

611990

FORM 1
REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1973

APPLICATION FOR A PATENT

We FUJI PHOTO FILM CO., LTD.

of No. 210 Nakanuma, Minami Ashigara-Shi, Kanagawa, JAPAN

hereby apply for the grant of a Patent for an invention entitled:

SILVER HALIDE COLOR LIGHT-SENSITIVE MATERIAL
COMPRISING PYRAZOLOAZOLE COUPLER

which is described in the accompanying complete specification. This Application is a Convention Application and is based on the Application numbered: 7859/88 for a Patent or similar protection made in Japan on 18 January 1988.

Our address for service is:

GRIFFITH HACK & CO.
71 YORK STREET
SYDNEY N.S.W. 2000
AUSTRALIA

DATED this 18th day of January, 1989.

FUJI PHOTO FILM CO., LTD.
By their Patent Attorneys



GRIFFITH HACK & CO.

TO: THE COMMISSIONER OF PATENTS
COMMONWEALTH OF AUSTRALIA



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68/10/81 0836001
1004880 18/01/89

B — APPLICATION BY ASSIGNEE OF INVENTOR

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

(Name of applicant) In support of an application made by: .Fuji Photo Film Co., Ltd.....

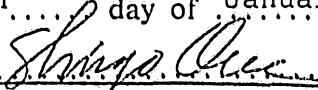
(Title) for a patent for an invention entitled:
.SILVER HALIDE COLOR LIGHT-SENSITIVE MATERIAL.....

(Full name and address of signatory) I, .Shingo Oue.....
of .No. 26-30, .Nishi Azabu 2-chome, .Minato-ku, .Tokyo, .Japan..

do solemnly and sincerely declare as follows:

1. I am authorised by the above mentioned applicant for the patent to make this declaration on its behalf.
- (Full name and address of inventor(s)) 2. The name and address of each actual inventor of the invention is as follows: Kazunori Hasebe, Masahiro Asami and Keisuke Shiba all of c/o Fuji Photo Film Co., Ltd., No. 210, Nakanuma, Minami Ashigara-shi, Kanagawa, Japan.....
.....
(State whether by assignment or contract of employment) and the facts upon which the applicant is entitled to make this application are as follows: Set out how Applicant derive title from actual inventors e.g. The Applicant is the assignee of the invention from the inventors..
.....
- (Delete paragraphs 3 and 4 for non-Convention application) 3. The basic application(s) as defined by Section 141 of the Act was (were) made as follows:
Country in Japan on January 18, 1988
in the name(s) .Fuji Photo Film Co., Ltd.....
and in on
in the name(s)
and in on
in the name(s)
4. The basic application(s) referred to in the preceding paragraph was(were) the first application(s) made in a Convention country in respect of the invention the subject of this application.

(Place and date of signing) Declared at Tokyo, Japan... this 5th day of January 1989.

Signed: 

Position: Managing Director.....

GRIFFITH HASSEL & FRAZER
G.P.O. BOX 4164 SYDNEY, AUSTRALIA

(12) PATENT ABRIDGMENT (11) Document No. AU-B-28595/89
 (19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 611990

(54) Title
 SILVER HALIDE COLOR LIGHT-SENSITIVE MATERIAL COMPRISING PYRAZOLOAZOLE COUPLER

International Patent Classification(s)
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 (51)⁵ G03F 007/06 G03C 001/005

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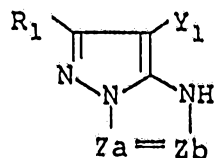
(71) Applicant(s)
 FUJI PHOTO FILM CO., LTD.

(72) Inventor(s)
 KAZUNORI HASEBE; MASAHIRO ASAMI; KEISUKE SHIBA

(74) Attorney or Agent
 GRIFFITH HACK & CO., GPO Box 4164, SYDNEY NSW 2001

(57) Claim

1. A silver halide color light-sensitive material comprising a support having provided thereon at least one light-sensitive emulsion layer containing surface latent image type silver halide grains, wherein said light-sensitive emulsion layer comprises a photographic emulsion containing silver bromochloride grains substantially free of silver iodide and having at least 90 mol% of average silver chloride content, said silver bromochloride grains having a localized silver bromide phase on the surface thereof in a discontinuous or isolated state, and at least one pyrazoloazole type coupler represented by formula (I) and said light-sensitive emulsion layer or at least one of other hydrophilic colloid layers comprises at least one compound represented by formula (II-a) or (II-b):

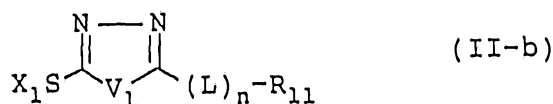


(I)

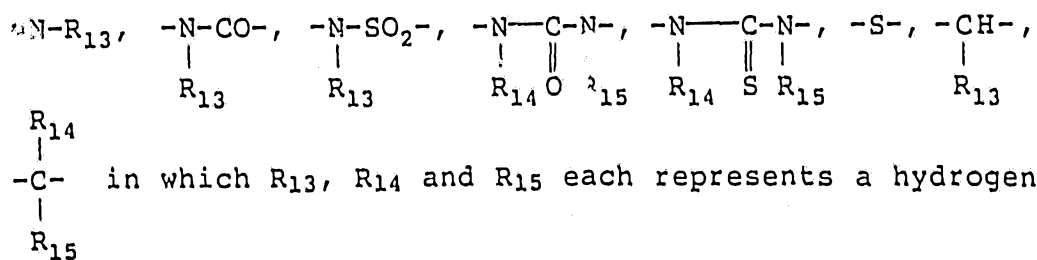
(11) AU-B-28595/89
(10) 611990

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wherein Z_a and Z_b each represents a methine group, a substituted methine group or $-N=$; R_1 represents a hydrogen atom or a substituent; and Y_1 represents a halogen atom or a group which can be released upon coupling reaction with an oxidation product of an aromatic primary amine developing agent (release group), with the proviso that a dimer or higher polymer may be formed via R_1 , Z_a , Z_b or Y_1 :



wherein R_{11} represents an alkyl group, an alkenyl group, a heterocyclic group or an aryl group; X_1 represents a hydrogen atom, an alkaline metal atom, an ammonium group or the precursor thereof; V_1 represents an oxygen atom, a sulfur atom, $=\text{NH}$, $=\text{N}-(\text{L})_{n'}-\text{R}_{12}$ in which R_{12} has the same meaning as R_{11} ; L represents a divalent linking group such as



atom, an alkyl group, or an aralkyl group; and n and n' each represents an integer 0 or 1.

611990

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

Form 10

COMPLETE SPECIFICATION

FOR OFFICE USE

Short Title:

Int. Cl:

Application Number:
Lodged:

Complete Specification-Lodged:
Accepted:
Lapsed:
Published:

Priority:

Related Art:

TO BE COMPLETED BY APPLICANT

Name of Applicant: FUJI PHOTO FILM CO., LTD.
Address of Applicant: No. 210 Nakanuma, Minami Ashigara-Shi,
Kanagawa, JAPAN
Actual Inventor: Kazunori Hasebe; Masahiro Asami and
Keisuke Shiba
Address for Service: GRIFFITH HACK & CO.
71 YORK STREET
SYDNEY NSW 2000
AUSTRALIA

Complete Specification for the invention entitled:

SILVER HALIDE COLOR LIGHT-SENSITIVE
MATERIAL COMPRISING PYRAZOLOAZOLE
COUPLER

The following statement is a full description of this invention,
including the best method of performing it known to me/us:-



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SILVER HALIDE COLOR LIGHT-SENSITIVE MATERIAL
COMPRISING PYRAZOLAZOLE COUPLER

FIELD OF THE INVENTION

The present invention relates to a silver halide color light-sensitive material having a rapid developing aptitude and an excellent color reproducibility. More particularly, the present invention relates to a surface latent image type silver halide color light-sensitive material excellent in stability of continuous development process and stability of sensitivity and gradation during the preparation thereof.

BACKGROUND OF THE INVENTION

In a silver halide color light-sensitive material, particularly a color negative light-sensitive material or color print light-sensitive material for use in photographing, it is known to use a silver bromochloride or silver chloride emulsion substantially free of silver iodide or having a high silver chloride content, e.g., at least 80 mol% to expedite or simplify the development process. However, it is known that such a high silver chloride content emulsion finds it difficult to provide a high sensitivity or inhibit the generation of fog. In order to overcome these problems, various approaches have been proposed. Examples of these approaches include the use of multilayer grains,



particularly core/shell type grains, the provision of a thin silver bromide or silver iodide layer on the surface of grains, the doping of grains with ions of different kinds of metals such as cadmium, zinc, lead, platinum, palladium, iridium, rhodium, nickel, and ruthenium, and the use of specific sensitizing dyes. These approaches are described in WO 87-4534, EP-A2-23,059, and EP-A2-231,861, and JP-A-58-95736, JP-A-58-108533, JP-A-62-153953, JP-A-62-194252, JP-A-62-250438, JP-A-60-222845, JP-A-60-222846, JP-A-62-246046 and JP-A-62-253142 to JP-A-62-253148 (the term "JP-A" as used herein means an "unexamined Japanese patent application"). It is also generally known that a water-soluble iridium salt may be used to improve the reciprocity law failure or provide a high sensitivity and contrast. This approach is described in JP-B-43-4935 (the term "JP-B" as used herein means an "examined Japanese patent publication"), DE-2,226,877, U.S. Patent 3,703,584, and JP-B-48-35373. It is further known that a water-soluble rhodium salt may be used as desensitizer or contrast improver, particularly for a direct positive silver halide emulsion. Particularly, JP-A-62-253145 describes that when silver halide grains having an entire silver chloride content of 80 to 99 mol% and comprising a high silver bromide content phase which can

be definitely distinguished as a peak by X-ray diffraction are doped with metal ions in the high silver chloride content phase, they are rendered highly pressure resistant.

JP-A-62-25314 gives a teaching that a high silver chloride content silver halide emulsion may comprise a mercapto heterocyclic compound to inhibit stress mark. In Example 3 of this Japanese patent application, it is described that a pyrazolotriazole magenta coupler may be incorporated in an emulsion of silver halide grains comprising high silver chloride content grains uniformly covered with a silver bromide layer on the surface thereof.

However, the Inventors' study revealed that when this type of a coupler is incorporated in a high silver chloride content emulsion adapted for rapid development, it can cause a photographically serious problem. Particularly, it was found that when a coating solution ages a long period of time during the preparation of the light-sensitive material, or the color developing solution is stained with some amount of the blix solution, a remarkably low contrast is given.

Since a silver halide color light-sensitive material has been required to exhibit a high image quality and provide an extremely high finished quality,

this problem cannot be solved simply by applying the above described approaches. It has been possible to provide a high sensitivity and inhibit the generation of fog. However, it has been impossible to obtain a color light-sensitive material which exhibits an excellent color reproducibility and a high stability of sensitivity and gradation during continuous development process as well.

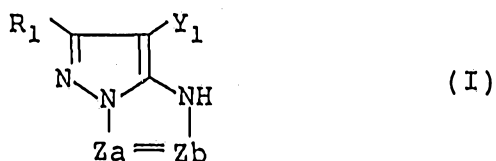
SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a silver halide color light-sensitive material which enables the inhibition of low contrast caused by the incorporation of a pyrazolo-triazole coupler excellent in color reproducibility into a high silver chloride content emulsion excellent in rapidity in processing.

These and other objects of the present invention will become more apparent from the following detailed description and examples.

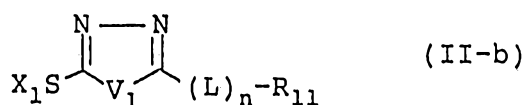
The Inventors studied the structure of high silver chloride content silver bromochloride grains and the defect of a coupler useful for the color reproduction. As a result, the objects of the present invention could be accomplished. Particularly, these objects of the present invention are accomplished with a

silver halide color light-sensitive material comprising a support having provided thereon at least one light-sensitive emulsion layer containing surface latent image type silver halide grains, wherein the light-sensitive emulsion layer comprises a photographic emulsion containing silver bromochloride grains substantially free of silver iodide and having at least 90 mol% of average silver chloride content, the silver bromochloride grains having a localized silver bromide phase on the surface thereof in a discontinuous or isolated state, and at least one pyrazoloazole type coupler represented by formula (I) and the light-sensitive emulsion layer or at least one of other hydrophilic colloid layers comprises at least one compound represented by formula (II-a) or (II-b).

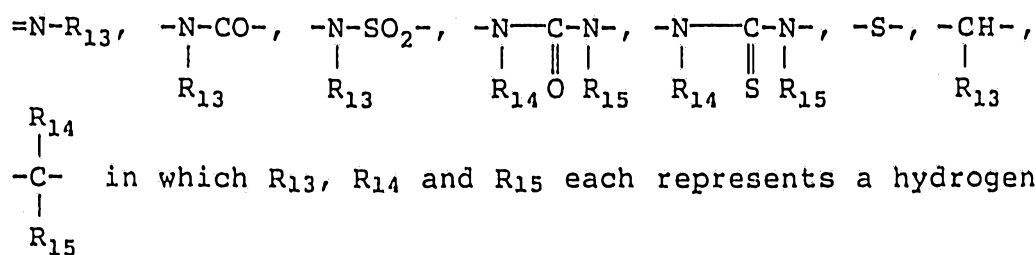


wherein Z_a and Z_b each represents a methine group, a substituted methine group or $-\text{N}=\text{}$; R_1 represents a hydrogen atom or a substituent; and Y_1 represents a halogen atom or a group which can be released upon coupling reaction with an oxidation product of an

aromatic primary amine developing agent (release group), with the proviso that a dimer or higher polymer may be formed via R_1 , Z_a , Z_b or Y_1 :



wherein R_{11} represents an alkyl group, an alkenyl group, a heterocyclic group or an aryl group; X_1 represents a hydrogen atom, an alkaline metal atom, an ammonium group or the precursor thereof; V_1 represents an oxygen atom, a sulfur atom, $=\text{NH}$, $=\text{N}-(\text{L})_{n'}-\text{R}_{12}$ in which R_{12} has the same meaning as R_{11} ; L represents a divalent linking group such as



atom, an alkyl group, or an aralkyl group; and n and n' each represents an integer 0 or 1.

DETAILED DESCRIPTION OF THE INVENTION

One of the preferred embodiments of the present invention is that at least one silver halide emulsion layer on a support comprises 50% or more, preferably 70% or more, particularly 90% or more by weight of a high silver chloride content emulsion as described above. The content of the emulsion means the proportion of the emulsion in a plurality of emulsions, if any, incorporated in one light-sensitive layer. It goes without saying that the emulsion of the present invention may be used singly (100% by weight).

The silver halide grain of the present invention consists of silver bromochloride grain wherein 90 mol% or more (average) of all the silver halide contents constituting the grain is silver chloride. More particularly, the silver halide grain of the present invention is silver bromochloride grain substantially free of silver iodide (that is, the silver iodide content is 1.0 mol% or less, preferably free of silver iodide) wherein 95 to 99.9 mol% of all the silver halide contents constituting the grain is silver chloride. The above described halogen content is represented on the average. This average value is obtained by averaging the halogen content of each of silver halide grains

contained in one silver halide emulsion used in the present invention.

The localized silver bromide phase in the present silver halide grain is present in an ununiform and discontinuous or isolated state rather than in a uniform continuous layer state. The silver bromide content in the localized phase differs substantially from that in the other parts of the grain. The silver halide grain having such a structure has a high rapid developability and a relatively high silver bromide content in the surface thereof, minimizing the generation of fog. The present silver halide grain also has a hetero structure, making it easy to provide a high sensitivity.

In most silver halide grain having such a hetero structure, development starting points tend to be concentrated at localized phases or its vicinity. Therefore, a fog inhibitor, a stabilizer or other additives can be adsorbed by such a silver halide grain without blocking development starting points, thus fully exhibiting its functions. This minimizes the generation of fog, making it possible to provide a high sensitivity. This also enables a smooth adjustment of the progress in development without changing the development starting speed.

In the present silver halide grain, the silver bromide content in the localized phases is preferably 5 mol% or more, more preferably 20 mol% or more, particularly 20 mol% to less than 70 mol%. If the silver bromide content in the localized phases exceeds this range, it causes pressure desensitization or some fluctuation in sensitivity or gradation during the continuous development process. If the localized phases grow so far as to cause protrusions of epitaxy particles to appear, it becomes difficult to obtain a high sensitivity. The silver bromide content in the localized phases and the difference in the silver bromide content between the localized phases and the substrate (portions of silver halide grain other than the localized phases) depend on the molar ratio of the amount of fine silver bromide grain or difficultly soluble bromide to be used to the host silver halide emulsion, the rate for supplying water-soluble bromide to the host silver halide emulsion, or the pAg or pH value of the reaction solution. In other words, the formation of the localized phases can be accomplished by adding a silver nitrate solution and halogen ions to a host silver halide emulsion at a predetermined rate while controlling the pAg or pH value of the reaction solution. Alternatively, the formation of the localized

phases can be accomplished by physical ripening of a host silver halide emulsion with a difficultly soluble bromide such as fine silver bromide or silver chlorobromide grains or substituting a host silver chloride by bromine ions. The ununiform, discontinuous or isolated localized phase particularly useful in the present invention may be formed by adding a water-soluble bromide and silver nitrate to a host silver halide emulsion with a so-called CR-compound as described in European Patents 0,273,429 and 0,273,430 or by physical ripening of a host silver halide emulsion with fine silver bromide or silver chlorobromide grains.

The measurement of the silver bromide content in the present localized phases can be accomplished by X-ray diffractometry as described in "Structural Analysis", Shinjikken Kagaku Koza 6 (Japan Chemistry Association), Maruzen, or XPS process as described in Surface Analysis "Application of IMA, Auger Electron and Photoelectron Spectrography", Kodansha. Particularly, silver bromide content in the localized phases present ununiformly or isolated on the surface, particularly edge or corner of silver halide grain can be measured by EDX process (Energy Dispersive X-ray analysis) as described in Takayoshi Fukushima, "Electron Ray Microanalysis", Nikkan Kogyo Shinbunsha, 1987. In this

process, a transmission type electromicroscope equipped with an EDX spectrometer is used. The specimen is placed in an aperture having a diameter of about 0.1 to 0.2 μm . This process provides an accuracy of about 5 mol%.

The silver halide grain to be used in the present invention may be preferably a regular crystal such as cube having (100) plane, hexagonal or tetradecahedral crystal, or octahedron crystal having (111) plane, or may be tabular crystal. These silver halide grains can be obtained by properly selecting the pAg or pH value of the reaction solution in which the silver halide grain is to be formed or selectively using CR-compounds (as described in the above cited European Patents 0,273,429 and 0,273,430) adsorbing substances by its (100) or (111) plane or other organic compounds. A particularly preferred silver halide grain is a hexagonal or tetradecahedral grain having (100) plane and having localized phases on the corners of the surface thereof or a tabular grain having localized phases on the corners or edges of the surface thereof.

The average size (as calculated in terms of mean diameter of sphere having the same volume as the grain) of silver halide grain in silver halide emulsion to be

used in the present invention may be preferably 0.1 to 2 μm , particularly 0.15 to 1.4 μm .

The distribution of grain size may be preferably narrow. A monodisperse emulsion may be preferably used. Particularly, a monodisperse emulsion of regular crystal grains may be preferably used in the present invention. An emulsion wherein 85% or more, particularly 90% or more of the total grains fall within of the average grain size $\pm 20\%$ by number or weight may be preferably used.

The preparation of the silver bromochloride emulsion to be used in the present invention may be accomplished by any suitable method as described in P. Glafkides, "Chimie et Physique Photographique", Paul Montel, 1967, G.F. Duffin, "Photographic Emulsion Chemistry", Focal Press, 1966, and V.L. Zelikman et al., "Making and Coating Photographic Emulsion", Focal Press, 1964. That is, the preparation of the present silver halide photographic emulsion can be accomplished by any one of acidic process, neutral process, and ammonia process. Particularly, the acidic process is preferred. The method for the reaction of the soluble silver salt with the soluble silver halide can be accomplished by single jet method, double jet method, or combination thereof. The preparation of the present monodisperse

emulsion may be preferably accomplished by double jet method. The preparation of the silver bromochloride emulsion to be used in the present invention may be accomplished by a process in which grains are formed in excess silver ions (so-called reversal mixing process). One form of the double jet method is a so-called controlled double jet method in which the pAg of the liquid phase in which silver halide is formed is kept constant. This process can provide a monodisperse silver halide emulsion suitable for the present invention having a regular crystal structure and a narrow grain size distribution. The above described silver halide grain which may be preferably used in the present invention may be preferably prepared on the basis of the double jet method.

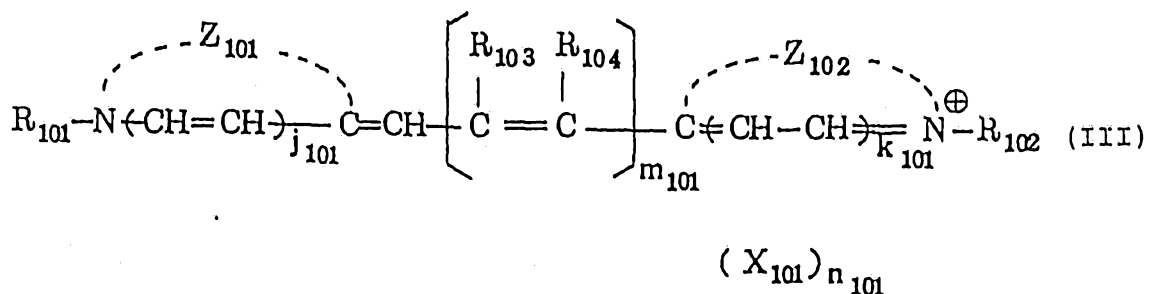
If the physical ripening is effected in the presence of a known silver halide solvent (e.g., ammonia, potassium thiocyanate, thioethers and thione compounds as described in U.S. Patent 3,271,157, JP-A-51-12360, JP-A-53-82408, JP-A-53-144319, JP-A-54-100717, and JP-A-54-155828), a preferred monodisperse emulsion of silver halide grain having a regular crystal structure and a narrow grain size distribution can be obtained.

