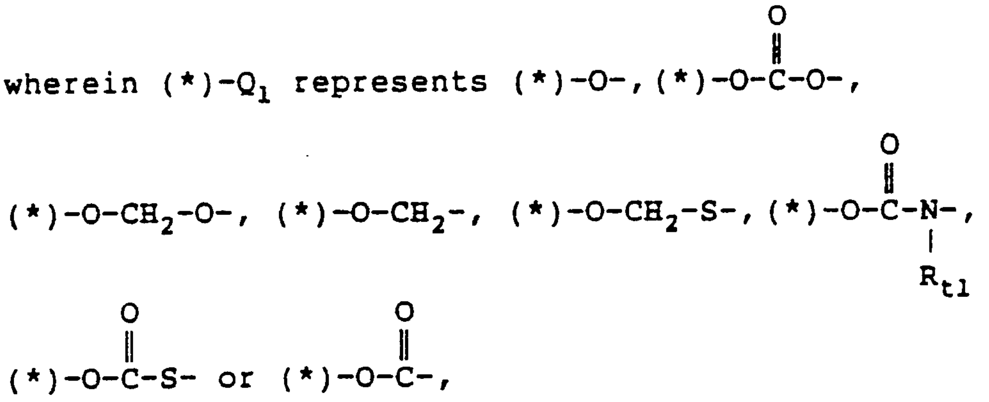
The divalent linking groups represented by Time include, for example, those capable of releasing a photographically useful group (hereinafter simply referred to as "PUG") upon an intramolecular ring-closing reaction of a p-nitrophenoxy derivative as described, for example, in U. S. Patent 4,248,962 (JP-A-54-145135); those capable of releasing PUG upon an intramolecular ring-closing reaction after the ring cleavage as described, for example, in U.S. Patents 4,310,612 (JP-A-55-53330) and 4,358,525; those capable of releasing PUG accompanied with the formation of an acid anhydride upon an intramolecular ring-closing reaction of a carboxy group of succinic acid mono-ester or analogues thereof as described, for example, in U.S. Patents 4,330,617, 4,446,216 and 4,483,919 and JP-A-59-121328; those capable of releasing PUG accompanied with the formation of quinon-monomethide or analogues thereof upon electron transfer via conjugated double bonds of an aryloxy group or a heterocyclic oxy group as described, for example, in U.S. Patents 4,409,323 and 4,421,845, Research Disclosure, No, 21228 (December, 1981), U.S. Patent 4,416,977 (JP-A-57-135944), JP-A-58-209736 and JP-A-58-209738; those capable of releasing PUG from the γ-position of enamine upon electron transfer in the enamine-structure portion of a nitrogen-containing hetero ring as described, for example, in U.S. Patent 4,420,554 (JP-A-57-136640), JP-A-57-135945, JP-A-57-188035, JP-A-58-98728 and JP-A-58-209737; those capable of releasing PUG upon an intramolecular ring-closing reaction of an oxy group formed by electron transfer to a carbonyl group which is conjugated with a nitrogen atom in a nitrogen-containing hetero ring as described, for example, in JP-A-57-56837; those capable of releasing PUG accompanied with the formation of an aldehyde as described, for example, in U.S. Patent 4,146,396 (JP-A 52-90932), JP-A-59-93442 and JP-A-59-75475; those capable of releasing PUG accompanied with decarboxylation of a carboxy group as described, for example, in JP-A-51-146828, JP-A-57-179842 and JP-A-59- 104641; those capable of releasing PUG accompanied with the formation of an isocyanate as described, for example, in JP-A-60-7429; and those capable of releasing PUG upon a coupling reaction with an oxidation product of a color developing agent as described, for example, in U.S. Patent 4,438,193.

Time may be composed of a combination of two or more divalent linking groups (for example, those represented by the general formulae (T-1) to (T-10) described hereinafter).

Preferable divalent timing groups represented by Time in the general formula (I) include those represented by the following general formulae (T-1) to (T-10) wherein the symbol (*) denotes the position at which V is bonded, and the symbol (**) denotes the position at which FA is bonded. Preferable timing groups also include those represented by combining two or more groups represented by the formulae.



(T-1)

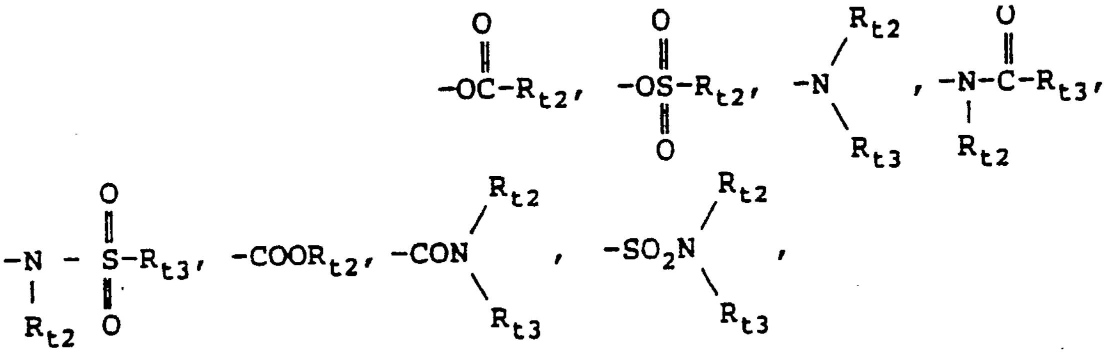


wherein $(*)\text{-}Q_1$ represents $(*)\text{-O-}$, $(*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-O-}$,

$(*)\text{-O-}CH_2\text{-O-}$, $(*)\text{-O-}CH_2\text{-}$, $(*)\text{-O-}CH_2\text{-S-}$, $(*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}\underset{R_{t1}}{\underset{|}{N}}\text{-}$,

$(*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-S-}$ or $(*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}$,

wherein $R_{t1}$ represents a hydrogen atom, an aliphatic group, an aromatic group, or a heterocyclic group; $X_1$ represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, $\text{-O-}R_{t2}$, $\text{-S-}R_{t2}$,

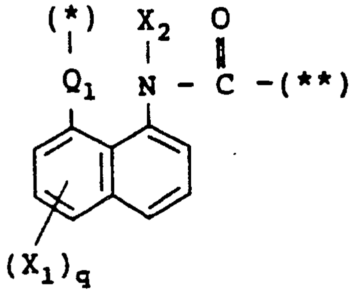


$\text{-O}\overset{O}{\overset{\|}{C}}\text{-}R_{t2}$, $\text{-O}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\text{-}R_{t2}$, $\text{-N}\genfrac{}{}{0pt}{}{\diagup R_{t2}}{\diagdown R_{t3}}$, $\text{-}\underset{R_{t2}}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R_{t3}$,

$\text{-}\underset{R_{t2}}{\underset{|}{N}}\text{ - }\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\text{-}R_{t3}$, $\text{-COO}R_{t2}$, $\text{-CON}\genfrac{}{}{0pt}{}{\diagup R_{t2}}{\diagdown R_{t3}}$, $\text{-SO}_2\text{N}\genfrac{}{}{0pt}{}{\diagup R_{t2}}{\diagdown R_{t3}}$,

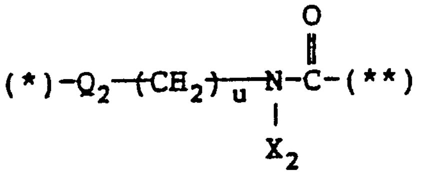
$\text{-CO-}R_{t2}$, $\text{-SO-}R_{t2}$, a cyano group, a halogen atom (e.g., fluorine, chlorine, bromine or iodine) or a nitro group, wherein $R_{t2}$ and $R_{t3}$, which may be the same or different, each has the same meaning as defined for $R_{t1}$; $X_2$ has the same meaning as defined for $R_{t1}$; q represents an integer of from 1 to 4, and when q is 2 or more, the substituents represented by $X_1$ may be the same or different, and when q is 2 or more, $X_1$ may connect with each other to form a ring; and r represents 0, 1 or 2.

The groups represented by the general formula (T-1) are described, for example, in U.S. Patent 4,248,962.



(T-2)

wherein (*)-Q₁, X₁, X₂ and q each has the same meaning as defined for the general formula (T-1).



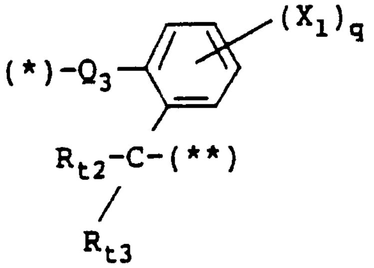
$$(*)\text{-}Q_2\text{-}(CH_2)_u\text{-}\underset{\underset{X_2}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}(**)$$

(T-3)

$$\text{wherein } (*)\text{-}Q_2 \text{ represents } (*)\text{-}O\text{-},\ (*)\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-},\ (*)\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{R_{t1}}{\|}}{N}\text{-},$$

$$(*)\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-},\ (*)\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}S\text{- or }(*)\text{-}O\text{-}\underset{\underset{R_{t1}}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-};$$

U represents an integer of from 1 to 4, preferably being 1, 2 or 3; and $R_{t1}$ and $X_2$ each has the same meaning as defined for the general formula (T-1).



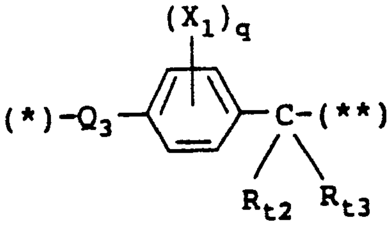
(T-4)

$$\text{wherein } (*)\text{-}Q_3 \text{ represents } (*)\text{-}O\text{-},\ (*)\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-},\ (*)\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{R_{t1}}{|}}{N}\text{-},$$

$$(*)\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}S\text{-},$$

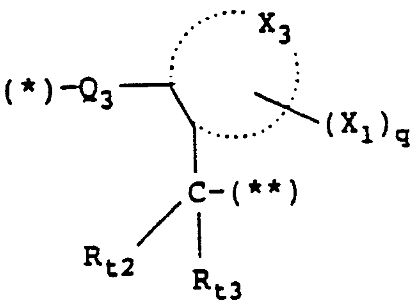
(*)-O-$CH_2$-O- or (*)-O-$CH_2$-S-; and $R_{t1}$, $R_{t2}$, $R_{t3}$, $X_1$ and q each has the same meaning as defined for the general formula (T-1).

An example of the group represented by the general formula (T-4) is the timing group as described in U.S. Patent 4,409,323.



(T-5)

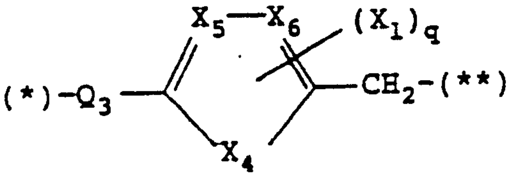
wherein (*)-$Q_3$, $R_{t2}$, $R_{t3}$, X and q each has the same meaning as defined for the general formula (T-4).



(T-6)

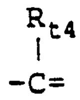
wherein $X_3$ represents an atomic group which contains at least one atom selected from the group consisting of carbon, nitrogen, oxygen and sulfur and which is necessary to form a 5-membered, 6-membered or 7-membered heterocyclic ring, which may be further condensed with a benzene ring or a 5-membered, 6-membered or 7-membered heterocyclic ring. Examples of preferable heterocyclic rings include pyrrole, pyrazole, imidazole, triazole, furan, oxazole, thiophene, thiazole, pyridine, pyridazine, pyrimidine, pyrazine, azepin, oxepin, indole, benzofuran, and quinoline. (*)-$Q_3$, $X_1$, q, $R_{t2}$ and $R_{t3}$ each has the same meaning as defined for the general formula (T-4).

An example of the group represented by the general formula (T-6) is the timing group as described in British Patent 2,096,783.



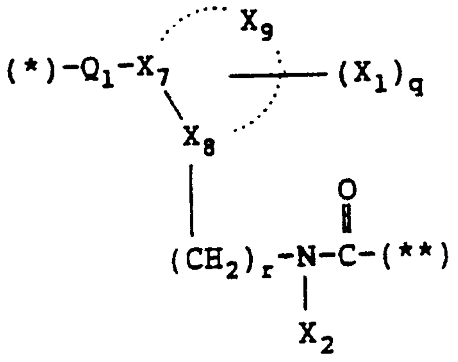
(T-7)

wherein $X_4$ represents an atomic group which contains at least one atom selected from the group consisting of carbon, nitrogen, oxygen and sulfur and which is necessary to form a 5-membered, 6-membered or 7-membered heterocyclic ring, which may be further condensed with a benzene ring or a 5-membered, 6-membered or 7-membered heterocyclic ring. Examples of preferable heterocyclic rings include pyrrole, imidazole, triazole, furan, oxazole, oxadiazole, thiophene, thiazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, azepin, oxepin and isoquinoline. $X_5$ and $X_6$ each represents



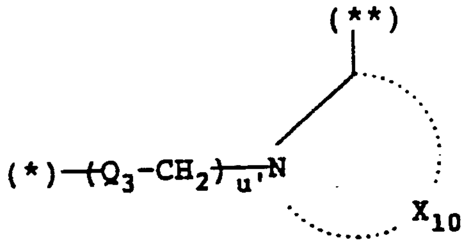
$$\overset{\overset{R_{t4}}{|}}{-C=}$$

or -N=, wherein $R_{t4}$ represents a hydrogen atom, an aliphatic group or an aromatic group; and (*)-$Q_3$, $X_1$ and q each has the same meaning as defined for the general formula (T-4).



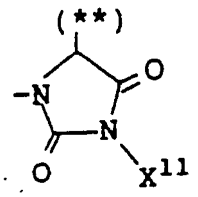
(T-8)

wherein $X_9$ represents an atomic group which contains at least one atom selected from the group consisting of carbon, nitrogen, oxygen, and sulfur and which is necessary to form a 5-membered, 6-membered or 7-membered heterocyclic ring, which may be further condensed with a benzene ring or a 5-membered, 6-membered or 7-membered heterocyclic ring. Examples of preferable heterocyclic rings include pyrrolidine, piperidine and benzotriazole besides those described for the general formula (T-6). $X_7$ and $X_8$ each represents $-\overset{|}{C}=$ or $-\overset{|}{N}-$; and $(^{*})\text{-}Q_1$, $X_1$, $X_2$, q and r each has the same meaning as defined for the general formula (T-1).



(T-9)

wherein $X_{10}$ has the same meaning as $X_9$ defined for the general formula (T-8); $(^{*})\text{-}Q_3$ has the same meaning as defined for the general formula (T-4); and $u'$ represents 0 or 1. Examples of preferable heterocyclic rings for $X_{10}$ are as follows.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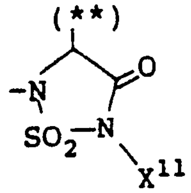
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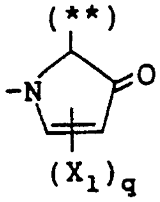
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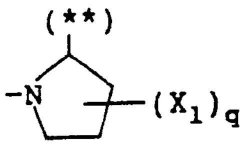
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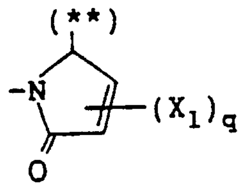
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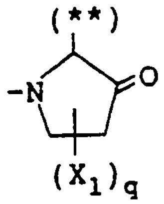
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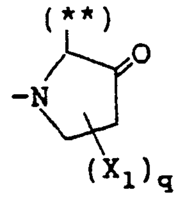
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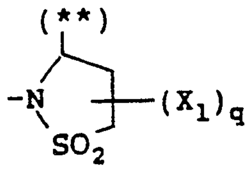
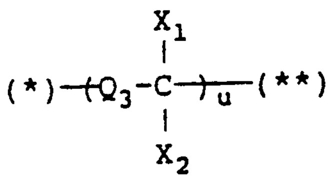

,

wherein $X_1$ and q each has the same meaning as defined for the general formula (T-1); and $X_{11}$ represents a hydrogen atom, an aliphatic group, and aromatic group, an acyl group, a sulfonyl group, an alkoxycarbonyl group, a sulfamoyl group, a heterocyclic group, or a carbamoyl group.


(T-10)

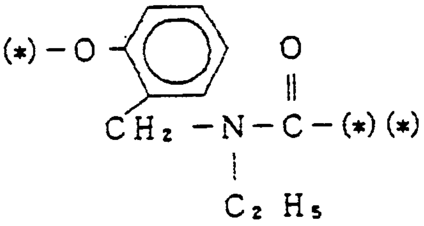
$$(*)-\!\left(Q_3-\underset{X_2}{\overset{X_1}{C}}\right)_u\!-(**)\qquad \text{(T-10)}$$

wherein $X_1$ and $X_2$ each has the same meaning as defined for the general formula (T-1); (*)-$Q_3$ has the same meaning as defined for the general formula (T-4); and u has the same meaning as defined for the general formula (T-3) and is preferably 1 or 2.

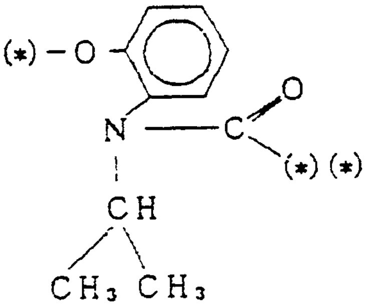
In the above described general formulae (T-1) to (T-10), when $X_1$, $X_2$, $R_{t1}$, $R_{t2}$, $R_{t3}$ and $R_{t4}$ contain a portion of an aliphatic group, the aliphatic group preferably has from 1 to 20 carbon atoms and may be saturated or unsaturated, substituted or unsubstituted, straight chain, branched chain or cyclic. When $X_1$, $X_2$, $R_{t1}$, $R_{t2}$, $R_{t3}$ and $R_{t4}$ described above contain a portion of an aromatic group, the aromatic group has from 6 to 20 carbon atoms, preferably from 6 to 10 carbon atoms, and is more preferably a substituted or unsubstituted phenyl group. Further, when $X_1$, $X_2$, $R_{t1}$, $R_{t2}$, $R_{t3}$ and $R_{t4}$ described above contain a portion of a heterocyclic group, the heterocyclic group is a 5-membered or 6-membered heterocyclic group containing at least one of a nitrogen atom, an oxygen atom and a sulfur atom as a hetero atom. Examples of preferable heterocyclic groups include a pyridyl group, a furyl group, a thienyl group, a triazolyl group, an imidazolyl group, a pyrazolyl group, a thiadiazolyl group, an oxadiazolyl group and a pyrrolidinyl group.

Specific examples of preferred divalent linking groups are set forth below, but the present invention should not be construed as being limited thereto.

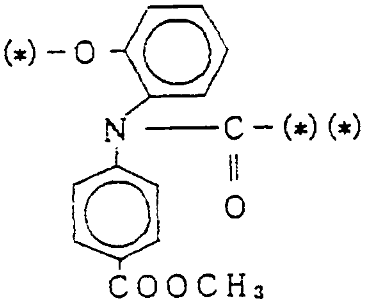
T- (1)



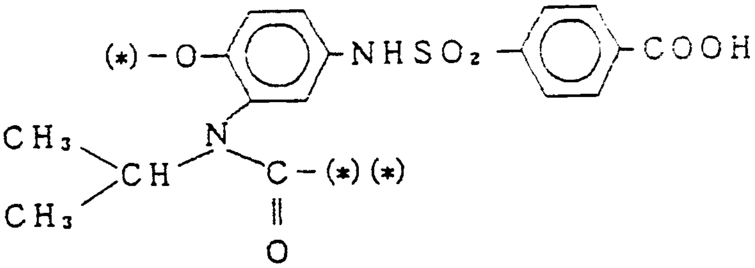
T- (2)



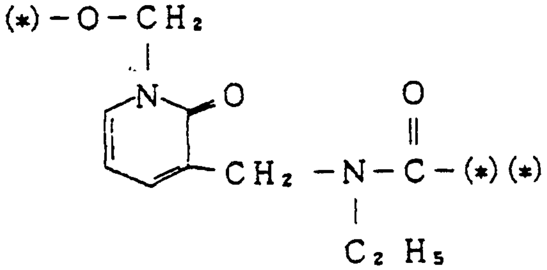
T- (3)



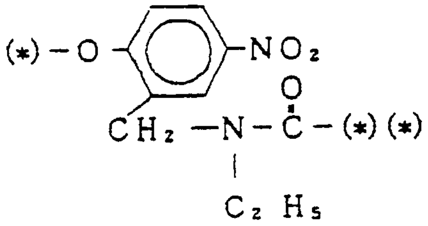
T- (4)



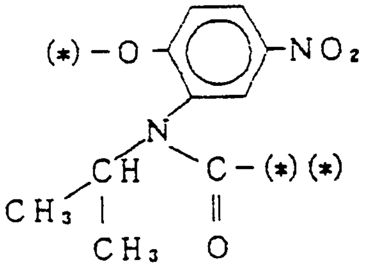
T- (5)



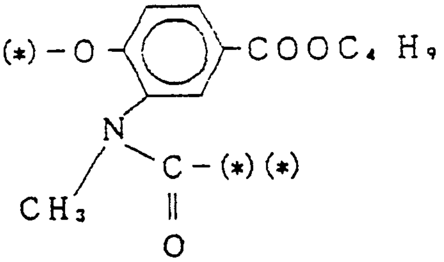
T- (6)



T- (7)



T- (8)



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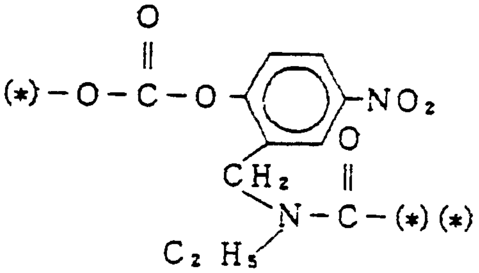
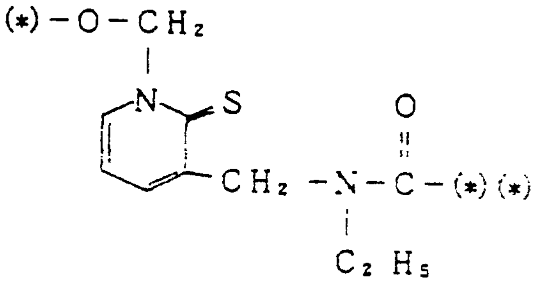
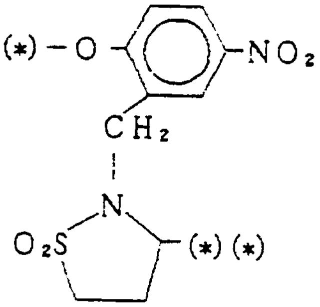


T− (10)



T− (11)



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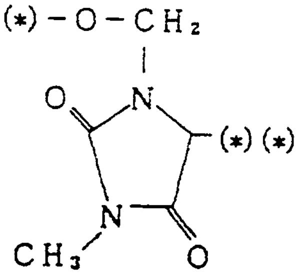
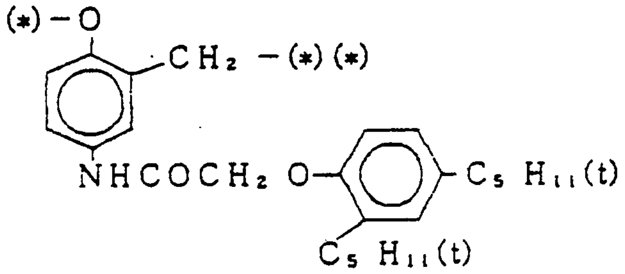


T-(13)



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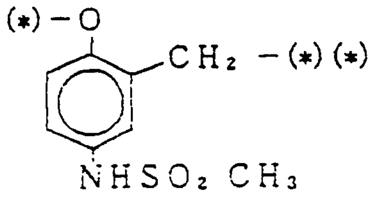

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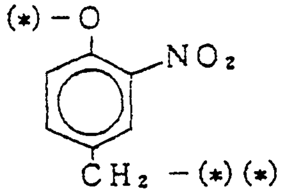

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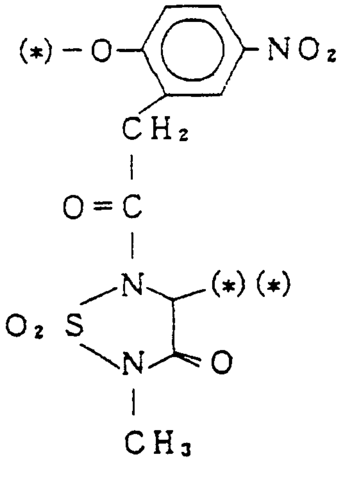

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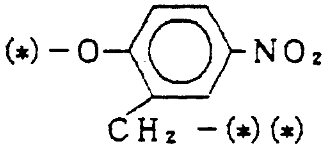

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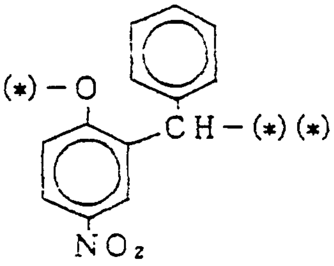
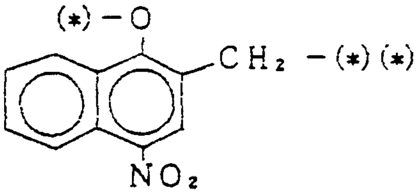


T- (19)



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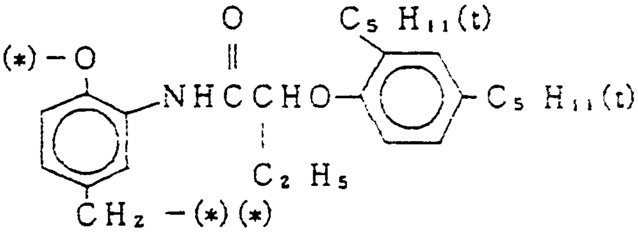

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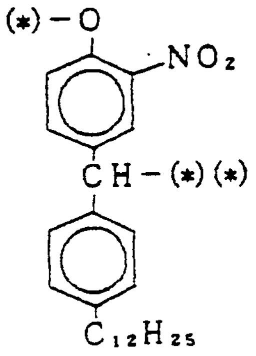

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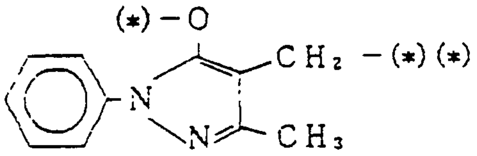

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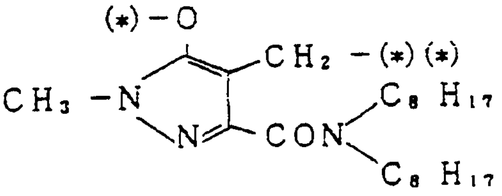

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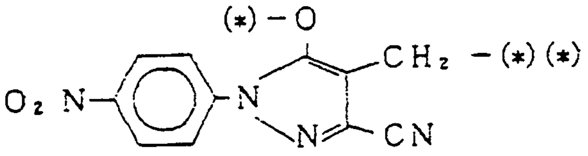

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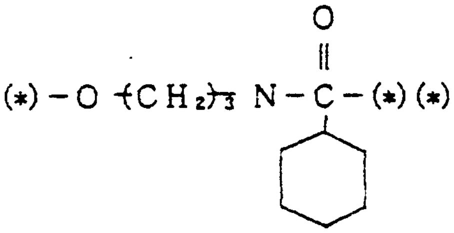

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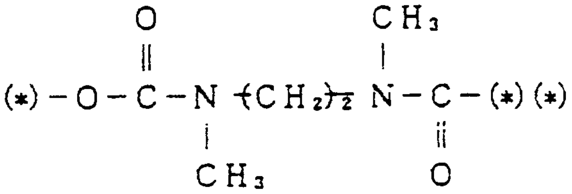
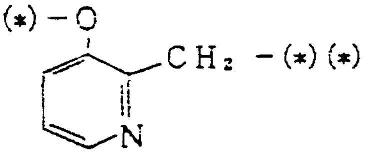
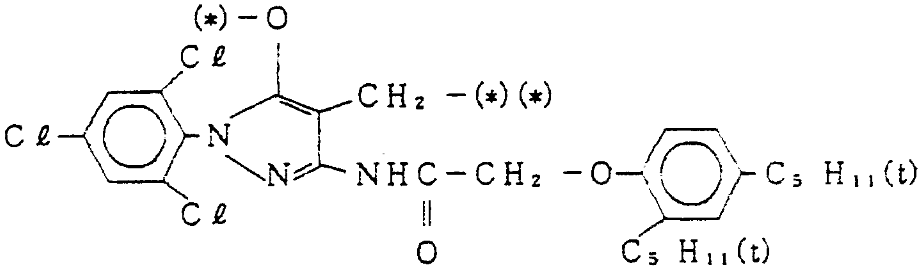


$$(*)-O-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{N}}-(CH_2)_2-\overset{CH_3}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}-(*)(*)$$

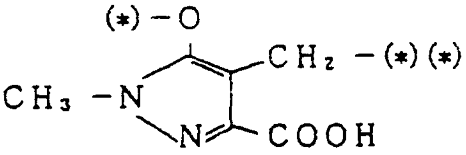
T－(27)



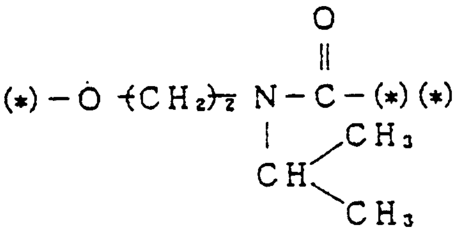
T－(28)



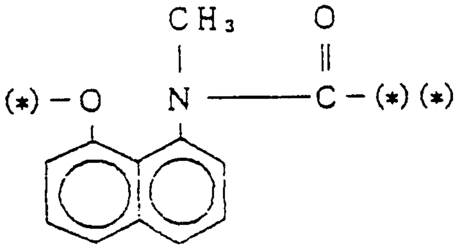
T－(29)



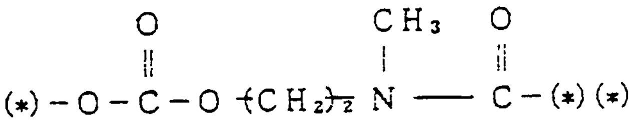
T-(30)



T-(31)



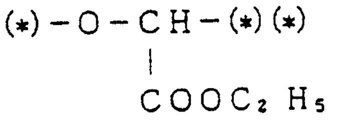
T-(32)



$(*)-O-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-\underset{}{\overset{CH_3}{\overset{|}{N}}}-\overset{O}{\overset{\|}{C}}-(*)(*)$

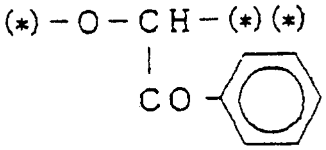
T-(33) $(*)-O-CH_2-(*)(*)$

T-(34)

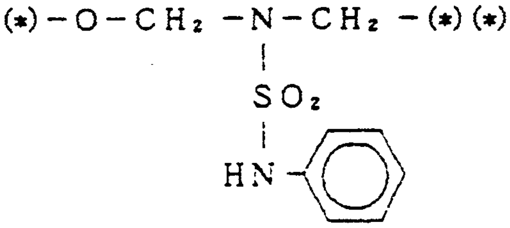


$(*)-O-\underset{\underset{COOC_2H_5}{|}}{CH}-(*)(*)$

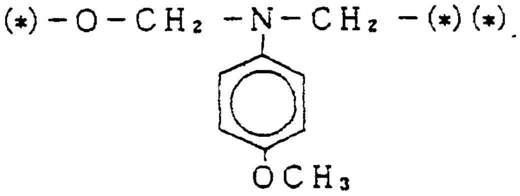
T-(35)



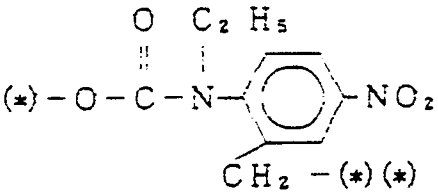
T-(36)



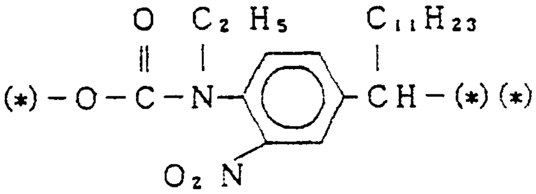
T-(37)



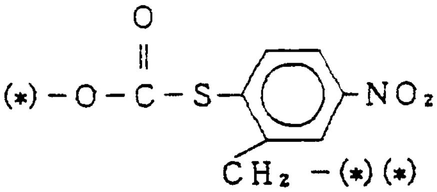
T-(38)



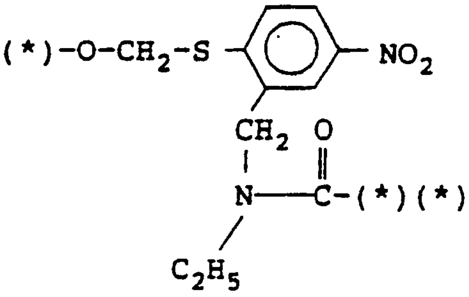
T-(39)



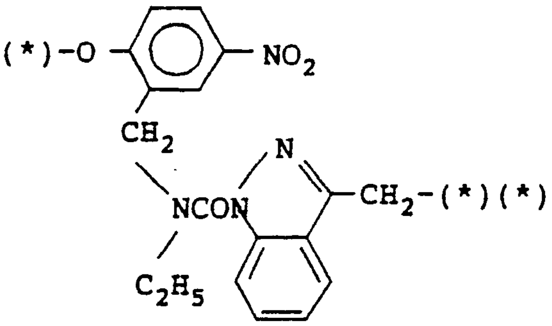
T-(40)



T-(41)



T-(41)



In the general formula (I), FA represents a moiety of a so-called nucleating agent which acts on silver halide grains to form fog nuclei capable of initiating development at the time of development, or a development accelerating agent. Suitable examples of FA include a group which acts reductively on silver halide grains to form fog nuclei at the time of development or a group which acts on silver halide grains to form silver sulfide nuclei which are fog nuclei capable of initiating development.

Preferred examples of FA include groups containing a group capable of adsorbing silver halide grains and being represented by the following general formula:

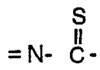
$AD-(L)_m-X$

wherein AD represents a group capable of adsorbing silver halide grains; L represents a divalent group; m represents 0 or 1; and X represents a reducing group or a group capable of acting on silver halide to form silver sulfide.

In the above general formula, when X is a group capable of acting on silver halide to form silver sulfide, X may also have the function of AD. In such a case, $AD-(L)_m-$ is not always necessary.

In a case where FA is a group containing $AD-(L)_m-X$, AD may be directly connected to Time, or L or X may be connected to Time so long as it is capable of being released from Time.

Examples of the group capable of adsorbing silver halide grains represented by AD include nitrogen-containing heterocyclic groups containing dissociable hydrogen atoms (e.g., pyrrole, imidazole, pyrazole, triazole, tetrazole, benzimidazole, benzopyrazole, benzotriazole, uracil, tetraazaindene, imidazotetrazole, pyrazolotriazole, or pentaazaindene), heterocyclic groups containing at least one nitrogen atom and other hetero atoms such as an oxygen atom, a sulfur atom and a selenium atom in its rings (e.g., oxazole, thiazole, thiazoline, thiazolidine, thiadiazole, benzothiazole, benzoxazole, or benzoselenazole), heterocyclic groups containing mercapto groups (e.g., 2-mercaptobenzothiazole, 2-mercaptopyrimidine, 2-mercaptobenzoxazole, or 1-phenyl-5-mercaptotetrazole), quaternary salts (e.g., a quaternary salts of tertiary amine, pyridine, quinoline, benzothiazole, benzimidazole, or benzoxazole), thiophenols, alkylthiols (e.g., cysteine), and compounds having a partial structure

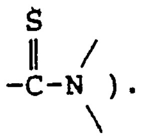


$=N-\overset{\overset{S}{\|}}{C}-$ (e.g., thiourea, dithiocarbamate, thioamide, rhodanine, thiazolidinethione, thiohydantoin, or thiobarbituric acid).

The divalent connecting group represented by L in FA includes an alkylene group, an alkenylene group, a phenylene group, a naphthylene group, -O-, -S-, -SO-, $-SO_2$ -N=N-, a carbonyl group, an amido group, a thioamido group, a sulfonamido group, a ureido group, a thioureido group or a heterocyclic group or a combination of two or more thereof.

When a group capable of being cleaved upon the action of a component (for example, hydroxide ion, hydroxylamine, or sulfite ion) contained in a developing solution is appropriately selected as one of the divalent connecting groups which constitutes L, it is possible to control or deactivate the nucleating function of FA.

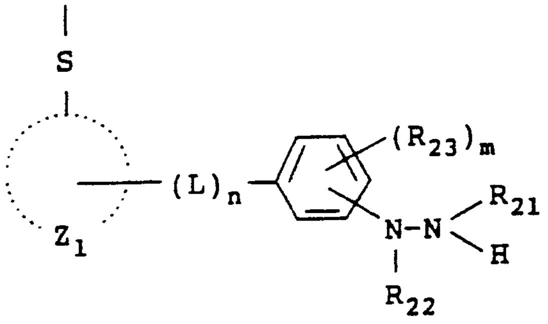
The group represented by X includes a group derived from reducing compounds (e.g., hydrazine, hydrazide, hydrazone, hydroquinone, catechol, p-aminophenol, p-phenylenediamine, 1-phenyl-3-pyrazolidinone, enamine, aldehyde, polyamine, acetylene, aminoborane, tetrazolium salts, quaternary salts such as ethylenebispyridinium, or carbazinic acid), compounds capable of forming silver sulfide at the time of development (e.g., thiourea, thioamide, dithiocarbamate, rhodanine, thiohydantoin, thiazolidinethione, and other compounds containing a partial structure



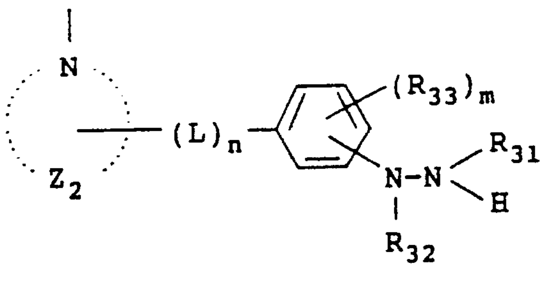
$$-\overset{S}{\overset{\|}{C}}-N\Big<\;).$$

Among the groups represented by X, some groups capable of forming silver sulfide at the time of development are themselves capable of adsorbing silver halide grains and therefore may serve as the above-described adsorptive group, i.e., AD.

Particularly preferred groups of FA are those represented by the following general formulae (II), (III) or (IV):



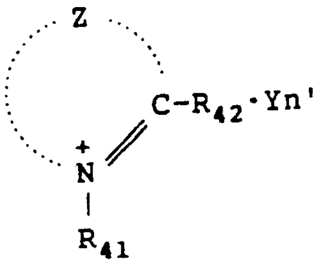
(II)



(III)

wherein $R_{21}$ and $R_{31}$ each represents an acyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group or a sulfamoyl group; $R_{22}$ and $R_{32}$ each represents a hydrogen atom, an acyl group, a sulfonyl group, an alkoxycarbonyl group or an aryloxycarbonyl group; $R_{23}$ and $R_{33}$ each represents a hydrogen atom, an alkoxy group, an alkyl group, an alkenyl group, an aryl group, an aryloxy group, an alkylthio group, an arylthio group, a carbonamido group or a sulfonamido group; m represents an integer of from 0 to 4, and when m is 2 or more, the substituents represented by $R_{23}$ or $R_{33}$ may be the same or different, and when m is 2 or more $R_{23}$ or $R_{33}$ may connect with each other to form a condensed ring; L represents a divalent connecting group; n represents 0 or 1; $Z_1$ represents a non-metallic atomic group necessary to form a monocyclic or condensed heterocyclic ring; and $Z_2$ represents a non-metallic atomic group necessary to form a monocyclic or condensed heterocyclic ring together with N.

In more detail, $R_{21}$ and $R_{31}$ each represents an acyl group (e.g., formyl, acetyl, propionyl, trifluoroacetyl, or pyruvoyl), a carbamoyl group (e.g., N,N-dimethylcarbamoyl), an alkylsulfonyl group (e.g., methanesulfonyl), an arylsulfonyl group (e.g., benzenesulfonyl), an alkoxycarbonyl group (e.g., methoxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl group) or a sulfamoyl group (e.g., methylsulfamoyl), $R_{22}$ and $R_{32}$ each represents a hydrogen atom, an acyl group (e.g., trifluoroacetyl), a sulfonyl group (e.g., methanesulfonyl, or benzenesulfonyl), an alkoxycarbonyl group (e.g., methoxycarbonyl) or an aryloxycarbonyl group (e.g, phenoxycarbonyl), and $R_{23}$ and $R_{33}$ each represents a halogen atom (e.g., fluorine or chlorine), an alkoxy group (e.g., methoxy or methoxy ethoxy), an alkyl group (e.g., methyl or hydroxymethyl), an alkenyl group (e.g., allyl), an aryl group (e.g., phenyl), an aryloxy group (e.g., phenoxy), an alkylthio group (e.g., methylthio), an arylthio group (e.g., phenylthio), a carbonamido group (e.g., acetamido) or a sulfonamido group (e.g., methanesulfonamido).



(IV)

wherein Z represents a non-metallic atomic group necessary for forming a substituted or unsubstituted 5-membered or 6-membered heterocyclic ring; $R_{41}$ represents a substituted or unsubstituted aliphatic group; $R_{42}$ represents a hydrogen atom, a substituted or unsubstituted aliphatic group or a substituted or unsubstituted aromatic group, or $R_{42}$ may be connected with Z to form a ring; provided that at least one of $R_{41}$, $R_{42}$ and Z contains an alkynyl group, an acyl group, a hydrazine group or a hydrazone group, or $R_{41}$ and $R_{42}$ are connected with each other to form a 6-membered dihydropyridinium ring; Y represents a counter ion required for charge balance; and $n'$ represents 0 or 1.

The general formula (IV) is now described in greater detail below. The heterocyclic ring formed by Z includes, for example, quinolinium, benzothiazolium, benzimidazolium, pyridinium, thiazolinium, thiazolium, naphthothiazolium, selenazolium, benzoselenazolium, imidazolium, tetrazolium, indolenium, pyrrolinium, acridinium, phenanthridium, isoquinolinium, oxazolium, naphthoxazolium and benzoxazolium nuclei. The group Z may be substituted, and the substituents therefore include, for example, an alkyl group, an alkenyl group, an aralkyl group, an aryl group, an alkynyl group, a hydroxyl group, an alkoxy group, an aryloxy group, an amino group, an alkylthio group, an arylthio group, an acyloxy group, an acylamino group, a sulfonyl group, a sulfonyloxy group, a sulfonylamino group, a carboxyl group, an acyl group, a carbamoyl group, a sulfamoyl group, a sulfo group, a cyano group, a ureido group, a urethane group, a carbonic acid ester group, a hydrazine group, a hydrazone group, an imino group, and a halogen atom. Z may be substituted with at least one substituent selected from the above-mentioned substituents, and when Z is substituted with two or more substituents, the plural substituents may be same or different. In addition, the substituents may be further substituted with any other substituents, for example, those described above.

Other substituents for Z include a heterocyclic quaternary ammonium group formed by Z via the connecting group L. In this case, the general formula (IV) forms a bis compound.

Preferred heterocyclic rings formed by Z include quinolinium, benzothiazolium, benzimidazolium, pyridinium, acridinium, phenanthridium and isoquinolinium nuclei. More preferably, the rings are quinolinium, benzothiazolium and benzimidazolium nuclei, and especially preferably they are quinolinium and benzothiazolium nuclei. Most preferably the ring is a quinolinium nucleus.

The aliphatic group represented by $R_{41}$ or $R_{42}$ includes an unsubstituted alkyl group having from 1 to 18 carbon atoms or a substituted alkyl group in which the alkyl moiety has from 1 to 18 carbon atoms. As substituents for the alkyl group, those described for Z above are included.

The aromatic group represented by $R_{42}$ includes those having from 6 to 20 carbon atoms, which may be, for example, a phenyl group or a naphthyl group. The aromatic group may optionally be substituted, and as substituents for the aromatic group, those described for Z above are included.

At least one of $R_{41}$, $R_{42}$ and Z contains an alkynyl group, an acyl group, a hydrazine group or a hydrazone group, or $R_{41}$ and $R_{42}$ form a 6-membered ring to complete a dihydropyridinium nucleus. These may also be substituted, and as substituents for the groups, those described for Z above are included.

The hydrazine group is particularly preferably substituted with an acyl group or a sulfonyl group.

The hydrazone group is particularly preferably substituted with an aliphatic group or an aromatic group.

The acyl group is preferably a formyl group or an aliphatic or aromatic ketone residue.

If an alkynyl group is contained in at least one of $R_{41}$, $R_{42}$ and Z, the alkynyl group preferably has from 2 to 18 carbon atoms, and includes, for example, an ethynyl group, propargyl group, a 2-butynyl group, a 1-methylpropargyl group, a 1,1-dimethylpropargyl group, a 3-butynyl group, and a 4-pentynyl group.

The alkynyl group may be substituted, and as the substituents for this group, those described for Z above are included. For example, there may be described a 3- phenylpropargyl group, a 3-methoxycarbonylpropargyl group and a 4-methoxy-2-butynyl group.

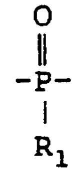
At least one substituent on the group or ring represented by $R_{41}$, $R_{42}$ or Z is preferably an alkynyl group or an acyl group, and it is also preferred that $R_{41}$ and $R_{42}$ are connected with each other to form a dihydropyridinium nuclei. Most preferably, at least one alkynyl group is substituted on the group or ring represented by $R_{41}$, $R_{42}$ or Z.

Particularly preferably, $R_{41}$ is a propargyl group.

The counter ion Y for charge balance may be any anion to neutralize the positive charge caused by the quaternary ammonium salt in the heterocyclic ring, and it may be a bromide ion, chloride ion, iodide ion, p-toluenesulfonate ion, ethylsulfonate ion, perchlorate ion, trifluoromethanesulfonate ion or thiocyanate ion. In this case, $n'$ is 1. When the heterocyclic quaternary ammonium salt in the general formula contains an anion substituent such as a sulfoalkyl substituent, the salt may be in the form of a betain. In this case, no pair ion is necessary and $n'$ is 0. When the heterocyclic quaternary ammonium salt has two anion substituents such as two sulfoalkyl groups, Y is a cationic pair ion, which may be, for example, an alkali metal ion (e.g., a sodium ion, or a potassium ion), or an ammonium ion (e.g., a triethylammonium ion).

In the general formula (I), V represents a carbonyl group, $-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-$,

a sulfonyl group, a sulfoxy group,



$$\overset{\overset{O}{\|}}{-P-}\atop{\underset{R_1}{|}}$$

(wherein $R_1$ represents an alkoxy group or an aryloxy group), an iminomethylene group or a thiocarbonyl group, and preferably represents a carbonyl group.

The aliphatic group represented by R in the general formula (I) includes a straight chain, branched chain or cyclic alkyl group, alkenyl group or alkynyl group, each containing preferably from 1 to 30 carbon atoms, more preferably from 1 to 20 carbon atoms. The branched chain alkyl group may contain one or more hetero atoms therein to form a saturated hetero ring.

Specific examples of the aliphatic group include a methyl group, a tert-butyl group, an n-octyl group, a tert-octyl group, a cyclohexyl group, a hexenyl group, a pyrrolidyl group, a tetrahydrofuryl group and an n-dodecyl group.

The aromatic group represented by R includes a monocyclic or dicyclic aryl group, for example, a phenyl group or a naphthyl group.

The heterocyclic group represented by R includes a 3-membered to 10-membered saturated or unsaturated heterocyclic group containing at least one of a nitrogen atom, an oxygen atom and a sulfur atom, and which may be a monocyclic ring or may form a condensed ring together with an aromatic ring or a heterocyclic ring. A 5-membered or 6-membered aromatic heterocyclic group is preferred. Specific examples of the heterocyclic group include a pyridyl group, an imidazolyl group, a quinolinyl group, a benzimidazolyl group, a pyrimidyl group, a pyrazolyl group, an isoquinolinyl group, a benzothiazolyl group and a thiazolyl group.

The group represented by R may be substituted with one or more substituents. Suitable examples of substituents include an alkyl group, an aralkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an aryl group, a substituted amino group, an acylamino group, a sulfonylamino group, a ureido group, a urethane group, an aryloxy group, a sulfamoyl group, a carbamoyl group, an alkylthio group, an arylthio group, a sulfonyl group, a sulfinyl group, a hydroxyl group, a cyano group, a sulfo group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyl group, an acyloxy group, a carboxy group and a halogen atom. These groups may be further substituted.

In the compound represented by the general formula (I), a ballast group which is conventionally employed in immobile photographic additives such as couplers, or a group which is capable of accelerating the adsorption of the compound represented by the general formula (I) onto silver halide may be incorporated into R or $(\text{Time})_t$FA of the general formula (I).

The ballast group is an organic group which provides a molecular weight sufficient to substantially prevent the compound represented by the general formula (I) from diffusing into other layers or processing solutions and includes, for example, alkyl, aryl, heterocyclic, ether, thioether, amido, ureido, methane, and sulfonamido groups or a combination of two or more thereof. The ballast group is preferably contains a substituted benzene ring, and more preferably contains a benzene ring substituted with a branched alkyl group.

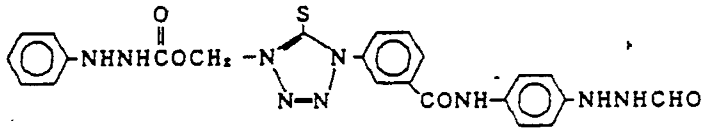
The adsorption accelerating group for silver halides includes specifically a cyclic thioamido group, for example, 4-thiazoline-2-thione, 4-imidazoline-2-thione, 2-thiohydantoin, rhodanine, thiocarbituric acid, tetrazoline-5-thione, 1,2,4-triazoline-3-thione, oxazoline-2-thione, benzimidazoline-2-thione, benzoxazoline-2-thione, benzothiazoline-2-thione, thiotriazine and 1,3-imidazoline-2-thione, a chain thioamido group, an aliphatic mercapto group, an aromatic mercapto group, a heterocyclic mercapto group (when the atom adjacent to the carbon atom bonded to the -SH group is a nitrogen atom, the mercapto group is the same as a cyclic thioamide group which is in a tautomeric relation therewith and specific examples thereof are the same as illustrated above), a group having a disulfido bond, a 5-membered or 6-membered nitrogen-containing heterocyclic ring comprises a combination of nitrogen with at least one atom selected from oxygen, sulfur, and carbon, for example, benzotriazole, triazole, tetrazole, indazole, benzimidazole, imidazole, benzothiazole, thiazole, thiazoline, benzoxazole, oxazole, oxazoline, thiadiazole, oxadiazole, triazine and azaindene, and a heterocyclic quaternary salt, for example, benzimidazolinium.

The adsorption accelerating groups may be further substituted with one or more appropriate substituents.

The substituents can be selected from those described for R above.

Specific examples of compounds represented by the general formula (I) according to the present invention are set forth below, but the present invention is not to be construed as being limited to these compounds.

(1)



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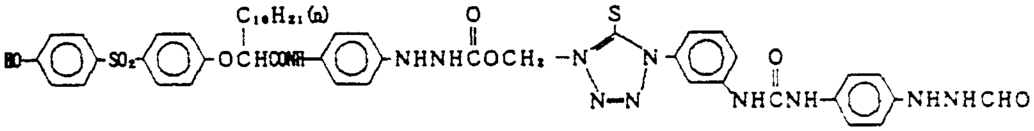

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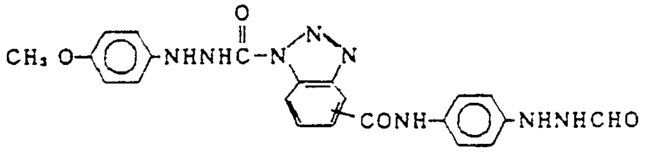

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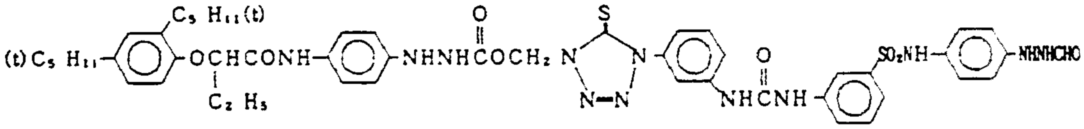

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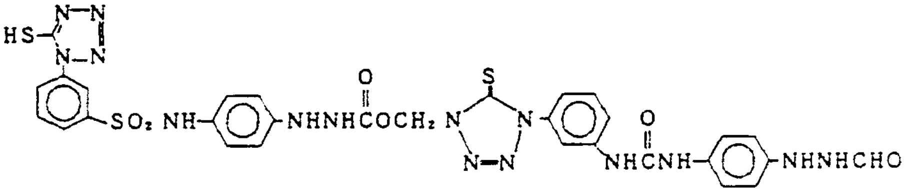

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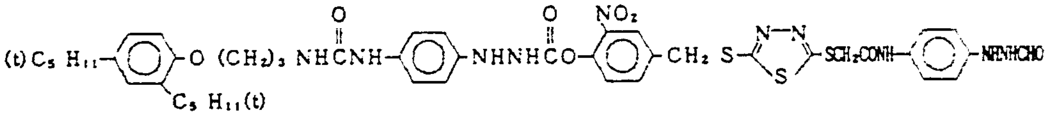

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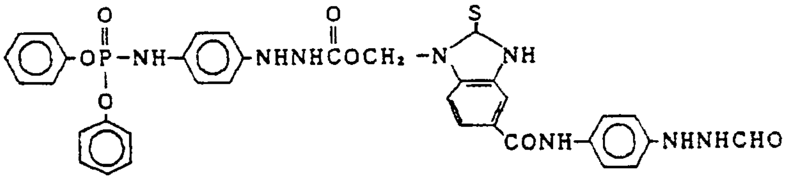

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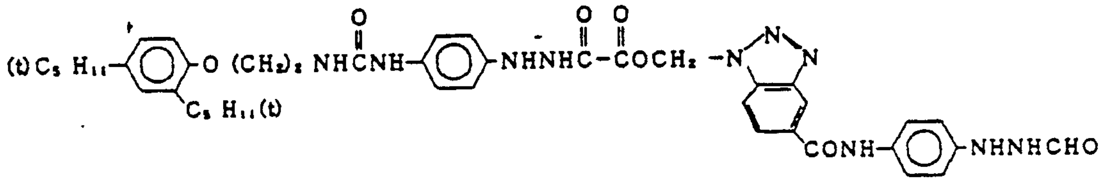

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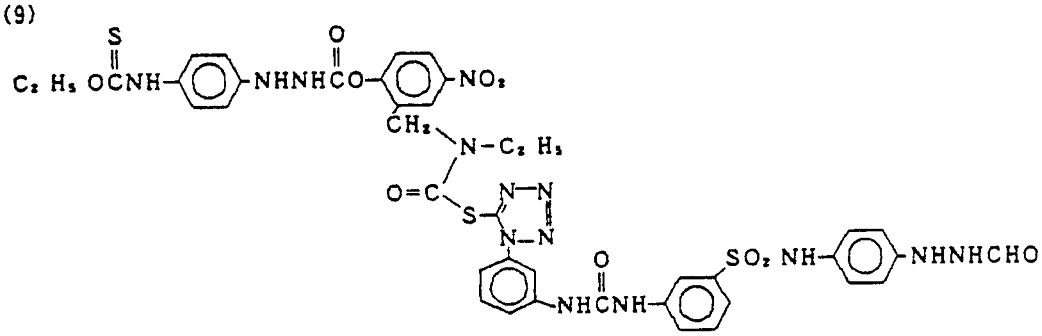

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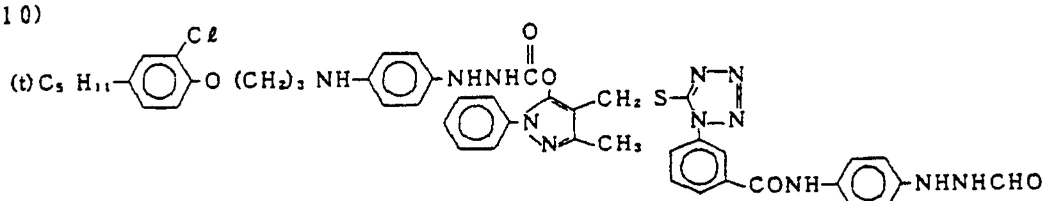

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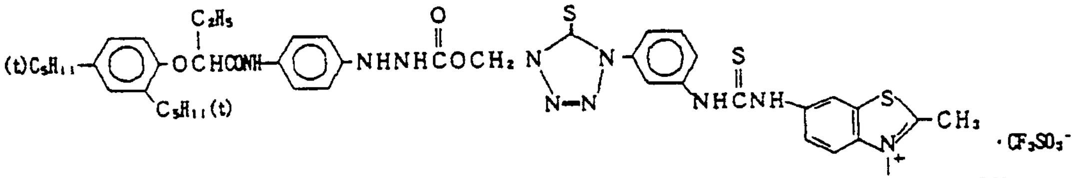

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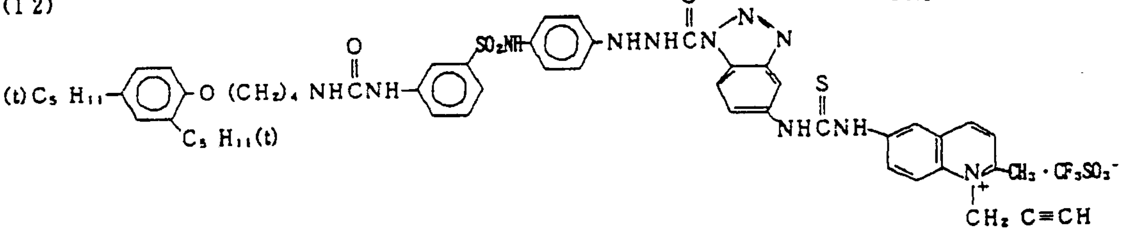

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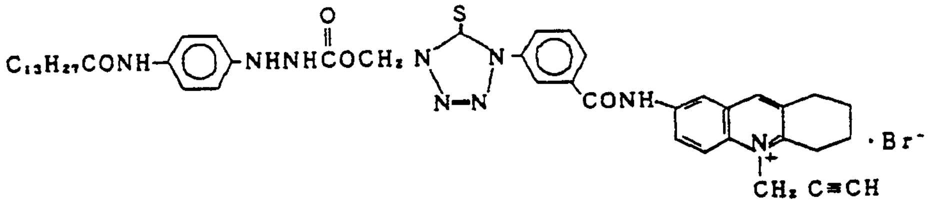

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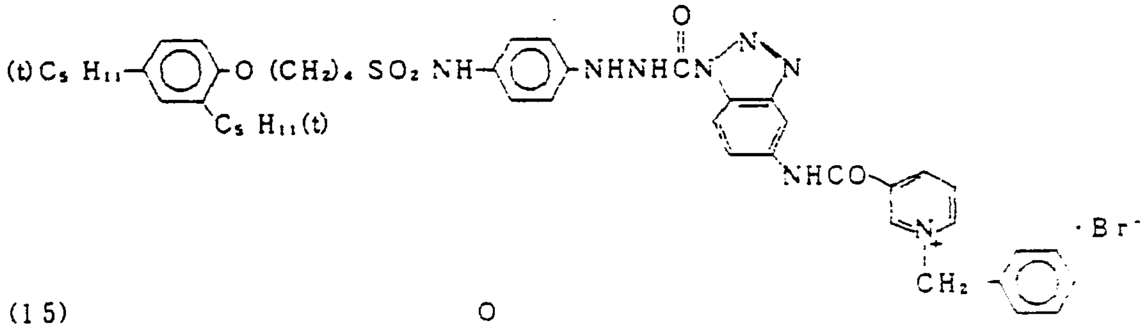

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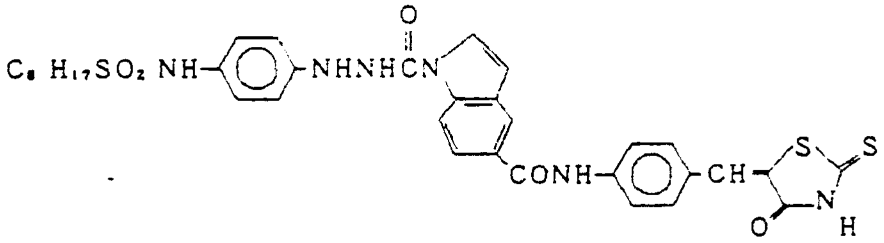


The compounds represented by general formula (I) described above and employed in the present invention can be synthesized with reference to the methods as described, for example, in JP-A-61-213847, JP-A-62-260153 and U.S. Patent 4,684,604 and the patents cited therein.