The removal of the soluble silver salts from the emulsion which has been subjected to physical ripening can be accomplished by noodle rinse process, flocculation sedimentation process or ultrafiltration process.

The chemical sensitization of the silver halide emulsion to be used in the present invention can be accomplished by sulfur sensitization process, selenium sensitization process, reduction sensitization process, or noble metal sensitization process, singly or in combination. Particularly, sulfur sensitization process using active gelatin or a sulfur-containing compound capable of reacting with silver ion (e.g., thiosulfates, thiourea compound, mercapto compound, rhodanine compound), reduction sensitization process using a reducing substance (e.g., stannous salt, amines, hydrazine derivatives, formamidinesulfinic acid, silane compound), or noble metal sensitization process using a metal compound (e.g., gold complex, complex of group VIII metals such as Pt, Ir, Pd, Rh, Fe) may be used, singly or in combination. The present monodisperse silver bromochloride emulsion may be preferably subjected to sulfur sensitization or selenium sensitization. These sensitization processes may be preferably effected in the presence of a hydroxyazaindene compound.

In the present invention the use of a spectral sensitizing dye is important. As a suitable spectral sensitizing dye for the present invention there may be used a cyanine dye, merocyanine dye, complex merocyanine dye, or the like. Other useful examples of spectral sensitizing dyes include complex cyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. As such a cyanine dye there may be preferably used simple cyanine dye, carbocyanine dye, or dicarbocyanine dye.

The addition of a spectral sensitizing dye may be preferably effected after the formation of host grains. Alternatively, the addition of a spectral sensitizing dye may be preferably effected before or during the chemical sensitization. A preferred example of cyanine dye will be shown hereinafter.



wherein Z₁₀₁ and Z₁₀₂ each represents an atomic group needed to form a heterocyclic nucleus.

As such a heterocyclic nucleus there may be preferably used a 5- or 6-membered cyclic nucleus containing as hetero atoms nitrogen atom, sulfur atom, oxygen atom, selenium atom, or tellurium atom, (condensed rings or substituents may further be connected to such a heterocyclic nucleus.)

Specific examples of such a heterocyclic nucleus include thiazole nucleus, benzothiazole nucleus, naphthothiazole nucleus, selenazole nucleus, benzo-selenazole nucleus, naphthoselenazole nucleus, oxazole nucleus, benzooxazole nucleus, naphthooxazole nucleus, imidazole nucleus, benzimidazole nucleus, naphthoimidazole nucleus, 4-quinoline nucleus, pyrroline nucleus, pyridine nucleus, tetrazole nucleus, indolenine nucleus, benzindolene nucleus, indole nucleus, tellurazole nucleus, benzotellurazole nucleus, naphhotellurazole nucleus, etc.

R₁₀₁ and R₁₀₂ each represents an alkyl group, an alkenyl group, an alkynyl group or an aralkyl group. These groups and groups as described hereinafter each is used in a sense of including substituted one in addition with unsubstituted one. Taking the case of the alkyl group, the alkyl group includes an unsubstituted alkyl

group and a substituted alkyl group, which groups may be straight, branched, or cyclic. The alkyl group preferably has 1 to 8 carbon atoms.

Examples of substituents for the substituted alkyl group includes a halogen atom (for example, chlorine, bromine, fluorine), a cyano group, an alkoxy group, a substituted or unsubstituted amino group, a carboxylic acid group, a sulfonic acid group, a hydroxy group, etc. The alkyl group may be substituted with one of them or two or more of them in combination.

Example of the alkenyl group includes a vinylmethyl group.

Example of the aralkyl group include a benzyl group and a phenethyl group.

In formula (III), m_{101} represents 0 or an integer of 1 to 3. When m_{101} represents 1, R_{103} represents a hydrogen atom, lower alkyl group, aralkyl group, or aryl group.

Specific examples of such an aryl group include substituted or unsubstituted phenyl group.

When m_{101} represents 1, R_{104} represents a hydrogen atom. When m_{101} represents 2 or 3, R_{103} represents a hydrogen atom, and R_{104} represents a hydrogen atom, lower alkyl group, or aralkyl group and may be connected to R_{102} to form a 5- or 6-membered ring.

When m_{101} represents 2 or 3, and R_{104} represents a hydrogen atom, R_{103} may be connected to another R_{103} to form a hydrocarbon ring or heterocyclic ring. Such a hydrocarbon ring or heterocyclic ring may be preferably a 5- or 6-membered ring. The suffixes j_{101} and k_{101} each represents 0 or 1. X_{101} represents an acid anion. The suffix n_{101} represents 0 or 1.

Among sensitizing dyes to be used in the present invention, a sensitizing dye to be used for a red-sensitive emulsion layer, i.e., emulsion layer whose wavelength range of 580 to 750 nm has been spectrally sensitized deteriorates the stability of sensitivity more remarkably than a sensitizing dye to be used for a blue-sensitive or green-sensitive emulsion layer. Particularly, this tendency is remarkable for a high silver chloride content silver bromochloride or silver chloride host emulsion.

However, among sensitizing dyes which spectrally sensitize the wavelength range of 580 to 750 nm, a sensitizing dye having a reduction potential of -1.27 or more negative (V. vs. SCE) exhibits a high sensitivity and an excellent stability of sensitivity and latent images. Particularly, a sensitizing dye having a reduction potential of -1.27 or more negative (V. vs. SCE) and a chemical structure wherein one or two of

conjugated methine chains between nitrogen atoms are used to make ring condensate may be preferably used. Examples of such a sensitizing dye include pentamethine cyanine dyes containing a benzothiazole nucleus, pentamethine cyanine dyes containing a benzoselenazole nucleus, and trimethine cyanine dyes containing 4-quinoline nucleus. The reduction potential of these dyes can be optimized by substituting this heterocyclic nucleus by an alkyl group, alkoxy group, halogen atom, hydroxyl group or the like.

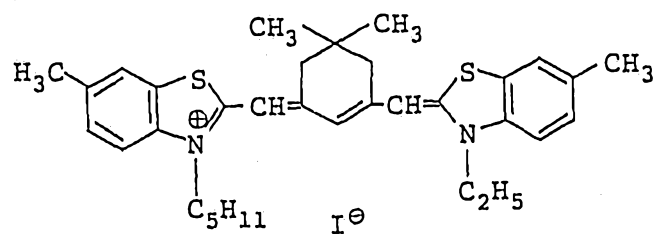
The reduction potential can be measured by means of a phase selected second harmonic alternating current polarography. A mercury dropping electrode is used as work electrode. A saturated calomel electrode is used as reference electrode. Platinum is used as opposite electrode.

The process for the measurement of reduction potential by means of a phase selected second harmonic alternating current voltmetry using platinum as work electrode is described in "Journal of Imaging Science", Vol. 30, pp. 27-35, 1986.

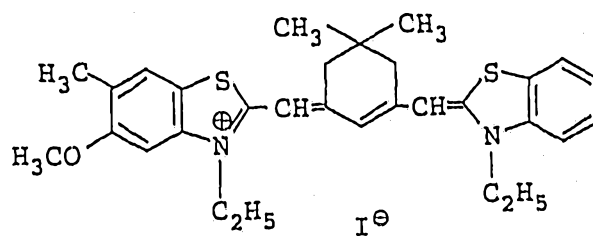
Specific examples of preferred red-sensitive sensitizing dyes which may be used in the present invention will be shown hereinafter, but the present

invention should not be construed as being limited thereto.

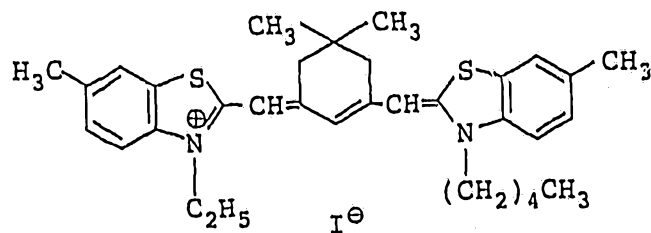
S-1



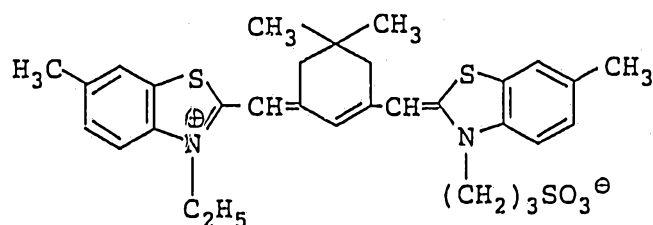
S-2



S-3

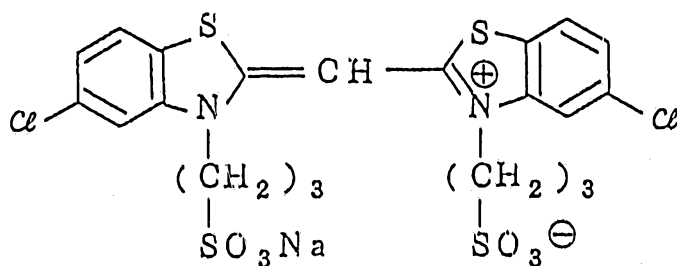


S-4

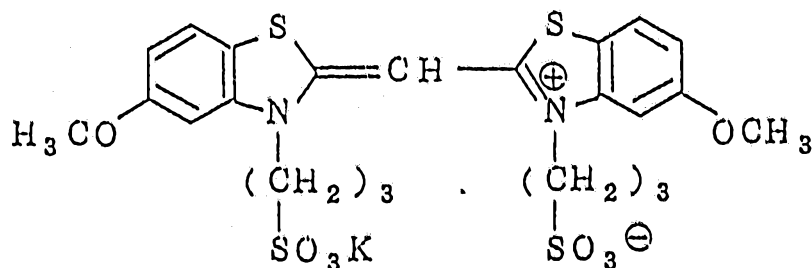


Specific examples of other typical sensitizing dyes which can be used in the present invention will be shown hereinafter.

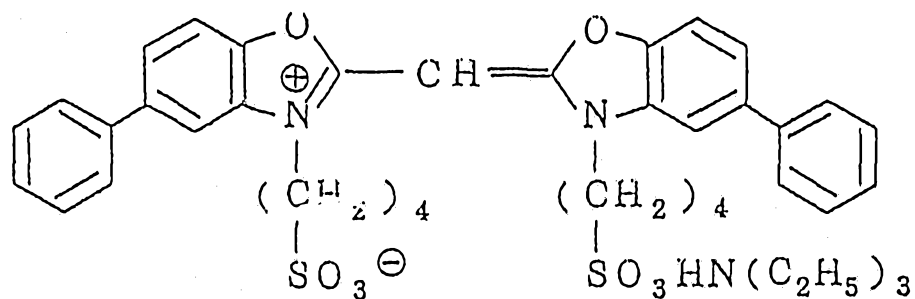
S - 5



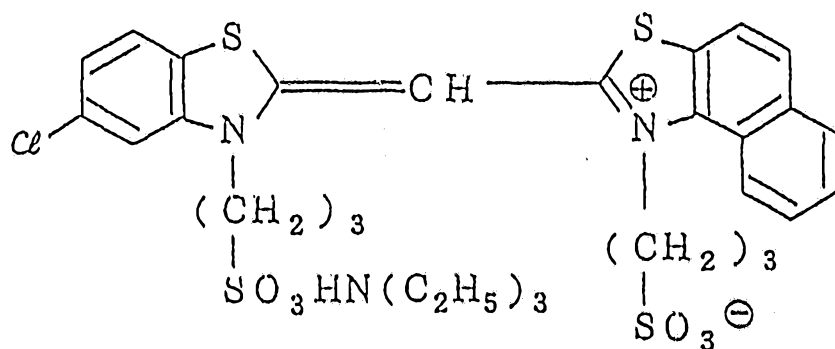
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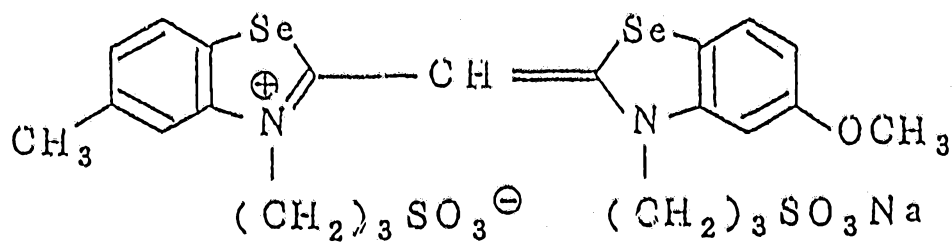
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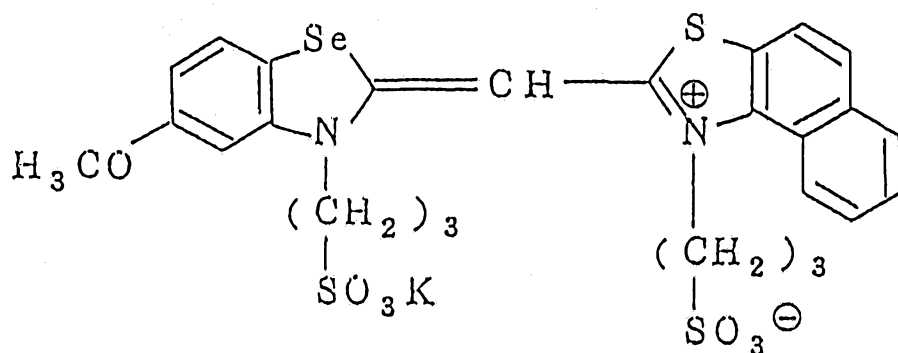
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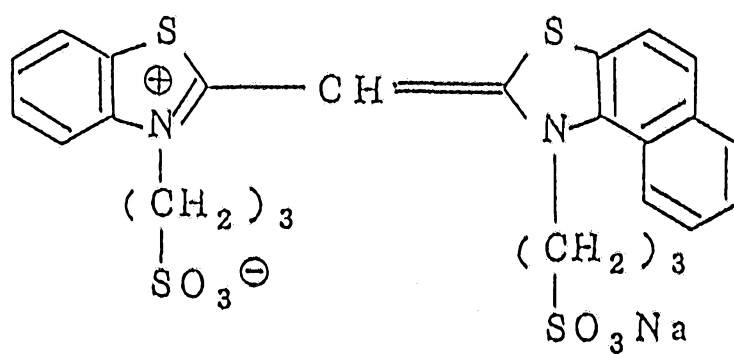
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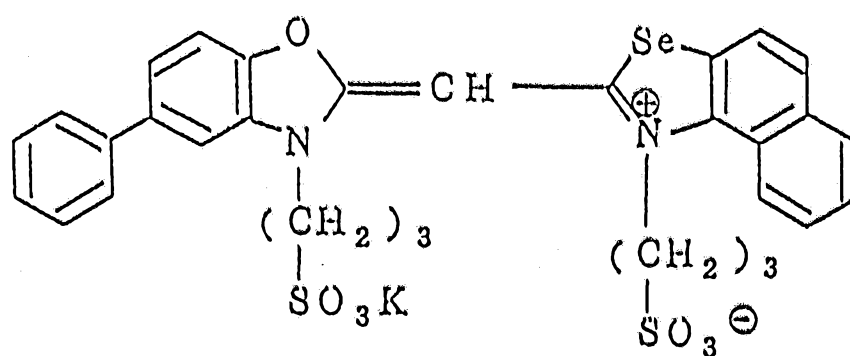
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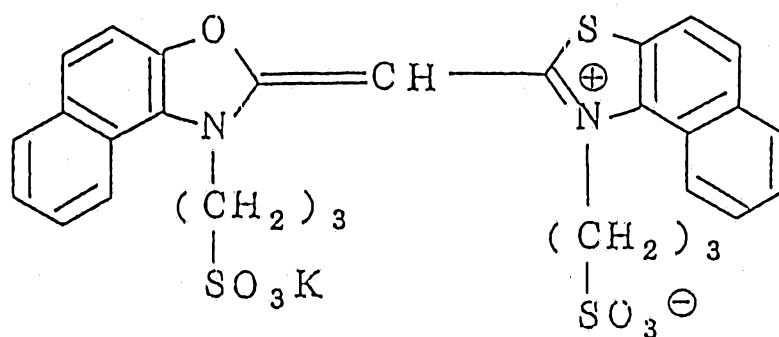
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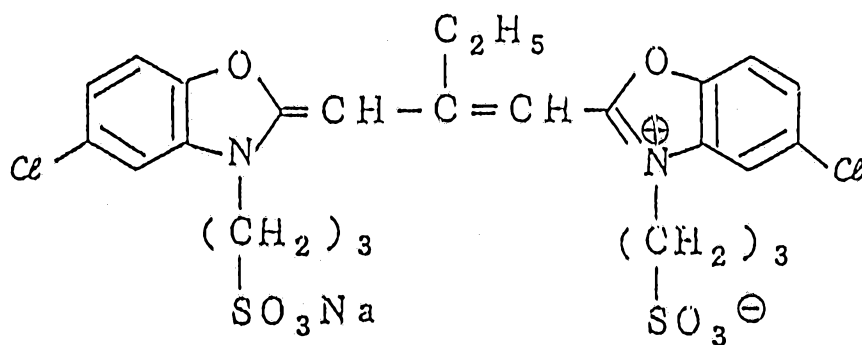
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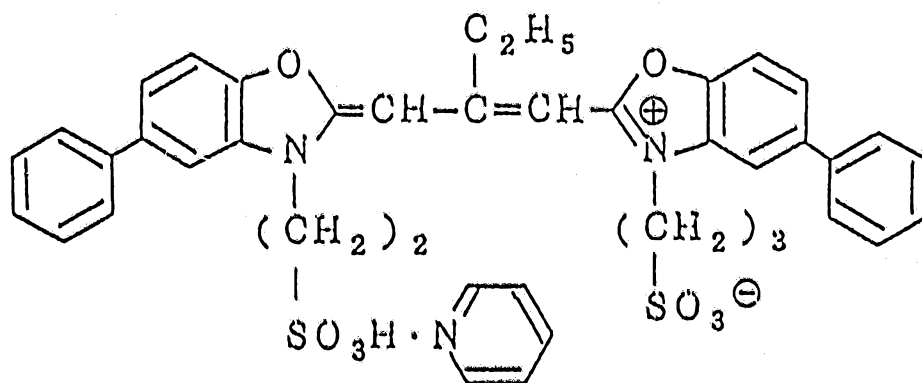
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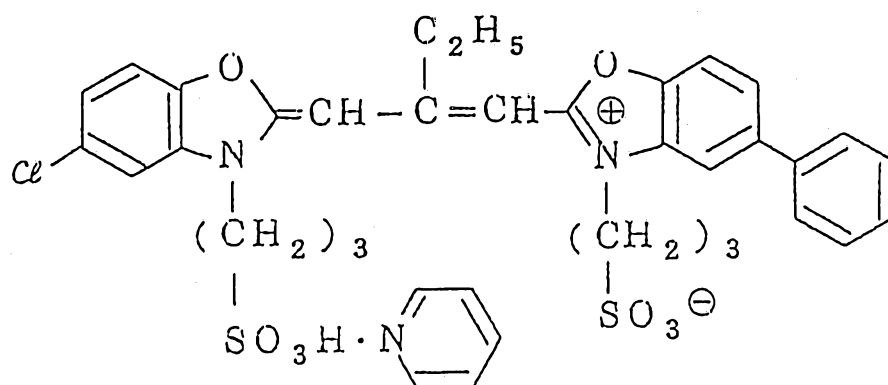
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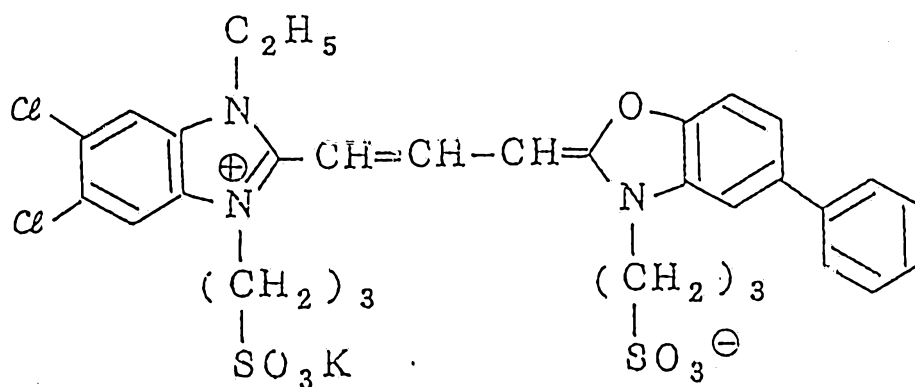
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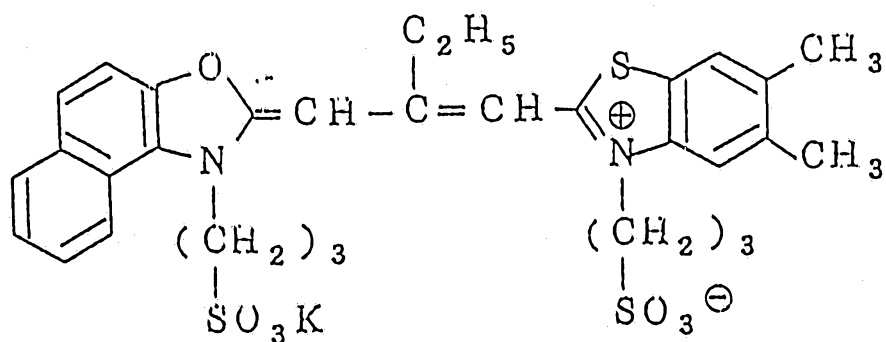
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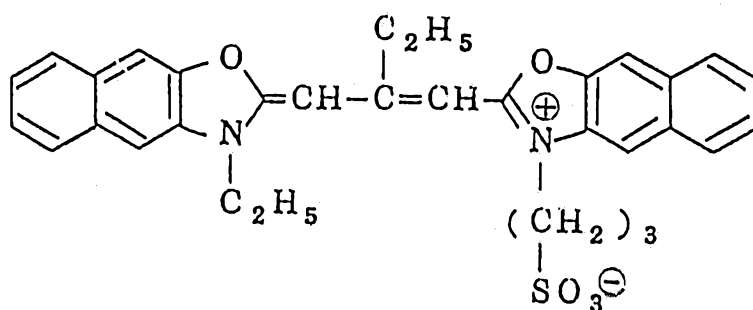
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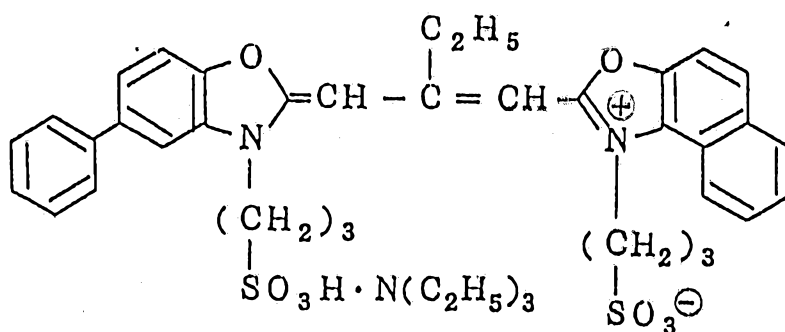
S - / 8