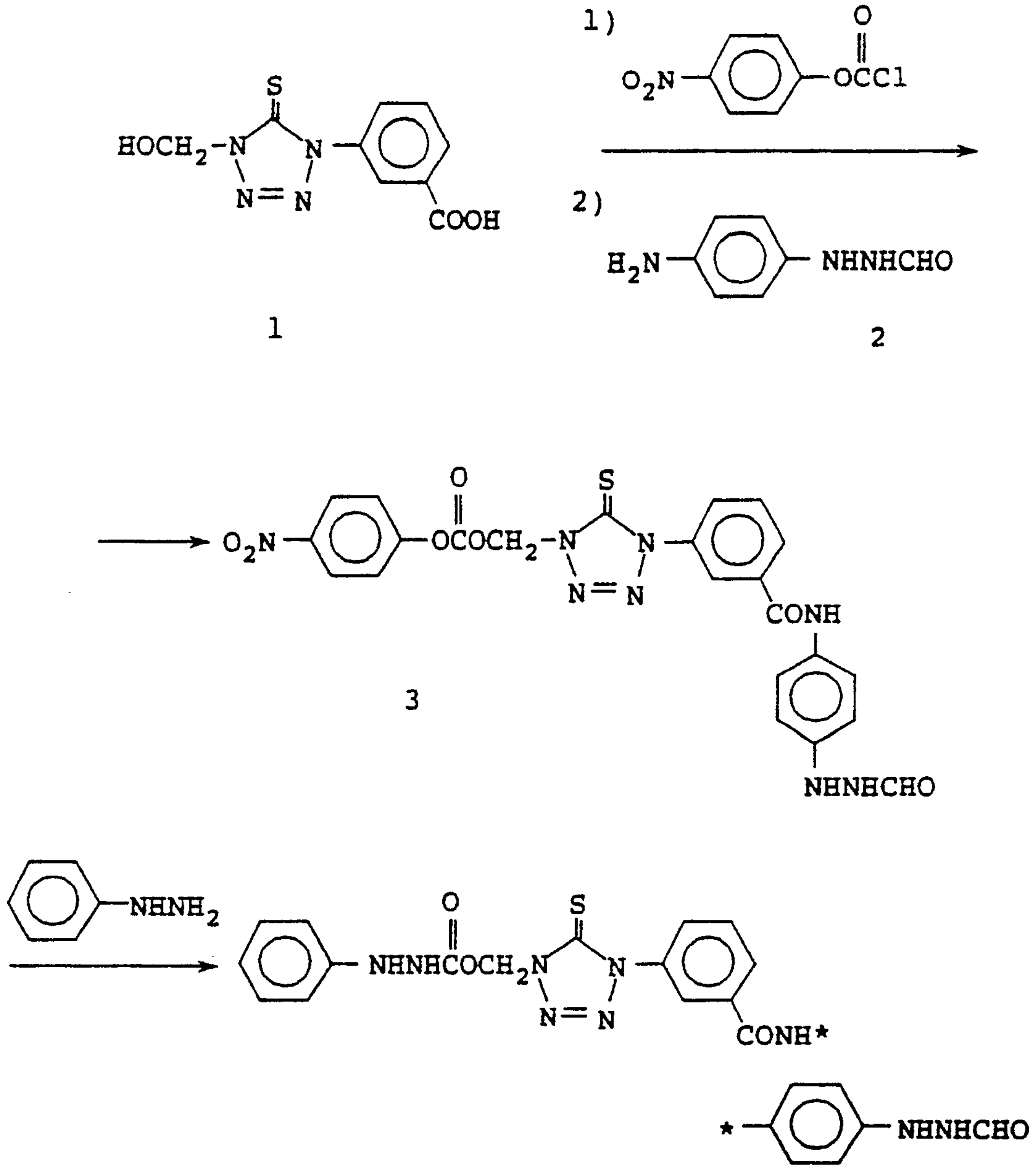
The FA compounds can be synthesized by the methods as described, for example, in the patents cited in Research Disclosure No. 22534 (January, 1983), pages 50 to 54, U.S. Patent 4,471,044, JP-A-57-150845, JP-A-59-157638 and JP-A-59-170840 or by methods which are similar to these methods.

Specific examples of the synthesis of the compounds will be described below.

## SYNTHESIS EXAMPLE 1

### Synthesis of Compound (1)

Compound (1) can be synthesized along the route shown below.



Compound (1)

(1) First Step: Synthesis of Compound 3

To 120 ml of acetonitrile were added 12.6 g of 4-(3-carboxyphenyl)-1-hydroxymethyl-5-thioxotetrazoline and 7.9 g of pyridine and then 20.2 g of 4-nitrophenyl chloroformate was added dropwise thereto with stirring under cooling with ice. After being reacted for 2 hours under cooling with ice, 40 ml of an N,N-dimethylacetamide solution containing 7.6 g of 2-(4-aminophenyl)-1-formylhydrazine was added dropwise thereto. After being reacted for 1 hour under cooling with ice and for 3 hours at room temperature, 100 ml of water was added to the reaction mixture, and the oily product thus separated was extracted with ethyl acetate. The organic layer was washed with water, concentrated by an evaporator, and the resulting oily product was separated and purified by silver gel column chromatography (eluent: chloroform/methanol = 20/l) to obtain 20.1 g (yield 73%) of Compound 3 as an oily product.

(2) Second Step: Synthesis of Compound (1)

19.3 g of Compound 3 and 3.8 g of phenylhydrazine were dissolved in 100 ml of methanol and reacted at room temperature for 5 hours. The reaction solution was concentrated by an evaporator and separated and purified by silica gel column chromatography (eluent: chloroform/methanol = 10/1) to obtain 11.8 g (yield: 65%) of the desired compound.

The compound represented by the general formula (I) according to the present invention can be incorporated into a silver halide emulsion layer or other hydrophilic colloid layer to achieve the desired purpose.

The amount of the compound to be added may be varied depending on the kind of photosensitive material, but is from $10^{-9}$ to $10^{\prime}$ mol, preferably from $10^{-7}$ to $10^{-2}$ mol, per mol of silver halide.

For introduction of the compound into the silver halide emulsion layer of the photographic material of the present invention, any known method, for example, the method as described in U.S. Patent 2,322,027, can be employed. For instance, the compound is first dissolved in a solvent, such as an alkyl phthalate (e.g., dibutyl phthalate, dioctyl phthalate), a phosphate (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, dioctylbutyl phosphate), a citrate (e.g., tributyl acetylcitrate), a benzoate (e.g., octyl benzoate), an alkylamide (e.g., diethyllaurylamide), a fatty acid ester (e.g., dibutoxyethyl succinate, diethyl azelate), a trimesate (e.g., tributyl trimesate) or the like, or in an organic solvent having a boiling point of from about 30 °C to about 150 °C, such as a lower alkyl acetate (e.g., ethyl acetate, butyl acetate), ethyl propionate, secondary butyl alcohol, methyl isobutyl ketone, β-ethoxyethyl acetate, methylcellosolve acetate or the like, and then the resulting solution is dispersed in a hydrophilic colloid. The above-described solvents may be used in the form of mixtures thereof.

In addition, the dispersion method using a polymer which is described in JP-B-51-39853 (the term "JP-B" as used herein means an "examined Japanese patent publication") and JP-A-51-59943 may also be employed.

In the photographic emulsion of the photographic material according to the present invention, any silver halide including silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide and silver chloride may be used.

The silver halide grains in the photographic emulsion may be regular grains having a regular crystalline form such as a cubic, octahedral or tetradecahedral crystalline form, or irregular grains having an irregular crystalline form such as a spherical crystalline form or having a crystal defect such as a twin plane, or may also be grains having a composite form of these crystalline forms. In addition, a mixture of grains with various crystalline forms may be used.

Regarding the grain size of the silver halide grains, the grains may be fine grains having a grain size of about 0.1 µm or less or may be large grains having a grain size, as a diameter of the projected area, of up to about 10 µm. The emulsion may be either a monodispersed emulsion having a narrow grain size distribution or a polydispersed emulsion having a broad grain size distribution.

The silver halide photographic emulsion for use in the present invention can be prepared by any conventional method, for example, in accordance with the methods as described, for example, in Research Disclosure, Vol. 176, No. 17643 (December, 1978), pages 22 to 23, "I. Emulsion Preparation and Type" and ibid., Vol. 187, No. 18716 (November, 1979), page 648.

The photographic emulsions for use in the present invention can also be prepared in accordance with the methods as described, for example, in P. Glafkides, Chemie et Physique Photographique (published by Paul Montel, 1967); G.F. Duffin, Photographic Emulsion Chemistry (published by Focal Press, 1966); V.L. Zelikman et al., Making and Coating Photographic Emulsion (published by Focal Press, 1954). More specifically, the silver halide emulsion may be prepared by an acid method, a neutral method, or an ammonia method. Also, as a method of reacting a soluble silver salt and soluble halide(s), a single jet method, a double jet method, or a combination thereof may be used. A reverse mixing method capable of forming silver halide grains in the presence of excess silver ions can also be employed. As one double jet method, a controlled double jet method of keeping a constant pAg in a liquid phase for forming silver halide grains can also be employed. According to the method, a silver halide emulsion containing silver halide grains having a regular crystal form and almost uniform grain sizes can be obtained.

The silver halide emulsion for use in the present invention can be physically ripened in the presence of a known silver halide solvent (for example, ammonia or potassium thiocyanate, as well as the thioethers and thione compounds as described, for example, in U.S. Patent 3,271,157, JP-A-51-12360, JP-A-53-82408, JP-A-53-144319, JP-A-54-100717 and JP-A-54-155828. According. to this method, a silver halide emulsion containing silver halide grains having a regular crystal form and almost uniform grain sizes can also be obtained.

The above-described silver halide emulsion containing regular crystal grains may be obtained by properly controlling the pAg value and the pH value in the formation of the grains. The details are described, for example, in Photographic Science and Engineering, Vol. 6, pages 159 to 165 (1962), Journal of Photographic Science, Vol. 12, pages 242 to 251 (1964), U.S. Patent 3,655,394 and British Patent 1,413,748.

As the monodispersed emulsion for use in the present invention, an emulsion in which the silver halide grains have a mean grain size (diameter) larger than about 0.05 µm and at least 95% by weight of the grains have a grain size falling within the range of the mean grain size ±40% is typical. Further, an emulsion in which the silver halide grains have a mean grain size of from 0.15 to 2 µm and at least 95% by weight or by number of the grains have a grain size falling within the range of the mean grain size ±20% can also be used. The method of preparing such emulsions is described, for example, in U.S. Patents 3,574,628 and 3,655,394 and British Patent 1,413,748. In addition, the monodispersed emulsions as described, for example, in JP-A-48-8600, JP-A-51-39027, JP-A-51-83097, JP-A-53-137133, JP-A-54-48521, JP-A-54-99419, JP-A-58-37635, JP-A-58-49938 are also preferably used.

Also, tabular grains having an aspect ratio of 5 or more may be used in the present invention. Tabular grains can easily be prepared by the methods as described, for example, in Gutoff, Photographic Science and Engineering, Vol. 14, pages 248 to 257 (1970); U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520 and British Patent 2,112,157. Tabular grains are preferably used since the covering power of the emulsion is increased and the spectral sensitizing efficiency by sensitizing dyes is elevated, and the details thereof are described in the aforesaid U.S. Patent 4,434,226.

In the formation of the silver halide grains for use in the present invention, a sensitizing dye or an additive can be added to the grains so as to properly control the crystal form of the grains formed.

The crystal structure of the grains may be uniform, or the inner part and the outer part of the grain may have different halogen compositions. The grain may also have a stratified structure. These emulsion grains are illustrated, for example, in British Patent 1,027,146, U.S. Patents 3,505,068 and 4,444,877 and JP-A-60-143331. Silver halides of different compositions may be combined by epitaxial junction, or the grains may also be combined with any compounds other than silver halides, such as silver thiocyanate or lead oxide, by a junction structure. The emulsion grains of this type are illustrated, for example, in U.S. Patents 4,094,684, 4,142,900 and 4,459,353, British Patent 2,038,792, U.S. Patents 4,349,622, 4,395,478, 4,433,501, 4,463,087, 3,656,962 and 3,852,067 and JP-A-59-162540.

Further, internal latent image type grains formed by surface chemical ripening of silver halide grains to give a light-sensitive nucleus (e.g., $Ag_2S$, $Ag_n$ (wherein n is an integer of 1 or more), Au) in the grain crystal and then growing a silver halide phase around the grains can also be used in the present invention.

The silver halide grains may also be formed or physically ripened in the presence of a cadmium salt, a zinc salt, a lead salt, a thallium salt, an iridium salt or a complex salt thereof, a rhodium salt or a complex salt thereof, an iron salt or a complex salt thereof.

The various kinds of emulsions may be surface latent image type emulsions which form a latent image mainly on the surface of the grain or internal latent image type emulsions which form a latent image mainly in the inside of the grain.

The emulsion may also be a direct reversal emulsion. The direct reversal emulsion may be any of a solarization type, an internal latent image type, a light fogging type or a nucleating agent-containing type, or a combination thereof.

Among them, it is preferred that a non-previously fogged internal latent image type emulsion be used, and this is fogged with a light before or during photographic processing, or a nucleating agent is used to obtain a direct positive photographic light-sensitive material.

The non-previously fogged internal latent image type silver halide emulsion for use in the present invention is such that the surface of the silver halide grain is not previously fogged and a latent image is formed mainly in the inside of the grain. More specifically, the term "internal latent image" emulsion as used herein is an emulsion defined as follows. A silver halide emulsion in a certain amount is coated on a transparent support and this is exposed to a light for a fixed period of time of from 0.01 to 10 seconds. Then this is developed with the following Developer (A) (internal developer) for 6 minutes at 20 °C and the maximum density obtained is measured by a conventional photographic densitometric method. A second portion of the same silver halide emulsion is coated in the same amount on another transparent support and then exposed in the same manner. This is then developed with the following Developer (B) (surface developer) for 5 minutes at 18 °C and the maximum density obtained is also measured in the same manner. Preferably, the former maximum density is at least five times larger than the latter maximum density, and more preferably, the former is at least ten times larger than the latter.

| Surface Developer B : | |
|---|---|
| Metol | 2.5 g |
| ℓ-Ascorbic Acid | 10 g |
| $NaBO_2 \cdot 4H_2O$ | 35 g |
| KBr | 1 g |
| Water to make | 1 liter |

| Internal Developer A : | |
|---|---|
| Metol | 2 g |
| Sodium Sulfite (anhydrous) | 90 g |
| Hydroquinone | 8 g |
| Sodium Carbonate (monohydrate) | 52.5 g |
| KBr | 5 g |
| KI | 0.5 g |
| Water to make | 1 liter |

Illustrative examples of the internal latent image type emulsion include conversion type silver halide emulsions as described, for example, in British Patent 1,011,062 and U.S. Patents 2.592.250 and 2,456.943, as well as core/shell type silver halide emulsions. Examples of core/shell type silver halide emulsions are described, for example, in JP-A-47-32813, JP-A-47-32814, JP-A-52-134721, JP-A-52-156614, JP-A-53-60222, JP-A-53-66218, JP-A-53-66727, JP-A-55-127549, JP-A-57-136641, JP-A-58-70221, JP-A-59-208540, JP-A-59-216136, JP-A-60-107641, JP-A-60-247237, JP-A-61-2148, JP-A-61-3137, JP-B-56-18939, JP-B-58-1412, JP-B-58-1415, JP-B-58-6935, JP-B-58-108528, JP-A-62-194248, U.S. Patents 3,206,313, 3,317,322, 3,761,266, 3,761,276, 3,850,637, 3,923,513, 4,035,185, 4,395,478 and 4,504,570, European Patent 17,148, and Research Disclosure, No. 16345 (November, 1977).

In order to remove soluble silver salts from the emulsion before and after physical ripening, the emulsion may be subjected to noodle washing, flocculation precipitation or ultrafiltration.

The emulsion for use in the present invention is, in general, physically ripened, chemically ripened or spectrally sensitized. The additives usable in the ripening steps are described in the above Research Disclosure, No. 17643 (December, 1978) and ibid., No. 18716 (November, 1979), and the relevant parts are listed in the following Table.

Known photographic additives which can be used in the present invention are also described in these publications and the relevant parts are also listed in the following Table.

| Kinds of Additives | RD 17643 | RD 18716 |
|---|---|---|
| 1 Chemical Sensitizers | p. 23 | p. 648 right column |
| 2 Sensitivity-Increasing Agents | | " |
| 3 Spectral Sensitizers and Super Sensitizers | pp. 23-24 | From p. 648 right column to p. 649 right column |
| 4 Whitening Agents | p. 24 | |
| 5 Anti foggants and Stabilizers | pp. 24-25 | p. 649 right column |
| 6 Light Absorbers, Filter Dyes and UV Ray Absorbers | pp. 25-26 | From p. 649 right column to p. 650, left column |
| 7 Antistaining Agents | p. 25, right column | p. 650, from left to right column |
| 8 Dye Image Stabilizers | p. 25 | |
| 9 Hardening Agents | p. 26 | p. 651, left column |
| 10 Binders | p. 26 | " |
| 11 Plasticizers and Lubricants | p. 27 | p. 650, right column |
| 12 Coating Aids and Surfactants | pp. 26-27 | " |
| 13 Antistatic Agents | p. 27 | " |

Various color couplers can be used in the present invention. Color couplers are compounds which can react with the oxidation product of an aromatic primary amine color developing agent by a coupling reaction to form or release a substantially non-diffusible dye, and the color couplers themselves are preferably substantially non-diffusible compounds. Specific examples of useful color couplers include naphthol or phenol compounds, pyrazolone or pyrazoloazole compounds and open-chain or heterocyclic ketomethylene compounds. Examples of cyan, magenta and yellow couplers for use in the present invention are described in Research Disclosure No. 17643 (December, 1978), page 25, VII-D, ibid., No. 18717 (November, 1979) and Japanese Patent Application No. 61-32462, as well as in the publications cited therein.

Preferably, the yellow couplers for use in the present invention include oxygen atom releasing type or nitrogen atom releasing type 2-equivalent yellow couplers as typical examples. In particular, α-pivaloylacetanilide couplers are excellent in fastness, especially light fastness of the dyes formed, while α-benzoylacetanilide couplers are excellent in color density.

The 5-pyrazolone magenta couplers which may be preferably used in the present invention include 5-pyrazolone couplers in which the 3-position is substituted with an arylamino group or an acylamino group (especially sulfur atom releasing type 2-equivalent couplers).

Further preferred are pyrazoloazole couplers, and the pyrazolo[5,1-c][1,2,4]triazoles as described in U.S. Patent 3,725,067 are especially preferred among them. In addition, the imidazo[1,2-b]pyrazoles as described in U.S. Patent 4,500,630 are more preferred from the view point of the small yellow side-absorption and the high light-fastness of the dyes formed, and the pyrazolo[1,5-b][1,2,4]triazoles as described in U.S. Patent 4,540,654 are particularly preferred.

The cyan couplers which can preferably be used in the present invention include the naphthol and phenol couplers as described, for example, in U.S. Patents 2,474,293 and 4,052,212, and the phenol cyan couplers having an alkyl group of two or more carbon atoms at the meta-position of the phenol nucleus as described in U.S. Patent 3,772,002. In addition, 2,5-diacylamino-substituted phenol couplers are also preferred from the viewpoint of the fastness of the color images formed.

Colored couplers for correcting any unnecessary absorption of the dyes formed in a short wavelength range, couplers forming dyes with an appropriate diffusibility, colorless couplers, DIR couplers which release a development inhibitor upon a coupling reaction and polymerized couplers can also be used in the present invention.

The standard amount of the color coupler for use in the present invention is from 0.001 to 1 mol per mol of the light-sensitive silver halide. Preferably, the amount is from 0.01 to 0.5 mol for a yellow coupler; it is from 0.03 mol to 0.3 mol for a magenta coupler; and it is from 0.002 mol to 0.3 mol for a cyan coupler.

A color forming enhancing agent can be used in the present invention so as to improve the color forming property of the couplers used. Specific examples of such compounds are those described in JP-A-62-215272.

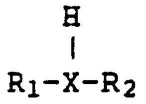
For incorporation of the couplers into emulsion layers in accordance with the present invention, the coupler is first dissolved in a high boiling point organic solvent and/or a low boiling point organic solvent and then emulsified and dispersed in gelatin or other aqueous hydrophilic colloid solution by high speed stirring with a homogenizer or the like, or by mechanical milling with a colloid mill or the like, or by means of an ultrasound technique, and the resulting dispersion is added to the intended emulsion layer. In this process, the high boiling point organic solvent is not always necessary but the compounds as described in JP-A-62-215272 are preferably used.

The couplers according to the present invention can be dispersed in a hydrophilic colloid by the method as described in JP-A-62-215272.

The photographic material of the present invention preferably contains one or more compounds capable of reacting with formaldehyde gas to fix the same, which are described in detail hereunder.

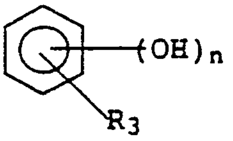
The compounds capable of reacting with formaldehyde gas to fix the same (hereinafter referred to as "formalin scavenger") for use in the present invention are those represented by the following general formulae (SI) or (SII), which have a relative molecular weight of 300 or less per one unit of the active hydrogen in the molecule. The relative molecular weight is defined as follows:

$$\text{(Relative Molecular Weight)} = \frac{\text{(Molecular Weight)}}{\text{(Active Hydrogen in Molecule)}}$$



$$R_1-\overset{\overset{\displaystyle H}{|}}{X}-R_2$$

(SI)



(SII)

wherein $R_1$ and $R_2$, which may be the same or different, each represents a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an acyl group, an alkoxycarbonyl group, a carbamoyl group or an amino group, or $R_1$ and $R_2$ may combine with each other to form a ring, provided that at least one of $R_1$ and $R_2$ is an acyl group, an alkoxycarbonyl group, a carbamoyl group or an amino group; X represents $-\overset{|}{C}H-$ or $-\overset{|}{N}-$; $R_3$ represents a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group, and $R_3$ may be connected to the phenyl ring to form a bicyclic compound; and n represents an integer of 2 or more.

The formalin scavenger described above can be incorporated into at least one of the silver halide emulsion layer, a subbing layer, a protective layer, an interlayer, a filter layer, an anti-halation layer and other auxiliary layers which constitute the silver halide color photographic material of the present invention. The formalin scavenger may be incorporated into a magenta polymer coupler-containing silver halide emulsion layer the photographic properties of which would be deteriorated by contact with formaldehyde gas, or into a layer which is nearer to the support than the emulsion layer or a layer which is farther from the support than the emulsion layer, and in any case, the object of the present invention can be attained.

When the photographic material of the present invention is a color photographic material, it may contain various color fading prevention agents. Specific examples of organic color fading prevention agents usable in the present invention include hindered phenols such as hydroquinones, 6-hydroxychromans, 5-hydroxycoumarans, spirochromans, p-alkoxyphenols and bisphenols, gallic acid derivatives, methylenedioxybenzenes, aminophenols, and hindered amines, as well as ether or ester derivatives formed by silylation or alkylation of the phenolic hydroxyl group in these compounds. In addition, metal complexes such as (bis-salicylaldoximato)nickel complexes and (bis-N,N-dialkyldithiocarbamato)nickel complexes may also be used.

For preventing the deterioration of yellow color images by heat, moisture and light, the compounds having both partial structures of hindered amines and hindered phenol moieties in one molecule as described in U.S. Patent 4,268,593 may advantageously be used. In order to prevent the deterioration of magenta color images, especially by light, the spiroindanes as described in JP-A-56-159644, and the hydroquinonediether or monoether-substituted chromans as described in JP-A-55-9835 may give a good result. These compounds may be added to a light-sensitive layer by co-emulsifying them with the corresponding color coupler in an amount of generally from 5 to 100% by weight of the coupler, whereby the intended object can be attained. In order to prevent the deterioration of cyan color images by heat and especially by light, incorporation of an ultraviolet light absorbing agent into both layers adjacent to the cyan color forming layer is effective. In addition, an ultraviolet light absorbing agent may also be added to a hydrophilic colloid layer such as a protective layer.

The photographic material of the present invention may contain a dye for anti-irradiation or anti-halation and may also contain an antistatic agent or a slide property-improving agent.

Specific examples of the additives are described in Research Disclosure, No. 17643 (December, 1979) and ibid., No. 18716 (November, 1979).

The present invention may also be applied to a multilayer and multicolor photographic material having at least two layers each having a different spectral sensitivity on a support. A multilayer natural color photographic material generally has at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer and at least one blue-sensitive emulsion layer on a support. The order of these layers as arranged on the support is not critical. Each of the emulsion layers may contain two or more emulsion layer parts each having a different speed; or a light insensitive layer may be between two or more emulsion layers having the same spectral sensitivity. It is typical that the red-sensitive emulsion layer contains a cyan forming coupler, the green-sensitive emulsion layer contains a magenta forming coupler and the blue-sensitive emulsion layer contains a yellow-forming coupler, but any other combinations may also be employed, as the case may be.

It is preferred that the photographic material of the present invention have auxiliary layers such as a protective layer, an interlayer, a filter layer, an anti-halation layer and a white reflective layer, if desired, in addition to the silver halide emulsion layers.

In the formation of the photographic material of the present invention, the photographic emulsion layers and other layers are coated on a support which is generally used in conventional photographic materials, for example, a flexible support such as a plastic film, paper or cloth, or a rigid support such as glass, porcelain or metal. As examples useful as a flexible support, there are films made of semi-synthetic or synthetic polymers such as cellulose nitrate, cellulose acetate, cellulose acetate butyrate, polystyrene, polyvinyl chloride, polyethylene terephthalate or polycarbonate, and paper coated or laminated with a baryta layer or an $\alpha$-olefin polymer (e.g., polyethylene, polypropylene or ethylene/butene copolymer). The support may be colored with a dye or pigment. The support may be blackened for the purpose of light-shielding. The surface of the support is generally coated with a subbing layer to improve adhesion of the emulsion layers and other layers. Before or after coating with the subbing layer, the surface of the support may be processed by glow discharge, corona discharge, ultraviolet ray irradiation or flame treatment.

For coating the silver halide photographic emulsion layers and other hydrophilic colloid layers on the support, various known coating methods, for example, dip coating, roller coating, curtain coating or extrusion coating, may be employed. If desired, plural layers may be coated simultaneously by the methods described in U.S. Patents 2,681,294, 2,761,791, 3,526,528 and 3,508,947.

When the photographic material of the present invention has a non-previously fogged internal latent image type emulsion as described above, the material is imagewise exposed, and then the material is fogged by light or a nucleating agent. The material is developed with a surface developer containing a p-phenylenediamine color developing agent, and thereafter subjected to bleaching and fixing to form a direct positive color image. Fogging may be an integral part of the development process.

For the above described fogging treatment to be applied to the photographic material of the present invention, either a "light fogging method" in which a second exposure is applied to the whole surface of the light-sensitive layer of the material, or a "chemical fogging method" in which the material is developed in the presence of a nucleating agent may be employed. In addition, the material may also be developed in the presence of both a nucleating agent and light. Further, a nucleating agent may previously be incorporated into the photographic material, which may be fogged by exposure.

The details of the light fogging method are described in JP-A-63-81337, and examples of nucleating agents which can be used in the present invention are also described therein from page 10 to page 14. In particular, the compounds of the general formula (N-1) or (N-2) described therein are preferred for use in the present invention.

Specific examples of the compounds of the general formula (N-1) are as follows:

(N-I-1): 5-Ethoxy-2-methyl-1-propargylquinolinium bromide
(N-I-2): 2,4-Dimethylpropargylquinolinium bromide
(N-I-3): 2-Methyl-1-{3-[2-(4-methylphenyl)hydrazono] butyl}quinolinium iodide
(N-I-4): 3,4-Dimethyldihydropyrido[2,1-b]benzothiazolium bromide
(N-I-5): 6-Ethoxythiocarbonylamino-2-methyl-1-propargylquinolinium trifluoromethanesulfonate
(N-I-6): 2-Methyl-6-(3-phenylthioureido)-1-propargylquinolinium bromide
(N-I-7): 6-(5-Benzotriazolecarboxamido)-2-methyl-1-propargylquinolinium trifluoromethanesulfonate
(N-I-8): 6-[3-(2-Mercaptoethyl)ureido]-2-methyl-1-propargylquinolinium trifluoromethanesulfonate
(N-I-9): 6-{3-[3-(5-Mercapto-1,3,4-thiadiazole-2-ylthio)propyl]ureido}-2-methyl-1-propargylquinolinium trifluoromethanesulfonate
(N-I-10): 6-(5-Mercaptotetrazol-1-yl)-2-methyl-1-propargylquinolinium iodide
(N-I-11): 1-Propargyl-2-(1-propenyl)quinolinium trifluoromethanesulfonate
(N-I-12): 6-Ethoxythiocarbonylamido-2-(2-methyl-1-propenyl)-1-propargylquinolinium trifluoromethanesulfonate

Specific examples of the compounds of the general formula (N-II) are as follows:

(N-II-1): 1-Formyl-2-{4-[3-(2-methoxyphenyl)ureido] propyl}hydrazine
(N-II-2) 1-Formyl-2-{4-[3-{3-[3-(2,4-di-tert-pentylphenoxy)propyl]ureido}phenylsulfonylamino]-phenyl}hydrazine
(N-II-3): 1-Formyl-2-{4-[3-(5-mercaptotetrazol-1-yl) benzamido}phenyl]hydrazine
(N-II-4): 1-Formyl-2-[4-{3-[3-(5-mercaptotetrazol-1-yl)phenyl]ureido}phenyl]hydrazine
(N-II-5): 1-Formyl-2-[4-{3-[N-(5-mercapto-4-methyl-1,2,4-triazol-3-yl)carbamoyl]propanamido} phenyl]-hydrazine
(N-II-6): 1-Formyl-2-{4-[3-{N-[4-(3-mercapto-1,2,4-triazol-4-yl)phenyl]cabamoyl}propanamido] phenyl}hydrazine
(N-II-7): 1-Formyl-2-[4-{3-[N-(5-mercapto-1,3,4-thiadiazol-2-yl)cabamoyl]propanamido}phenyl]-hydrazine
(N-II-8): 2-[4-Benzotriazol-5-carboxamido)phenyl]-1-formylhydrazine
(N-II-9): 2-[4-{3-(N-Benzotriazole-5-carboxamido) carbamoylpropanamide]phenyl}-1-formylhydrazine
(N-II-10): 1-Formyl-2-{4-[1-(N-phenylcarbamoyl)thiosemicarbamido}phenyl]hydrazine

Nucleation accelerating agents which can be used in the present invention include tetraazaindenes, triazaindenes and pentaazaindenes having at least one mercapto group which may optionally be substituted with an alkali metal atom or an ammonium group, as well as the compounds as described in JP-A-63-106506.

Specific examples of nucleation accelerating agents which can be used in the present invention are set forth below, but the present invention is not to be construed as being limited thereto:

(A-1): 3-Mercapto-1,2,4-triazolo[4,5-a]pyridine
(A-2): 3-Mercapto-1,2,4-triazolo[4,5-a]pyrimidine
(A-3): 5-Mercapto-1,2,4-triazolo[1,5-a]pyrimidine
(A-4): 7-(2-Dimethylaminoethyl)-5-mercapto-1,2,5-triazolo[1,5-a]pyrimidine
(A-5): 3-Mercapto-7-methyl-1,2,4-triazolo[4,5-a]pyrimidine
(A-6): 3,6-Dimercapto-1,2,4-triazolo[4,5-b]pyridazine
(A-7): 2-Mercapto-5-methylthio-1,3,4-thiadiazole
(A-8): 3-Mercapto-4-methyl-1,2,4-triazole
(A-9): 2-(3-Dimethylaminopropylthio)-5-mercapto-1,3,4-thiadiazole hydrochloride
(A-10): 2-(2-Morpholinoethylthio)-5-mercapto-1,3,4-thiadiazole hydrochloride

Although the nucleation accelerating agents may be incorporated into either the photographic light-sensitive material or a processing solution, it is preferred that they be incorporated into the photographic light-sensitive material, especially into the internal latent image type silver halide emulsion layer or other hydrophilic colloid layers (e.g., an interlayer or a protective layer) of the material. Particularly preferably, they are incorporated into the silver halide emulsion layer or into the layers adjacent thereto in the photographic material.

The amount of nucleation accelerating agents to be added is preferably from $10^{-6}$ to $10^{-2}$ mol, more preferably from $10^{-5}$ to $10^{-2}$ mol, per mol of silver halide in the material.

When the nucleation accelerating agent is incorporated into a processing solution, i.e., the developing solution or a prebath thereof, the amount of the agent is preferably from $10^{-8}$ to $10^{-3}$ mol, more preferably from $10^{-7}$ to $10^{-4}$ mol, per liter of the processing solution.

Two or more kinds of nucleation accelerating agents can be used in a mixture.

When the photographic material of the present invention is used in a color diffusion transfer process, a dye developer can be used as the coloring agent. It is preferable that a coloring agent which itself is non-diffusible (or immobile) in an alkaline condition (e.g., in a developing solution), but which may release a diffusible dye (or a precursor thereof) as a result of development be used in this process. The diffusible dye releasing coloring agents (DRR compounds) include couplers or redox compounds which are capable of releasing a diffusible dye. These are useful not only for the color diffusion transfer process (wet type) but also for heat-developable photographic materials (dry type) as described, for example, in JP-A-58-58543.

The diffusible dye releasing redox compounds (hereinafter referred to as "DRR compounds") can be represented by the following general formula:

(Ballast )——( Redox-cleaving Atomic Groups )——D

wherein, the Ballast and the Redox-cleaving Atomic Group may be those derived from the compounds as described in JP-A-58-163938, pages 12 to 22, and D represents a dye moiety (or precursor thereof). The dye moiety may be connected to the Redox-cleaving Atomic Group via a linking group. As the dye moiety for D, the dyes described in the following publications are preferably used.

### Examples of Yellow Dyes:

The dyes described in U.S. Patents 3,597,200, 3,309,199, 4,013,633, 4,245,028, 4,156,609, 4,139,383, 4,195,992, 4,145,641, 4,148,643 and 4,336,322, JP-A-51-114930, JP-A-56-71072, Research Disclosure, No. 17630 (1978) and ibid., No. 16475 (1977) are preferred.

### Examples of Magenta Dyes:

The dyes described in U.S. Patents 3,453,107, 3,544,545, 3,932,380, 3,931,144, 3,932,308, 3,954,476, 4,233,237, 4,255,509, 4,250,246, 4,142,891, 4,207,104 and 4,287,292, JP-A-52-106727, JP-A-53-23628, JP-A-55-36804, JP-A-56-73057, JP-A-56-71060 and JP-A-55-134 are preferred.

### Examples of Cyan Dyes:

The dyes described in U.S. Patents 3,482,972, 3,929,760, 4,013,635, 4,268,625, 4,171,220, 4,242,435, 4,142,891, 4,195,994, 4,147,544 and 4,148,642, British Patent 1,551,138, JP-A-54-99431, JP-A-52-8827, JP-A-53-47823, JP-A-53-143323, JP-A-54-99431, JP-A-56-71061, European Patents (EPC) 53037 and 53040, and Research Disclosure, No. 17630 (1978) and ibid., No. 16475 (1977) are preferred.

The amount of the dye compound to be coated is generally from about $1 \times 10^{-4}$ to $1 \times 10^{-2}$ mol/m$^2$, preferably from $2 \times 10^{-4}$ to $2 \times 10^{-2}$ mol/m$^2$.

In the photographic material of the present invention, the coloring agent can be incorporated into the corresponding silver halide emulsion layer or into the layers adjacent thereto.

When the photographic material of the present invention is used in a color diffusion transfer process, the photographic emulsion may be coated on the same support having an image receiving layer, or alternatively, it may be coated on a different support. The silver halide photographic emulsion layer (light-sensitive element) and the image-receiving layer (image-receiving element) may be combined to provide a combined slim unit, or they may be provided independently in the form of the respective separate photographic material units. Regarding the combined film unit type, it may be either a completely integrated type for exposure, development and observation of transfer images formed or a semi-integrated type for exposure and development where the developed sheet is released to observe the image formed. The latter type is preferred for the present invention.

The present invention can be applied to various kinds of photographic materials.

For example, these include black-and-white negative films, black-and-white reversal films, color negative films for general use or for movies, color reversal films for slides or television use, color reversal papers and instant color films. In addition, the present invention may also be applied to color hard copies for preservation of images from full color duplicators or CRT. Further, the present invention can be applied to black-and-white photographic materials consisting of three color coupler mixtures as described in Research Disclosure, No. 17123 (July, 1978).

The color developing solution to be used for development of the photographic material of the present invention is preferably an alkaline aqueous solution consisting mainly of an aromatic primary amine color developing agent. As the color developing agent, p-phenylenediamine compounds are preferably used although aminophenol compounds are also useful. Specific examples of the compounds include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline and sulfates, hydrochlorides and p-toluenesulfonates thereof. These compounds can be used in the form of a mixture of two or more of them, in accordance with the object thereof.

The color developing solution generally contains a pH buffer such as carbonates, borates or phosphates of alkali metals, as well as a development inhibitor or an anti-foggant such as bromides, iodides, benzimidazoles, benzothiazoles or mercapto compounds.

The color developing solution has a pH value of generally from 9 to 12, preferably from 9.5 to 11.5. The amount of the replenisher for the developing solution, although depending upon the kind of color photographic material to be processed, is generally one liter or less per m$^2$ of the material being processed, and the amount may be reduced to 300 ml or less if the bromide ion concentration in the replenisher is lowered. When the amount of the replenisher is reduced, it is preferred to reduce the contact area between the processing bath and air so as to prevent evaporation and aerial oxidation of the processing solution. In addition, the amount of the replenisher may be reduced by means of inhibiting the accumulation of bromide ions in the developing solution.

After color development, the photographic emulsion layer thus processed is generally bleached. Bleaching may be carried out simultaneously with fixing (i.e., a bleach-fixing step), or may be carried out separately therefrom. In order to accelerate the photographic processing, bleaching may be followed by bleach-fixing. In addition, other various modifications, for example, bleach-fixing in two continuous bleach-fixing bathes, fixing prior to bleach-fixing, or bleach fixing followed by bleaching, may also be employed in accordance with the object of the photographic processing.

Suitable bleaching agents include compounds of polyvalent metals such as iron(III), cobalt(III), chromium(VI) or copper(II), as well as peracids, quinones and nitro compounds. Specific examples of bleaching agents include ferricyanides; bichromates; organic complexes with iron(III) or cobalt(III), for example, complexes with an aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid or glycoletherdiaminetetraacetic acid, or an organic acid such as citric acid, tartaric acid or malic acid; persulfates; bromates; permanganates; and nitrobenzenes. Among them, aminopolycarboxylic acid/iron(III) complexes such as ethylenediaminetetraacetic acid.iron(III) complex and persulfates are preferred from the viewpoint of rapid processability and prevention of environmental pollution. Aminopolycarboxylic acid iron(III) complexes are especially useful both in bleaching solutions and in bleach-fixing solutions.

The pH value of the bleaching solution or bleach-fixing solution containing the aminopolycarboxylic acid.iron(III) complex is generally from 5.5 to 8, but the solution may have a lower pH value so as to accelerate processing.

The bleaching solution, bleach-fixing solution and any prebath thereof may contain a bleach accelerating agent, if desired.

Suitable fixing agents include thiosulfates, thiocyanates, thioether compounds, thioureas and a large number of iodides. Use of thiosulfates is general, and ammonium thiosulfate in particular is preferred. As preservatives for the bleach-fixing solution, sulfites, bisulfites or carbonyl-bisulfite adducts are preferred.

The silver halide color photographic material of the present invention is generally subjected to washing with water and/or stabilization after being desilvered. The amount of wash water may be determined within a broad range in accordance with the characteristics of the photographic material to be processed (for example, the nature of the couplers and other components), the intended use of the material, as well as the temperature of the wash water, the number of washing tanks (stages), the kind of replenishment system (countercurrent or ordinary current) and various other conditions. Among these conditions, the relation between the number of washing tanks and the amount of wash water may be determined by the method described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, pages 248 to 253, (May, 1955).

In the processing of the photographic material of the present invention, the pH value of the wash water is from 4 to 9, preferably from 5 to 8. The temperature of the wash water and the washing time may vary within a broad range, in accordance with the characteristics of the photographic material to be processed and the intended use thereof, and in general, the range of from 15 °C to 45 °C and from 20 seconds to 10 minutes, preferably from 25 °C to 40 °C and from 30 seconds to 5 minutes, may be selected. In place of the above-described water washing step, the photographic material of the present invention may be processed directly by a stabilizing solution. In such a stabilization step, the methods described in JP-A-57-

8543, JP-A-58-14834 and JP-A-60-220345 can be utilized.

The stabilizing bath for the stabilization step may contain various kinds of chelating agents and fungicides. The overflow solution resulting from the replenishment of the water washing bath and/or stabilizing bath may be re-used in the previous desilvering step or in other steps.

The silver halide color photographic material of the present invention can contain a color developing agent for the purpose of simplifying and accelerating processing of the material. For incorporation of a color developing agent into the material, a precursor of the color developing agent is preferably used. As precursors, for example, there may be the indoaniline compounds described in U.S. Patent 3,342,597, the Schiff's base compounds described in U.S. Patent 3,342,599, Research Disclosure, No. 14850 and ibid., No. 15159, the aldol compounds described in Research Disclosure, No. 13924, the metal complexes described in U.S. Patent 3,719,492 and the urethane compounds described in JP-A-53-135628.

The respective processing solutions for the photographic material of the present invention are used at from 10° C to 50° C. Although a standard temperature is from 33° C to 38° C, the processing temperature may be increased so as to accelerate the processing step and shorten the processing time, or the processing temperature may be decreased so as to improve the quality of the image formed and to improve the stability of the processing solution.

Regarding the amount of replenisher to be replenished in the respective processing steps, it is preferable to use as small an amount as possible. Specifically, the amount of replenisher is preferably from 0.1 to 50 times, more preferably from 3 to 30 times, the amount of the solution carried over from the preceding bath, per unit area of the material.

When the photographic material of the present invention is black-and-white photographic material, it may be developed with various kinds of known developing agents. For example, polyhydroxybenzenes such as hydroquinone, 2-chlorohydroquinone, 2-methylhydroquinone, catechol or pyrogallol; aminophenols such as p-aminophenol, N-methyl-p-aminophenol or 2,4 diaminophenol; 3-pyrazolidones such as 1-phenyl-3-pyrazolidones, 1-phenyl-4,4′-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidones or 5,5-dimethyl-1-phenyl-3-pyrazolidone; and ascorbic acids can be used, alone or in combination. In addition, the developing solution described in JP-A-58-55928 may be used. The developing agent may be incorporated into an alkaline processing composition (processing element) or into an appropriate layer in the light-sensitive element.

The internal latent image type emulsion photographic material of the present invention can be developed with a surface developer to obtain a direct positive image. The surface developer is such that the development therewith is induced substantially by the latent image or fog nuclei existing on the surface of the silver halide grains. Although the surface developer preferably does not contain a silver halide solvent, it may contain a silver halide solvent (for example, sulfites) provided that the silver halide solvent does not substantially participate in developing the internal latent image before the completion of the development of the silver halide grains by the surface development.

The developing solution may contain, as an alkaline agent or as a buffer, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, trisodium phosphate or sodium metaborate. The content of these agents in the developing solution may be selected so that the pH value of the resulting solution falls within the range of from 9 to 13, preferably from 10 to 11.2.

It is preferable that the developing solution contains a compound which is generally used as an anti-foggant, such as a benzimidazole (e.g., 5-nitrobenzimidazole), a benzotriazole (e.g., benzotriazole or 5-methylbenzotriazole) or the like, so as to further lower the minimum density of the direct positive image to be formed.

The details of developing agents, preservatives, buffers and developing methods for black-and-white photographic materials as well as specific examples thereof and the use of the materials are described, for example, in Research Disclosure, No. 17643 (December, 1978), XIX to XXI.

The developing agent can be incorporated into an alkaline development processing solution (processing element) or may also be incorporated into an appropriate layer of the photographic element. Examples of the developing agents which may be used in the present invention include hydroquinone, an aminophenol such as N-methylaminophenol, 1-phenyl-3-pyrazolidinone, 1-phenyl-4,4-dimethyl 3 pyrazolidinone, 1-phenyl-4-methyl-4-oxymethyl-3-pyrazolidinone, N,N-diethyl-p-phenylenediamine, 3-methyl-N,N-diethyl-p-phenylenediamine and 3-methoxy-N-ethoxy-p-phenylenediamine.

Among those described above, black-and-white developing agents which are capable of reducing stains in an image-receiving layer (mordant layer) are especially preferred for same reasons as in the case of the above described alkaline development processing solution.

When the photographic material of the present invention is used as a film unit for a diffusion transfer process, it is preferably processed with a viscous developing solution. The viscous developing solution is a liquid composition containing components necessary for development of silver halide emulsions (and formation of diffusion transferred dye images), and the main component of the solvent is water, which may often contain other hydrophilic solvents such as methanol or methyl cellosolve. Preferably, the processing composition contains a hydrophilic polymer such as a macromolecular polyvinyl alcohol, hydroxyethyl cellulose or sodium carboxymethyl cellulose. It is preferred that the polymer be added to the composition in such an amount to give a processing composition having a viscosity of 1 poise or more, preferably from about 500 to 1000 poises, at room temperature.

The above described processing composition is preferably employed in a container capable of being ruptured under pressure, for example, as described in U.S. Patents 2,543,181, 2,643,886, 2,653,732, 2,723,051, 3,056,491, 3,056,492 and 3,152,515.

The following examples are provided to further illustrate the present invention, but are not to be construed as limiting the invention in any way.

## EXAMPLE 1

The following First to Fourteenth layers were coated on the front side of a paper support (having a thickness of 100 µm), both surfaces of which were laminated with polyethylene, and the following Fifteenth and Sixteenth layers were coated on the back side of the paper support to prepare a color photographic light sensitive material. The polyethylene laminated on the First layer side of the support contained titanium dioxide (4 g/m$^2$) as a white pigment and a slight amount (0.003 g/m$^2$) of ultramarine as a bluish dye (chromaticity of the surface of the support was 88.0, -0.20 and -0.75 in an L*, a* and b* system).

### Construction of Layers

The composition of each layer is shown below. The coating amounts of the components are in g/m$^2$. With respect to silver halide, the coating amount is indicated in terms of a silver coating amount. The emulsion used in each layer was prepared according to the method for preparation of Emulsion EM1. The emulsion used in the Fourteenth layer was a Lippmann emulsion not being chemically sensitized on the surfaces of grains.

| First Layer: Antihalation Layer | |
|---|---|
| Black colloidal silver | 0.10 |
| Gelatin | 0.70 |

| Second Layer: Intermediate Layer | |
|---|---|
| Gelatin | 0.70 |

| Third Layer: Low-Sensitive Red-Sensitive Layer | |
|---|---|
| Silver bromide emulsion spectrally sensitized with red-sensitizing dyes (ExS-1, 2, 3) (average grain size: 0.25 µm, size distribution (coefficient of variation): 8%, octahedral) | 0.04 |
| Silver chlorobromide emulsion spectrally sensitized with red-sensitizing dyes (ExS-1, 2, 3) (silver chloride: 5 mol%, average grain size: 0.40 µm, size distribution: 10%, octahedral) | 0.08 |
| Gelatin | 1.00 |
| Cyan coupler (ExC-1, 2, 3, mixing ratio: 1/1/0.2) | 0.30 |
| Color fading preventing agent (Cpd-1, 2, 3, 4, mixing ratio: 1/1/1/1) | 0.18 |
| Stain preventing agent (Cpd-5) | 0.003 |
| Coupler dispersing medium (Cpd-6) | 0.03 |
| Coupler solvent (Solv-1, 2, 3, mixing ratio: 1/1/1) | 0.12 |

| Fourth Layer: High-Sensitive Red-Sensitive Layer | |
|---|---|
| Silver bromide emulsion spectrally sensitized with red-sensitizing dyes (ExS-1, 2, 3) (average grain size: 0.60 µm, size distribution: 15%, octahedral) | 0.14 |
| Gelatin | 1.00 |
| Cyan coupler (ExC-1, 2, 3, mixing ratio: 1/1/0.2) | 0.30 |
| Color fading preventing agent (Cpd-1, 2, 3, 4, mixing ratio: 1/1/1/1) | 0.18 |
| Coupler dispersing medium (Cpd-6) | 0.03 |
| Coupler solvent (Solv-1, 2, 3, mixing ratio: 1/1/1) | 0.12 |

| Fifth Layer: Intermediate Layer | |
|---|---|
| Gelatin | 1.00 |
| Color mixing preventing agent (Cpd-7) | 0.08 |
| Color mixing preventing agent solvent (Solv-4, 5, mixing ratio: 1/1) | 0.16 |
| Polymer latex (Cpd-8) | 0.10 |

| Six Layer: Low-Sensitive Green-Sensitive Layer | |
|---|---|
| Silver bromide emulsion spectrally sensitized with green-sensitizing dye (ExS-4) (average grain size: 0.25 µm, size distribution: 8%, octahedral) | 0.04 |
| Silver chlorobromide emulsion spectrally sensitized with green-sensitizing dye (ExS-4) (silver chloride: 5 mol%, average grain size: 0.40 µm, size distribution: 10%, octahedral) | 0.06 |
| Gelatin | 0.80 |
| Magenta coupler (ExM-1, 2, 3, mixing ratio: 1/1/1) | 0.11 |
| Color fading preventing agent (Cpd-9, 26, mixing ratio: 1/1) | 0.15 |
| Stain preventing agent (Cpd-10, 11, 12, 13, mixing ratio: 10/7/7/1) | 0.025 |
| Coupler dispersing medium (Cpd-6) | 0.05 |
| Coupler solvent (Solv-4, 6, mixing ratio: 1/1) | 0.15 |

| Seventh Layer: High-Sensitive Green-Sensitive Layer | |
|---|---|
| Silver bromide emulsion spectrally sensitized with green-sensitizing dye (ExS-4) (average grain size: 0.65 µm, size distribution: 16%, octahedral) | 0.10 |
| Gelatin | 0.80 |
| Magenta coupler (ExM-1, 2, 3, mixing ratio: 1:1:1) | 0.11 |
| Color fading preventing agent (Cpd-9, 26, mixing ratio: 1:1) | 0.15 |
| Stain preventing agent (Cpd-10, 11, 12, 13, mixing ratio: 10:7:7:1) | 0.025 |
| Coupler dispersing medium (Cpd-6) | 0.05 |
| Coupler solvent (Solv-4, 6, mixing ratio: 1:1) | 0.15 |

Eighth Layer: Intermediate Layer

Same as Fifth Layer

| Ninth Layer: Yellow Filter Layer | |
|---|---|
| Yellow colloidal silver (grain size: 100Å) | 0.12 |
| Gelatin | 0.70 |
| Color mixing preventing agent (Cpd-7) | 0.03 |
| Color mixing preventing agent solvent (Solv-4, 5, mixing ratio: 1:1) | 0.10 |
| Polymer latex (Cpd-8) | 0.07 |

Tenth Layer: Intermediate Layer

Same as Fifth Layer

| Eleventh Layer: Low-Sensitive Blue-Sensitive Layer | |
|---|---|
| Silver bromide emulsion spectrally sensitized with blue-sensitizing dyes (ExS-5, 6) (average grain size: 0.40 µm, size distribution: 8%, octahedral) | 0.07 |
| Silver chlorobromide emulsion spectrally sensitized with blue-sensitizing dyes (ExS-5, 6) (silver chloride: 8 mol%, average grain size: 0.60 µm, size distribution: 11%, octahedral) | 0.14 |
| Gelatin | 0.80 |
| Yellow coupler (ExY-1, 2, mixing ratio: 1:1) | 0.35 |
| Color fading preventing agent (Cpd-14) | 0.10 |
| Stain preventing agent (Cpd-5, 15, mixing ratio: 1:5) | 0.007 |
| Coupler dispersing medium (Cpd-6) | 0.05 |
| Coupler solvent (Solv-2) | 0.10 |

| Twelfth Layer: High-Sensitive Blue-Sensitive Layer | |
|---|---|
| Silver bromide emulsion spectrally sensitized with blue-sensitizing dyes (ExS-5, 6) (average grain size: 0.85 µm, size distribution: 18%, octahedral) | 0.15 |
| Gelatin | 0.60 |
| Yellow coupler (ExY-1, 2: mixing ratio: 1/1) | 0.30 |
| Color fading preventing agent (Cpd-14) | 0.10 |
| Stain preventing agent (Cpd-5, 15, mixing ratio: 1/5) | 0.007 |
| Coupler dispersing medium (Cpd-6) | 0.05 |
| Coupler solvent (Solv-2) | 0.10 |

| Thirteenth Layer: Ultraviolet Light Absorbing Layer | |
|---|---|
| Gelatin | 1.00 |
| Ultraviolet light absorbing agent (Cpd-2, 4, 16, mixing ratio: 1/1/1) | 0.50 |
| Color mixing preventing agent (Cpd-7, 17, mixing ratio: 1/1) | 0.03 |
| Dispersing medium (Cpd-6) | 0.02 |
| Ultraviolet light absorbing agent solvent (Solv-2, 7 mixing ratio: 1/1) | 0.08 |
| Irradiation preventing dye (Cpd-18, 19, 20, 21, 27, mixing ratio: 10/10/13/15/20) | 0.05 |

| Fourteenth Layer: Protective Layer | |
|---|---|
| Silver chlorobromide fine particles (silver chloride: 97 mol%, average grain size: 0.1 µm) | 0.03 |
| Acryl-modified copolymer of polyvinylalcohol (molecular weight: 50,000) | 0.01 |
| Polymethyl methacrylate particles (average particle size: 2.4 µm) and silicon oxide (average particle size: 5 µm, mixing ratio: 1/1) | 0.05 |
| Gelatin | 1.80 |
| Gelatin hardener (H-1, 2; mixing ratio: 1/1) | 0.18 |

| Fifteenth Layer: Back Layer | |
|---|---|
| Gelatin | 2.50 |
| Ultraviolet light absorbing agent (Cpd-2, 4, 16, mixing ratio: 1/1/1) | 0.50 |
| Dye (Cpd-18, 19, 20, 21, 27, mixing ratio: 1/1/1/1/1) | 0.06 |

| Sixteenth Layer: Back Protective Layer | |
|---|---|
| Polymethyl methacrylate particles (average particle size: 2.4 µm) and silicon oxide (average particle size: 5 µm), mixing ratio: 1/1 | 0.05 |
| Gelatin | 2.00 |
| Gelatin hardener (H-1, 2, mixing ratio: 1/1) | 0.14 |

Preparation of Emulsion EM-1

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were added simultane ously to an aqueous gelatin solution at 75 °C over a period of 15 minutes while vigorously stirring, to obtain an octahedral silver bromide emulsion having an average grain diameter of 0.40 µm. At that time, 0.3 g of 3,4-dimethyl-1,3-thiazoline-2-thione per mol of silver was added. Then, 6 mg of sodium thiosulfate and 7 mg of chloroauric acid (tetrahydrate) were added to the emulsion per mol of silver in order and the emulsion was heated to 75 °C for 80 minutes to be chemically sensitized. The thus-prepared silver bromide grains were used as cores and were further grown under the same precipitation conditions as above to obtain a monodispersed octahedral core-shell type silver bromide emulsion having an average grain diameter of 0.7 µm. The coefficient of variation of the grain size was about 10%.

1.5 mg of sodium thiosulfate and 1.5 mg of chloroauric acid (tetrahydrate) were added to the emulsion per mol of silver, and the emulsion was heated to 60 °C for 60 minutes to be chemically sensitized, thus an internal latent image type silver halide emulsion was obtained.

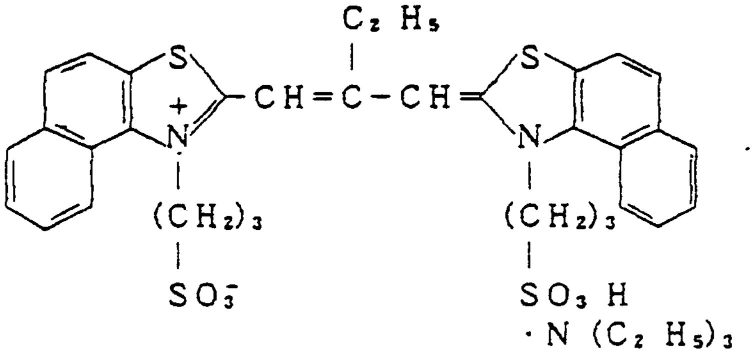
To each light-sensitive layer were added as a nucleating agent, ExZK-1 in an amount of $10^{-3}$ % by weight based on silver halide, and as a nucleation accelerating agent, Cpd-22 in an amount of $10^{-2}$ % by weight based on silver halide.

Also, to each layer, as emulsifying dispersing aids, Alkanol XC (manufactured by Du Pont) and sodium alkylbenzenesulfonate, and as coating aids, succinic acid ester and Megafac F-120 (manufactured by Dai Nippon Ink and Chemical Co, Ltd.) were added. Furthermore, to the layers containing silver halide or colloidal silver, as stabilizers, Cpd-23, 24, and 25 were added.

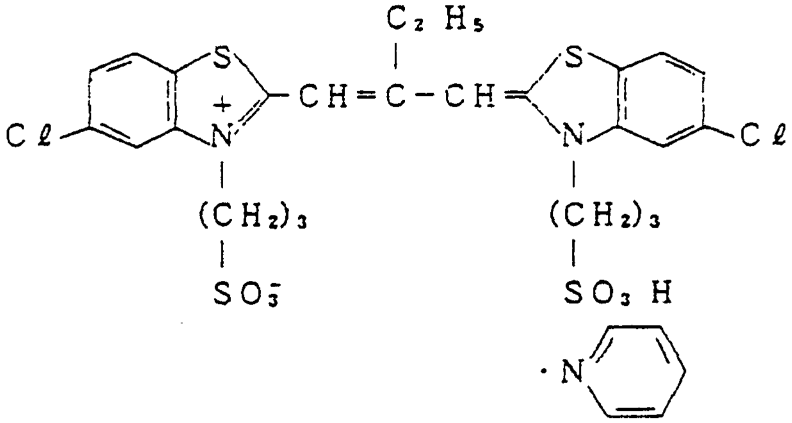
The sample thus-prepared was designated Sample 101.