S - 1 9



S - 2 0



Metal ions selected from the group VIII metal ions or its complex ions may be preferably contained in the localized phases or its substrate of the present silver halide grain. The type and concentration of metal ions may be altered between the localized phases and its substrate. One or more metal ions can be used,

singly or in combination. Particularly, iridium ion may be incorporated in the localized phases, and metal ion selected from osmium, iridium, platinum, ruthenium, rhodium, palladium, iron, cobalt, and nickel ions, or its complex ion may be incorporated in its substrate. Furthermore, metal ions selected from cadmium, zinc, lead, mercury and thallium ions may be used. In this manner, a silver halide emulsion excellent in the reciprocity law failure and the stability of sensitivity and gradation can be obtained. The amount of these metal ions or complex ions to be added is preferably in the range of 10^{-8} to 10^{-5} mol based on the amount of silver halide.

Particularly, if iridium ion is incorporated in silver bromide localized phases, the reciprocity law failure can be improved, a high sensitivity and contrast can be obtained, and the stability of latent images can be improved.

The present chemical sensitization can be effected in any ordinary manner as described above so that latent images are formed mainly on the surface of silver halide grain. Particularly, in the present silver halide grain comprising localized phases on the surface thereof, the chemical sensitization should be effected so that the balance between the substrate grain

and the localized phase is controlled. This control can be effected by a method as described in European Patents 0,273,429 and 0,273,430, particularly proper use of CR-compounds.

The decrease in the sensitivity or gradation due to the addition of the present pyrazolotriazole type couplers can be effectively prevented by the combined use of a mercapto heterocyclic compound represented by formula (II-a) or (II-b).

These mercapto heterocyclic compounds will be further described hereinafter.



wherein R_{11} represents an alkyl group, alkenyl group, heterocyclic group or aryl group; and X_1 represents a hydrogen atom, alkaline metal atom, ammonium group or precursor. Examples of such an alkaline metal atom include sodium atom, and potassium atom. Examples of such an ammonium group include tetramethylammonium group, and trimethylbenzyl ammonium group. The term "precursor" as used herein means a group which can be $\text{X}_1=\text{H}$ or alkaline metal under an alkaline condition.

Examples of such a precursor include acetyl group, cyanoethyl group, and methanesulfonylethyl group.

Examples of the alkyl group or alkenyl group represented by R_{11} include substituted, unsubstituted and alicyclic alkyl or alkenyl groups. Examples of substituents for the substituted alkyl group include halogen atom, nitro group, cyano group, hydroxyl group, alkoxy group, aryl group, acylamino group, alkoxy-carbonylamino group, ureide group, amino group, heterocyclic group, acyl group, sulfamoyl group, sulfonamido group, thioureide group, carbamoyl group, alkylthio group, arylthio group, heterocyclic thio group, carboxylic acid group, sulfonic acid group, and salts thereof.

Examples of the above described ureide group, thioureide group, sulfamoyl group, carbamoyl group, and amino group include unsubstituted, N-alkyl-substituted and N-aryl-substituted groups. Examples of the above described aryl group include phenyl group, substituted phenyl group and naphthyl group. Examples of the substituents for the substituted phenyl and naphthyl group include those described with reference to the above described substituted alkyl group.

Specific examples of the heterocyclic group represented by R_{11} include pyridyl group.

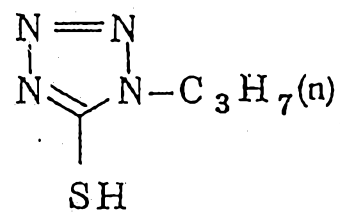
The alkyl group or aryl group represented by R_{11} and R_{12} in formula (II-b) are as defined with reference to formula (II-a).

The amount of the compound represented by formula (II-a) or (II-b) to be incorporated is preferably in the range of 1×10^{-5} to 5×10^{-2} mol, particularly 1×10^{-4} to 1×10^{-2} mol per 1 mol of silver halide.

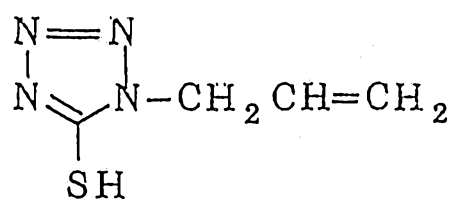
Specific examples of the compound represented by formula (II-a) or (II-b) include Compounds A-366 to A-530, A-3, A-592 to A-644, A-729 to A-746, and A-795 to A-812 described in JP-A-62-215272 (pp. 51-68).

Particularly preferred examples of such compounds will be shown hereinafter.

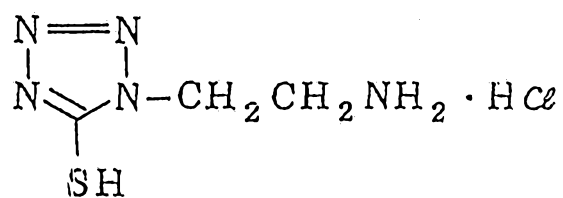
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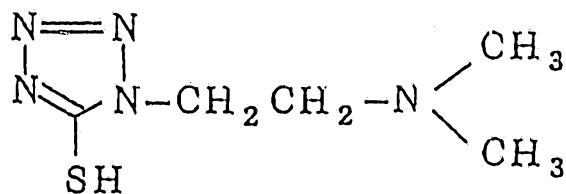
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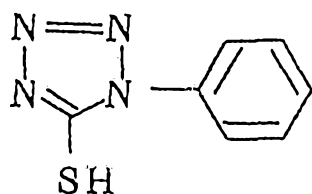
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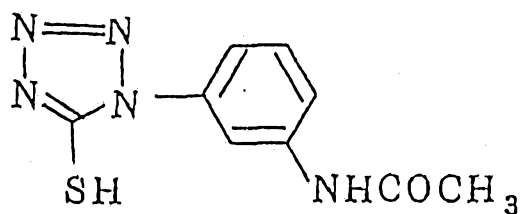
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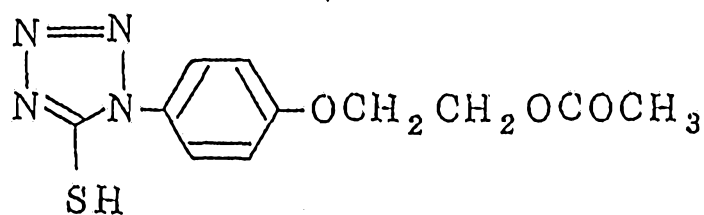
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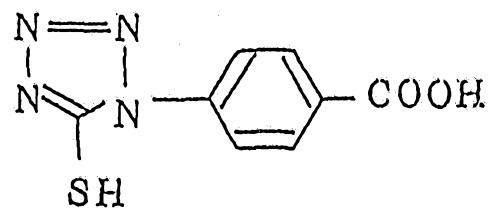
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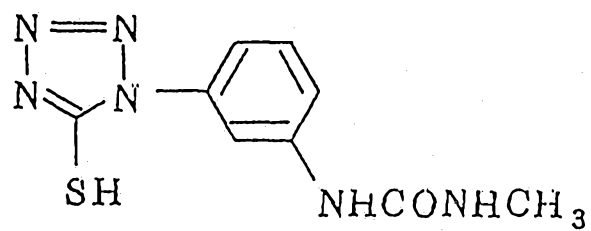
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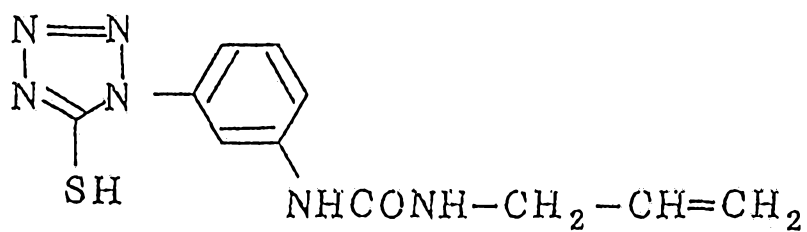
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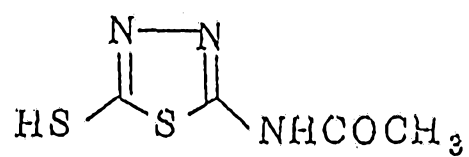
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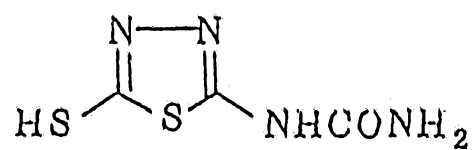
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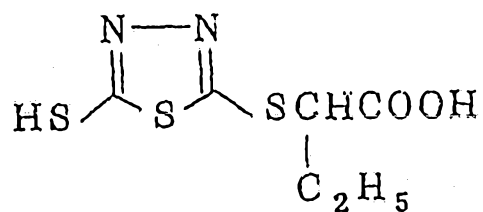
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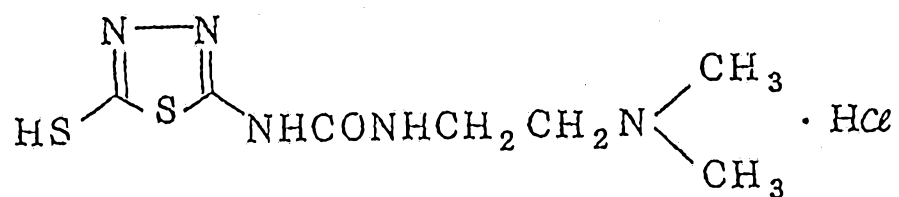
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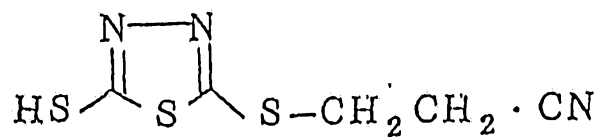
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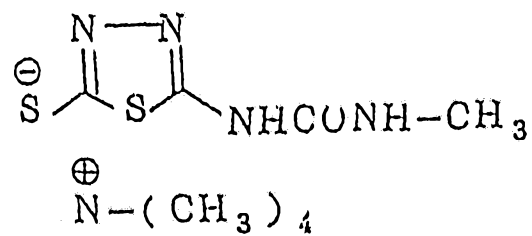
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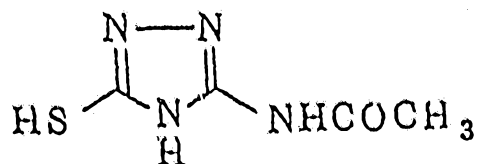
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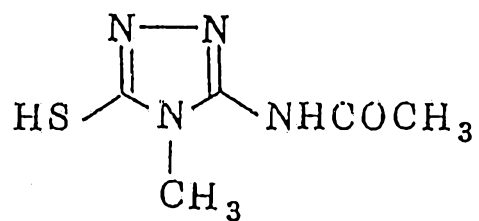
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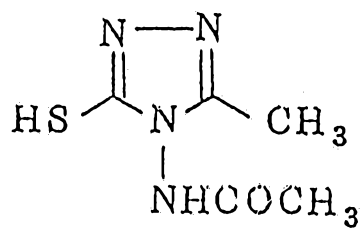
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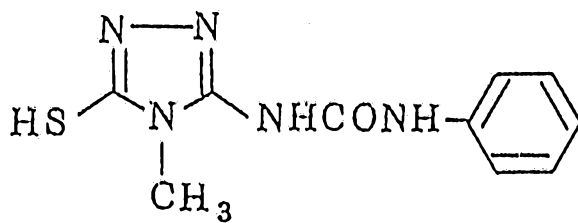
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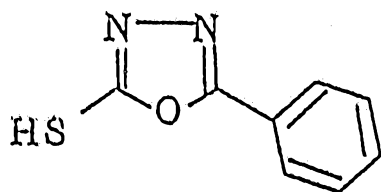
(19)



(20)



(21)



As described above, in a high silver chloride content emulsion excellent in rapid developability, if iridium is incorporated in the localized phases on the silver halide grain, the reciprocity law failure can be improved, and a high sensitivity and contrast can be obtained but the toe gradation tends to become low. This disadvantage can be solved by doping the material with rhodium ion or its complex ion. However, the inventors' study showed that if the material doped with rhodium ion or its complex ion is exposed to safelight or the like, this effect is drastically impaired.

In order to further improve the effect of stabilizing the sensitivity and gradation in the present invention, a dye may be preferably used having a maximum absorption wavelength of 570 to 660 nm in a gelatin film. A strong absorption may lie in a wavelength lower or higher than the maximum absorption wavelength range. However, if too strong an absorption lies in the major sensitive wavelength range of a blue-sensitive, green-sensitive or red-sensitive layer, e.g., 400 to 485 nm, 530 to 560 nm or 630 to 700 nm, the effective sensitivity of each light-sensitive layer is lowered. A dye having a molar absorptivity of, preferably 10^2 to 10^3 $\text{mol}\cdot\text{cm}^{-1}$ in the maximum absorption range may be preferably used. Such a dye can be selected from

commonly known dyes such as arylidene dye, styryl dye, butadiene dye, oxonol dye, cyanine dye, merocyanine dye, hemicyanine dye, diarylmethane dye, triarylmethane dye, azomethine dye, azo dye, metal chelate dye, anthraquinone dye, stilbene dye, chalkone dye, and indophenol dye. Furthermore, such a dye can be selected from compounds as described in U.S. Patents 3,880,658, 3,931,144, 3,932,380, 3,932,381, and 3,942,987, and J. Fabian, H. Hartmann, "Light Absorption of Organic Colorants", Springer Verlag, or its nondiffusive analogues. The dye which may be used in the present invention can be selected from functional dyes as disclosed in Japanese Patent Application No. 106893/87, or dyes as described in JP-A-62-215270, JP-A-62-293243 (pp. 109-117) and JP-A-63-208846 which conform the above spectral absorption characteristics and cause no color stain after development.

The present high silver chloride content silver halide emulsion containing localized phases exhibits an excellent rapid developability as a silver chloride emulsion and provides the same sensitivity as a silver bromochloride emulsion having a silver bromide content of 20 mol% or more. The combined use of the following fog inhibitors can practically fully stop the generation of fog.

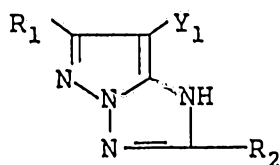
Preferred examples of such fog inhibitors include mercaptotetrazoles, mercaptotriazoles, benzotriazoles, mercaptothiadiazoles, mercaptooxadiazoles, mercaptotriazoles and decomposition products of nucleic acids such as adenines. These fog inhibitors can be mostly adsorbed by the surface of grains other than development starting points to inhibit the generation of fog during the development process without lowering the development starting speed.

Examples of the pyrazoloazole coupler of formula (I) which can be used in the present invention include pyrazolo[5,1-c][1,2,4]triazoles as described in U.S. Patent 3,725,067. Among these couplers, imidazo[1,2-b]pyrazoles as described in U.S. Patent 4,500,630 may be preferably used because they exhibit little yellow side absorption and excellent fastness to light. Particularly preferred among such couplers are pyrazolo[1,5-b][1,2,4]triazoles as described in U.S. Patent 4,540,654.

Other suitable examples of such pyrazoloazole couplers include pyrazolotriazole couplers containing branched alkyl group connected to the 2-, 3- or 6-position of the pyrazolotriazole ring as described in JP-A-61-65245, pyrazoloazole couplers containing sulfon-amido groups in its molecule as described in JP-A-61-

65246, pyrazoloazole couplers containing alkoxyphenyl-sulfonamido ballast group as described in JP-A-61-147254, and pyrazolotriazole couplers containing alkoxy group or aryloxy group in the 6-position as described in EP-A-226,849.

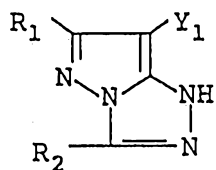
Specific examples of typical pyrazoloazole couplers which can be used in the present invention will be shown hereinafter.



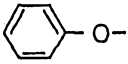
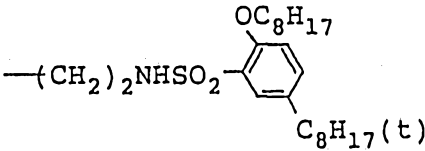
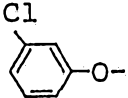
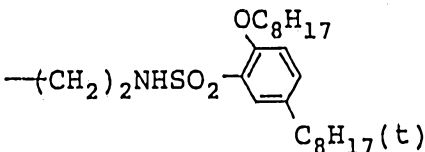
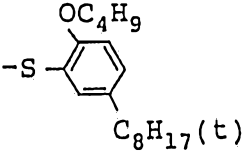
Compound	R ₁	R ₂	Y ₁
M-1	CH ₃ -		-Cl
M-2	Same as above		Same as above

Compound	R ₁	R ₂	Y ₁
M-3	Same as above	$ \begin{array}{c} \text{OC}_8\text{H}_{17} \\ \\ -\text{CHCH}_2\text{NHSO}_2-\text{C}_6\text{H}_3(\text{OC}_8\text{H}_{17})_2 \\ \\ \text{CH}_3 \end{array} $	$ -\text{O}-\text{C}_6\text{H}_4-\text{CH}_3 $
M-4	$ \text{OCH}_3 \\ \\ \text{C}_6\text{H}_4-\text{O}- $	$ \begin{array}{c} \text{OC}_8\text{H}_{17} \\ \\ \text{C}_6\text{H}_4-\text{NHSO}_2-\text{C}_6\text{H}_3(\text{OC}_8\text{H}_{17})_2 \\ \\ \text{C}_8\text{H}_{17}(\text{t}) \end{array} $	$ \begin{array}{c} \text{OC}_4\text{H}_9 \\ \\ -\text{S}-\text{C}_6\text{H}_3(\text{C}_8\text{H}_{17}(\text{t}))_2 \end{array} $
M-5	CH ₃ -	$ \begin{array}{c} \text{OC}_2\text{H}_4\text{OC}_2\text{H}_5 \\ \\ -\text{CHCH}_2\text{NHSO}_2-\text{C}_6\text{H}_3(\text{NHSO}_2-*)_2 \\ \\ \text{CH}_3 \end{array} $ $ \begin{array}{c} \text{OC}_8\text{H}_{17} \\ \\ *-\text{C}_6\text{H}_3(\text{C}_8\text{H}_{17}(\text{t}))_2 \end{array} $	-Cl
M-6	Same as above	$ \begin{array}{c} \text{CH}_3 \\ \\ -\text{CCH}_2\text{NHSO}_2-\text{C}_6\text{H}_3(\text{NHSO}_2-*)_2 \\ \\ \text{CH}_3 \end{array} $ $ \begin{array}{c} \text{OC}_8\text{H}_{17} \\ \\ *-\text{C}_6\text{H}_3(\text{C}_8\text{H}_{17}(\text{t}))_2 \end{array} $	Same as above

Compound	R ₁	R ₂	Y ₁
M-7			
M-8	CH ₃ CH ₂ O-	Same as above	Same as above
M-9			Same as above
M-10			-Cl



Compound	R ₁	R ₂	Y ₁
M-11	CH ₃ -	$\text{HO}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-\text{OCHCONH}-\text{C}_{10}\text{F}_{21}$	-Cl
		$*\text{-C}_6\text{H}_4\text{-}(\text{CH}_2)_3$	
M-12	Same as above	$\begin{array}{l} (n)\text{C}_6\text{H}_{13} \\ (n)\text{C}_8\text{H}_{17} \end{array} \text{CHCH}_2\text{SO}_2(\text{CH}_2)_2$	Same as above
M-13	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH-} \\ \diagdown \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{OC}_4\text{H}_9 \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{SO}_2(\text{CH}_2)_3 \\ \\ \text{C}_8\text{H}_{17}(t) \end{array}$	Same as above
M-14	$\begin{array}{c} \text{-(CH-CH}_2\text{)}_{50}^* \\ \\ \text{COOCH}_2\text{CH}_2\text{OCH}_3 \\ \\ \text{CH}_3 \\ \\ \text{*(CH}_2\text{-C)}_{50} \\ \\ \text{CONH-} \end{array}$	$\begin{array}{c} \text{CH}_3\text{-CH-} \\ \\ \text{CH}_2\text{NHSO}_2\text{CH}_3 \end{array}$	Same as above

Compound	R ₁	R ₂	Y ₁
M-15			-Cl
M-16			

5-Pyrazolone couplers may be used in combination with pyrazoloazole couplers. As such 5-pyrazolone couplers there may be preferably used couplers substituted by an arylamino group or acylamino group in the 3-position in the light of color hue of color dye and color density. Typical examples of such dyes are described in U.S. Patents 2,311,082, 2,343,703, 2,600,788, 2,908,573, 3,062,653, 3,152,896, and 3,936,015. As release groups for two-equivalent 5-pyrazolone couplers there may be preferably used nitrogen atom linked release groups as described in U.S. Patent 4,310,619 or arylthio groups as described in U.S. Patent 4,351,897. 5-Pyrazolone couplers containing a ballast group as described in European Patent 73,636 and WO 88/04795 can provide a high color density.