The compounds used in this example are illustrated below.

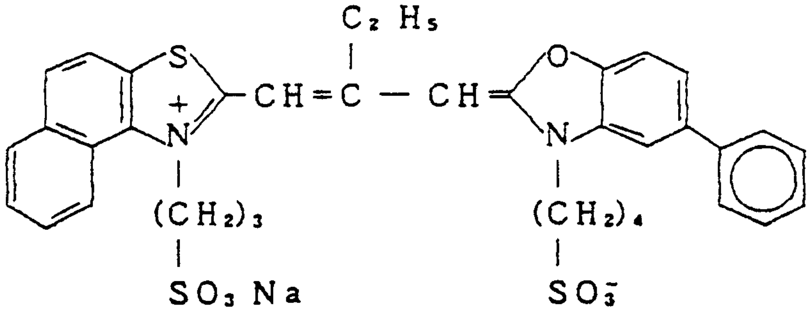
ExS-1



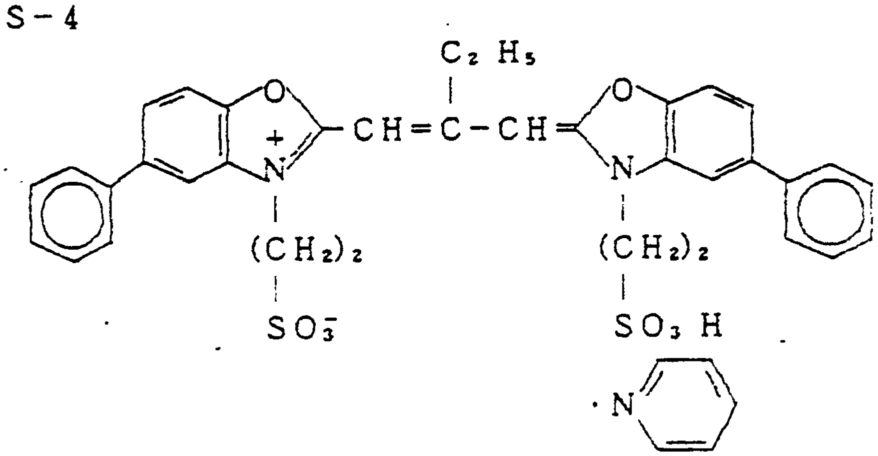
ExS-2



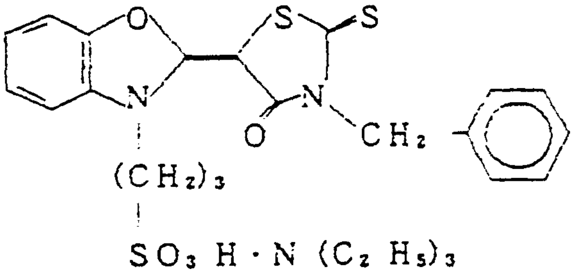
ExS-3



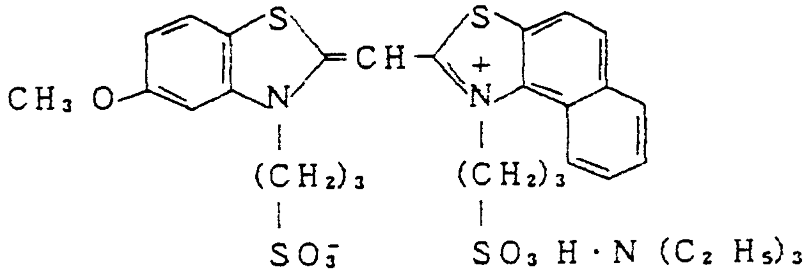
ExS-4



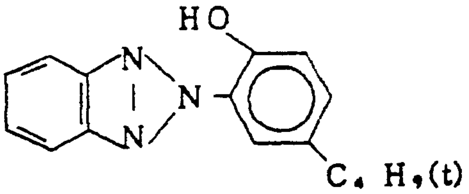
ExS-5



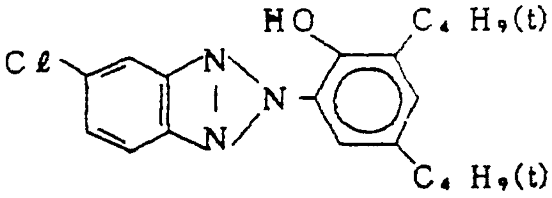
ExS-6



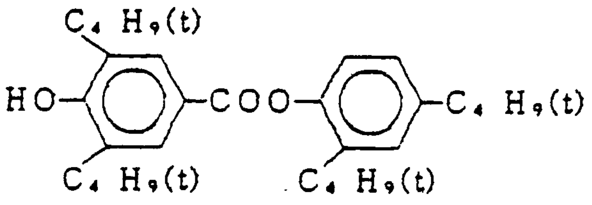
Cpd-1



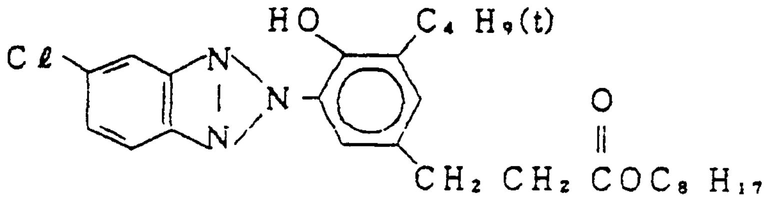
Cpd-2



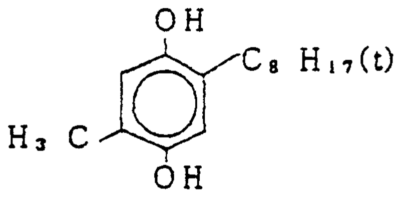
Cpd-3



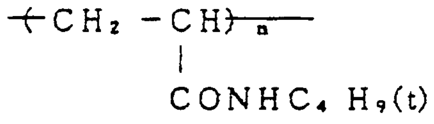
Cpd-4



Cpd-5



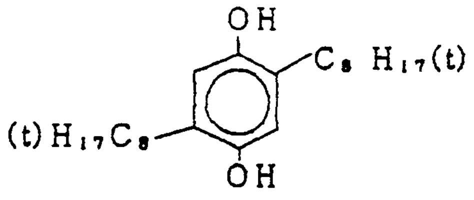
Cpd-6



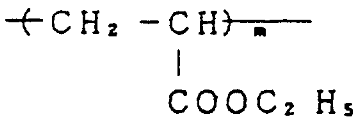
$-\!\left(CH_2-\underset{\displaystyle CONHC_4H_9(t)}{CH}\right)_{n}\!-$

$n = 100 \sim 1000$

Cpd-7



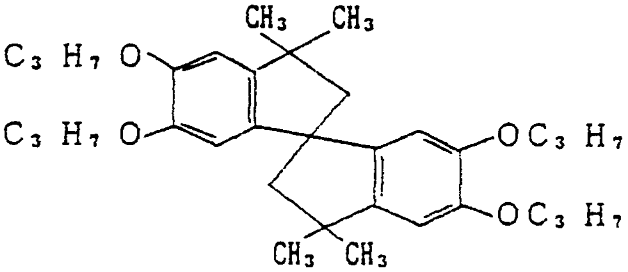
Cpd-8



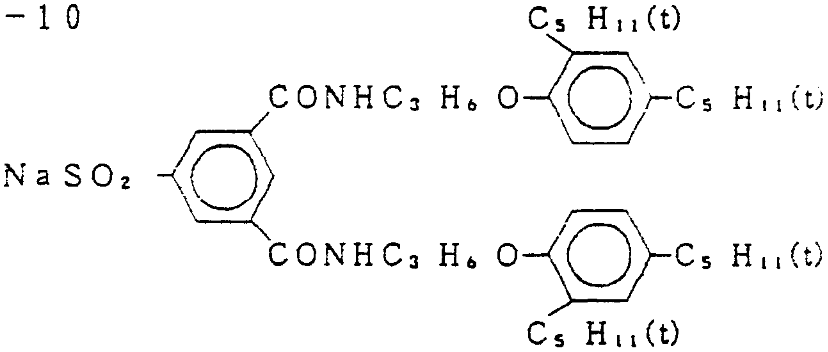
$-\!\left(CH_2-\underset{\displaystyle COOC_2H_5}{CH}\right)_{m}\!-$

m = 1,000 - 5,000

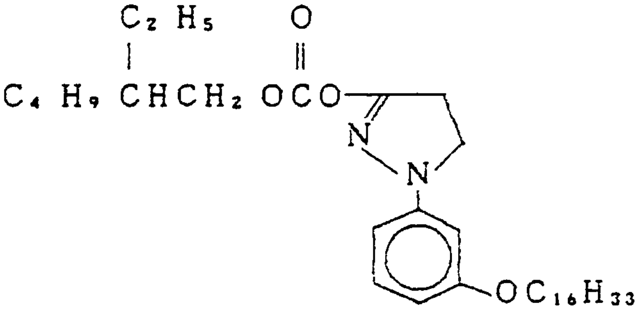
Cpd−9



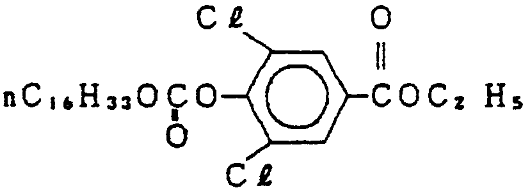
Cpd−10



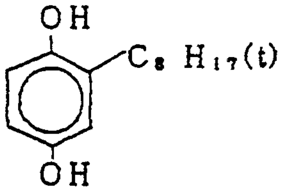
Cpd−11



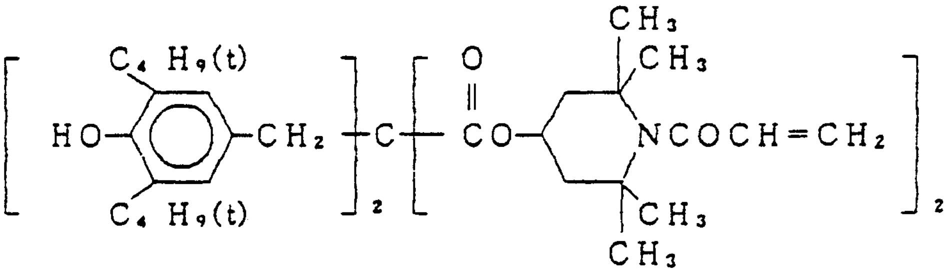
Cpd−12



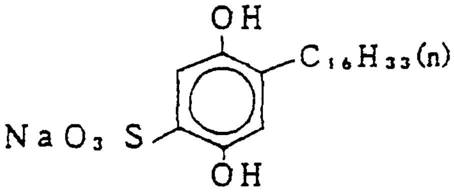
Cpd−13



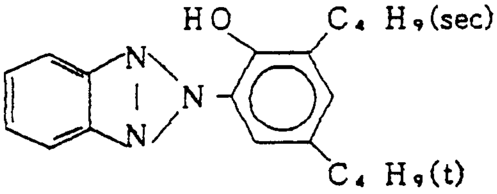
Cpd-14



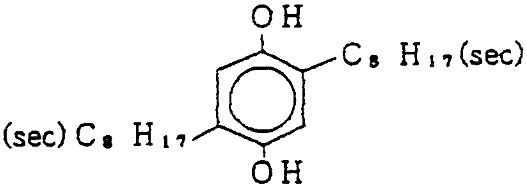
Cpd-15



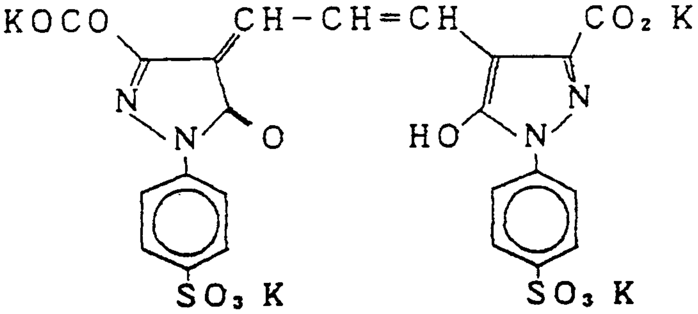
Cpd-16



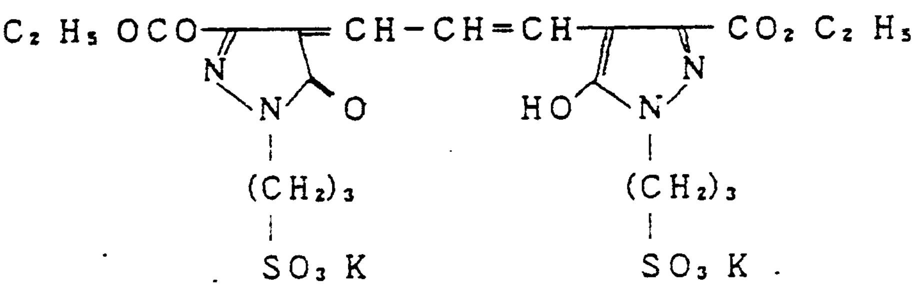
Cpd-17



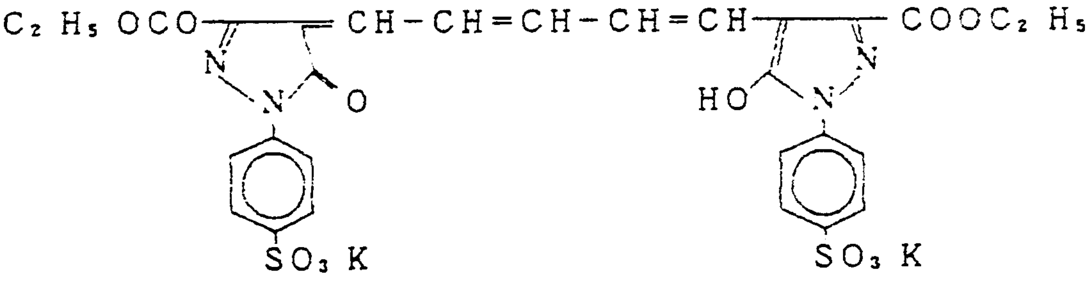
Cpd-18



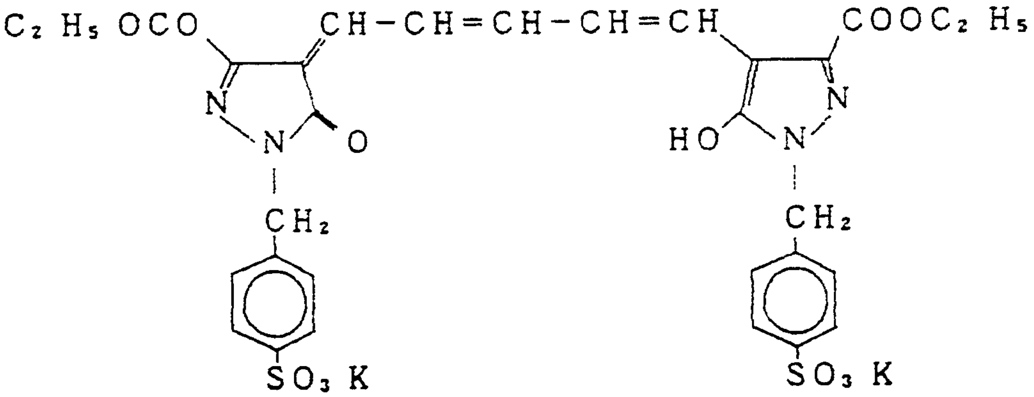
Cpd-19



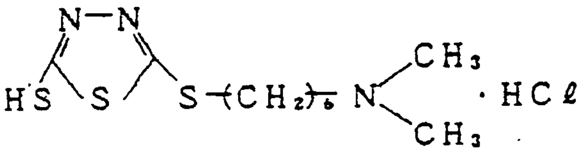
Cpd-20



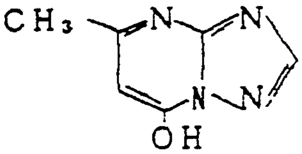
Cpd-21



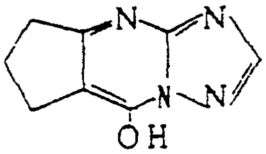
Cpd-22



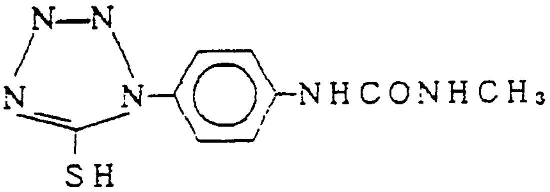
Cpd-23



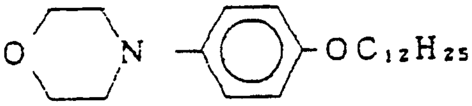
Cpd-24



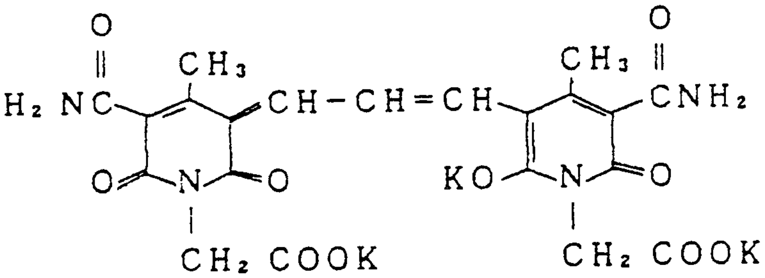
Cpd-25



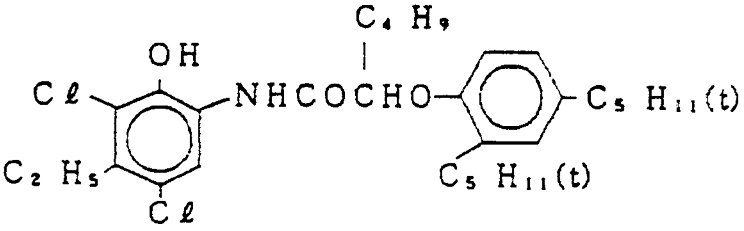
Cpd-26



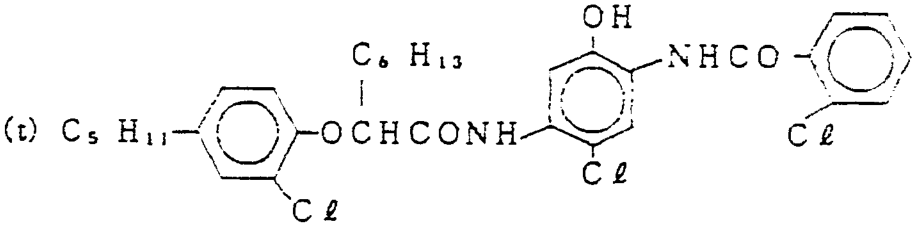
Cpd-27



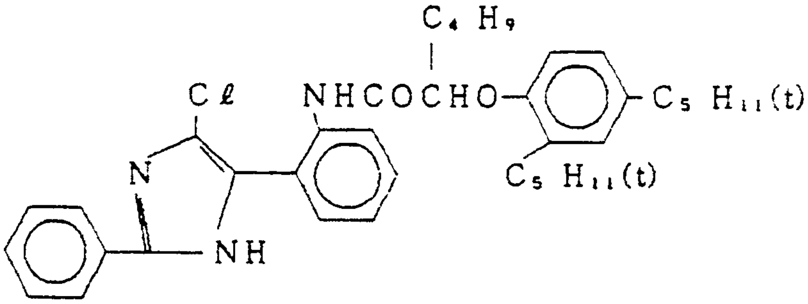
ExC-1



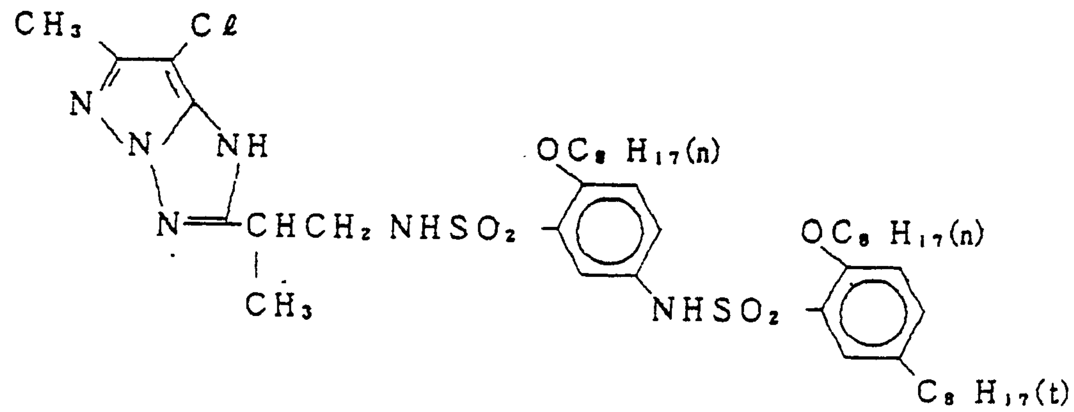
ExC-2



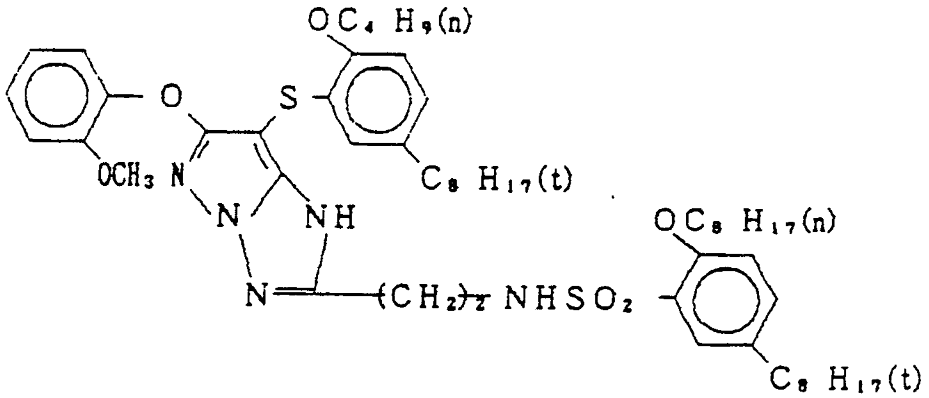
ExC-3



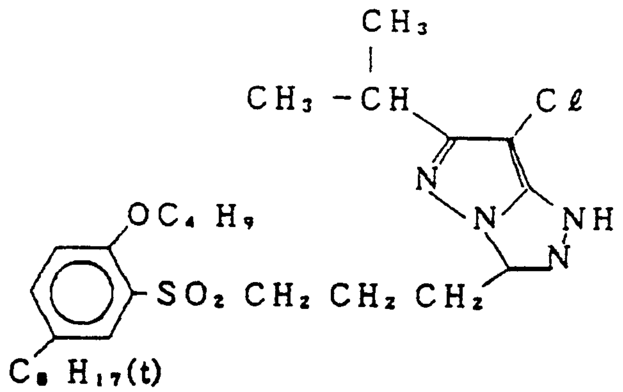
ExM-1



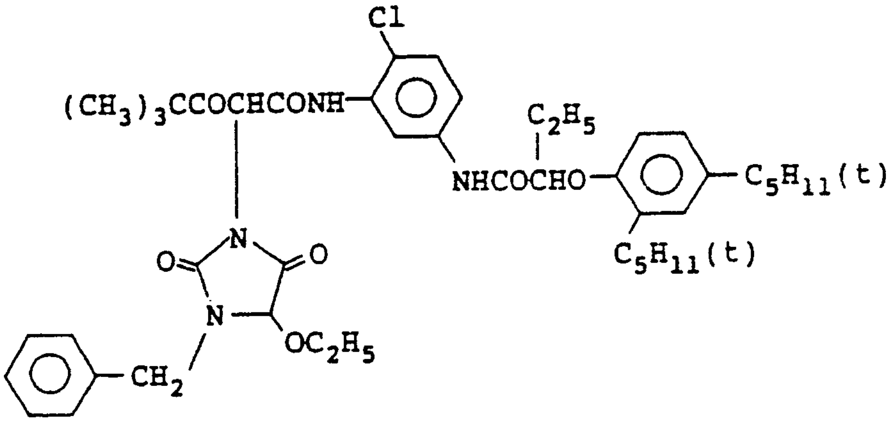
ExM-2



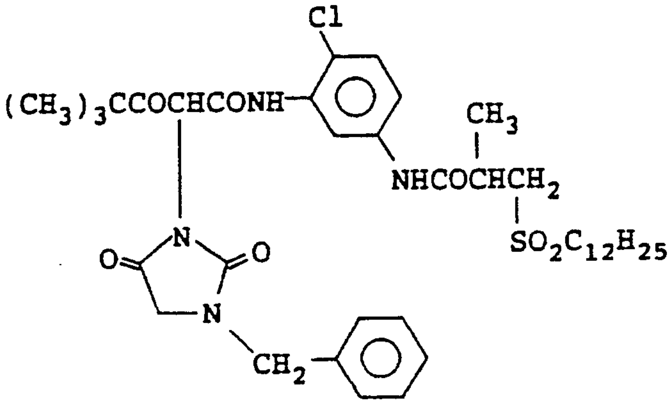
ExM-3



ExY-1



ExY-2



Solv-1 Di(2-ethylhexyl) sebacate
Solv-2 Trinonyl phosphate
Solv-3 Di(3-methylhexyl) phthalate
Solv-4 Tricresyl phosphate
Solv-5 Dibutyl phthalate
Solv-6 Trioctyl phosphate
Solv-7 Di(2-ethylhexyl) phthalate
H-1 1,2-Bis(vinylsulfonylacetamido)ethane
H-2 4,6-Dichloro-2-hydroxy-1,3,5-triazine sodium salt
ExZK-1 7-(3-Ethoxythiocarbonylaminobenzamido)-9-methyl-10-propargyl-1,2,3,4-tetrahydroacridinium trifluoromethanesulfonate

Samples 102 to 112 were prepared in the same manner as described for Sample 101, except that a compound represented by the general formula (I) according to the present invention or a comparative compound as shown in Table 1 below were added in the amount of $4.5 \times 10^{-3}$ mol per mol of silver to the sixth and seventh layers, respectively.

A group of samples thus-obtained were stored for 3 days in an atmosphere of 40 °C and 80% RH (incubation), then subjected to wedge exposure (1/10 sec, 10 CMS) together with a group of samples which were not stored in incubation. All samples were then continuously processed in accordance with the processing method described below by an automatic developing machine until the total amount of replenisher added equaled three times the tank capacity.

| Processing Step | Time | Temperature | Tank Capacity | Amount of Replenishment |
|---|---|---|---|---|
| | (sec) | (°C) | (ℓ) | (ml/m$^2$) |
| Color Development | 135 | 38 | 15 | 300 |
| Bleach-Fixing | 40 | 33 | 3 | 300 |
| Washing with Water (1) | 40 | 33 | 3 | - |
| Washing with Water (2) | 40 | 33 | 3 | 320 |
| Drying | 30 | 80 | | |

The replenishment system for the wash water was a countercurrent replenishment system in which a replenisher was added to water washing bath (2) and the overflow solution from water washing bath (2) was introduced into water washing bath (1). In the processing method, the amount of the bleach-fixing solution carried over from the bleach-fixing bath to water washing bath (1) was 35 ml/m$^2$ of photographic material being processed, and the volume of the replenisher added to water washing bath (2) was 9.1 times the amount of bleach-fixing solution carried over.

The compositions of the processing solutions used were as follows:

| Color Developing Solution | Mother Solution | Replenisher |
|---|---|---|
| D-Sorbitol | 0.15 g | 0.20 g |
| Sodium naphthalenesulfonate and formaldehyde condensate | 0.15 g | 0.20 g |
| Ethylenediaminetetramethylenephosphonic acid | 1.5 g | 1.5 g |
| Diethylene glycol | 12.0 ml | 16.0 ml |
| Benzyl alcohol | 13.5 ml | 18.0 ml |
| Potassium bromide | 0.80 g | - |
| Benzotriazole | 0.003 g | 0.004 g |
| Sodium sulfite | 2.4 g | 3.2 g |
| N,N-Bis(carboxymethyl)hydrazine | 6.0 g | 8.0 g |
| D-Glucose | 2.0 g | 2.4 g |
| Triethanolamine | 6.0 g | 8.0 g |
| N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate | 6.4 g | 8.5 g |
| Potassium carbonate | 30.0 g | 25.0 g |
| Fluorescent whitening agent (diaminostilbene type) | 1.0 g | 1.2 g |
| Water to make | 1,000 ml | 1,000 ml |
| pH (at 25°C) | 10.25 | 10.75 |

| Bleach-Fixing Solution (both Mother Solution and Replenisher) | |
|---|---|
| Disodium ethylenediaminetetraacetate dihydrate | 4.0 g |
| Ammonium iron(III) ethylenediaminetetraacetato dihydrate | 70.0 g |
| Ammonium thiosulfate (700 g/liter) | 180 ml |
| Sodium p-toluenesulfinate | 20.0 g |
| Sodium bisulfite | 20.0 g |
| 5-Mercapto-1,3,4-triazole | 0.5 g |
| Ammonium nitrate | 10.0 g |
| Water to make | 1,000 ml |
| pH (at 25°C) | 6.20 |

Washing Water (both Mother Solution and Replenisher)

City water was passed through a mixed bed type column filled with an H-type strong acidic cation exchange resin (Amberlite IR-120B manufactured by Rohm & Haas Co.) and an OH-type anion exchange resin (Amberlite IR-400 manufactured by Rohm & Haas Co.) to prepare water containing not more than 3 mg/liter of · calcium ion and magnesium ion. To the water thus-treated were added sodium dichloroisocyanurate in an amount of 20 mg/liter and sodium sulfate in an amount of 1.5 g/liter. The pH of the solution was in a range from 6.5 to 7.5.