In the present invention, as yellow couplers there may be preferably used pivaloylacetanilide yellow couplers, benzoylacetanilide yellow couplers, or the like. Pivaloylacetanilide yellow couplers are further described in U.S. Patents 4,622,287 (15th line on 3rd column to 39th line on 8th column) and 4,623,616 (50th line on 14th column to 41st line on 19th column).

Benzoylacetanilide yellow couplers are further described in U.S. Patents 3,408,194, 3,933,501, 4,046,575, 4,133,958, and 4,401,752.

Specific examples of such pivaloylacetanilide yellow couplers include Compounds (Y-1) to (Y-39) described in U.S. Patent 4,622,287 (37th column to 54th column). Particularly preferred among these compounds are (Y-1), (Y-4), (Y-6), (Y-7), (Y-15), (Y-21), (Y-22), (Y-23), (Y-26), (Y-35), (Y-37), (Y-38) and (Y-39).

Other specific examples of pivaloylacetanilide yellow couplers include exemplary compounds (Y-1) to (Y-33) described in U.S. Patent 4,623,616 (19th column to 24th column). Particularly preferred among these compounds are (Y-2), (Y-7), (Y-8), (Y-12), (Y-20), (Y-21), (Y-23), and (Y-29).

Further specific examples of such yellow couplers preferably include typical exemplary compound (34) described in U.S. Patent 3,408,194 (6th column),

exemplary compounds (16) and (19) described in U.S. Patent 3,933,501, exemplary compound (9) described in U.S. Patent 4,046,575 (7th column to 8th column), exemplary compound (1) described in U.S. Patent 4,133,958 (5th column to 6th column), and an exemplary compound described in U.S. Patent 4,401,752 (5th column). Particularly, two-equivalent couplers having nitrogen atom linked release groups may be preferably used.

In the present invention, as cyan couplers there may be preferably used phenolic cyan couplers or naphtholic cyan couplers.

Examples of such phenolic cyan couplers include couplers containing an acylamino group in the 2-position of the phenol nucleus and an alkyl group in the 5-position of the phenol nucleus and their polymer couplers as described in U.S. Patents 2,369,929, 4,518,687, 4,511,647, and 3,772,002. Specific typical examples of such couplers include couplers as described in Example 2 in Canadian Patent 625,822, Compound (1) described in U.S. Patent 3,772,002, Compounds (I-4) and (I-5) described in U.S. Patent 4,564,590, Compounds (1), (2), (3) and (24) described in JP-A-61-39045, and Compound (C-2) described in JP-A-62-70846.

Examples of phenolic cyan couplers include 2,5-diacylaminophenolic couplers as described in U.S.

Patents 2,772,162, 2,895,826, 4,334,011, and 4,500,653, and JP-A-59-164555. Specific typical examples of such couplers include Compound (V) described in U.S. Patent 2,895,826, Compound (17) described in U.S. Patent 4,557,999, Compounds (2) and (12) described in U.S. Patent 4,565,777, Compound (4) described in U.S. Patent 4,124,396, and Compound (I-19) described in U.S. Patent 4,613,564.

Other examples of phenolic cyan couplers include couplers containing nitrogen-containing heterocyclic group fused to a phenol nucleus as described in U.S. Patents 4,327,173, 4,564,586, and 4,430,423, JP-A-61-390441, and JP-A-62-257158. Specific typical examples of such couplers include Couplers (1) and (3) described in U.S. Patent 4,327,173, Compounds (3) and (16) described in U.S. Patent 4,564,586, and Compounds (1) and (3) described in U.S. Patent 4,430,423.

Further examples of phenolic cyan couplers include ureide couplers as described in U.S. Patents 4,333,999, 4,451,559, 4,444,872, 4,427,767, and 4,579,813, and European Patent 067,689. Specific typical examples of such ureide couplers include Coupler (7) described in U.S. Patent 4,333,999, Coupler (1) described in U.S. Patent 4,451,559, Coupler (14) described in U.S. Patent 4,444,872, Coupler (3)

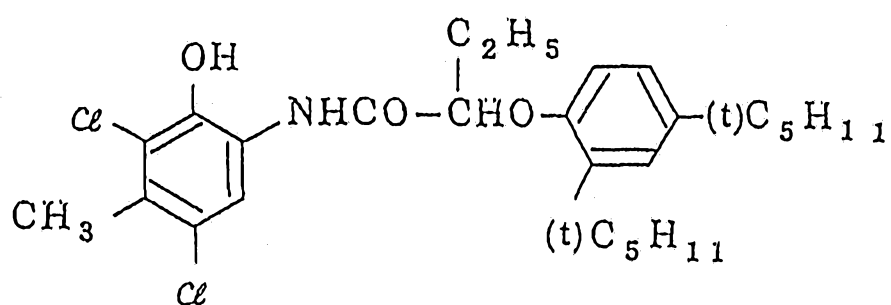
described in U.S. Patent 4,427,767, Couplers (6) and (24) described in U.S. Patent 4,609,619, Couplers (1) and (11) described in U.S. Patent 4,579,813, Couplers (45) and (50) described in European Patent 067,689, and Coupler (3) described in JP-A-61-42658.

Examples of naphtholic cyan couplers include couplers containing N-alkyl-N-arylcarbamoyl group in the 2-position of the naphthol nucleus as described in U.S. Patent 2,313,586, couplers containing alkylcarbamoyl group in the 2-position of the naphthol nucleus as described in U.S. Patent 2,474,293, couplers containing arylcarbamoyl group in the 2-position of the naphthol nucleus as described in JP-B-50-14523 (the term "JP-B" as used herein means an examined Japanese patent publication), couplers containing carbonamido or sulfonamido group in the 5-position of the naphthol nucleus as described in JP-A-60-237448, JP-A-61-145557, and JP-A-61-153640, couplers containing aryloxy release group as described in U.S. Patent 3,476,563, couplers containing substituted alkoxy release group as described in U.S. Patent 4,296,199, and couplers containing glycolic acid release group as described in JP-B-60-39217.

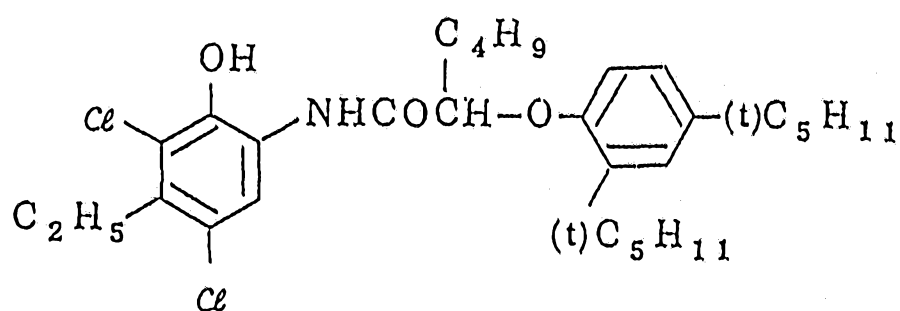
Specific typical examples of cyan couplers, 5-pyrazolone magenta couplers and yellow couplers which

can be preferably used in the present invention will be shown hereinafter.

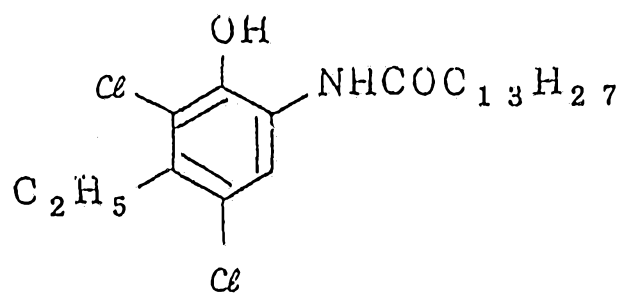
C - (1)



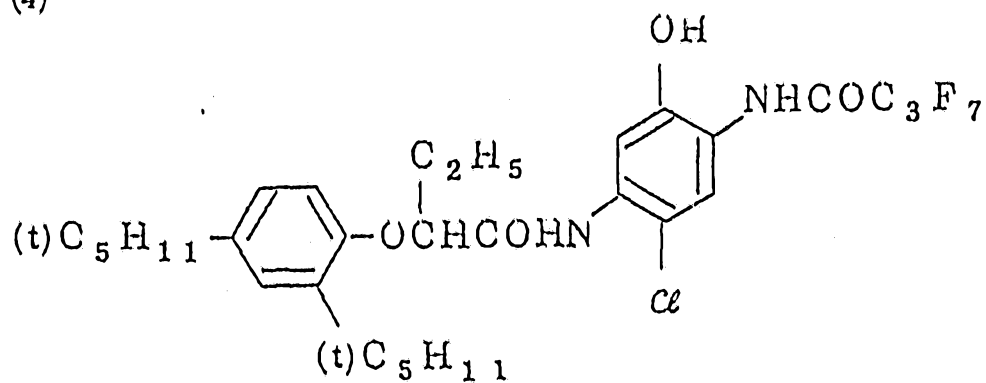
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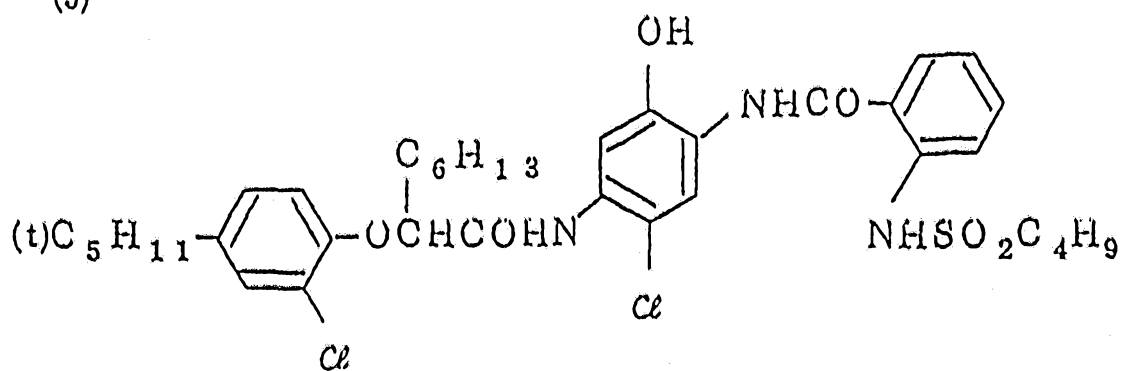
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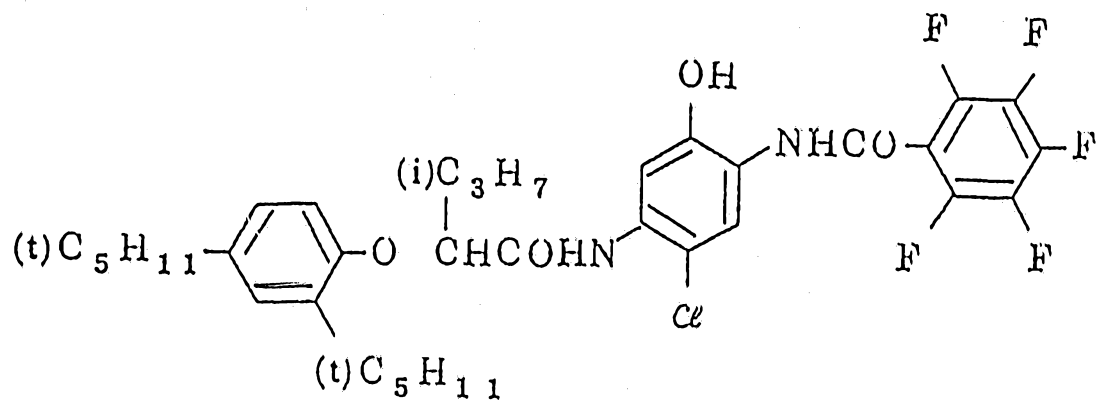
(4)



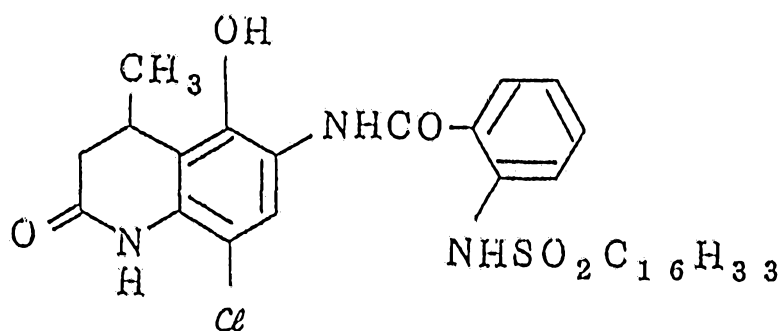
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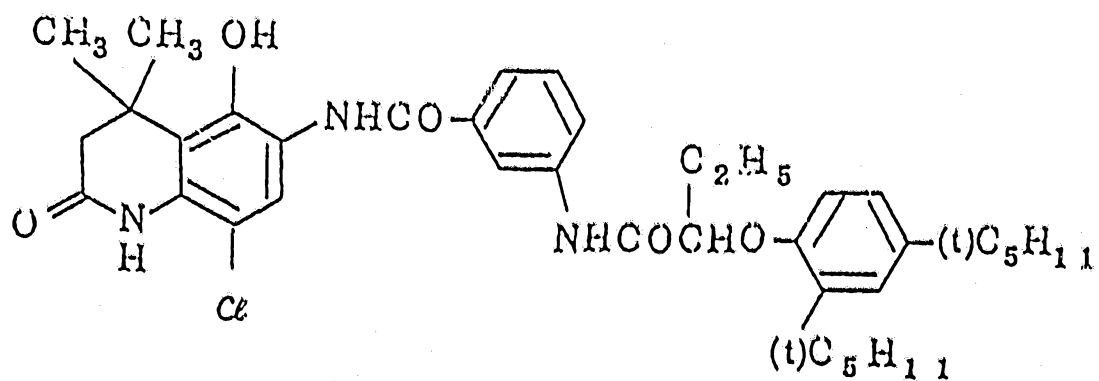
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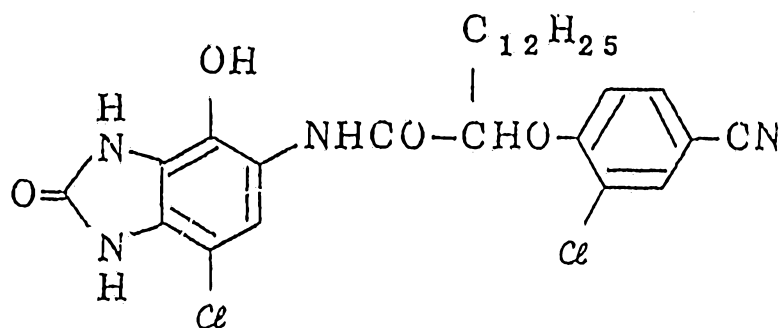
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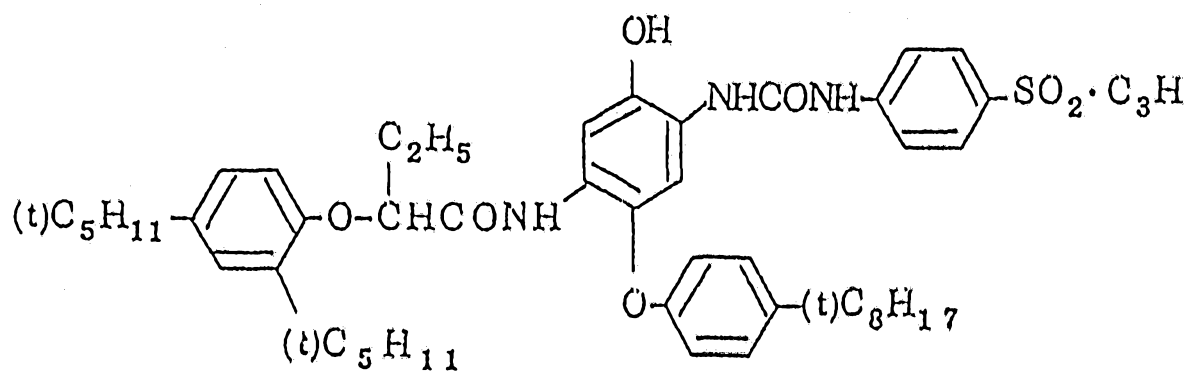
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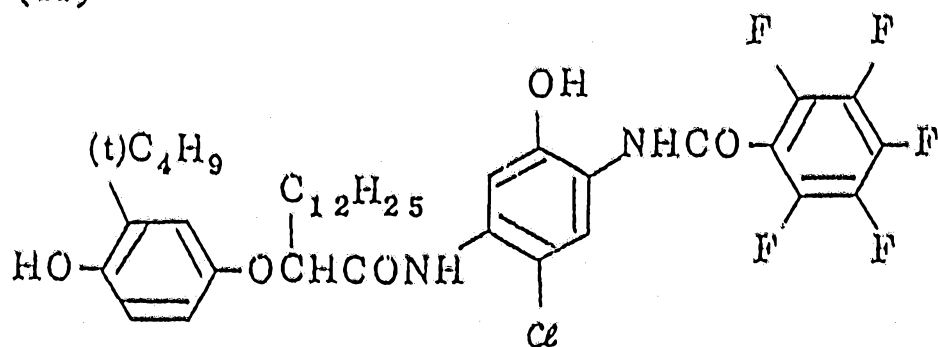
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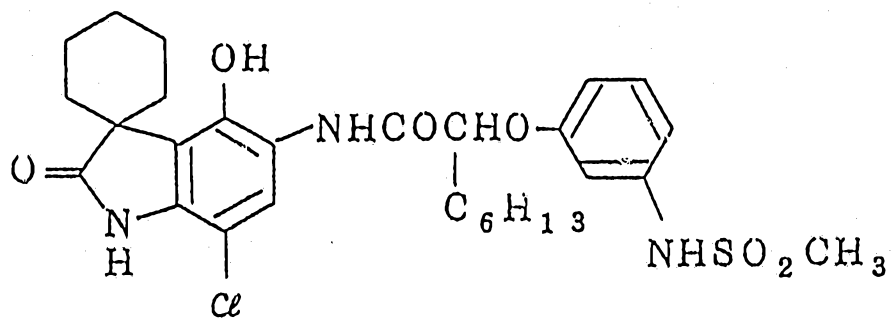
(10)



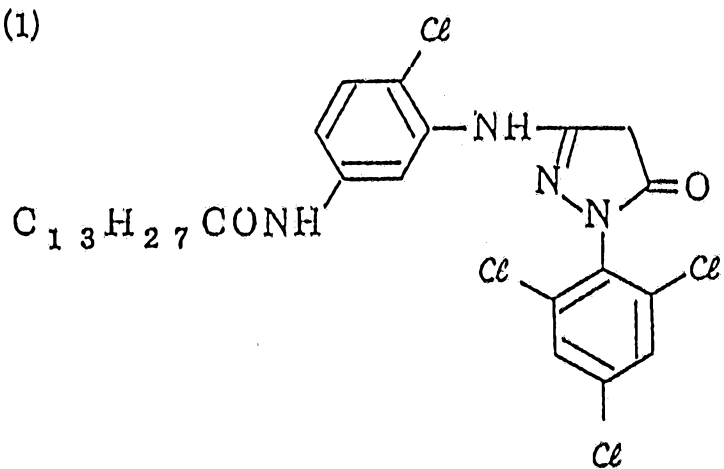
(11)



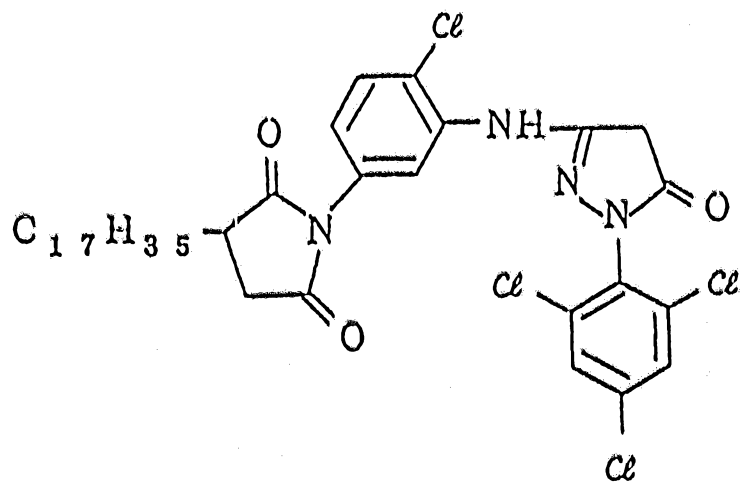
(12)



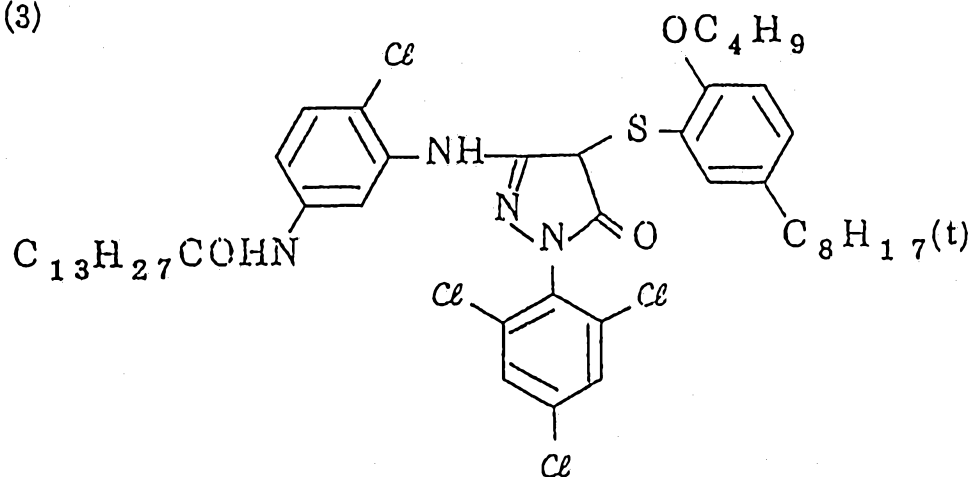
M - (1)



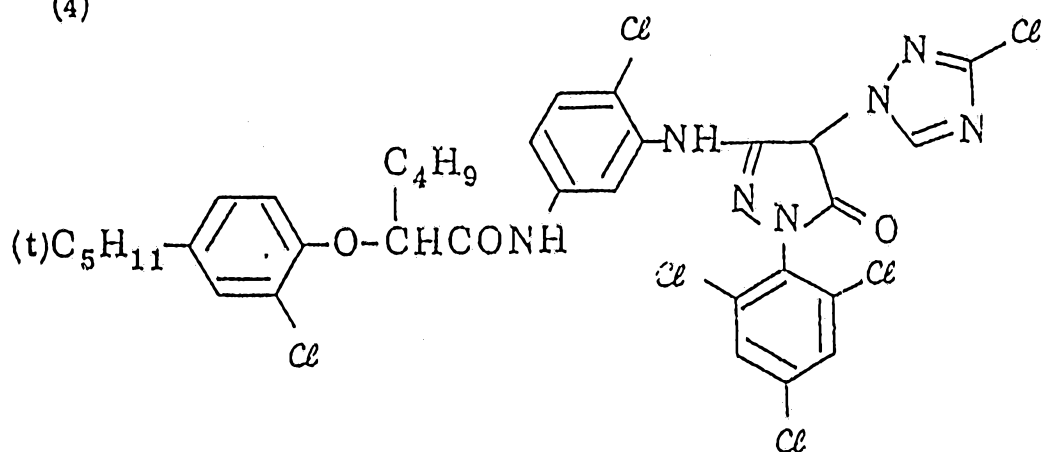
(2)



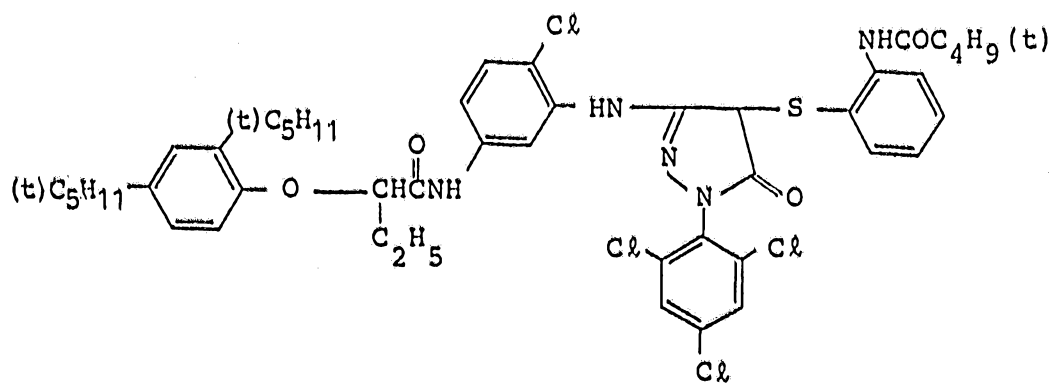
(3)



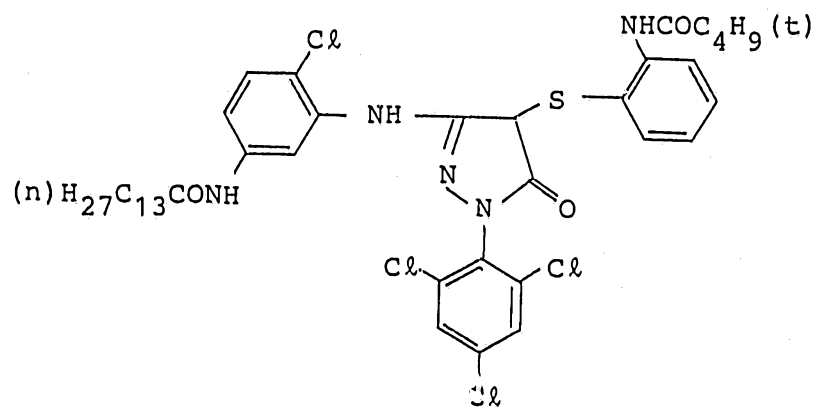
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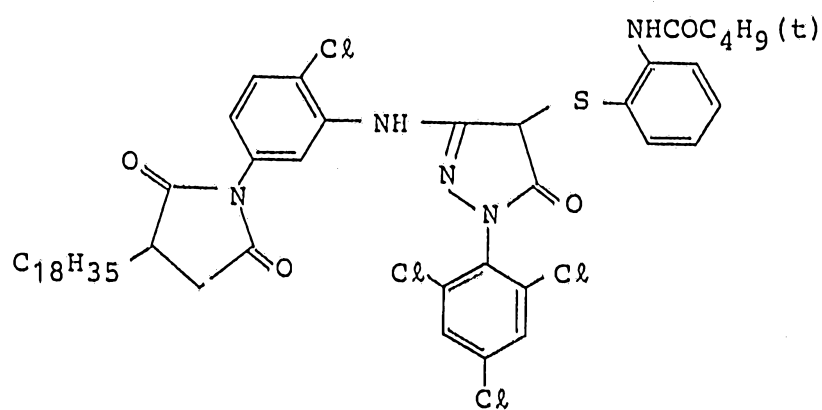
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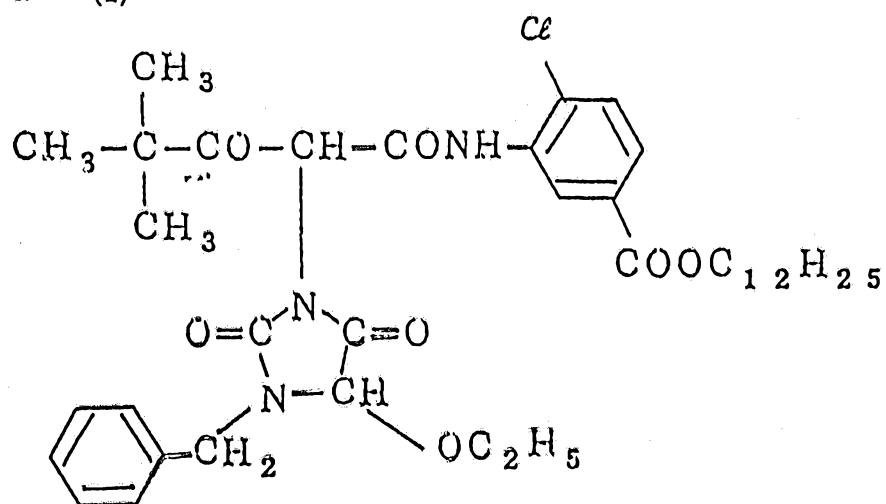
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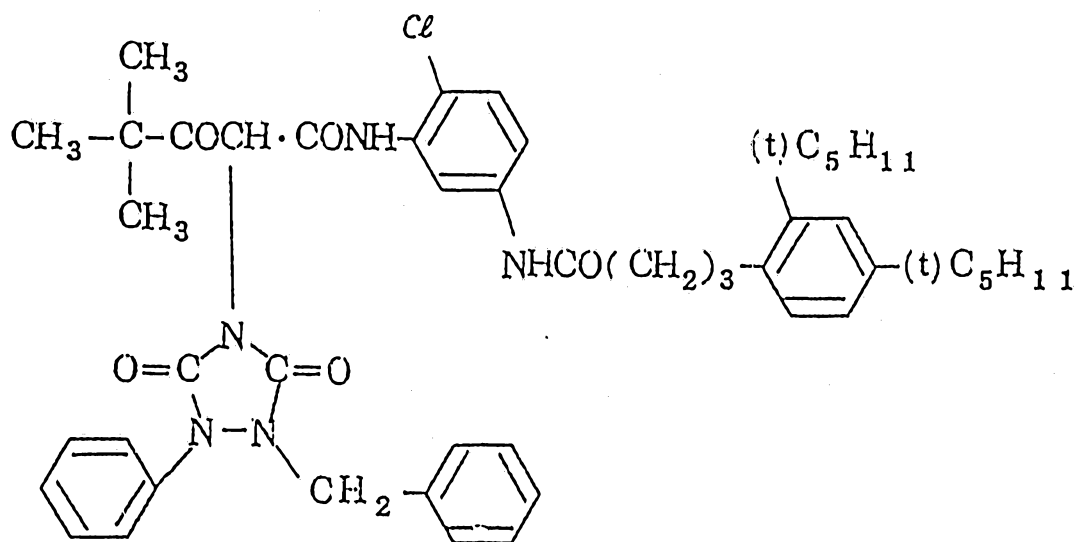
(7)



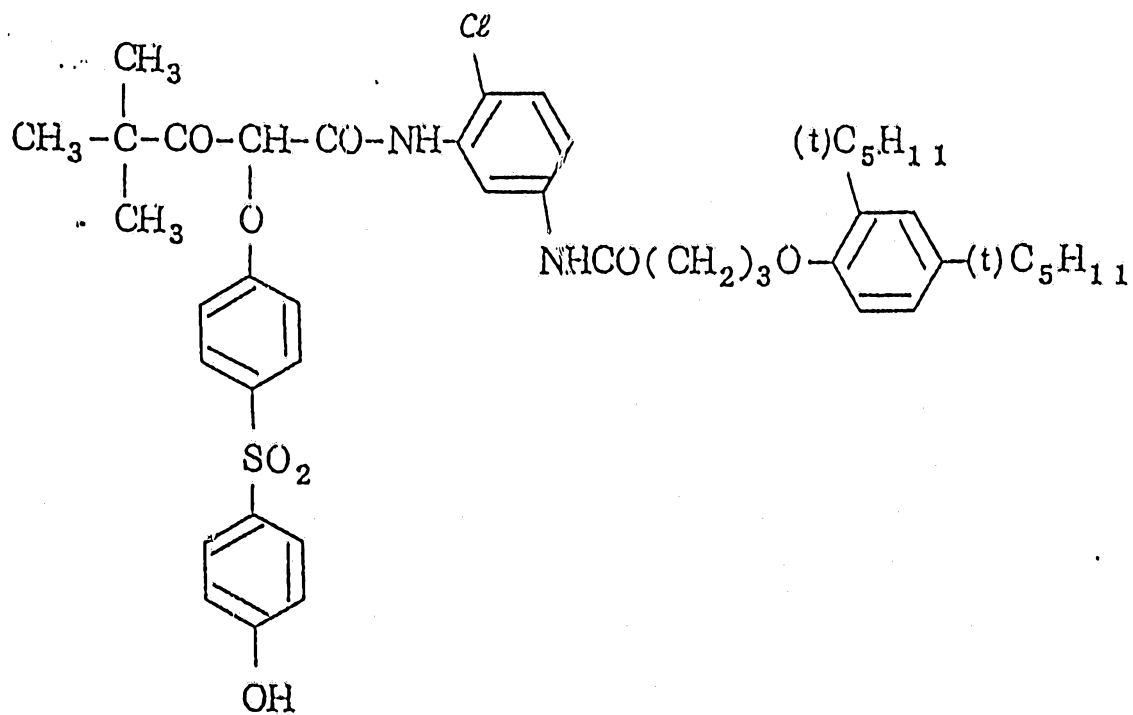
Y - (1)



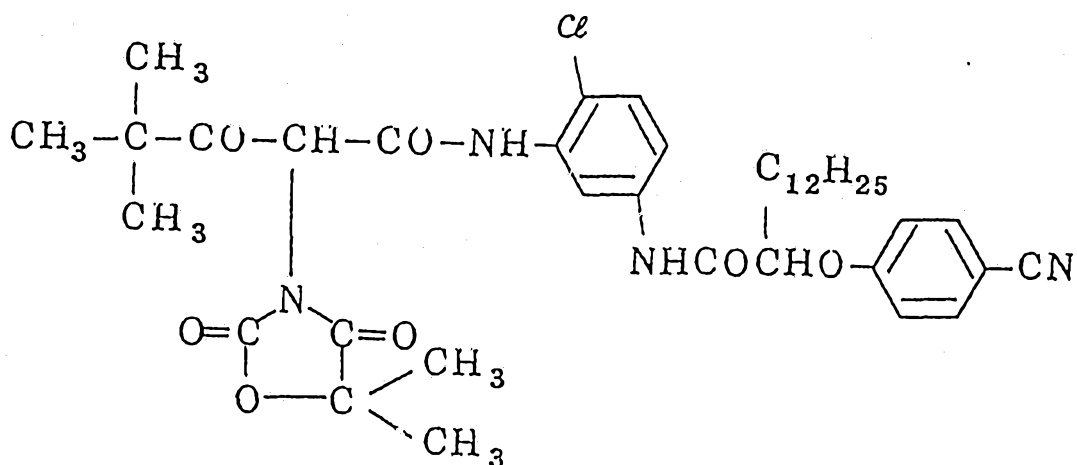
(2)



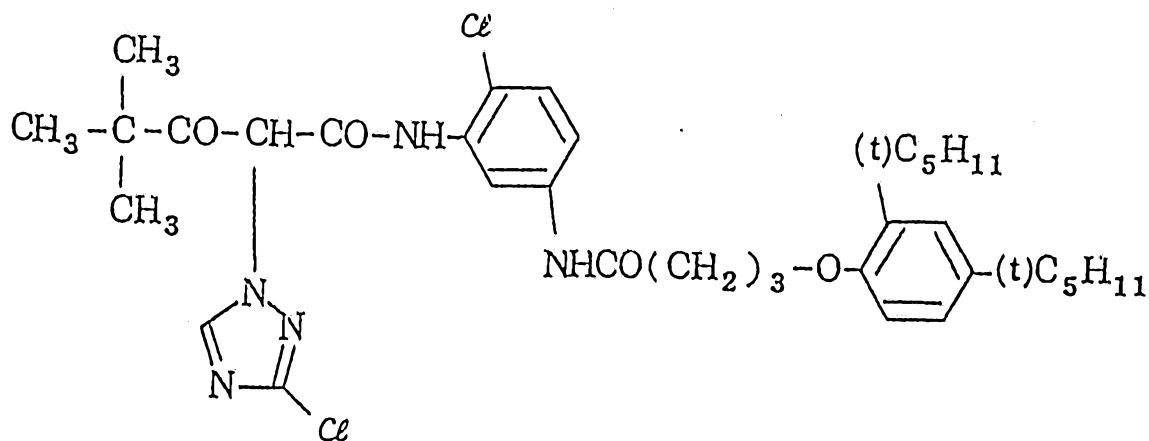
(3)



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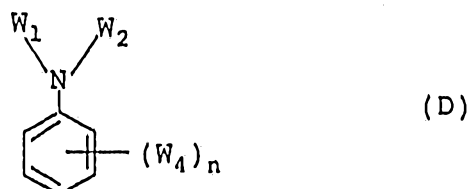
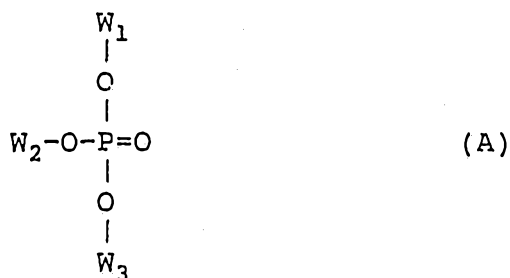


The standard amount of such a color coupler to be used is in the range of 0.001 to 1 mol per 1 mol of light-sensitive silver halide. Particularly, the amount of a yellow coupler to be used is preferably in the

range of 0.01 to 0.5 mol per 1 mol of light-sensitive silver halide. The amount of a magenta coupler to be used is preferably in the range of 0.003 to 0.3 mol per 1 mol of light-sensitive silver halide. The amount of a cyan coupler to be used is preferably in the range of 0.002 to 0.3 mol per 1 mol of light-sensitive silver halide.

In a light-sensitive material comprising the present color coupler, the coated amount of silver halide is preferably in the range 0.1 to 1.5 g/m², particularly 1.2 g/m² or less if a reflective support is used, or in the range of 0.2 to 7 g/m², particularly 5 g/m² or less if a transparent support is used.

The incorporation of these couplers in the emulsion layer can be accomplished by an oil dispersion process. In this process, these couplers are dispersed in the emulsion layer together with at least one high boiling organic solvent. Preferably, high boiling organic solvents represented by formulae (A) to (E) may be used.



wherein W_1 , W_2 , and W_3 each represents a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, aryl or heterocyclic group; W_4 represents W_1 , $O-W_1$ or $S-W_1$; and n represents an integer 1 to 5. When n is 2 or more, the plurality of W_4 's may be the same or different. In formula (E), W_1 and W_2 may together form a condensed ring.

The details of these high boiling organic solvents are described in JP-A-62-215272, from page 137, right lower column to page 144, right upper column.

These couplers can be emulsion-dispersed in an aqueous solution of a hydrophilic colloid by impregnating them in a loadable latex polymer (for example, U.S. Patent 4,203,716) in the presence of or in the absence of the above-described high boiling organic solvents, or dissolving them in a water-insoluble and organic solvent-soluble polymer. A homopolymer or a copolymer as described in WO 88/00723, pages 12 to 30 can be preferably used as the water-insoluble and organic solvent-soluble polymer, with the use of a acrylamide-series polymer being particularly preferred in view of stabilizing a color image, etc.

The light-sensitive material prepared in accordance with the present invention may comprise as color fog inhibitor or color stain preventing agent a hydroquinone derivative, aminophenol derivative, amine, gallic acid derivative, catechol derivative, ascorbic acid derivative, colorless compound forming coupler, color dye elution type coupler, sulfonamide phenol derivative or the like.

The present light-sensitive material may comprise various discoloration inhibitors. Typical

examples of organic discoloration inhibitors for cyan, magenta and/or yellow images include hydroquinones, 6-hydroxychromans, 5-hydroxycoumarans, spirochromans, p-alkoxyphenols, bisphenols and other hindered phenols, gallic acid derivatives, methylenedioxybenzenes, aminophenols, hindered amines, and ether or ester derivatives obtained by silylating or alkylating the phenolic hydroxyl group of these compounds. Other examples of discoloration inhibitors which can be used include metal complexes such as (bissalicylaldoximato)nickel complex and (bis-N,N-dialkyldithiocarbamato)nickel complex.

Specific examples of organic discoloration inhibitors are described in the following patent specifications.