For each sample, the maximum and minimum densities of the magenta color images formed were measured. The results are shown in Table 1 below.

TABLE 1

| Incubation | | | | | | |
|---|---|---|---|---|---|---|
| | | No | | Yes | | |
| Sample No. | Compound | $D_{max}$ | $D_{min}$ | $D_{max}$ | $D_{min}$ | Remarks |
| 101 | none | 2.1 | 0.10 | 1.2 | 0.13 | Comparison |
| 102 | Comparative Compound A | 2.2 | " | 2.0 | 0.10 | " |
| 103 | Comparative Compound B | 2.1 | " | 1.9 | " | " |
| 104 | (1) | 2.4 | " | 2.3 | " | Present Invention |
| 105 | (2) | 2.5 | " | 2.3 | " | " |
| 106 | (3) | 2.4 | " | 2.3 | " | " |
| 107 | (4) | 2.6 | " | 2.5 | " | " |
| 108 | (6) | 2.5 | " | 2.3 | " | " |
| 109 | (8) | 2.5 | " | 2.3 | " | " |
| 110 | (10) | 2.4 | " | 2.3 | " | " |
| 111 | (12) | 2.5 | " | 2.4 | " | " |
| 112 | (15) | 2.3 | " | 2.2 | " | " |

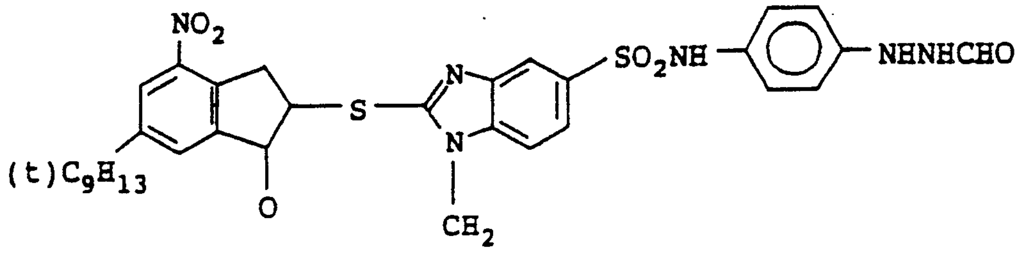
From the results shown in Table 1 above, it can be seen that Samples 104 to 112 which contain a compound represented by the general formula (I) according to the present invention exhibit higher maximum image density ($D_{max}$) in comparison with Sample 101 (containing no compound), Sample 102 (containing comparative Compound A) and Sample 103 (containing Comparative Compound B) in the case of no incubation. Further, with Samples 104 to 112, the decrease in maximum image density ($D_{max}$) and the increase in minimum image density ($D_{min}$) due to the incubation are less in comparison with Sample 101 (containing no compound).

Further, each of Compounds (1), (4), (5), (7), (9), (13) or (14) according to the present invention were added to the third and fourth layers of test materials and color printing paper samples were prepared in the same manner as the preparation of Sample 101. These samples were incubated under the same conditions as above then exposed and developed in the same manner as above, and similar results were obtained.

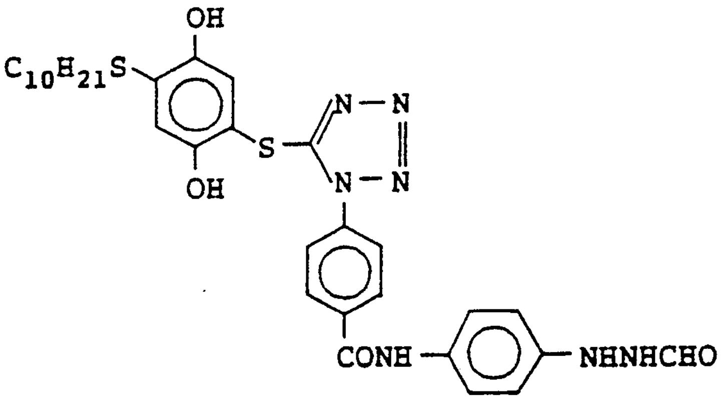
Moreover, each of Compounds (2), (4), (8), (11) or (14) according to the present invention were added to the eleventh and twelfth layers of test materials and color printing paper samples were prepared in the same manner as above. Similar results were obtained.

From the above results, it is evident that: (i) maximum image density is increased, and (ii) storage stability is improved by the addition of compounds according to the present invention to direct positive color photographic materials.

Comparative Compound A: (described in JP-A-59-170840)



Comparative Compound B: (described in JP-A-60-107029)



## EXAMPLE 2

Color printing paper samples were prepared in the same manner as in Example 1, except the nucleating agent ExZK-1 was eliminated from each of the light-sensitive layers. The samples were subjected to incubation, exposure to light and processing in the same manner as described in Example 1. During color development, 15 seconds after the initiation of the development, fogging exposure was conducted for a period of 10 seconds (0.5 lux on the surface of the photographic material processed, with color temperature of 5400° K).

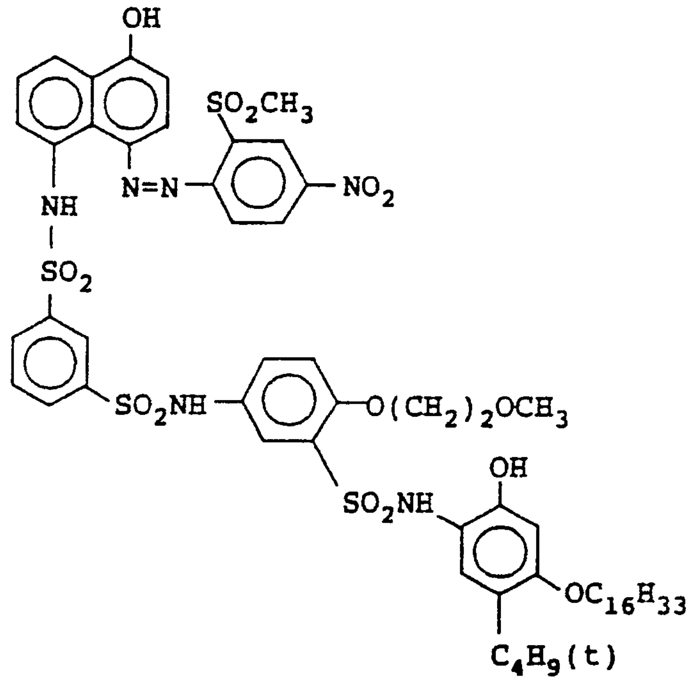
Results similar to those in Example 1 were obtained.

## EXAMPLE 3

The following Layers (1) to (11) were coated on a black support in order to prepare a light-sensitive sheet.

(1) Layer containing the following Cyan DRR Compound (0.36 mmol/m$^2$), tricyclohexyl phosphate (0.09 g/m$^2$), 2,5-di(tert-pentadecyl)hydroquinone (0.01 g/m$^2$) and gelatin (0.44 g/m$^2$).

Cyan DRR Compound:



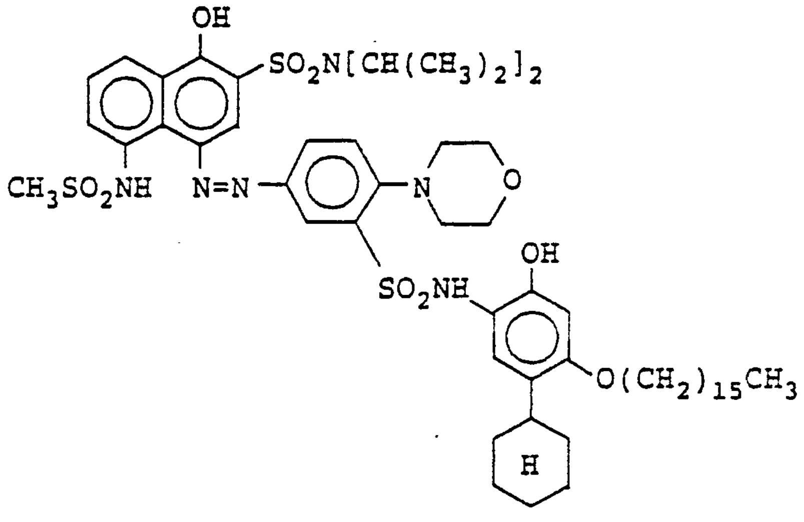
(2) Layer containing a red-sensitive internal latent image type direct reversal silver bromide emulsion (Emulsion A which is similar to the Emulsion EM-1 of Example 1) containing Red-sensitive Sensitizing Dye described in Example 1) (0.5 g/m$^2$ as silver), gelatin (0.78 g/m$^2$), Nucleating Agent N-II-11 (27 $\mu$g/m$^2$) and sodium pentadecylhydroquinone sulfonate (0.06 g/m$^2$).

(3) Layer containing 2,5-di(tert-pentadecyl)hydroquinone (0.71 g/m$^2$), vinylpyrrolidone/vinyl acetate copolymer (7/3, by molar ratio) (0.24 g/m$^2$) and gelatin (0.4 g/m$^2$).

(4) Layer containing gelatin (0.3 g/m$^2$).

(5) Layer containing the following Magenta DRR Compound (0.49 g/m$^2$), tricyclohexyl phosphate (0.08 g/m$^2$), 2,5-di(tert-pentadecyl)hydroquinone (0.01 g/m$^2$ and gelatin (0.5 g/m$^2$).

Magenta DRR Compound:



(6) Layer containing a green-sensitive internal latent image type direct reversal silver bromide

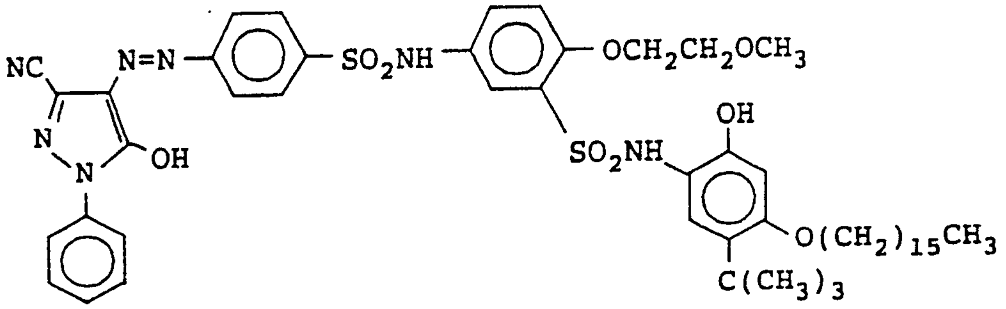
emulsion (Emulsion A which is similar to the Emulsion EM-1 of Example 1 containing Green-sensitive Sensitizing Dye described in Example 1) (0.34 g/m$^2$ as silver), gelatin (0.66 g/m$^2$ , the same nucleating agent as Layer (2) (12.9 µg/m$^2$) and sodium pentadecylhydroquinonesulfonate (0.04 g/m$^2$).

(7) Layer containing 2,5-di(tert-pentadecyl)hydroquinone (0.71 g/m$^2$), vinylpyrrolidone/vinyl acetate copolymer (7/3, by molar ratio) (0.24 g/m$^2$) and gelatin (0.4 g/m$^2$).

(8) Layer containing gelatin (0.25 g/m$^2$).

(9) Layer containing the following Yellow DRR Compound (0.48 g/m$^2$), tricyclohexyl phosphate (0.03 g/m$^2$ , 2,5-di(tert-pentadecyl)hydroquinone (0.004 g/m$^2$) and gelatin (0.43 g/m$^2$).

Yellow DRR Compound:



(10) Layer containing a blue-sensitive internal latent image type direct reversal silver bromide emulsion (Emulsion A containing Blue-sensitive Sensitizing Dye described in Example 1) (0.84 g/m$^2$ as silver), gelatin (0.9 g/m$^2$), the same nucleating agent as Layer (2) (29 mg/m$^2$) and sodium pentadecylhydroquinonesulfonate (0.05 g/m$^2$).

(11) Layer containing gelatin (1.0 g/m$^2$).

A processing solution (0.8 g) having the following composition was put in a container capable of being ruptured under pressure.

| Processing Solution : | |
|---|---|
| Benzyl Alcohol | 0.2 ml |
| 1-(p-Tolyl)-4-hydroxymethyl-4-methyl-3-pyrazolidinone | 0.3 g |
| Methylhydroquinone | 0.012 g |
| 5-Methylbenzotriazole | 0.6 g |
| Sodium Sulfite | 0.18 g |
| Hydroxymethyl Cellulose | 4 g |
| Potassium Hydroxide (28% aqueous solution) | 22.4 ml |
| Water | 67 ml |

The following Layers (12) to (16) were coated in order on the surface of a white support the opposite surface of which had been coated with a carbon black layer and a titanium white layer in order, to prepare a dye image receiving sheet.

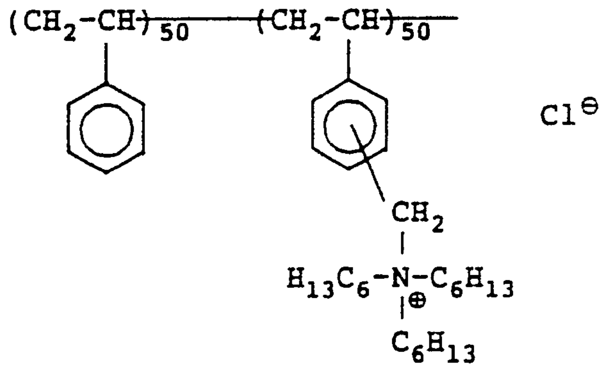
(12) Layer containing acrylic acid/butyl acrylate copolymer (80/20, by weight) (22 g/m$^2$) and 1,4-bis-(2,3-epoxypropoxy)butane (0.44 g/m$^2$).

(13) Layer containing acetyl cellulose (capable of providing 39.4 g of acetyl group by hydrolysis of 100 g of acetyl cellulose) (3.8 g/m$^2$), styrene/maleic anhydride copolymer (60/40, by weight; molecular weight, about 50,000) (0.2 g/m$^2$) and 5-(β-cyanoethylthio)-1-phenyltetrazole (0.115 g/m$^2$).

(14) Layer containing vinylidene chloride/methyl acrylate/acrylic acid copolymer latex (85/12/3), by weight) (3.5 g/m$^2$) and polymethyl methacrylate latex (grain size, 1 to 3 µm) (0.05 g/m$^2$).

(15) Mordant layer containing the following mordanting agent (3.0 g/m$^2$) and gelatin (3.0 g/m$^2$).

Mordanting Agent:



(16) Layer containing phthalated gelatin (1 g/m²).

The above described light-sensitive sheet was designated Sample 301. Other samples were prepared in the same manner as the preparation of the Sample 301, except that the comparative Compound B described in Example 1 or a compound according to the present invention was added to Layer (2) in an amount of $1 \times 10^{-5}$ mol per mol of silver as indicated in Table 3 below.

The thus-prepared samples were incubated in an atmosphere of 40 °C and 80% RH for 3 days and then exposed to light. The thus-exposed samples were super posed on the above described dye image receiving sheet in face-to-face relation and the above described processing solution was spread therebetween in a thickness of 60 µm by the use of a pressing means. Thus transferred color images were obtained.

The maximum cyan image density obtained was measured for every sample. The results obtained are shown in Table 3 below.

TABLE 3

| | | $D_{max}$ | | |
|---|---|---|---|---|
| Sample No. | Compound | Before Incubation | After Incubation | Remarks |
| 301 | none | 2.2 | 1.5 | Comparison |
| 302 | Comparative Compound B | 2.4 | 2.2 | " |
| 303 | (1) | 2.5 | 2.4 | Present Invention |
| 304 | (2) | 2.5 | 2.4 | " |
| 305 | (4) | 2.6 | 2.5 | " |
| 306 | (8) | 2.5 | 2.4 | " |
| 307 | (13) | 2.7 | 2.5 | " |
| 308 | (15) | 2.4 | 2.3 | " |

The results obtained are similar to those in Example 1.

Further, a compound of the invention was added to the sixth layer or the tenth layer and the same experiment was repeated using the respective samples. Similar results were obtained.

## EXAMPLE 4

Core/shell type emulsions I, II and III were prepared in accordance with the methods described below.

Emulsion I:

An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to an aqueous solution of gelatin with vigorous stirring over a period of about 20 minutes, while the pAg value of the reaction system was controlled to 7.90 at 40° C. A cubic monodispersed silver bromide emulsion having an average grain size of 0.08 µm was obtained. To the emulsion were added sodium thiosulfate and chloroauric acid (tetra-hydrate) each in an amount of 580 mg per mol of silver, and the emulsion was heated at 75° C for 80 minutes to effect chemical sensitization. The thus-obtained silver bromide grains, as cores, were further grown under the same precipitation conditions as in the first step to obtain a core/shell type monodispersed cubic silver bromide emulsion having an average grain size of 0.18 µm. After washing with water and desalting, sodium thiosulfate and chloroauric acid (tetra-hydrate) were added to the emulsion each in an amount of 6.2 mg per mol of silver and the emulsion was heated for 60 minutes at 65° C to effect chemical sensitization. Thus Emulsion I was obtained.

Emulsion II:

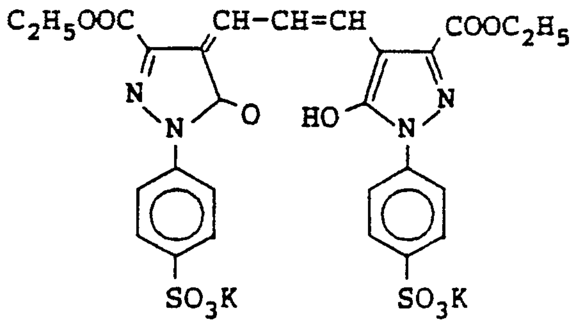
An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to an aqueous solution of gelatin with vigorous stirring over a period of about 40 minutes, while the pAg value of the reaction system was controlled to 9.70 at 45° C. An octahedral silver bromide emulsion having an average grain size of 0.2 µm was obtained. To the emulsion were added sodium thiosulfate and chloroauric acid (tetrahydrate) each in an amount of 5 mg per mol of silver, and the emulsion was heated at 75° C for 80 minutes to effect chemical sensitization. The thus-obtained silver bromide grains, as cores, were grown for a further 40 minutes under the same precipitation conditions as in the first step to obtain a core/shell type monodispersed octahedral silver bromide emulsion having an average grain size of 0.35 µm. To the emulsion were added sodium thiosulfate and chloroauric acid (tetrahydrate) each in an amount of 4.5 mg per mol of silver, and the emulsion was heated for 60 minutes at 65° C to effect chemical sensitization. Thus an internal latent image type silver halide emulsion (Emulsion II) was obtained.

Emulsion III:

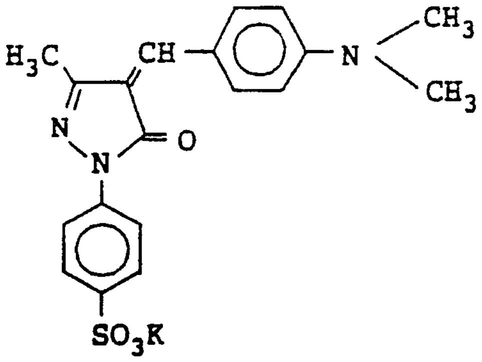
An aqueous solution of potassium bromide and an aqueous solution of silver nitrate were simultaneously added to an aqueous solution of gelatin with vigorous stirring over a period of about 40 minutes, while the pAg value of the reaction system was controlled to 8.60 at 75° C. An octahedral monodispersed silver bromide emulsion having an average grain size of 0.4 µm was obtained. To the emulsion were added sodium thiosulfate and chloroauric acid (tetra-hydrate) each in an amount of 4 mg per mol of Ag, and the emulsion was heated at 75° C for 80 minutes to effect chemical sensitization. The thus-obtained silver bromide grains, as cores, were grown for a further 40 minutes under the same precipitation conditions as in the first step to obtain a core/shell type monodispersed octahedral silver bromide emulsion having an average grain size of 0.6 µm. After washing with water and desalting, sodium thiosulfate was added to the emulsion in an amount of 0.9 mg per mol of silver, and the emulsion was heated for 60 minutes at 65° C to effect chemical sensitization. Thus an internal latent image type silver halide emulsion (Emulsion III) was obtained.

On a 100 µm thick polyethylene terephthalate film support having a subbing layer were coated an anti-halation layer (lower layer) composed of Anti-halation Dyes (A), (B) and (C) (65 mg/m$^2$, 80 mg/m$^2$ and 40 mg/m$^2$, respectively) and gelatin (5 g/m$^2$), and a protective layer (upper layer) composed of barium strontium sulfate (average grain size 1.0 um) (0.1 g/m$^2$) and polymethyl methacrylate (average grain size 1.3 µm) (0.07 g/m$^2$), as matting agents, Coating Aid (D) (30 mg/m$^2$), Antistatic Agent (E) (1 mg/m$^2$), Hardening Agent (F), (100 mg/m$^2$) and gelatin (1 g/m$^2$ to prepare a two-layered backing layer.

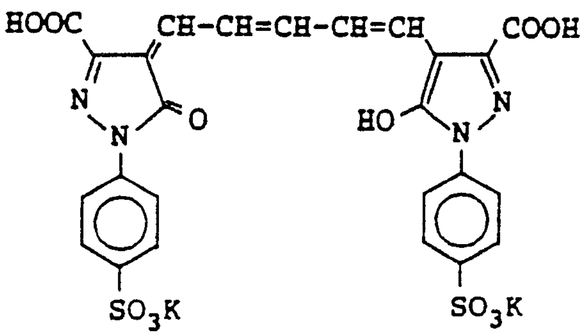
Dye (A):


C2H5OOC
CH-CH=CH
COOC2H5
N
N
O
HO
N
N
SO3K
SO3K

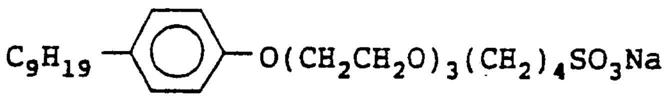
Dye (B):


H3C
CH
N
CH3
CH3
N
N
O
SO3K

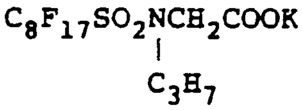
Dye (C):



Coating Aid (D):



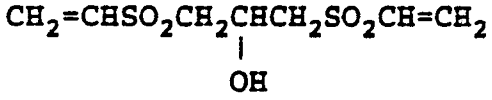
Antistatic Agent (E):



$C_8F_{17}SO_2\underset{\substack{|\\C_3H_7}}{N}CH_2COOK$

Megafac F-120 (manufactured by Dai Nippon Ink and Chemical Co., Ltd.)

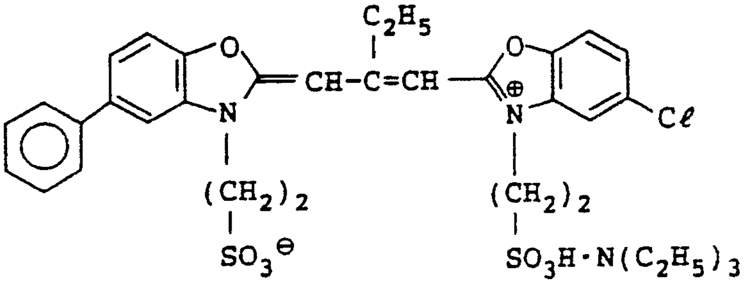
Hardening Agent (F):



$CH_2{=}CHSO_2CH_2\underset{\substack{|\\OH}}{C}HCH_2SO_2CH{=}CH_2$

Sensitizing Dye (G) was added to Core/shell Emulsions I, II and III, in an amount of 150 mg, 200 mg and 180 mg, respectively, per mol of silver, and Nucleating Agent (N-II-1) was also added in an amount of $1.0\times10^{-3}$ mol per mol of silver. Further, sodium dodecylbenzenesulfonate as a coating aid and a viscosity increasing agent were added so as to balance the surface tension and the viscosity. Thus coating compositions for a first, second, and third layer were prepared.

Sensitizing Dye (G):



Antistatic agent (E), sodium dodecylbenzenesulfonate (coating aid) and a viscosity increasing agent were added to gelatin to prepare a coating composition for a fourth layer (protective layer).

The thus-prepared coating compositions for the first to fourth layers were coated in order on the above described support on the surface opposite to that coated with the backing layer. The amount of silver halide in the first layer was 1 g/m$^2$ (as silver); that in the second layer was 0.8 g/m$^2$ (as silver); and that in the third layer was 1.5 g/m$^2$ (as silver). The amount of gelatin in the first layer was 1.3 g/m$^2$; that in the second layer was 1.3 g/m$^2$; that in the third layer was 2.4 g/m$^2$; and that in the fourth layer was 1.7 g/m$^2$. Thus a direct positive photographic material (Sample 401) was prepared.

Other samples were prepared in the same manner as in the preparation of Sample 401, except that the Comparative Compound B described in Example 1 or a compound according to the present invention was added to the emulsion layer in an amount of $1 \times 10^{-4}$ mol per mol of silver, as shown in Table 4 below.

The thus-prepared samples were exposed with a 1 kw tungsten lamp (color temperature: 2854° K) for one second through a step wedge and then developed by an automatic developing machine (FMCP-4800 Type Camera Processor manufactured by Fuji Photo Film Co., Ltd.) using Developer (D) which was prepared by mixing the following Replenisher (A) (one liter) and Starter (B) (20 ml), at 36° C for one minute. After development, the samples were stopped, fixed, washed with water and then dried in a conventional manner. The maximum density ($D_{max}$) and the minimum density ($D_{min}$) of the image formed in each sample were measured. The results obtained are shown in Table 4 below.

| Replenisher (A) : | |
|---|---|
| Sodium sulfite | 100 g |
| Potassium carbonate | 20 g |
| 1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone | 3 g |
| Hydroquinone | 45 g |
| 5-Methylbenzotriazole | 40 mg |
| Water to make | 1 liter |
| Potassium hydroxide to adjust | pH of 11.8 |
| Starter (B) : | |
| Sodium bromide | 175 g |
| Glacial acetic acid | 63 ml |
| Water to make | 1 liter |

As is apparent from Table 4 below, the compounds according to the present invention were advantageous since they were effective in increasing $D_{max}$ without increasing $D_{min}$ as compared with the comparative samples.

TABLE 4

| Sample No. | Compound | $D_{max}$ | $D_{min}$ | Remarks |
|---|---|---|---|---|
| 401 | none | 2.82 | 0.15 | Comparison |
| 402 | Comparative Compound B | 2.92 | 0.17 | " |
| 403 | (2) | 3.12 | 0.15 | Present Invention |
| 404 | (4) | 3.26 | 0.15 | " |
| 405 | (5) | 3.24 | 0.15 | " |
| 406 | (10) | 3.23 | 0.15 | " |
| 407 | (12) | 3.27 | 0.17 | " |
| 408 | (14) | 3.11 | 0.16 | " |

## EXAMPLE 5

An aqueous solution of silver nitrate and an aqueous solution of potassium bromide were simultaneously added to an aqueous solution of gelatin (pH 5.5, 75 °C) containing 20 mg/liter of thioether(1,8-dihydroxy-3,6-dithiaoctane) at a constant rate with thorough stirring, while the silver electrode potential was kept such that regular octahedral grains could grow. 1/8 Mol of silver nitrate was added over a period of 5 minutes. Thus an octahedral monodispersed silver bromide emulsion having an average grain size of about 0.14 μm was obtained. Sodium thiosulfate and chloroauric acid (tetra-hydrate) were added to the emulsion each in an amount of 20 mg per mol of the silver halide and it was thoroughly stirred at pH 7.5 at 75 °C for 80 minutes to effect chemical sensitization. A core emulsion was obtained. Afterward an aqueous solution of silver nitrate (containing 7/8 mol of silver nitrate) and an aqueous solution of potassium bromide were added to the emulsion simultaneously at the same temperature as above over a period of 40 minutes with thorough stirring, whereupon the silver electrode potential was kept such that regular octahedral grains could grow, so that the cores were coated with shells. Thus a monodispersed octahedral core/shell type emulsion having an average grain size of about 0.3 μm was obtained. The thus-prepared emulsion was washed with water and desalted in a conventional manner, and then melted under heat. After the pH value of the emulsion was adjusted to 6.5, sodium thiosulfate and chloroauric acid (tetra-hydrate) were added thereto each in an amount of 5 mg per mol of the silver halide and the emulsion was ripened for 60 minutes at 95 °C whereby the shell surfaces were chemically sensitized. Thus an internal latent image type monodispersed octahedral core/shell emulsion (Emulsion X) was obtained. The grain size distribution of the emulsion was measured from an electro-microscopic photograph. The average grain size was 0.30 μm and the coefficient of variation (average grain size × 100/standard deviation) was 10%.

A panchromatic sensitizing dye (3,3′-diethyl-9-methylthiacarbocyanine) was added to the emulsion in an amount of 5 mg per mol of the silver halide, and then Nucleating Agent (N-II-4) ($1.0 \times 10^{-5}$ mol per mol of silver halide) and Nucleation Accelerating Agent (A-16) ($1 \times 10^{-3}$ mol per mol of silver halide) were added thereto. The resulting composition was coated on a polyethylene terephthalate film support in an amount of 2.8 $g/m^2$ as silver, and a protective layer containing gelatin and a hardening agent was simultaneously coated thereover. Thus a direct positive photographic material sensitive to red light (Sample 501) was prepared.