Specific examples of hydroquinones are described in U.S. Patents 2,360,290, 2,418,613, 2,700,453, 2,701,197, 2,728,659, 2,732,300, 2,735,765, 3,982,944, 4,430,425, 2,710,801, and 2,816,028, and British Patent 1,363,921. Specific examples of 6-hydroxychromans, 5-hydroxycoumarans, and spirochromans are described in U.S. Patents 3,432,300, 3,573,050, 3,574,627, 3,698,909, and 3,764,337, and JP-A-52-152225. Specific examples of spiroindans are described in U.S. Patent 4,360,589. Specific examples of p-alkoxyphenols are described in U.S. Patent 2,735,765, British Patent 2,066,975, JP-A-

59-10539, and JP-B-57-19764. Specific examples of hindered phenols are described in U.S. Patents 3,700,455, and 4,228,235, JP-A-52-72225, and JP-B-52-6623. Specific examples of gallic acid derivatives, methylenedioxybenzenes, and aminophenols are described in U.S. Patents 3,457,079 and 4,332,886, and JP-B-56-21144. Specific examples of hindered amines are described in U.S. Patents 3,336,135, and 4,268,593, British Patents 1,326,889, 1,354,313, and 1,410,846, JP-B-51-1420, and JP-A-58-114036, JP-A-59-53846, and JP-A-59-78344. Specific examples of ether and ester derivatives of phenolic hydroxyl groups are described in U.S. Patents 4,155,765, 4,174,220, 4,254,216, 4,264,720, and 4,279,990, JP-A-54-145530, JP-A-55-6321, JP-A-58-105147, and JP-A-59-10539, and JP-B-57-37856, and JP-B-53-3263. Specific examples of metal complexes are described in U.S. Patents 4,050,938, and 4,241,155, and British Patent 2,027,731(A). These compounds may be incorporated in the light-sensitive layer in the form of a coemulsion with its corresponding color coupler in an amount of 5 to 100% by weight based on the amount of the color coupler to accomplish its objects. In order to prevent the deterioration of a cyan dye image due to heat, particularly light, it is more effective to

incorporate an ultraviolet absorber in both the two layers adjacent to the cyan coloring layer.

Particularly preferred among the above described discoloration inhibitors are spiroindanes, and hindered amines.

In the present invention, the following compounds may be preferably used in combination with the above described couplers, particularly pyrazoloazole couplers.

In other words, a compound (A) which is chemically bonded to an aromatic amine developing agent left after the color development to produce a chemically inert and substantially colorless compound and/or a compound (B) which is chemically bonded to an oxidation product of an aromatic amine color developing agent left after the color development to produce a chemically inert and substantially colorless compound may preferably be used simultaneously or separately to inhibit the generation of stain or other side effects due to the production of color dyes caused by the reaction of a coupler with a color developing agent or its oxidation product left in the film during preservation after the development.

As a suitable compound (A) there may be used a compound which reacts with p-aminidine at a second-order

reaction rate constant k_2 of $1.0 \text{ l/mol}\cdot\text{sec}$ to $1 \times 10^{-5} \text{ l/mol}\cdot\text{sec}$ in trioctyl phosphate at 80°C . The second-order reaction rate constant can be measured according to a method as described in JP-A-63-158545.

If k_2 exceeds this range, the compound itself becomes so unstable that it may react with gelatin or water to undergo decomposition. On the other hand, if k_2 is smaller than this range, the compound reacts with the remaining aromatic amine developing agent at a lower rate, making it impossible to inhibit the side effects of the remaining aromatic amine developing agent.

A preferred example of such a compound (A) can be represented by formula (AI) or (AII):



wherein R_1 and R_2 each represents an aliphatic group, aromatic group or heterocyclic group; n represents 0 or 1; A represents a group that can react with the aromatic amine developing agent to form a chemical bond; X represents a group that can react with the aromatic amine developing agent to split off; B represents a hydrogen atom, an aliphatic group, an aromatic group,

a heterocyclic group, an acyl group or a sulfonyl group; Y represents a group that can facilitate the addition of the aromatic amine developing agent to the compound having formula (AII); and R₁ and X together or Y and R₂ or B together may combine to form a ring structure.

Of ways wherein the remaining aromatic amine developing agent and the compound (A) chemically combine, typical ways are substitution reactions and addition reactions.

The preferred examples of the compounds represented by formula (AI) or (AII) include the compounds as described in JP-A-63-158545, JP-A-62-283338, Japanese patent application No. 158342/87, EP-A-277589, etc.

More preferred examples of the compounds (B) that can chemically combine with the oxidation product of the aromatic amine developing agent remaining after the color development processing to form a chemically inactive and substantially colorless compound are those represented by the following formula (BI):



wherein R represents an aliphatic group, an aromatic group, or a heterocyclic group, and Z represents a nucleophilic group or a group that can decompose in the

photographic material to release a nucleophilic group. In the compounds represented by the formula (BI), Z preferably represents a group having a Pearson's nucleophilic $n\text{CH}_3\text{I}$ value [R.G. Pearson et al., J. Am. Chem. Soc., 90, 319 (1968)] of 5 or more, or the group derived therefrom.

The preferred examples of the compounds represented by the formula (BI) include the compounds as described in EP-A-255722, EP-A-277589, JP-A-62-143048, JP-A-62-229145, Japanese patent application Nos. 136724/88, 214681/87 and 158342/87, etc.

The detailed explanation on combination of the aforementioned compound (A) and compound (B) is described in EP 277589.

In order to improve the preservability, particularly light fastness of a cyan image, a benzotriazole ultraviolet absorber may be preferably incorporated in the light-sensitive material. Such an ultraviolet absorber may be incorporated in the form of a coemulsion with a cyan coupler.

The coated amount of such an ultraviolet absorber may be such that it renders the cyan dye image stable to light. However, if such an ultraviolet absorber is used in too large an amount, it may cause the unexposed portion (background) of the color

photographic light-sensitive material to grow yellowish. Therefore, the coated amount of such an ultraviolet absorber is normally in the range of 1×10^{-4} to 2×10^{-3} mol/m², particularly 5×10^{-4} to 1.5×10^{-3} mol/m².

In the light-sensitive material layer structure of a normal color paper, an ultraviolet absorber may be incorporated in either, preferably both of the two layers adjacent to a cyan coupler-containing red-sensitive emulsion layer. If an ultraviolet absorber is incorporated in an intermediate layer between a green-sensitive layer and a red-sensitive layer, it may be co-emulsified with a color stain preventing agent. If an ultraviolet absorber is incorporated in a protective layer, another protective layer may be provided as an outermost layer. This protective layer may comprise a mixture of matt agents having any grain diameters or latexes having different grain diameters.

In the present light-sensitive material, an ultraviolet absorber may be incorporated in a hydrophilic colloidal layer.

As a suitable reflective support for the present invention there may be used a material which improves the reflectivity of the light-sensitive material so that a dye image formed on the silver halide emulsion layer is made sharp. Examples of such a reflective support

include a support coated with a hydrophobic resin comprising a reflective substance such as titanium oxide, zinc oxide, calcium carbonate or calcium sulfate dispersed therein and a vinyl chloride resin comprising a reflective substance dispersed therein. Specific examples of such supports include baryta paper, polyethylene-coated paper, polypropylene synthetic paper, and transparent support such as glass plate, polyester film (e.g., polyethylene terephthalate, cellulose triacetate, cellulose nitrate), polyamide film, polycarbonate film, and polystyrene film combined with a reflective layer or a reflective substance. These supports can be properly selected depending on the purpose of application. Alternatively, supports having a mirror-like surface reflection or a second type diffused reflection surface as described in JP-A-60-210346, JP-A-63-118154 and JP-A-63-24247 may be used. In the present invention, a transparent support may be used.

As described above, the present invention may be advantageously applied to a multilayer multicolor photographic material having at least two different spectral sensitivities on a support. A multilayer natural color photographic material normally comprises at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer and at least one red-

sensitive emulsion layer on a support. The order of arrangement of these sensitive layers can be properly selected as necessary. Each of these emulsion layers may consist of two or more emulsion layers having different sensitivities or may consist two or more emulsion layers having the same color sensitivity and a light-insensitive layer provided interposed therebetween.

The color light-sensitive material according to the present invention may comprise a protective layer, intermediate layer, filter layer, antihalation layer, back layer or the like besides a silver halide emulsion layer on a support.

As a suitable binder or protective colloid to be incorporated in the emulsion layer or intermediate layer in the present light-sensitive material there can be advantageously used gelatin. Other hydrophilic colloids can be used in the present invention.

Examples of such hydrophilic colloids which can be used in the present invention include protein such as gelatin derivative, graft polymer of gelatin with other high molecular compounds, albumin, and casein, sugar derivative such as hydroxyethyl cellulose, carboxymethyl cellulose, cellulose ester sulfate, sodium alginate, and starch derivative, homopolymer or copolymer such as

polyvinyl alcohol, polyvinyl alcohol-partial acetal, poly-N-vinyl pyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole, and polyvinyl pyrazole, and other synthetic hydrophilic high molecular compounds.

As gelatin there may be used lime-processed gelatin, acid-processed gelatin, or enzyme-processed gelatin as described in Bull. Soc. Sci. Phot. Japan. No. 16, page 30 (1966). Alternatively, hydrolyzate or enzymatic decomposition product of gelatin may be used.

Besides the above described additives, the present light-sensitive material may comprise various stabilizers, stain inhibitors, developing agents or the precursors thereof, development accelerators or the precursors thereof, lubricants, mordants, matt agents, antistatic agents, plasticizers, or other various additives useful for photographic light-sensitive materials. Typical examples of these additives are described in Research Disclosure Nos. 17,643 (December, 1978) and 18,716 (November, 1979).

The present light-sensitive material may comprise a water-soluble dye in the hydrophilic colloid layer as a filter dye or for the purpose of inhibiting irradiation or halation or other various purposes.

The photographic emulsion layer or other hydrophilic colloid layers of the present light-sensitive material may comprise a stilbene series, triazine series, oxazole series or coumarine series whitening agent. A water-soluble whitening agent may be used. Alternatively, a water-insoluble whitening agent may be used in the form of a dispersion.

Another feature of the present invention is a high rapidity and stability in the color development. In other words, the color development can be effected in a time shorter than 3 minutes and 40 seconds, preferably 3 minutes, particularly 2 minutes and 30 seconds in accordance with the present invention. This requires a small amount of silver halide to be coated. This extremely favors the color development as well as rapidity in the desilvering process.

As a suitable aromatic primary amine color developing agent to be incorporated in the present color developing solution there may be used any known developing solution commonly used in various color photographic processes. Examples of these developing agents include aminophenolic and p-phenylenediamine derivatives. Preferred examples of such derivatives include p-phenylenediamine derivatives. Typical examples of such p-phenylenediamine derivatives will be

shown hereinafter, but the present invention should not be construed as being limited thereto.

- D-1: N,N-diethyl-p-phenylenediamine
- D-2: 2-Amino-5-diethylaminotoluene
- D-3: 2-Amino-5-(N-ethyl-N-laurylamino)toluene
- D-4: 4-[N-ethyl-N-(β -hydroxyethyl)amino]aniline
- D-5: 2-Methyl-4-[N-ethyl-N-(β -hydroxyethyl)amino]-aniline
- D-6: 4-Amino-3-methyl-N-ethyl-N-[β -(methanesulfonamido)ethyl]aniline
- D-7: N-(2-amino-5-diethylaminophenylethyl)methanesulfonamide
- D-8: N,N-dimethyl-p-phenylenediamine
- D-9: 4-Amino-3-methyl-N-ethyl-N-methoxyethylaniline
- D-10: 4-Amino-3-methyl-N-ethyl-N- β -ethoxyethylaniline
- D-11: 4-Amino-3-methyl-N-ethyl-N- β -butoxyethylaniline

These p-phenylenediamine derivatives may be used in the form of sulfate, hydrochloride, sulfite, or p-toluenesulfonate. The amount of the above described aromatic primary amine developing agent to be incorporated is preferably in the range of about 0.1 to about 20 g, particularly about 0.5 g to about 10 g per l of developing solution.

The present color developing solution may optionally comprise as preservative a sulfite such as sodium sulfite, potassium sulfite, sodium bisulfite,

potassium bisulfite, sodium metasulfite, and potassium metasulfite, or a carbonyl-sulfurous acid addition product. However, in order to improve the color development property of the color developing solution, the added amount of sulfurous ions may be preferably minimized.

In order to directly preserve the above described color developing agent, various hydroxylamines, hydroxamic acids as described in JP-A-63-43132, hydrazines and hydrazides as described in Japanese Patent Application No. 170756/86, phenols as described in JP-A-63-44657 and JP-A-63-58443, α -hydroxyketones and α -aminoketones as described in JP-A-63-44656, and/or various saccharides as described in JP-A-63-36244 may be used. These compounds may be used in combination with monoamines as described in Japanese Patent Application No. 164515/86, JP-A-63-4235, JP-A-63-24254, JP-A-63-21647, JP-A-63-27841, and JP-A-63-25654, diamines as described in Japanese Patent Application No. 164515/86, JP-A-63-30845, and JP-A-63-43139, polyamines as described in JP-A-63-21647, and JP-A-63-26655, polyamines as described in JP-A-63-44655, nitroxy radicals as described in JP-A-63-53551, alcohols as described in JP-A-63-43140, and JP-A-63-53549, oxims as

described in JP-A-63-56654, and tertiary amines as described in Japanese Patent Application No. 265149/86.

The presents color light-sensitive material may further comprise as preservative various metals as described in JP-A-57-44148, and JP-A-57-53749, salicylic acids as described in JP-A-59-180588, alcanolamines as described in JP-A-54-3532, polyethylene imines as described in JP-A-56-94349, and aromatic polyhydroxy compounds as described in U.S. Patent 3,746,544 as necessary. Particularly preferred among these compounds are aromatic polyhydroxy compounds and triethanol amines, and compounds as described in Japanese Patent Application No. 265149/86.

The color developing solution to be used in the present invention has a pH value of 9 to 12, preferably 9 to 11.0. The present color developing solution may further comprise known developing solution components.

In order to maintain the above described pH range, various buffers may be preferably used. As such buffers there may be used carbonates, phosphates, borates, tetraborates, hydroxybenzoates, glycyl salts, N,N-dimethylglycine salts, leucine salts, norleucine salts, guanine salts, 3,4-dihydroxyphenyl alanine salts, alanine salts, aminobutyrate, 2-amino-2-methyl-1,3-propandiol salts, valine salts, proline salts, tris-

hydroxyaminomethane salts, and lysine salts. Particularly, carbonates, phosphates, tetraborates and hydroxybenzoates are advantageous in that they have an excellent solubility and buffer capacity at a high pH range of 9.0 or higher, exhibit no bad effect (e.g., fog) on the photographic properties even when added to a color developing solution, and are inexpensive. These buffers may be preferably used.

Specific examples of these buffers include sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, tri-potassium phosphate, disodium phosphate, dipotassium phosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-sulfosalicylate), and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate). However, the present invention should not be construed as being limited to these compounds.

The amount of such a buffer to be incorporated in the color developing solution is preferably in the range of 0.1 mol/l or more, particularly 0.1 to 0.4 mol/l. Furthermore, the color developing solution may comprise various chelating agents for the purpose of

inhibiting precipitation of calcium or magnesium or improving the stability of the color developing solution.

As suitable chelating agents there may be used organic acid compounds. Examples of such organic acid compounds include aminopolycarboxylic acids as described in JP-B-48-30496, and JP-B-44-30232, organic phosphonic acids as described in JP-A-56-97347, JP-B-56-39359 and West German Patent No. 2,227,639, phosphonocarboxylic acids as described in JP-A-52-102726, JP-A-53-42730, JP-A-54-121127, JP-A-55-126241, and JP-A-55-659506, and compounds as described in JP-A-58-195845, and JP-A-58-203440, and JP-B-53-40900. Specific examples of such chelating agents will be described hereinafter, but the present invention should not be construed as being limited thereto.

Specific examples of such chelating agents include nitriletriacetic acid, diethylenetriaminepentaacetic acid, ethylenediaminetetraacetic acid, N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, trans-cyclohexanediamine-tetraacetic acid, 1,2-diaminopropanetetraacetic acid, glycoletherdiaminetetraacetic acid, ethylenediamine-ortho-hydroxyphenylacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic

acid, and N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid.

These chelating agents may be optionally used in combination.

The amount of these chelating agents to be added may be enough to hinder metal ions in the color developing solution. For example, the added amount may be in the range of 0.1 to 10 g per 1 l.

The present color developing solution may optionally comprise any development accelerator. However, the present color developing solution may preferably be substantially free of benzyl alcohol in the light of prevention of pollution, inhibition of color stain, and easiness of solution preparation. The term "substantially" means that the present color developing solution may contain benzyl alcohol in an amount of 2 ml or less per 1 l, preferably none.

The above described compounds can produce a remarkable effect at a processing step using a color developing solution substantially free of benzyl alcohol.

Other examples of development accelerators which can be optionally incorporated in the color developing solution include thioether compounds as described in JP-B-37-16088, JP-B-37-5987, JP-B-38-7826, JP-B-44-12380,

and JP-B-45-9019, and U.S. Patent 3,813,247, p-phenylenediamine compounds as described in JP-A-52-49829, and JP-A-50-15554, quaternary ammonium salts as described in JP-A-50-137726, JP-A-56-156826, and JP-A-52-43429, and JP-B-44-30074, amine compounds as described in U.S. Patents 2,494,903, 3,128,182, 4,230,796, 3,253,919, 2,482,546, 2,596,926, and 3,582,346, and JP-B-41-11431, polyalkylene oxide as described in JP-B-37-16088, JP-B-42-25201, JP-B-41-11431, and JP-B-42-23883, and U.S. Patents 3,128,183, and 3,532,501, 1-phenyl-3-pyrazolidones, and imidazoles.

In the present invention, any fog inhibitors may be optionally incorporated. As such fog inhibitors there may be used alkaline metal halides such as sodium chloride, potassium bromide, and potassium iodide, or organic fog inhibitors. Typical examples of such organic fog inhibitors include benzotriazole, 6-nitrobenzimidazole, 5-nitroisindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chloro-benzotriazole, 2-thiazolyl-benzimidazole, 2-thiazolylmethylbenzimidazole, indazole, hydroxyazaindolizine, adenine, and other nitrogen-containing heterocyclic compounds.

The color developing solution to be used in the present invention may preferably contain a brightening agent. As such a brightening agent there may be used a

4,4'-diamino-2,2'-disulfostilbene compound. The amount of such a brightening agent to be incorporated is in the range of 0 to 5 g/l, preferably 0.1 to 4 g/l.

The color developing solution to be used in the present invention may optionally comprise various surface active agents such as alkylsulfonyl acid, arylphosphonic acid, aliphatic carboxylic acid, and aromatic carboxylic acid.

The processing temperature for the present color developing solution is in the range of 20 to 50°C, preferably 30 to 40°C. The processing time is in the range of 20 seconds to 5 minutes, preferably 30 seconds to 2 minutes. The replenishment amount of the color developing solution may be preferably minimized. The replenishment amount of the color developing solution is in the range of 20 to 600 ml, preferably 50 to 300 ml per 1 m² of the light-sensitive material. Further preferably, the replenishment amount of the color developing solution is in the range of 100 to 200 ml per 1 m² of the light-sensitive material.

The desilvering process in the present invention will be described hereinafter. The desilvering process may consist in bleach process-fixing process, fixing process-blix process, bleach process-blix process, blix process or the like. In the present invention, the time

of the desilvering process can be minimized to produce a more remarkable effect of the present invention. Particularly, the desilvering time may be 2 minutes or less, preferably 15 seconds to 60 seconds.

The bleaching solution, blix solution and fixing solution to be used in the desilvering process will be described hereinafter.

As a bleaching agent to be incorporated in the bleaching solution or blix solution there may be used any bleaching agent. Particularly, complexes of iron (III) with an organic acid (e.g., aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, and diethylenetriaminepentaacetic acid, and organic phosphonic acid such as aminopolyphosphonic acid, phosphonocarboxylic acid, and organic phosphonic acid), organic acid such as citric acid, tartaric acid, and malic acid, persulfates, or hydrogen peroxide.

Among these compounds, organic complexes of iron (III) may be particularly preferably used in the light of rapidity in development and pollution prevention. Examples of aminopolycarboxylic acids, aminopolyphosphonic acids, organic phosphonic acids, or the salts thereof useful for the formation of these organic complexes of iron (III) include ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, 1,3-

diaminopropanetetraacetic acid, propylenediaminetetraacetic acid, nitriletriacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, iminodiacetic acid, and glycoetherdiaminetetraacetic acid.

These compounds may be sodium salts, potassium salts, lithium salts, or ammonium salts. Among these compounds, complexes of iron (III) with ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, 1,3-diaminopropanetetraacetic acid, and methyliminodiacetic acid have a high bleaching effect and may be preferably used.

These ferric complexes may be used in the form of a complex. Alternatively, a ferric salt such as ferric sulfate, ferric chloride, ferric nitrate, ferric ammonium sulfate, or ferric phosphate may be chelated with a chelating agent such as aminopolycarboxylic acid, aminopolyphosphonic acid, or phosphonocarboxylic acid in a solution to form a ferric complex. Such a chelating agent may be used in excess of the stoichiometric amount for the formation of a ferric complex. Preferred among these iron complexes are aminopolycarboxylic acid iron complexes. The amount of such a complex to be incorporated is in the range of 0.01 to 1.0 mol/l, preferably 0.05 to 0.50 mol/l. The bleaching solution, blix solution and/or its prebath may comprise various

compounds as bleach accelerator. For example, compounds containing mercapto group or disulfide bond as described in U.S. Patent 3,893,858, German Patent 1,290,812, JP-A-53-95630, and Research Disclosure, No. 17,129 (July, 1978), thiourea compounds as described in JP-B-45-8506, JP-A-52-20832, and JP-A-53-32735, and U.S. Patent 3,706,561, and halides such as iodide and bromide have an excellent bleaching capacity and may be preferably used.

The bleaching solution or blix solution to be used in the present invention may further comprise a rehalogenating agent such as bromide (e.g., potassium bromide, sodium bromide, ammonium bromide), chloride (e.g., potassium chloride, sodium chloride, ammonium chloride), or iodide (e.g., ammonium iodide). The bleaching solution or blix solution may optionally comprise a corrosion inhibitor such as one or more inorganic or organic acids or alkaline metal salts or ammonium salts thereof (e.g., boric acid, borax, sodium metaborate, acetic acid, sodium acetate, sodium carbonate, potassium carbonate, phosphorous acid, phosphoric acid, sodium phosphate, citric acid, sodium citrate, tartaric acid) having a pH buffering capability, ammonium nitrate, or guanidine.

As a fixing agent to be incorporated in the present blix solution or fixing solution there may be used a known fixing agent. Examples of such a fixing agent include thiosulfate such as sodium thiosulfate and ammonium thiosulfate, thiocyanate such as sodium thiocyanate, and ammonium thiocyanate, thioether compound such as ethylenebisthioglycolic acid, and 3,6-dithia-1,8-octanediol, and water-soluble silver halide solvent such as thiourea. These fixing agents may be used singly or in combination. Alternatively, a special blix solution made of a combination of a fixing agent and a large amount of a halide such as potassium iodide as described in JP-A-55-155354 may be used. In the present invention, a thiosulfate, particularly ammonium thiosulfate may be preferably used. The amount of such a fixing agent to be incorporated is preferably in the range of 0.3 to 2 mol, particularly 0.5 to 1.0 mol/l. The pH range of the blix solution or fixing solution is preferably in the range of 3 to 10, particularly 5 to 9.

The blix solution may further comprise various brightening agents, antifoaming agents, surface active agents, or organic solvents such as polyvinyl pyrrolidone, and methanol.

The present blix solution or fixing solution may comprise as preservative a sulfite (e.g., sodium

sulfite, potassium sulfite, ammonium sulfite), a bisulfite (e.g., ammonium bisulfite, sodium bisulfite, potassium bisulfite), a metabisulfite (e.g., potassium metabisulfite, sodium metabisulfite, ammonium metabisulfite), or other sulfurous acid ion-releasing compounds. These compounds may be preferably incorporated in an amount of about 0.02 to 0.50 mol/l, particularly 0.04 to 0.40 mol/l as calculated in terms of sulfurous acid ion.

As such a preservative there may be normally used a sulfite. Other examples of preservatives which can be used in the present invention include ascorbic acid, carbonyl-bisulfurous acid addition product, and carbonyl compound.

Furthermore, a buffering agent, brightening agent, chelating agent, anti-foaming agent, anti-fungal agent, or the like may be optionally incorporated.

In the present processing steps, the desilvering process by fixing or blix process is normally followed by the rinsing and/or stabilizing process.

The amount of water to be used in the rinsing process can be widely selected depending on the properties of the light-sensitive material (e.g., determined by the materials used, such as coupler), the application of the light-sensitive material, the

temperature of the rinsing water, the number of the rinsing tanks (stages), the replenishment system (i.e., whether countercurrent or forward current replenishment system), and other various conditions. Among these conditions, the relationship between the number of the rinsing tanks and the amount of water to be used in the multistage countercurrent replenishment system can be determined by the method as described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, pp. 248-253, (May, 1955). In general, the number of stages in the multistage countercurrent replenishment system is preferably 2 to 6, particularly 2 to 4.

In accordance with the multistage countercurrent replenishment system, the amount of rinsing water to be used can be drastically reduced, for example, to 0.5 to 1 ℓ per 1 m^2 of the light-sensitive material, exhibiting a remarkable effect of the present invention. However, the multistage countercurrent replenishment system is disadvantageous in that the time of water retention in the tanks is increased, causing proliferation of bacterial which produces suspended materials that will be attached to the light-sensitive material. In the process for the processing of the present light-sensitive material, the approach as described in JP-A-62-288838 which comprises reducing the calcium and

magnesium ion concentration can be extremely effectively used to overcome such a problem. Such a problem can also be solved by the use of a proper sterilizer such as isothiazolone compounds and thiabendazoles as described in JP-A-57-8542, chlorine sterilizers such as sodium chlorinated isocyanurate as described in JP-A-61-120145, benzotriazole as described in JP-A-61-267761, copper ion, and sterilizers as described in Hiroshi Horiguchi, "Chemistry of Anti-bacterial and Anti-fungal Agents", Eisei Gijutsukai, "Technic for Sterilization and Fungi-proofing of Microorganism", and Nihon Bokin Bobai Gakkai, "Dictionary of Anti-bacterial and Anti-fungal Agents".

The rinsing water may further comprise as hydro-extracting agent a surface active agent, or as water hardener a chelating agent such as EDTA.

Alternatively, the desilvering process can be directly followed by the stabilizing process rather than the rinsing process. The stabilizing solution may comprise a compound capable of stabilizing images. Examples of such a compound include aldehyde compounds such as formalin, buffering agents for adjusting the film pH value to that suitable for the stabilization of a dye, and ammonium compounds. Furthermore, the stabilizing solution may comprise the above described

sterilizers or anti-fungal agents to prevent the proliferation of bacteria or fungi-proof the light-sensitive material which has been processed.

The stabilizing solution may further comprise a surface active agent, a brightening agent, and a film hardener. In the processing of the present light-sensitive material, if the stabilizing process is effected directly after the desilvering process without passing through the rinsing process, any known process as described in JP-A-57-8543, JP-A-58-14834, and JP-A-60-220345 may be used.

In a preferred embodiment of the present invention, a chelating agent such as 1-hydroxyethylidene-1,1-diphosphonic acid and ethylenediamine-tetramethylenephosphonic acid, magnesium compound, or bismuth compound may be used.

In the present invention, as a rinsing water or stabilizing solution to be used after the desilvering process there may be used a so-called rinse solution.

The pH value at the present rinsing process or stabilizing process is in the range of 4 to 10, preferably 5 to 8. The processing temperature can be widely determined depending on the application and properties of the light-sensitive material to be processed. The processing temperature is normally in

the range of 15 to 45°C, preferably 20 to 40°C. The processing time can be properly determined. The shorter the processing time is, the more remarkable is the effect of the present invention. The processing time is preferably in the range of 30 seconds to 4 minutes, particularly 30 seconds to 2 minutes. The amount of a processing solution to be replenished to each processing step is preferably small in the light of running cost, amount of discharge, and handleability. The smaller the replenishment amount is, the more remarkable is the effect of the present invention.

The replenishment amount of each processing solution is preferably 0.5 to 50 times, particularly 3 to 40 times the amount of the processing solution carried over from the prebath per unit area of the light-sensitive material to be processed or 1 ℓ or less, preferably 500 ml or less per 1 m² of the light-sensitive material to be processed. The replenishment of the processing solution may be effected continuously or intermittently.

The processing solution which has been used at the rinsing and/or stabilizing process may be further used at the previous process. For example, the overflow of the rinsing water given by the saving accomplished by the multistage countercurrent replenishment system may

be flown into the prebath such as blix bath while a concentrated processing solution may be replenished to the blix bath so that the amount of discharge can be reduced.

The present invention can be applied to any processing methods such as processing of color paper, color reversal paper, color direct positive light-sensitive material, color positive film, color negative film, and color reversal film. Particularly, the present invention may be preferably applied to color paper or color reversal paper.

The present invention will be further described in the following examples, but the present invention should not be construed as being limited thereto.

EXAMPLE 1

6.4 g of sodium chloride was added to 1000 ml of a 3% aqueous solution of lime-processed gelatin. 3.2 ml of a 1% aqueous solution of N,N'-dimethylimidazolidine-2-thione was added to the mixture. An aqueous solution containing 0.2 mol of silver nitrate and an aqueous solution containing 0.04 mol of potassium bromide and 0.16 mol of sodium chloride were added to the solution with vigorous stirring at a temperature of 52°C. An aqueous solution containing 0.8 mol of silver nitrate and an aqueous solution containing 0.16 mol of potassium

bromide and 0.64 mol of sodium chloride were added to the solution with vigorous stirring at a temperature of 52°C. When 1 minute passed after the completion of the addition of the aqueous solution of silver nitrate and the aqueous solution of halogenated alkali, 286.7 mg of pyridinium 2-[5-phenyl-2-{2-[5-phenyl-3-(2-sulfonatoethyl)benzooxazoline-2-ylidenemethyl]-1-butenyl}-3-benzooxazolio]ethanesulfonate was added to the solution. The solution was then kept at a temperature of 52°C for 15 minutes. The solution was then desalted and rinsed. The emulsion was then subjected to optimum chemical sensitization with 90.0 g of lime-processed gelatin and an optimum amount of triethylthiourea so that a surface latent image type emulsion was obtained. Thus, a silver bromochloride emulsion A-1 (silver bromide content: 20 mol%) was prepared.

3.3 g of sodium chloride was added to 1000 ml of a 3% aqueous solution of lime-processed gelatin. 3.2 ml of a 1% aqueous solution of N,N'-dimethylimidazolidine-2-thione was added to the mixture. An aqueous solution containing 0.2 mol of silver nitrate and an aqueous solution containing 0.004 mol of potassium bromide and 0.196 mol of sodium chloride were added to the solution with vigorous stirring at a temperature of 52°C. An aqueous solution containing 0.8 mol of silver nitrate

and an aqueous solution containing 0.016 mol of potassium bromide and 0.784 mol of sodium chloride were then added to the solution with vigorous stirring at a temperature of 52°C. When 1 minute passed after the completion of the addition of the aqueous solution of silver nitrate and the aqueous solution of halogenated alkali, 286.7 mg of pyridinium 2-[5-phenyl-2-(2-[5-phenyl-3-(2-sulfonatoethyl)benzooxazoline-2-ylidene-methyl]-1-butenyl)-3-benzooxazolio]ethanesulfonate was added to the solution. After being kept at a temperature of 52°C for 15 minutes, the solution was then desilvered and rinsed. The emulsion was then subjected to optimum chemical sensitization with 90.0 g of lime-processed gelatin and an optimum amount of triethylthiourea so that a surface latent image type emulsion was obtained. Thus, a silver bromochloride emulsion B-1 (silver bromide content: 2 mol%) was prepared.

3.3 g of sodium chloride was added to 1000 ml of a 3% aqueous solution of lime-processed gelatin. 3.2 ml of a 1% aqueous solution of N,N'-dimethylimidazolidine-2-thione was added to the mixture. An aqueous solution containing 0.2 mol of silver nitrate and an aqueous solution containing 0.2 mol of sodium chloride were then added to the solution with vigorous stirring at a

temperature of 52°C. An aqueous solution containing 0.75 mol of silver nitrate and an aqueous solution containing 0.75 mol of sodium chloride were then added to the solution with vigorous stirring at a temperature of 52°C. When 1 minute passed after the completion of the addition of the aqueous solution of silver nitrate and the aqueous solution of sodium chloride, 286.7 mg of pyridinium 2-[5-phenyl-2-(2-[5-phenyl-3-(2-sulfonatoethyl)benzooxazoline-2-ylidenemethyl]-1-butenyl}-3-benzooxazolio]ethanesulfonate was added to the solution. After being kept at a temperature of 52°C for 15 minutes, an aqueous solution containing 0.05 mol of silver nitrate and an aqueous solution containing 0.02 mol of potassium bromide and 0.03 mol of sodium chloride were added to the solution with vigorous stirring at a temperature of 40°C. The solution was then desalted and rinsed. The solution was then subjected to optimum chemical sensitization with 90.0 g of lime-processed gelatin and an optimum amount of triethylthiourea so that a surface latent image type emulsion was obtained. Thus, a silver bromochloride emulsion C-1 (silver bromide content: 2 mol%) was prepared.

3.3 g of sodium chloride was added to 1000 ml of a 3% aqueous solution of lime-processed gelatin. 3.2 ml of a 1% aqueous solution of N,N'-dimethylimidazolidine-

2-thione was added to the mixture. An aqueous solution containing 0.2 mol of silver nitrate and an aqueous solution containing 0.2 mol of sodium chloride were then added to the solution with vigorous stirring at a temperature of 52°C. An aqueous solution containing 0.775 mol of silver nitrate and an aqueous solution containing 0.775 mol of sodium chloride were then added to the solution with vigorous stirring at a temperature of 52°C. When 1 minute passed after the completion of the addition of the aqueous solution of silver nitrate and the aqueous solution of sodium chloride, 286.7 mg of pyridinium 2-[5-phenyl-2-{2-[5-phenyl-3-(2-sulfonatoethyl)benzooxazoline-2-ylidenemethyl]-1-butenyl}-3-benzooxazolio]ethanesulfonate was added to the solution. The solution was then kept at a temperature of 52°C for 15 minutes. An aqueous solution containing 0.025 mol of silver nitrate and an aqueous solution containing 0.02 mol of potassium bromide and 0.005 mol of sodium chloride were then added to the solution with vigorous stirring at a temperature of 40°C. The solution was then desalted and rinsed. The solution was then subjected to optimum chemical sensitization with 90.0 g of lime-processed gelatin and an optimum amount of triethylthiourea so that a surface latent image type

emulsion was obtained. Thus, a silver bromochloride D-1 (silver bromide content: 2 mol%) was prepared.

Emulsion C-2 and Emulsion D-2 were prepared in the same manner as in Emulsion C-1 and Emulsion D-1 except that potassium hexacyanoferrate (II) (trihydrate) was incorporated in the aqueous solution of sodium chloride to be added at second time in an amount of 2.0 mg and potassium hexachloroiridiumate (IV) was incorporated in the aqueous solution of halogenated alkali to be added at third time in an amount of 1.0 mg.

The crystal shape, grain size and the grain size distribution of Emulsions A-1 to D-2 were determined from electron microscope photography. The silver halide grains incorporated in Emulsions A-1 to D-2 were all cubic. The grain size was determined by the average of the diameter of circles having the same area as the projected area of grains. The grain size distribution was obtained by dividing the standard deviation of the grain sizes by the average grain size.

The X-ray diffraction from the silver halide crystal was measured to determine the halogen composition of the emulsion grains. The diffraction angle of the diffraction ray from (200) plane was accurately measured. Monochromatized Cu γ ray was used as light source. The diffraction ray from crystals having a

uniform halogen composition gave a single peak while the diffraction ray from crystals containing localized phases having different compositions gave a plurality of peaks corresponding to these compositions. The halogen composition of silver halide constituting the crystals can be determined by calculating the lattice constant from the measured peak diffraction angle. The results are shown in Table 1.

10 1 00 28595

Table 1

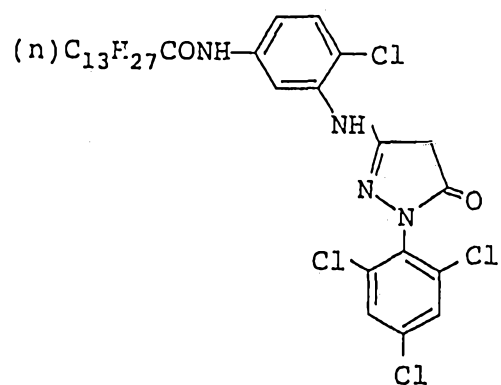
<u>Emulsion</u>	<u>Crystal shape</u>	<u>Grain size (distribution)</u>	<u>Primary peak</u>	<u>Secondary peak</u>	<u>Remarks</u>	
					<u>Localized silver bromide phase</u>	<u>Polyvalent metal ion impurity</u>
A-1	Cube	0.51 μ (0.08)	Cl 80% (Br 20%)	-	None	-
B-1	"	0.50 μ (0.07)	Cl 98% (Br 2%)	-	None	-
C-1	"	0.50 μ (0.08)	Cl 100%	Cl 83%- 90%	Present	-
C-2	"	0.50 μ (0.08)	Cl 100%	Cl 83%- 90%	Present	Fe(II), Ir(IV)
D-1	"	0.50 μ (0.08)	Cl 100%	Cl 61%- 90%	Present	-
D-2	"	0.50 μ (0.08)	Cl 100%	Cl 61%- 90%	Present	Fe(II), Ir(IV)

29.6 g of a magenta coupler (a), 5.9 g of a dye image stabilizer (b) and 11.8 g of a dye image stabilizer (c) were dissolved in 30.0 ml of ethyl acetate and 38.5 ml of a solvent (d). The solution was then emulsion-dispersed in 320 ml of a 10% aqueous solution of gelatin containing 20 ml of 10% sodium dodecylbenzenesulfonate. Thus an emulsion dispersion (a) was prepared.

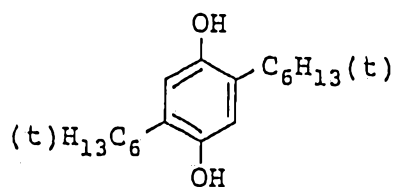
31.5 g of a magenta coupler (e), 13.7 g of a dye image stabilizer (c), 2.7 g of a stain inhibitor (f) and 2.2 g of a stain inhibitor (g) were dissolved in 45 ml of ethyl acetate, 11.3 ml of a solvent (h) and 22.6 ml of a solvent (i). The solution was emulsion-dispersed in 320 ml of a 10% aqueous solution of gelatin containing 20 ml of 10% sodium dodecylbenzenesulfonate. Thus, an emulsion dispersion (b) was prepared.

The silver halide emulsions and the emulsion dispersions of magenta coupler thus prepared were combined to prepare coating solutions having compositions as shown in Table 2. These coating solutions were coated on a paper support laminated with polyethylene on both sides thereof to prepare 24 light-sensitive materials having layer structures as shown in Table 2. As a gelatin hardener for each layer there was used sodium 1-oxy-3,5-dichloro-s-triazine.

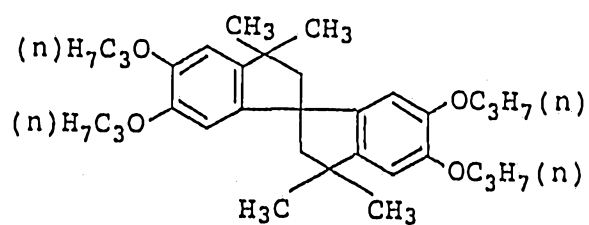
(a) Magenta coupler



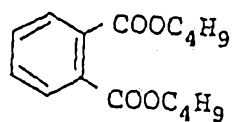
(b) Dye image stabilizer



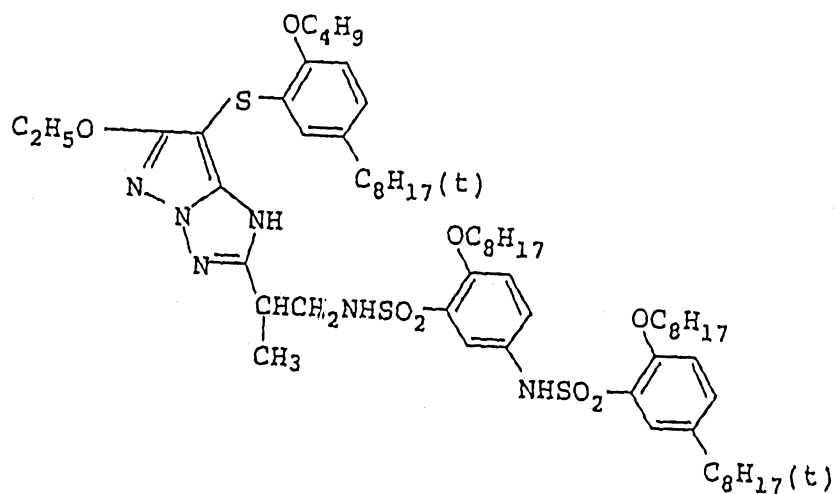
(c) Dye image stabilizer



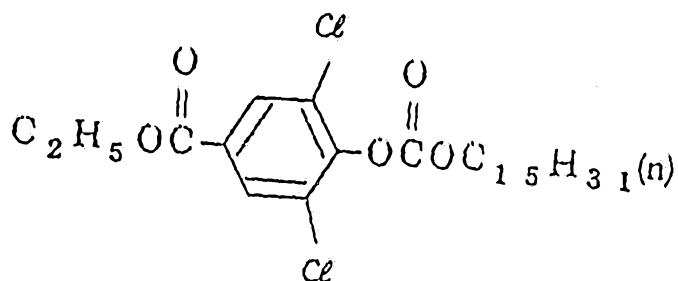
(d) Solvent



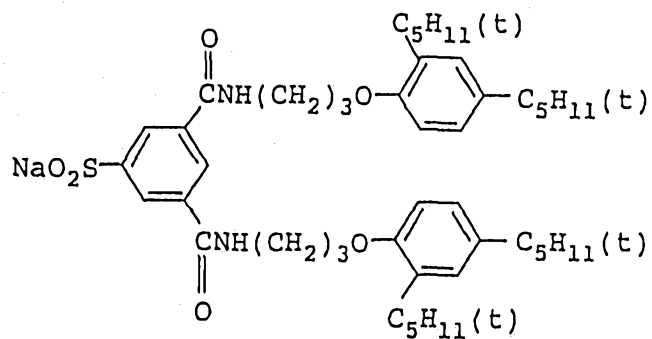
(e) Magenta coupler



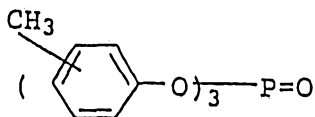
(f) Stain inhibitor



(g) Stain inhibitor



(h) Solvent



(i) Solvent

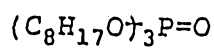


Table 2

Layer	Specimen a-1 to a-12	Specimen b-1 to b-12
2nd layer	(Protective layer)	
	Gelatin	1.33 g/m ²
	Acryl-modified polymer of polyvinyl alcohol (modification degree: 17%)	0.17 g/m ²
1st layer	(Green-sensitive emulsion layer)	(Green-sensitive emulsion layer)
	Silver bromochloride emulsion 0.36 g/m ²	Silver bromochloride emulsion 0.14 g/m ²
	See Table 3	See Table 3
	Magenta coupler (a) 0.32 g/m ²	Magenta coupler (e) 0.43 g/m ²
	Dye image stabilizer (b) 0.06 g/m ²	Dye image stabilizer (c) 0.19 g/m ²
	Dye image stabilizer (c) 0.13 g/m ²	Stain inhibitor (f) 0.04 g/m ²
	Solvent (d) 0.42 ml/m ²	Stain inhibitor (g) 0.03 g/m ²
	Gelatin 1.00 g/m ²	Solvent (h) 0.16 ml/m ²
		Solvent (i) 0.31 ml/m ²
		Gelatin 1.24 g/m ²
Paper support laminated with polyethylene on both sides (containing TiO ₂ in polyethylene on 1st layer side)		

Table 3

<u>Specimen</u>	<u>Silver Halide Emulsion</u>	<u>Emulsion Dispersion of Coupler</u>	<u>Exemplary Compound (9)</u>
a-1	A-1	(a)	-
a-2	B-1	"	-
a-3	C-1	"	-
a-4	C-2	"	-
a-5	D-1	"	-
a-6	D-2	"	-
a-7	A-1	"	5×10^{-4}
a-8	B-1	"	"
a-9	C-1	"	"
a-10	C-2	"	"
a-11	D-1	"	"
a-12	D-2	"	"
b-1	A-1	(b)	-
b-2	B-1	"	-
b-3	C-1	"	-
b-4	C-2	"	-
b-5	D-1	"	-
b-6	D-2	"	-
b-7	A-1	"	5×10^{-4}
b-8	B-1	"	"
b-9	C-1	"	"
b-10	C-2	"	"

Table 3 (cont'd)

<u>Specimen</u>	<u>Silver Halide Emulsion</u>	<u>Emulsion Dispersion of Coupler</u>	<u>Exemplary Compound (9)</u>
b-11	D-1	(b)	5×10^{-4}
b-12	D-2	"	"

The figure in the 4th column indicates the molar number of Exemplary Compound (9) added per 1 mol of silver. Exemplary Compound (9) was added in the form of methanol solution during the preparation of Emulsions A-1 to D-2.