Other samples were prepared in the same manner as in the preparation of Sample 501, except that Comparative Compound B as described in Example 1 or a compound according to the present invention was added to the emulsion layer in an amount of $1 \times 10^{-4}$ mol per mol of silver, as shown in Table 5 below.

The thus prepared light-sensitive materials were wedgewise exposed using a sensitometer with a 1 kw tungsten lamp (color temperature: 2854 °K) for 0.1 second through a step-wedge. Then, the thus exposed samples were developed with an automatic developing machine (Kodak Proster I Processor) using Kodak Proster Plus processing solution (developing solution: pH 10.7) at 38 °C for 18 seconds and successively with the developing machine washed with water, fixed, washed with water and dried. The maximum density ($D_{max}$) and the minimum density ($D_{min}$) of the direct positive image formed in each sample were measured. The results obtained are shown in Table 5 below.

TABLE 5

| Sample No. | Compound | $D_{max}$ | $D_{min}$ | Remarks |
|---|---|---|---|---|
| 501 | none | 2.62 | 0.06 | Comparison |
| 502 | Comparative Compound B | 2.68 | 0.07 | " |
| 503 | (1) | 2.78 | 0.07 | Present Invention |
| 504 | (3) | 2.76 | 0.07 | " |
| 505 | (4) | 2.85 | 0.07 | " |
| 506 | (9) | 2.83 | 0.07 | " |
| 507 | (13) | 2.87 | 0.07 | " |

As is apparent from the results shown in Table 5 above, the compounds according to the present invention (Samples 503 to 507) are advantageous since they are effective for increasing the $D_{max}$ value without increasing the $D_{min}$ value, as compared with the comparative sample (Sample 502).

## EXAMPLE 6

### Preparation of Sample 601:

The layers having the compositions described below were coated in order on a cellulose triacetate film support having a subbing layer to prepare a multi-layer color photographic material (Sample 601).

The amounts of the respective components are represented in units of g/m$^2$, and the amount of the silver halide is indicated as an amount of silver therein. The amount of the sensitizing dye is represented in units of mol per mol of the silver halide present in the layer.

| First Layer : Antihalation Layer | |
|---|---|
| Black colloidal silver | 0.18 as Ag |
| Gelatin | 0.40 |

| Second Layer : Interlayer | |
|---|---|
| 2,5-Di-tert-pentadecylhydroquinone | 0.18 |
| EX-1 | 0.07 |
| EX-3 | 0.02 |
| EX-11 | 0.005 |
| U-1 | 0.08 |
| U-2 | 0.08 |
| HBS-1 | 0.10 |
| HBS-2 | 0.02 |
| Gelatin | 1.04 |

| Third Layer : First Red-sensitive Emulsion Layer | |
|---|---|
| Silver iodobromide emulsion (silver iodide: 6 mol%, average grain size: 0.70 μm) | 0.55 as Ag |
| Sensitizing Dye I | $6.9\times10^{-5}$ |
| Sensitizing Dye II | $1.8\times10^{-5}$ |
| Sensitizing Dye III | $3.1\times10^{-4}$ |
| Sensitizing Dye IV | $4.0\times10^{-5}$ |
| EX-2 | 0.350 |
| HBS-1 | 0.005 |
| EX-10 | 0.042 |
| Gelatin | 1.20 |

| Fourth Layer : Second Red-sensitive Emulsion Layer | |
|---|---|
| Silver iodobromide emulsion (silver iodide: 8 mol%, average grain size: 0.75 μm) | 1.20 as Ag |
| Sensitizing Dye I | $5.1\times10^{-5}$ |
| Sensitizing Dye II | $1.4\times10^{-5}$ |
| Sensitizing Dye III | $2.3\times10^{-4}$ |
| Sensitizing Dye IV | $3.0\times10^{-5}$ |
| EX-2 | 0.300 |
| EX-3 | 0.050 |
| EX-10 | 0.004 |
| HBS-2 | 0.050 |
| Gelatin | 1.30 |

| Fifth Layer : Third Red-sensitive Emulsion Layer | |
|---|---|
| Silver iodobromide emulsion (silver iodide: 14 mol%, average grain size: 1.00 μm) | 1.60 as Ag |
| Sensitizing Dye IX | $5.4\times10^{-5}$ |
| Sensitizing Dye II | $1.4\times10^{-5}$ |
| Sensitizing Dye III | $2.4\times10^{-4}$ |
| Sensitizing Dye IV | $3.1\times10^{-5}$ |
| EX-5 | 0.150 |
| EX-3 | 0.055 |
| EX-4 | 0.060 |
| HBS-1 | 0.32 |
| Gelatin | 1.63 |

| Sixth Layer : Interlayer | |
|---|---|
| HBS-3 | 0.01 |
| Gelatin | 1.06 |
| EX-14 | 0.02 |

| Seventh Layer : First Green-sensitive Emulsion Layer | |
|---|---|
| Silver iodobromide emulsion (silver iodide: 6 mol%, average grain size: 0.65 µm) | 0.40 as Ag |
| Sensitizing Dye V | $3.0 \times 10^{-5}$ |
| Sensitizing Dye VI | $1.0 \times 10^{-4}$ |
| Sensitizing Dye VII | $3.8 \times 10^{-4}$ |
| EX-6 | 0.260 |
| EX-1 | 0.021 |
| EX-7 | 0.030 |
| EX-8 | 0.025 |
| HBS-1 | 0.100 |
| HBS-4 | 0.060 |
| Gelatin | 0.75 |

| Eighth Layer : Second Green-sensitive Emulsion Layer | |
|---|---|
| Silver iodobromide emulsion (silver iodide: 9 mol%, average grain size: 0.70 µm) | 0.80 as Ag |
| Sensitizing Dye V | $2.1 \times 10^{-5}$ |
| Sensitizing Dye VI | $7.0 \times 10^{-5}$ |
| Sensitizing Dye VII | $2.6 \times 10^{-4}$ |
| EX-6 | 0.150 |
| EX-8 | 0.010 |
| EX-1 | 0.008 |
| EX-7 | 0.012 |
| HBS-1 | 0.60 |
| HBS-4 | 0.050 |
| Gelatin | 0.10 |

| Ninth Layer : Third Green-sensitive Emulsion Layer | |
|---|---|
| Silver iodobromide emulsion (silver iodide: 12 mol%, average grain size: 1.0 µm) | 1.2 as Ag |
| Sensitizing Dye V | $3.5 \times 10^{-5}$ |
| Sensitizing Dye VI | $8.0 \times 10^{-5}$ |
| Sensitizing Dye VII | $3.0 \times 10^{-4}$ |
| EX-6 | 0.065 |
| EX-1 | 0.025 |
| HBS-2 | 0.55 |
| Gelatin | 1.74 |

| Tenth Layer : Yellow Filter Layer | |
|---|---|
| Yellow colloidal silver | 0.05 as Ag |
| EX-14 | 0.04 |
| HBS-1 | 0.02 |
| Gelatin | 0.95 |

| Eleventh Layer : First Blue-sensitive Emulsion Layer | |
|---|---|
| Silver iodobromide emulsion (silver iodide: 6 mol%, average grain size: 0.6 µm) | 0.24 as Ag |
| Sensitizing Dye VIII | $3.5 \times 10^{-4}$ |
| EX-9 | 0.85 |
| EX-8 | 0.12 |
| HBS-1 | 0.28 |
| Gelatin | 1.28 |

| Twelfth Layer : Second Blue-sensitive Emulsion Layer | |
|---|---|
| Silver iodobromide emulsion (silver iodide: 10 mol%, average grain size: 0.80 µm) | 0.45 as Ag |
| Sensitizing Dye VIII | $2.1 \times 10^{-4}$ |
| EX-9 | 0.20 |
| EX-8 | 0.015 |
| HBS-1 | 0.03 |
| Gelatin | 0.46 |

| Thirteenth Layer : Third Blue-sensitive Emulsion Layer | |
|---|---|
| Silver iodobromide emulsion (silver iodide: 16 mol%, average grain size: 1.2 µm) | 0.77 as Ag |
| Sensitizing Dye VIII | $2.2 \times 10^{-4}$ |
| EX-9 | 0.20 |
| HBS-1 | 0.07 |
| Gelatin | 0.69 |

| Fourteenth Layer : First Protective Layer | |
|---|---|
| Silver iodobromide emulsion (silver iodide: 1 mol%, average grain size: 0.07 µm) | 0.08 as Ag |
| U-1 | 0.11 |
| U-2 | 0.17 |
| HBS-1 | 0.90 |
| Gelatin | 1.00 |

| Fifteenth Layer : Second Protective Layer | |
|---|---|
| Polymethyl methacrylate particles (diameter: about 1.5 µm) | 0.54 |
| S-1 | 0.04 |
| S-2 | 0.04 |
| Gelatin | 0.72 |

In addition to the above described components, a gelatin hardening agent (H-1) and a surface active agent were added to the respective layers.

Preparation of Samples 602 to 613:

Samples 602 to 613 were prepared in the same manner as the preparation of the Sample 601, except that a compound according to the present invention or Comparative Compound A or B as described in Example 1 was added to the thirteenth layer in an amount of $5\times10^{-5}$ mol per mol of silver as shown in Table 6 below.

Several of these samples were preserved in a refrigerator for 7 days and several others were stored under the conditions of 40°C and 80% RH for 7 days. Then all samples were sensitometrically exposed with a white light and subjected to color development processing in accordance with the steps described below. The density of the thus-processed samples was measured with a blue light. The results obtained are shown in Table 6 below.

The color development processing was effected in accordance with the following steps at 38°C.

| | |
|---|---|
| Color Development | 3 min. 15 sec. |
| Bleaching | 6 min. 30 sec. |
| Washing with Water | 2 min. 10 sec. |
| Fixing | 4 min. 20 sec. |
| Washing with Water | 3 min. 15 sec. |
| Stabilizing | 1 min. 05 sec. |

The processing solutions used in the respective steps had the following compositions:

| Color Developing Solution : | |
|---|---|
| Diethylenetriaminepnetaacetic acid | 1.0 g |
| 1-Hydroxyethylidene-1,1-diphosphonic acid | 2.0 g |
| Sodium sulfite | 4.0 g |
| Potassium carbonate | 30.0 g |
| Potassium bromide | 1.4 g |
| Potassium iodide | 1.3 mg |
| Hydroxylamine sulfate | 2.4 g |
| 4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate | 4.5 g |
| Water to make | 1.0 liter |
| | pH 10.0 |

| Bleaching Solution : | |
|---|---|
| Ammonium ferric ethylenediaminetetraacetate | 100.0 g |
| Disodium ethylenediaminetetraacetate | 10.0 g |
| Ammonium bromide | 150.0 g |
| Ammonium nitrate | 10.0 g |
| Water to make | 1.0 liter |
| | pH 6.0 |

| Fixing Solution : | |
|---|---|
| Disodium ethylenediaminetetraacetate | 1.0 g |
| Sodium sulfite | 4.0 g |
| Ammonium thiosulfate aqueous solution (70%) | 175.0 ml |
| Sodium bisulfite | 4.6 g |
| Water to make | 1.0 liter |
| | pH 6.6 |

| Stabilizing Solution : | |
|---|---|
| Formalin (40%) | 2.0 ml |
| Polyoxyethylene-p-monononylphenylether (average polymerization degree 10) | 0.3 g |
| Water to make | 1.0 liter |

TABLE 6

| | | Samples Preserved in Refrigerator | | Samples stored under High Temperature and High Humidity conditions | | |
|---|---|---|---|---|---|---|
| Sample No. | Compound | Minimum density | Relative Sensitivity * | Minimum density | Relative Sensitivity * | Remarks |
| 601 | none | 0.50 | 100 | 0.50 | 98 | Comparison |
| 602 | Comparative Compound A | 0.52 | 105 | 0.53 | 102 | " |
| 603 | Comparative Compound B | 0.53 | 106 | 0.55 | 101 | " |
| 604 | (1) | 0.51 | 116 | 0.53 | 115 | Present Invention |
| 605 | (2) | 0.51 | 115 | 0.52 | 113 | " |
| 606 | (3) | 0.51 | 118 | 0.53 | 115 | " |
| 607 | (4) | 0.52 | 122 | 0.53 | 120 | " |
| 608 | (6) | 0.51 | 119 | 0.53 | 115 | " |
| 609 | (8) | 0.51 | 117 | 0.52 | 115 | " |
| 610 | (9) | 0.51 | 119 | 0.53 | 114 | " |
| 612 | (12) | 0.52 | 118 | 0.53 | 116 | " |
| 613 | (15) | 0.52 | 121 | 0.54 | 119 | " |

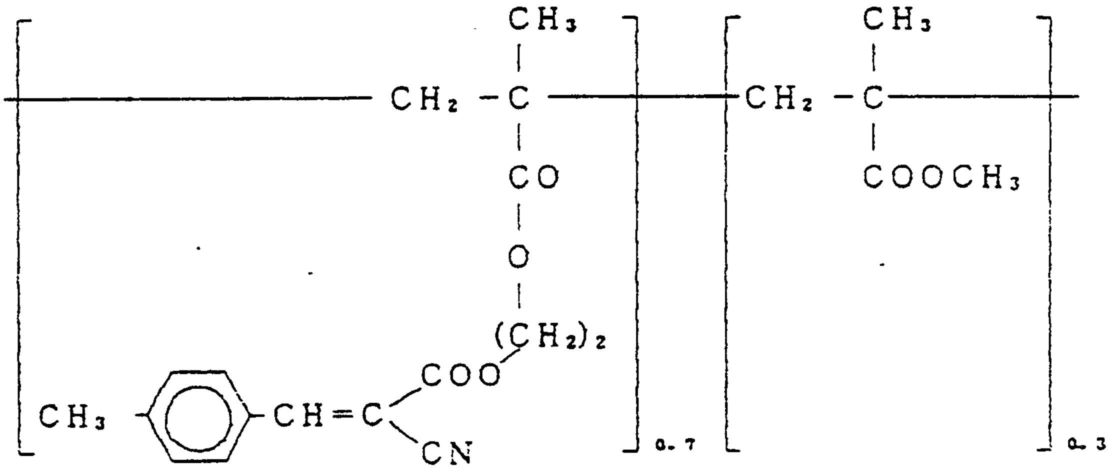
(*) Relative Sensitivity:

This corresponds to the reciprocal of an exposure amount giving a color density of (fog + 0.2), based on the standardized value (100) of Sample 601 stored in a refrigerator.

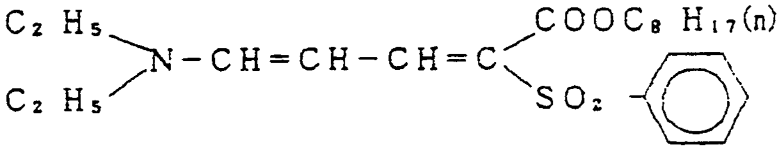
From the results shown in Table 6 above, it can be seen that the compounds according to the present invention (Samples 604 to 613) are effective for increasing sensitivity, while the fog level was almost same in both the samples of the present invention and the Comparative Samples (Samples 602 and 603).

The compounds used in Example 6 had the following structural formulae:

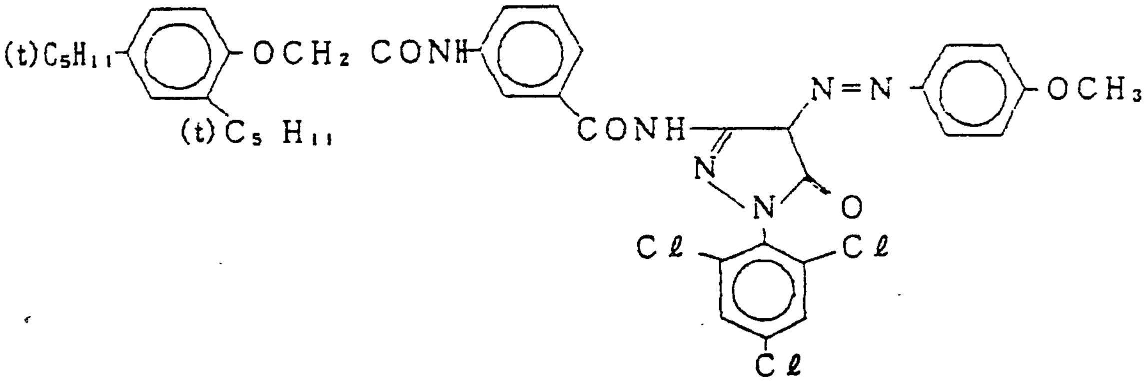
U-1



U-2



EX-1



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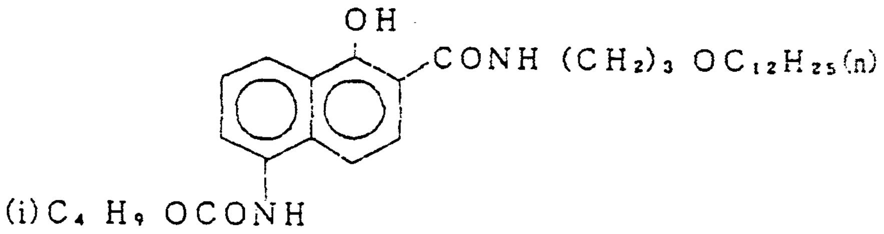

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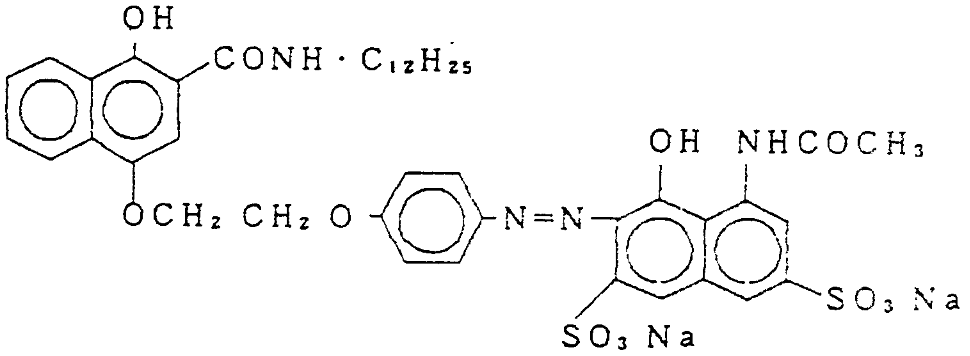
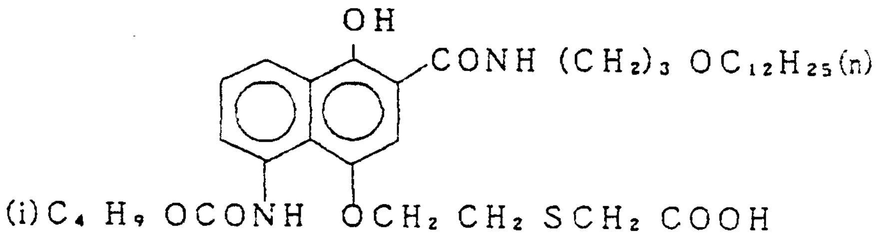


EX-4



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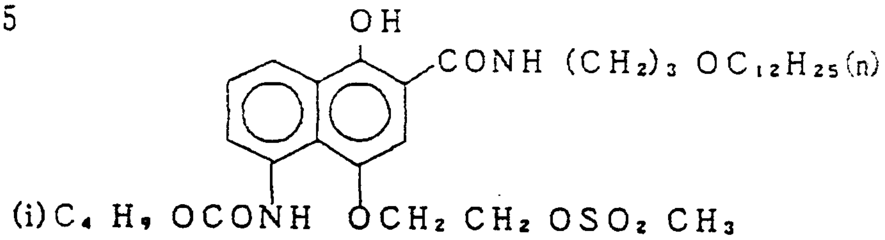
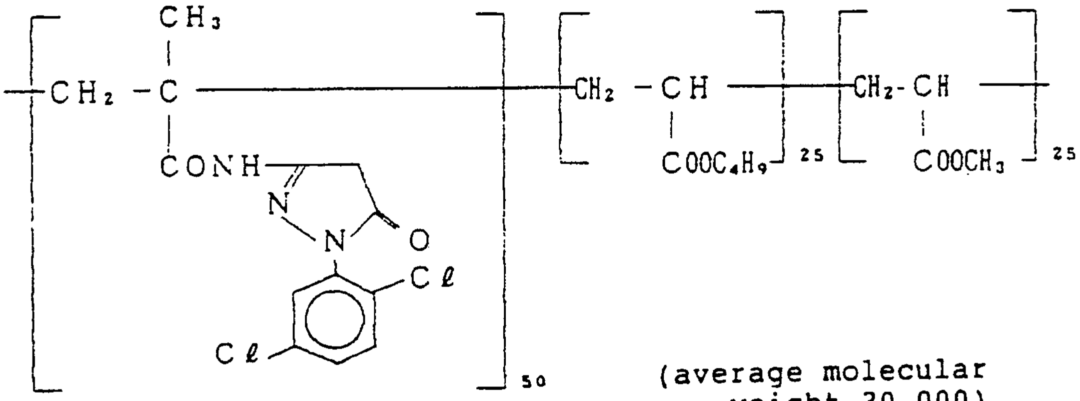
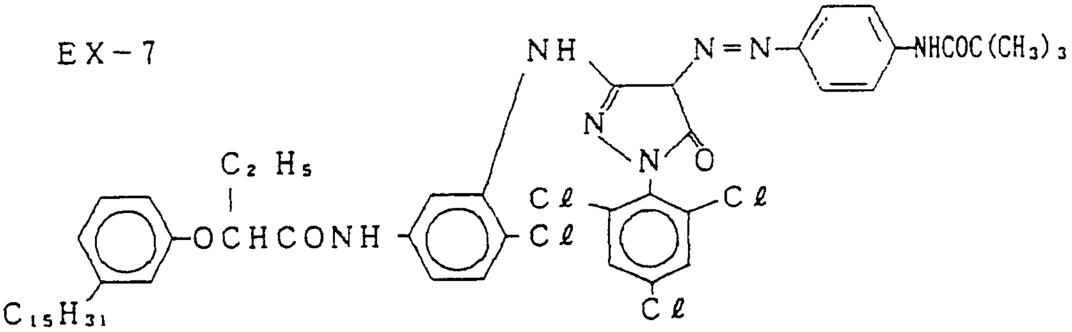


EX-6 (coupler included in JP-A-58-28745)

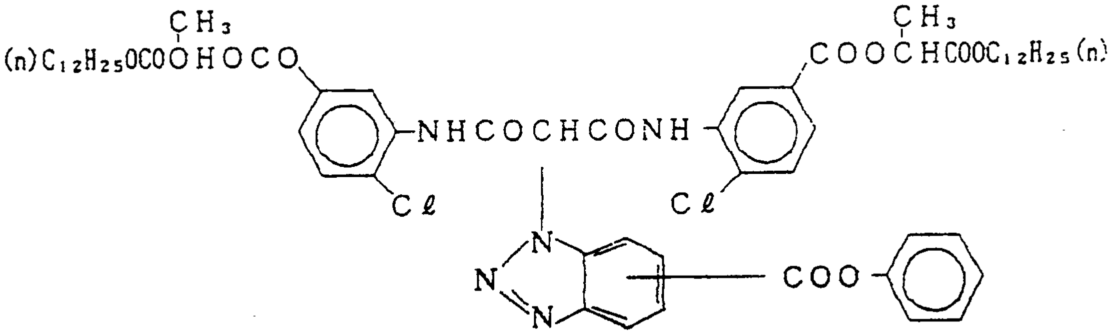


(average molecular weight 30,000)

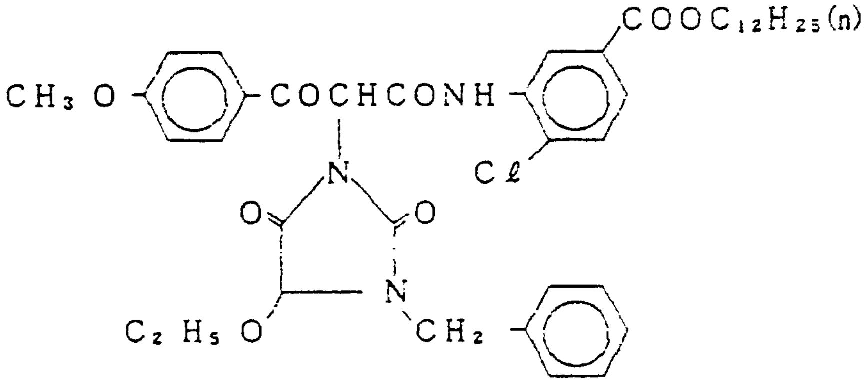
EX-7



EX-8



EX-9



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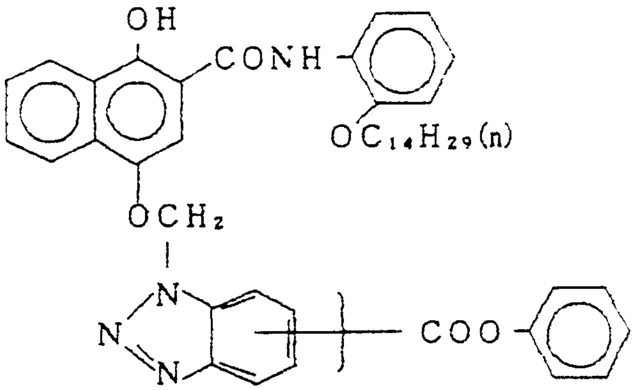

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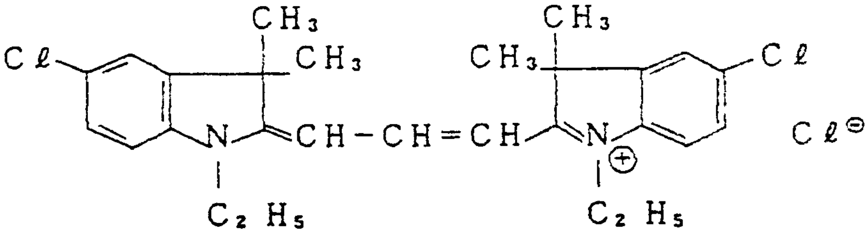
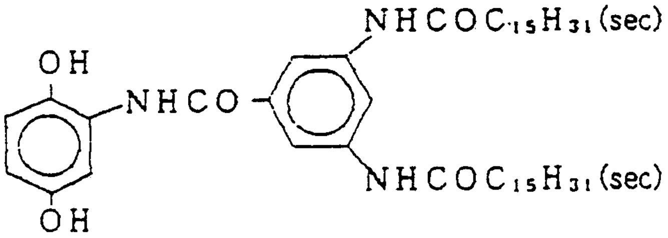


EX-14

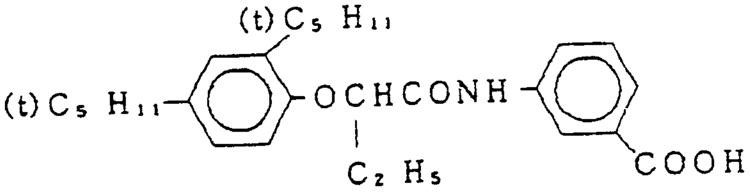


HBS-1 Tricresyl phosphate

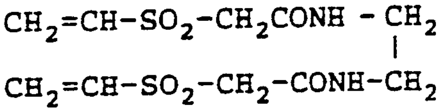
HBS-2 Dibutyl phthalate

HBS-3 Bis(2-ethylhexyl) phthalate

HBS-4

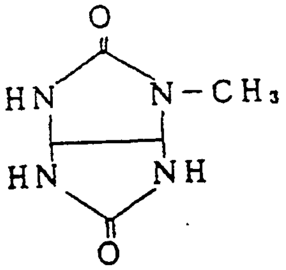


H-1

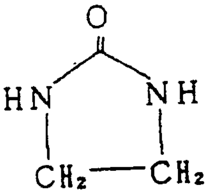


$$\begin{array}{l} CH_2{=}CH{-}SO_2{-}CH_2CONH - CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2 \end{array}$$

S-1

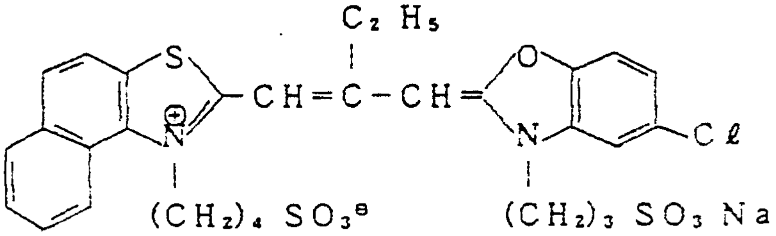


S-2



Sensitizing Dye

I



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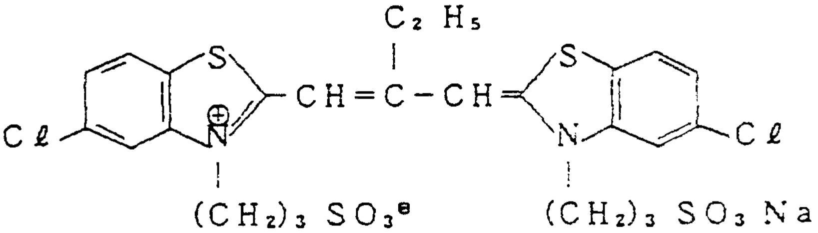

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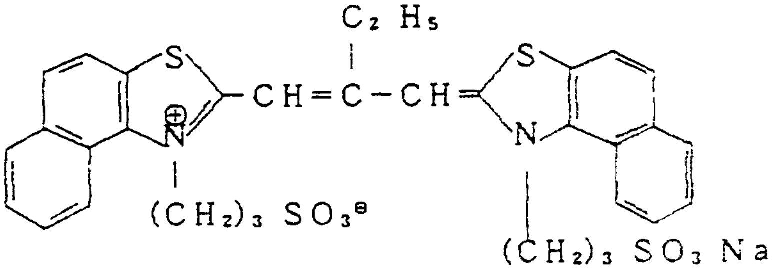

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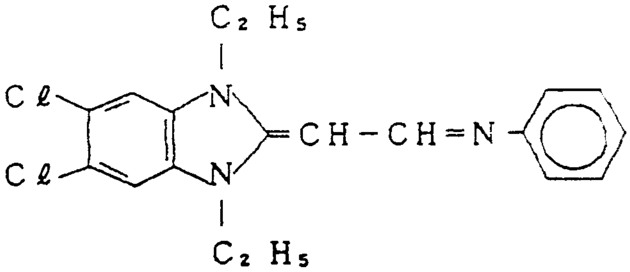
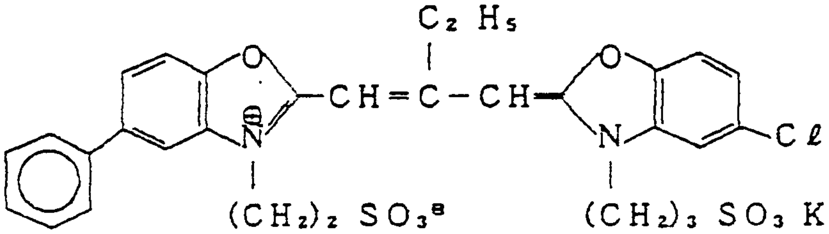


V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Cℓ
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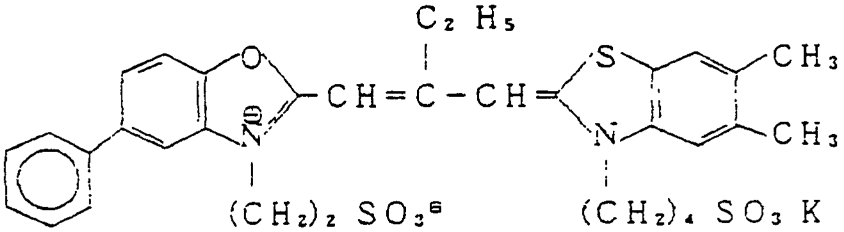
VI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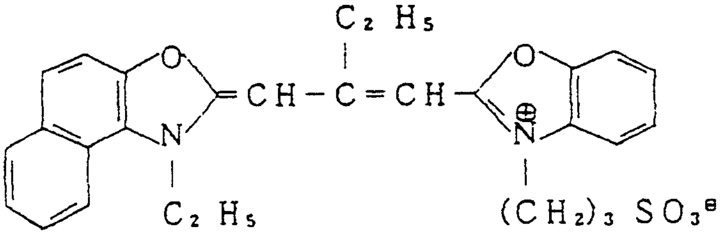
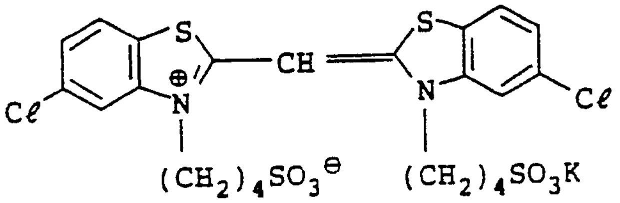
(CH₂)₄ SO₃ K

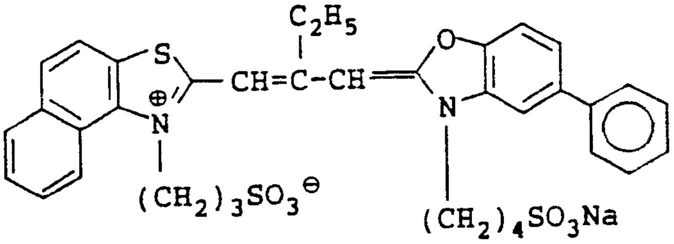
VII


C₂ H₅
O
=CH-C=CH
N
N⊕
C₂ H₅
(CH₂)₃ SO₃⊖

VIII



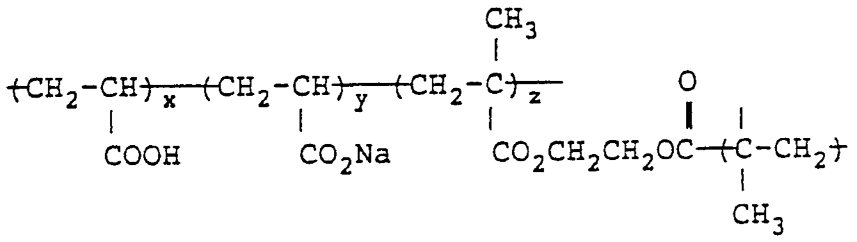
IX



## EXAMPLE 7

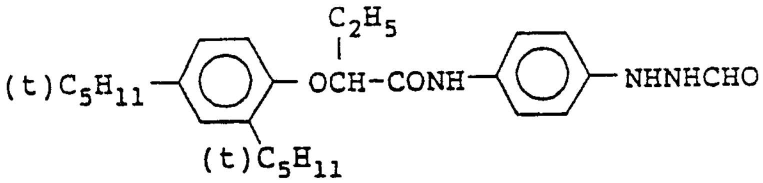
Potassium hexachloroiridium (III) ($4 \times 10^{-7}$ mol per mol of silver) was added to an aqueous gelatin solution kept at 50° C. An aqueous silver nitrate solution and an aqueous solution containing potassium iodide and potassium bromide were simultaneously added thereto over a period of 60 minutes in the presence of ammonia, while the pAg value of the reaction system was kept at 7.8. Thus a cubic monodispersed emulsion having an average grain size of 0.25 µm and an average silver iodide content of 1 mol% was obtained. To the silver iodobromide emulsion were added sodium 5,5′-dichloro-9-ethyl-3,3′-bis(3-sulfopropyl)oxacarbocyanine, as a sensitizing dye, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, as a stabilizer, a dispersion of polyethylacrylate, 1,3-vinylsulfonyl-2-propanol and Nucleating Agent N described below ($5 \times 10^{-3}$ mol per mol of silver), and then Acidic Polymer Latex H described below (400 mg/m$^2$) was further added thereto. Then the resulting composition was coated on a polyethylene terephthalate film in an amount of 3.4 g/m$^2$ as silver, to prepare a photographic material (Sample 701).

Acidic Polymer Latex H:



x:y:z =40:10:50

N:



Other samples were prepared in the same manner as the preparation of Sample 701, except that a compound according to the present invention or Comparative Compound B as described in Example 1 was added in an amount of $1 \times 10^{-2}$ mol per mol of silver as shown in Table 7 shown below.

The thus prepared samples were exposed and developed, and the photographic characteristics of the respective samples were determined. The development processing was effected with a developing solution having the composition described below, in an automatic developing machine (FG-660F type manufactured by Fuji Photo Film Co., Ltd.), at 38° C for 30 seconds.

| Developing Solution : | |
|---|---|
| Hydroquinone | 45.0 g |
| N-methyl-p-aminophenol 1/2-sulfate | 0.8 g |
| Sodium hydroxide | 18.0 g |
| Potassium hydroxide | 55.0 g |
| 5-Sulfosalicylic acid | 45.0 g |
| Boric acid | 25.0 g |
| Potassium sulfite | 110.0 g |
| Disodium ethylenediaminetetraacetate | 1.0 g |
| Potassium bromide | 6.0 g |
| 5-Methylbenzotriazole-n-butyldiethanolamine | 15.0 g |
| Water to make | 1 liter |
| | pH 11.6 |

In Table 7 below, the relative sensitivity is defined as the reciprocal of the exposure amount giving a density of 1.5 by development at 38° C for 30 seconds, based on the standardized value (100) of Sample 701.

The black spots were evaluated by microscopic observation by way of 5-stage evaluation, in which "5" means the best quality and "1" means the worst quality. The stages "5" and "4" indicate useful products; the stage "3" indicates rough but marginally useful products; and the stages "2" and "1" indicate unusable products. The intermediate between "4" and "3" was represented by "3.5".

TABLE 7

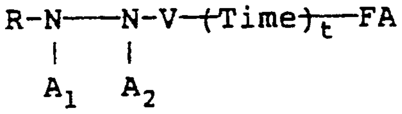
| Sample No. | Compound | Sensitivity | $\gamma$ | $D_{max}$ | Black spot | Remarks |
|---|---|---|---|---|---|---|
| 701 | none | 100 | 14 | 3.9 | 5.0 | Comparison |
| 702 | Comparative Compound B | 103 | 15 | 4.0 | 4.0 | " |
| 703 | (1) | 103 | 17 | 4.3 | 5.0 | Present Invention |
| 704 | (4) | 104 | 18 | 4.4 | 5.0 | " |
| 705 | (5) | 102 | 17 | 4.3 | 4.5 | " |
| 706 | (8) | 101 | 18 | 4.3 | 5.0 | " |
| 707 | (12) | 105 | 17 | 4.2 | 4.5 | " |

As is apparent from the results shown in Table 7, the compounds according to the present invention are advantageous in view of the increase in $D_{max}$ and $\gamma$ and the prevention of occurrence of black spot as compared with the comparative compound.

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 silver halide photographic material comprising a support having thereon at least one light-sensitive silver halide emulsion layer, wherein the silver halide photographic material contains at least one compound represented by the following general formula (I):

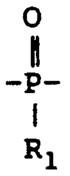


$$\underset{A_1}{\underset{|}{R-N}}-\underset{A_2}{\underset{|}{N}}-V-(Time)_t-FA \qquad (I)$$

wherein $A_1$ and $A_2$ each represents a hydrogen atom or one of them represents a hydrogen atom and the other represents a sulfonyl group or $-(\underset{\underset{O}{\|}}{C})_{\ell}-R_0$

(wherein $R_0$ represents an alkyl group, an alkenyl group, an aryl group, an alkoxy group or an aryloxy group; and $\ell$ represents 1 or 2); Time represents a divalent linking group; t represents 0 or 1; FA represents a moiety of a nucleating agent or a development accelerating agent; V represents a carbonyl group, $-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-$,

a sulfonyl group, a sulfoxy group,

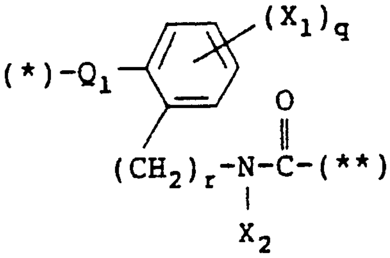


$$-\overset{\overset{O}{\|}}{\underset{\underset{R_1}{|}}{P}}-$$

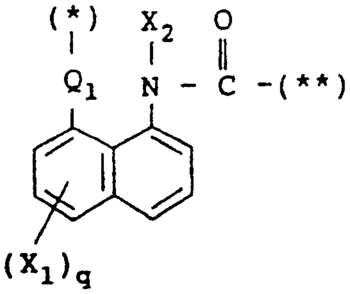
(wherein $R_1$ represents an alkoxy group or an aryloxy group), an iminomethylene group or a thiocarbonyl group; and R represents an aliphatic group, an aromatic group or a heterocyclic group.

2. A silver halide photographic material as claimed in Claim 1, wherein both $A_1$ and $A_2$ are hydrogen atoms.

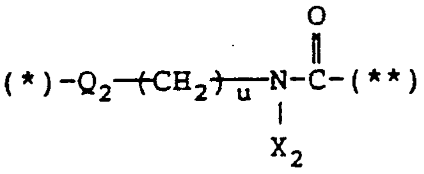
3. A silver halide photographic material as claimed in Claim 1, wherein the divalent linking group represented by Time is selected from the groups represented by the following general formulae (T-1), (T-2), (T-3), (T-4), (T-5), (T-6), (T-7), (T-8), (T-9) or (T-10):



(T-1)

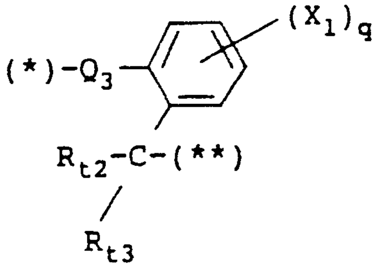


(T-2)

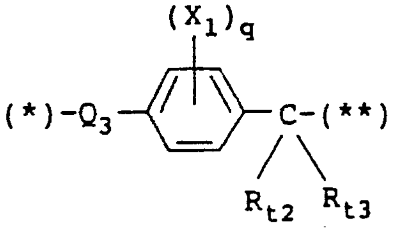


$$(*)\text{-}Q_2\text{-}(CH_2)_u\text{-}\underset{\underset{X_2}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}(**)$$

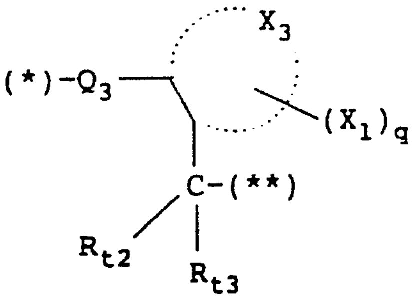
(T-3)



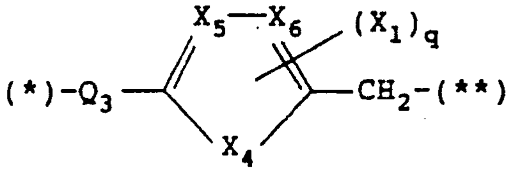
(T-4)



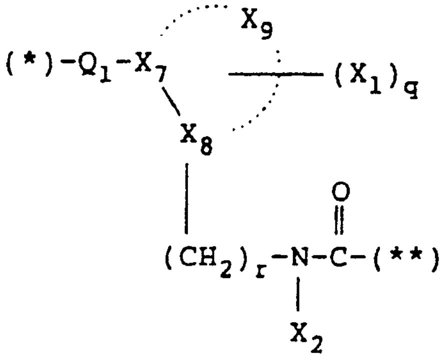
(T-5)



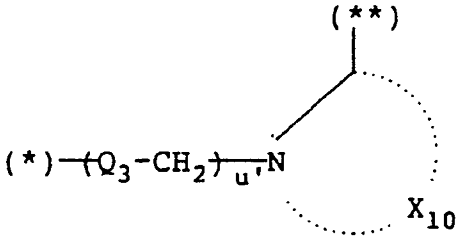
(T-6)



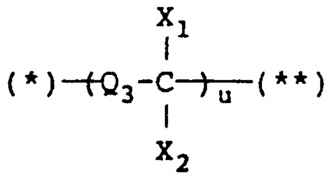
(T-7)



(T-8)



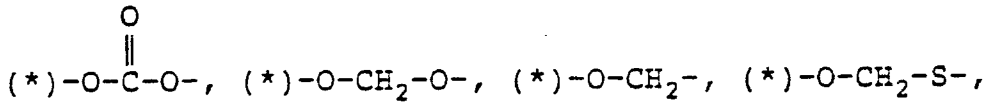
(T-9)



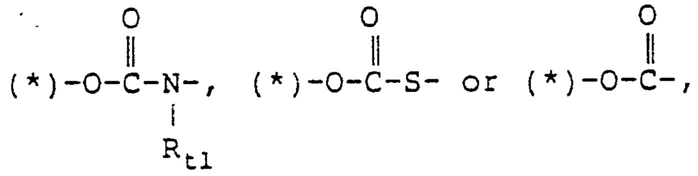
$$(*)-\!\left(Q_3-\underset{\textstyle X_2}{\overset{\textstyle X_1}{\underset{|}{\overset{|}{C}}}}\right)_u\!-(**)$$

(T-10)

wherein a symbol (*) denotes the position at which V is bonded, and a symbol (**) denotes the position at which FA is bonded; wherein (*)-$Q_1$ represents (*)-O-,

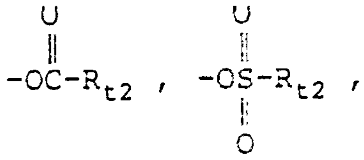


$$(*)\text{-O-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-O-},\quad (*)\text{-O-CH}_2\text{-O-},\quad (*)\text{-O-CH}_2\text{-},\quad (*)\text{-O-CH}_2\text{-S-},$$

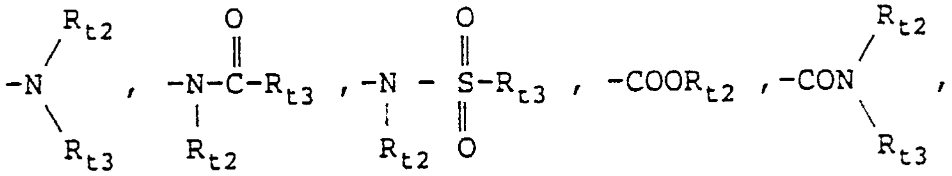


$$(*)\text{-O-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\underset{\underset{\displaystyle R_{t1}}{|}}{N}\text{-},\quad (*)\text{-O-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-S- or } (*)\text{-O-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-},$$

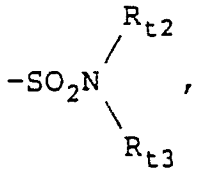
wherein $R_{t1}$ represents a hydrogen atom, an aliphatic group, an aromatic group, or a heterocyclic group; $X_1$ represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group. $-O-R_{t2}$, $-S-R_{t2}$,



$$\text{-O}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R_{t2},\quad \text{-O}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}\text{-}R_{t2},$$

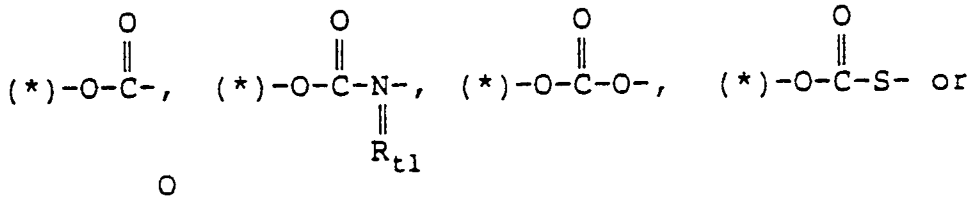


$$\text{-N}\begin{matrix}R_{t2}\\ R_{t3}\end{matrix},\quad \text{-}\underset{\underset{\displaystyle R_{t2}}{|}}{N}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R_{t3},\quad \text{-}\underset{\underset{\displaystyle R_{t2}}{|}}{N}\text{ - }\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}\text{-}R_{t3},\quad \text{-COOR}_{t2},\quad \text{-CON}\begin{matrix}R_{t2}\\ R_{t3}\end{matrix},$$

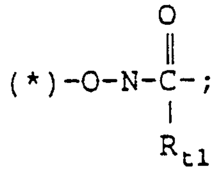


$$\text{-SO}_2\text{N}\begin{matrix}R_{t2}\\ R_{t3}\end{matrix},$$

$-CO-R_{t2}$ , $-SO-R_{t2}$ , a cyano group, a halogen atom or a nitro group, wherein $R_{t2}$ and $R_{t3}$, which may be the same or different, each has the same meaning as defined for $R_{t1}$; $X_2$ has the same meaning as defined for $R_{t1}$; q represents an integer of from 1 to 4, and when q is 2 or more, the substituents represented by $X_1$ may be the same or different, and when q is 2 or more, $X_1$ may connect with each other to form a ring; and r represents 0, 1 or 2; (*)-$Q_2$ represents (*)-O-,

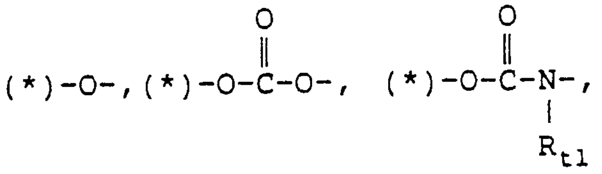


$(*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-},\ (*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}\underset{R_{t1}}{\underset{\|}{N}}\text{-},\ (*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-O-},\ (*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-S-}$ or

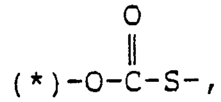


$(*)\text{-O-}\underset{R_{t1}}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-};$ u represents an integer of from 1 to 4;

$(*)\text{-}Q_3$ represents

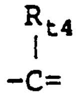


$(*)\text{-O-},(*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-O-},\ (*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}\underset{R_{t1}}{\underset{|}{N}}\text{-},$



$(*)\text{-O-}\overset{O}{\overset{\|}{C}}\text{-S-},$

(*)-O-CH$_2$-O- or (*)-O-CH$_2$-S-; X$_3$ represents an atomic group which contains at least one atom selected from the group consisting of carbon, nitrogen, oxygen and sulfur and which is necessary to form a 5-membered, 6-membered or 7-membered heterocyclic ring, which may be further condensed with a benzene ring or a 5-membered, 6-membered or 7-membered heterocyclic ring; X$_4$ represents an atomic group which contains at least one atom selected from the group consisting of carbon, nitrogen, oxygen and sulfur and which is necessary to form a 5-membered, 6-membered or 7-membered heterocyclic ring, which may be further condensed with a benzene ring or a 5 membered, 6-membered or 7-membered heterocyclic ring; X$_5$ and X$_6$ each represents



$\overset{R_{t4}}{\overset{|}{\text{-C=}}}$

or -N=, wherein R$_{t4}$ represents a hydrogen atom, an aliphatic group or an aromatic group; X$_9$ and X$_{10}$ each represents an atomic group which contains at least one atom selected from the group consisting of carbon, nitrogen, oxygen, and sulfur and which is necessary to form a 5-membered, 6-membered or 7-membered heterocyclic ring, which may be further condensed with a benzene ring or a 5-membered, 6-membered or 7-membered heterocyclic ring; X$_7$ and X$_8$ each each represents $\text{-}\overset{|}{C}\text{=}$ or $\text{-}\overset{|}{N}\text{-}$; and u$'$ represents 0 or 1.

4. A silver halide photographic material as claimed in Claim 1, wherein the moiety represented by FA is a group represented by the following general formula:

AD-(L)$_m$-X

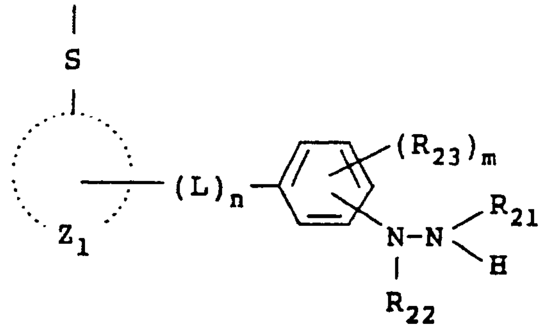
wherein AD represents a group capable of adsorbing silver halide grains; L represents a divalent group; m represents 0 or 1; and X represents a reducing group or a group capable of acting on silver halide to form silver sulfide.

5. A silver halide photographic material as claimed in Claim 4, wherein the group capable of adsorbing silver halide grains represented by AD is a nitrogen-containing heterocyclic group containing a dissociable hydrogen atom, a heterocyclic group containing at least one nitrogen atom and at least one other hetero atom in its ring, a heterocyclic group containing a mercapto group, a quaternary salt, a thiophenol, an alkylthiol or a compound having a partial structure

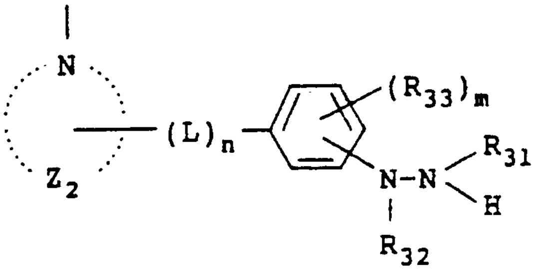
$\text{=N-}\overset{S}{\overset{\|}{C}}\text{-}$.

6. A silver halide photographic material as claimed in Claim 4, wherein the divalent connecting group represented by L is selected from an alkylene group, an alkenylene group, a phenylene group, a naphthylene group, -O-, -S-, -SO-, -SO$_2$-, -N=N-, a carbonyl group, an amido group, a thioamido group, a sulfonamido group, a ureido group, a thioureido group or a heterocyclic group or a combination of two or more thereof.

7. A silver halide photographic material as claimed in Claim 1, wherein the moiety represented by FA is a group represented by the following general formula (II) or (III):



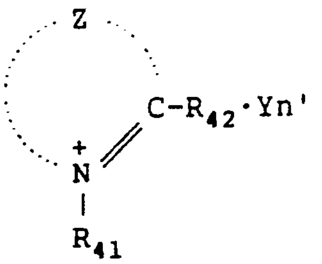
(II)



(III)

wherein $R_{21}$ and $R_{31}$ each represents an acyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group or a sulfamoyl group; $R_{22}$ and $R_{32}$ each represents a hydrogen atom, an acyl group, a sulfonyl group, an alkoxycarbonyl group or an aryloxycarbonyl group; $R_{23}$ and $R_{33}$ each represents a hydrogen atom, an alkoxy group, an alkyl group, an alkenyl group, an aryl group, an aryloxy group, an alkylthio group, an arylthio group, a carbonamido group or a sulfonamido group; m represents an integer of from 0 to 4, and when m is 2 or more, the substituents represented by $R_{23}$ or $R_{33}$ may be the same or different, and when m is 2 or more $R_{23}$ or $R_{33}$ may connect with each other to form a condensed ring; L represents a divalent connecting group; n represents 0 or 1; $Z_1$ represents a non-metallic atomic group necessary to form a monocyclic or condensed heterocyclic ring; and $Z_2$ represents a non-metallic atomic group necessary to form a monocyclic or condensed heterocyclic ring together with N.

8. A silver halide photographic material as claimed in Claim 1, wherein the moiety represented by FA is a group represented by the following general formula (IV):



(IV)

wherein Z represents a non-metallic atomic group necessary for forming a substituted or unsubstituted 5-membered or 6-membered heterocyclic ring; $R_{41}$ represents a substituted or unsubstituted aliphatic group; $R_{42}$ represents a hydrogen atom, a substituted or unsubstituted aliphatic group or a substituted or unsubstituted aromatic group, or $R^{42}$ may be connected with Z to form a ring; provided that at least one of $R_{41}$, $R_{42}$ and Z contains an alkynyl group, an acyl group, a hydrazine group or a hydrazone group, or $R_{41}$ and $R_{42}$ are connected with each other to form a 6-membered dihydropyridinium ring; Y represents a counter ion required for charge balance; and $n'$ represents 0 or 1.

9. A silver halide photographic material as claimed in Claim 8, wherein the heterocyclic ring formed by Z is selected from quinolinium, benzothiazolium, benzimidazolium, pyridinium, thiazolinium, thiazolium, naphthothiazolium, selenazolium, benzoselenazolium, imidazolium, tetrazolium, indolenium, pyrrolinium,

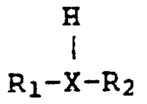
acridinium, phenanthridium, isoquinolinium, oxazolium, naphthoxazolium and benzoxazolium nuclei, which may be substituted with one or more substituents selected from an alkyl group, an alkenyl group, an aralkyl group, an aryl group, an alkynyl group, a hydroxyl group, an alkoxy group, an aryloxy group, an amino group, an alkylthio group, an arylthio group, an acyloxy group, an acylamino group, a sulfonyl group, a sulfonyloxy group, a sulfonylamino group, a carboxyl group, an acyl group, a carbamoyl group, a sulfamoyl group, a sulfo group, a cyano group, a ureido group, a urethane group, a carbonic acid ester group, a hydrazine group, a hydrazone group, an imino group, and a halogen atom.

10. A silver halide photographic material as claimed in Claim 1, wherein V is a carbonyl group.

11. A silver halide photographic material as claimed in Claim 1, wherein the group represented by R has one or more substituents selected from an alkyl group, an aralkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an aryl group, a substituted amino group, an acylamino group, a sulfonylamino group, a ureido group, a urethane group, an aryloxy group, a sulfamoyl group, a carbamoyl group, an alkylthio group, an arylthio group, a sulfonyl group, a sulfinyl group, a hydroxyl group, a cyano group, a sulfo group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyl group, an acyloxy group, a carboxy group and a halogen atom.

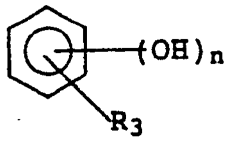
12. A silver halide photographic material as claimed in Claim 1, wherein the compound represented by the general formula (I) is present in an amount of from $10^{-9}$ to $10^{1}$ mol per mol of silver halide.

13. A silver halide photographic material as claimed in Claim 1, wherein the silver halide photographic material further contains a formalin scavenger represented by the following general formulae (SI) or (SII):



$$R_1-\overset{\overset{\displaystyle H}{|}}{X}-R_2$$

(SI)



(SII)

wherein $R_1$ and $R_2$, which may be the same or different, each represents a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an acyl group, an alkoxycarbonyl group, a carbamoyl group or an amino group, or $R_1$ and $R_2$ may combine with each other to form a ring, provided that at least one of $R_1$ and $R_2$ is an acyl group, an alkoxycarbonyl group, a carbamoyl group or an amino group; X represents $-\overset{|}{C}H-$ or $-\overset{|}{N}-$; $R_3$ represents a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group or a substituted aryl group, and $R_3$ may be connected to the phenyl ring to form a bicyclic compound; and n represents an integer of 2 or more.

14. A silver halide photographic material as claimed in Claim 1, wherein the silver halide photographic material further contains a color forming coupler.

15. A silver halide photographic material as claimed in Claim 14, wherein the silver halide photographic material contains at least one red-sensitive silver halide emulsion layer containing at least one cyan color forming coupler, at least one green-sensitive silver halide emulsion layer containing at least one magenta color forming coupler, and at least one blue-sensitive silver halide emulsion layer containing at least one yellow color forming coupler.

16. A silver halide photographic material as claimed in Claim 1, wherein the silver halide emulsion layer contains a non-previously fogged internal latent image type silver halide emulsion.

17. A silver halide photographic material as claimed in Claim 16, wherein the silver halide photographic material further contains a nucleating agent.

18. A silver halide photographic material as claimed in Claim 17, wherein the silver halide photographic material further contains a nucleation accelerating agent.

19. A silver halide photographic material as claimed in Claim 1, wherein the silver halide photographic material further contains a diffusible dye releasing redox compound.