The 24 coated specimens thus prepared were then subjected to performance test.

The difference in photographic properties between specimens coated with a coating solution which has passed 30 minutes since preparation and specimens coated with a coating solution which has passed 6 hours since preparation.

These coated specimens were exposed to light of 200 CMS through an optical wedge and a green filter for 0.1 second, and then subjected to color development with the developing solution described later in the development process described later.

The reflective density of these specimens which had been processed were then measured to determine a so-called characteristic curve. The sensitivity of these

specimens was represented by the reciprocal of the exposure which gives a density of 0.5 higher than the fog density. The sensitivity value was represented relative to that of the specimen coated with Specimen a-1 which had passed 30 minutes since preparation as 100. The contrast was obtained by determining the difference between the density corresponding to the exposure which is 0.5 higher than the exposure by which the sensitivity was obtained and the density of the point at which the sensitivity was obtained.

The specimens coated with a coating solution which had passed 30 minutes since preparation were processed and then subjected to light discoloration test by means of a xenon tester with a illuminance of 100,000 lux for 24 hours. The degree of discoloration due to light irradiation was represented by the density change at the portion of a density of 1.5 before light irradiation after light irradiation.

Furthermore, the specimens coated with a coating solution which had passed 30 minutes since preparation were developed with a color developing solution mixed with 0.3 ml/l of a blix solution and then examined for photographic properties.

The results are shown in Table 4.

<u>Processing Step</u>	<u>Temperature</u>	<u>Time</u>
Color development	35°C	45 seconds
Blix	30-35°C	45 seconds
Rinse 1	30-35°C	20 seconds
Rinse 2	30-35°C	20 seconds
Rinse 3	30-35°C	20 seconds
Rinse 4	30-35°C	30 seconds
Drying	70-80°C	60 seconds

(The rinsing step was effected in a counter-current process in which the water flew from the tank 4 to the tank 1 through the tanks 3 and 2.)

The composition of the various processing solutions will be described hereinafter.

Color Developing Solution

Water	800 ml
Ethylenediamine-N,N,N,N-tetramethylene-phosphonic acid	1.5 g
Triethylenediamine(1,4-diazabicyclo-(2,2,2)octane	5.0 g
Sodium chloride	1.4 g
Potassium carbonate	25 g
N-ethyl-N-(β -methanesulfoneamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
N,N-diethylhydroxylamine	4.2 g
Brightening agent (UVITEX CK, Ciba Geigy)	2.0 g
Water to make	1,000 ml

pH (25°C) 10.10

Blix Solution

Water 400 ml

Ammonium thiosulfate (70%) 100 ml

Sodium sulfite 18 g

Ammonium ethylenediaminetetraacetato
ferrate 55 g

Disodium ethylenediaminetetraacetate 3 g

Ammonium bromide 40 g

Glacial acetic acid 8 g

Water to make 1,000 ml

pH (25°C) 5.5

Rinsing Solution

Ion-exchanged water (calcium and magnesium
concentration: 3 ppm or less for each)

10 100 2000

Table 4

<u>Specimen</u>	<u>Coated with solution 30 minutes after preparation</u>		<u>Coated with solution 6 hours after preparation</u>		<u>Light discoloration ($\Delta D_{1.5}$) 100,000 lux, 24 hours</u>	<u>Developing solution mixed with blix solution</u>		<u>Remarks</u>
	<u>Relative Sensitivity</u>	<u>Contrast</u>	<u>Relative Sensitivity</u>	<u>Contrast</u>		<u>Relative sensitivity</u>	<u>Contrast</u>	
a-1	100	1.06	95	1.05	0.47	121	1.49	Comparative
a-2	63	1.44	60	1.45	0.45	78	1.68	"
a-3	184	1.39	175	1.39	0.46	222	1.61	"
a-4	199	1.46	192	1.47	0.48	238	1.69	"
a-5	237	1.41	227	1.40	0.46	284	1.62	"
a-6	245	1.47	234	1.48	0.47	291	1.71	"
a-7	88	0.98	81	0.97	0.48	93	1.04	"
a-8	51	1.42	46	1.41	0.45	56	1.47	"
a-9	167	1.36	153	1.35	0.47	183	1.43	"
a-10	182	1.43	164	1.43	0.45	198	1.51	"
a-11	214	1.38	192	1.36	0.46	237	1.44	"
a-12	222	1.45	203	1.45	0.48	241	1.53	"

10

100

2000

Table 4 (cont'd)

Specimen	Coated with solution 30 minutes after preparation		Coated with solution 6 hours after preparation		Light discoloration ($\Delta D_{1.5}$) 100,000 lux, 24 hours	Developing solution mixed with blix solution		Remarks
	Relative Sensitivity	Contrast	Relative Sensitivity	Contrast		Relative sensitivity	Contrast	
b-1	94	1.05	86	0.68	0.06	76	0.57	Comparative
b-2	55	1.44	49	1.15	0.06	45	1.07	"
b-3	178	1.37	162	1.08	0.07	142	1.01	"
b-4	190	1.42	173	1.10	0.08	153	1.03	
b-5	229	1.36	207	1.04	0.05	182	0.98	"
b-6	237	1.43	216	1.12	0.06	189	1.02	"
b-7	101	1.11	100	1.10	0.07	99	1.10	"
b-8	64	1.49	63	1.48	0.06	64	1.47	"
b-9	185	1.43	184	1.43	0.05	183	1.42	Present invention
b-10	199	1.49	199	1.49	0.06	196	1.48	"
b-11	239	1.44	237	1.44	0.07	237	1.43	"
b-12	247	1.50	246	1.49	0.07	245	1.48	"

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The comparison of these emulsions shows that Specimens a-1, a-7, b-1 and b-7 comprising Emulsion A-1 exhibit a low development speed which gives a low contrast. On the other hand, the specimens comprising Emulsion B-1 having a high silver chloride content exhibit an improved development speed but provide too low a sensitivity to be fit for practical use. It can be seen that Emulsions C-1, C-2, D-1 and D-2 having localized silver bromide phases exhibit a high development speed and a high sensitivity. However, if these emulsions are combined with the present magenta coupler excellent in the resistance to light discoloration, the contrast shows a remarkable drop when the specimen is formed of a coating solution which has aged or when the specimen is processed with a developing solution mixed with a blix solution, disabling practical use thereof.

In accordance with the present invention, an emulsion which exhibits a high development speed and a coupler excellent in the resistance to light discoloration can be used in combination to obtain an excellent light-sensitive material which exhibits a small fluctuation in properties during the preparation and a small fluctuation in processing.

Emulsions C-2 and D-2 which have been doped with Fe(II) and Ir(IV) as impurity ions can provide a higher contrast.

EXAMPLE 2

An emulsion of silver halide grain having a grain size of 1.3 μm was prepared in the same manner as Emulsion D-2 of Example 1 except that the temperature at which silver halide grain is formed and the time necessary for the addition of the aqueous solution of silver nitrate and the aqueous solution of halogenated alkali were altered, the added amount of potassium hexacyanoferrate (II) (trihydrate) was changed to 0.4 mg, the added amount of potassium hexachloroiridiumate (IV) was changed to 0.12 mg, and 286.7 mg of pyridinium 2-[5-phenyl-2-{2-[5-phenyl-3-(2-sulfonatoethyl)-benzooxazolin-2-ylidenemethyl]-1-butenyl}-3-benzooxazolio]ethanesulfonate was replaced by 172.8 mg of triethylammonium 3-{2-[5-chloro-3-(3-sulfonatopropyl)benzothiazolin-2-ylidenemethyl]-3-naphtho[1,2-d]thiazolio}propanesulfonate. Thus, Emulsion E-1 was obtained. Emulsion E-1 exhibited a grain size distribution of 0.07. The X-ray diffraction of Emulsion E-1 gave a primary peak of silver chloride content of 100% and a secondary peak corresponding to a silver chloride content of 53 to 90%.

Emulsion F-1 was then prepared in the same manner as in Emulsion D-1 of Example 1 except that 286.7 mg of pyridinium 2-[5-phenyl-2-(2-[5-phenyl-3-(2-sulfonatoethyl)benzooxazolin-2-ylidenemethyl]-1-butenyl}-3-benzooxazolio]ethanesulfonate was replaced by 60.0 mg of 2-[2,4-(2,2-dimethyl-1,3-propano)-5-(6-methyl-3-pentyl-benzothiazolin-2-ylidene)-1,3-pentadiethyl]-3-ethyl-6-methylbenzothiazolium iodide.

Eight multilayer color light-sensitive material specimens having compositions, layer structures and emulsions as shown in Tables 5, 6 and 7 were prepared by using these emulsions. The preparation of the coating solution for each layer was accomplished in the same manner as in Example 1. As a gelatin hardener for each layer there was used sodium 1-oxy-3,5-dichloro-S-triazine.

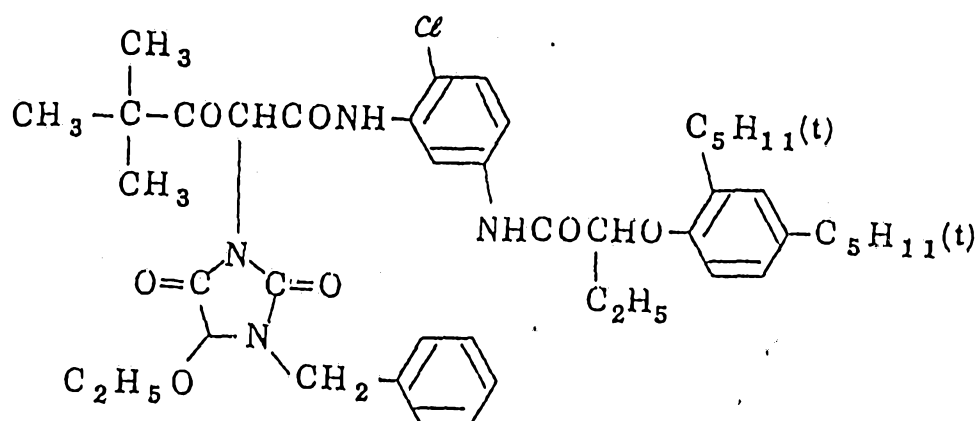
Table 5

<u>Layer</u>	<u>Main composition</u>	
7th layer (protective layer)	Gelatin	1.33 g/m ²
	Acryl-modified copolymer of polyvinyl alcohol (modification degree: 17%)	0.17 g/m ²
6th layer (ultraviolet absorbing layer)	Gelatin	0.54 g/m ²
	Ultraviolet absorber (m)	0.21 g/m ²
	Solvent (o)	0.09 ml/m ²

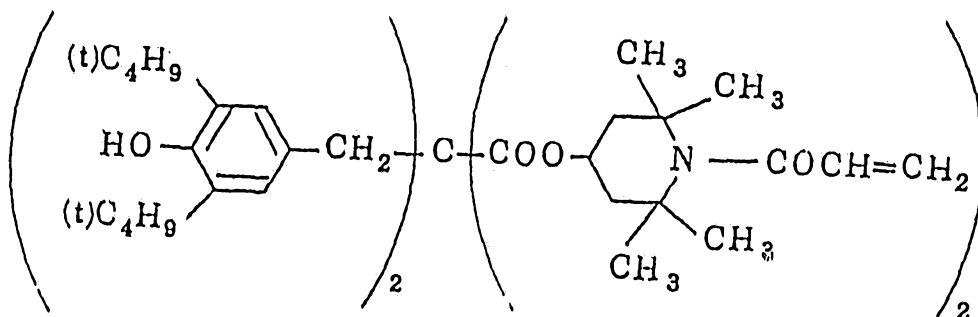
5th layer (red- sensitive layer)	Silver halide emulsion F-1	0.24 g/m ²
	Gelatin	0.95 g/m ²
	Cyan coupler (p)	0.40 g/m ²
	Dye image stabilizer (q)	0.24 g/m ²
	Stabilizer (r)	0.44 g/m ²
	Stabilizer (s)	0.05 g/m ²
	Solvent (t)	0.15 g/m ²
4th layer (ultraviolet absorbing layer)	Solvent (u)	0.14 ml/m ²
	Solvent (o)	0.14 ml/m ²
	Gelatin	1.60 g/m ²
	Ultraviolet absorber (m)	0.62 g/m ²
	Color stain inhibitor (n)	0.05 g/m ²
3rd layer (green- sensitive layer)	Solvent (o)	0.26 ml/m ²
	For composition and others, see Table 6.	
2nd layer (color stain inhibiting layer)	Gelatin	0.99 g/m ²
	Color stain inhibitor (e)	0.08 g/m ²
1st layer (blue- sensitive layer)	Silver halide emulsion E-1	0.27 g/m ²
	Gelatin	1.20 g/m ²
	Yellow coupler (j)	0.68 g/m ²
	Dye image stabilizer (k)	0.17 g/m ²
	Solvent (d)	0.27 ml/m ²
Support	Polyethylene-laminated paper (containing TiO ₂ and ultramarine blue in polyethylene on 1st layer side)	

The amount of silver halide emulsion is represented as calculated in terms of amount of silver.

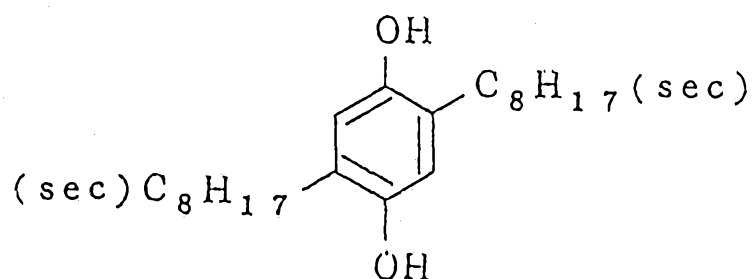
(j) Yellow coupler



(k) Dye image stabilizer

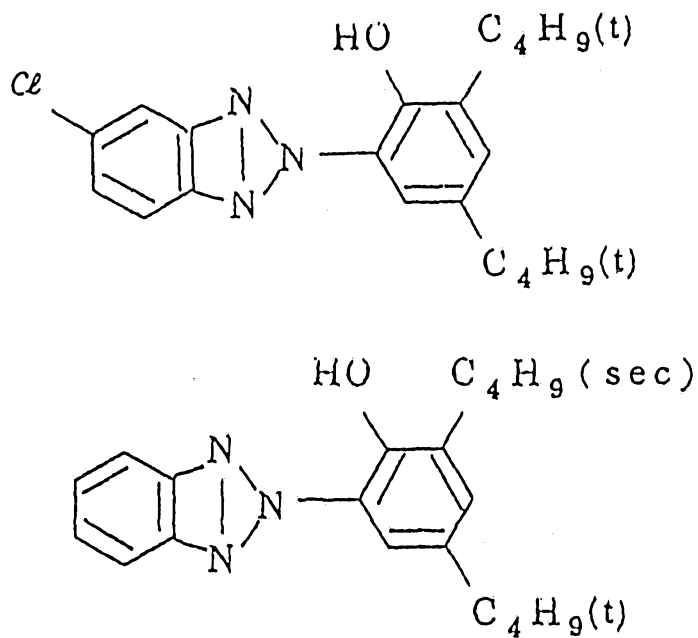


(e) Color stain inhibitor

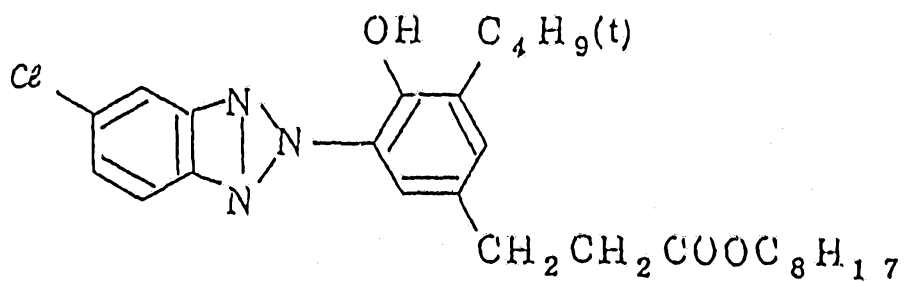


(m) Ultraviolet absorber

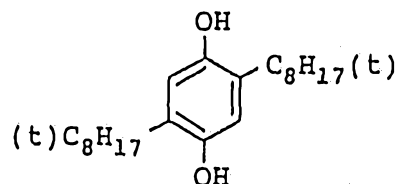
1:5:3 mixture (molar ratio) of



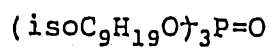
and



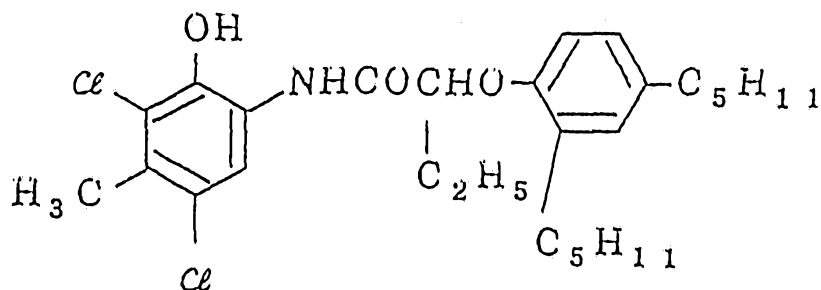
(n) Color stain inhibitor



(o) Solvent

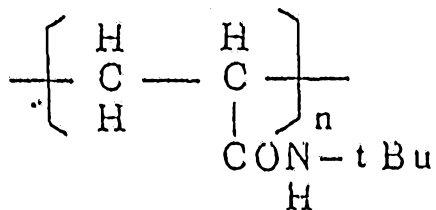


(p) Cyan coupler



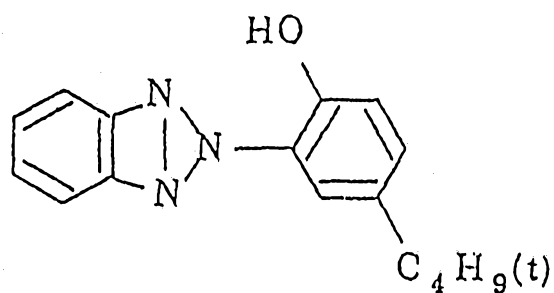
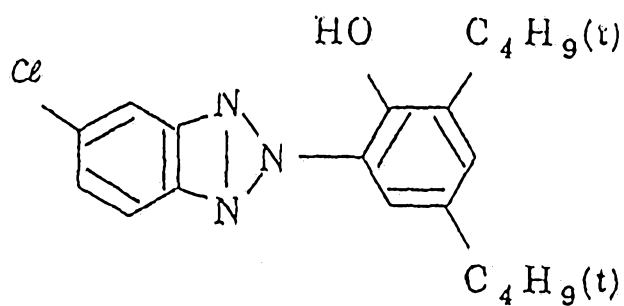
(r) Stabilizer

Polymer having a number of average molecular weight of 60,000

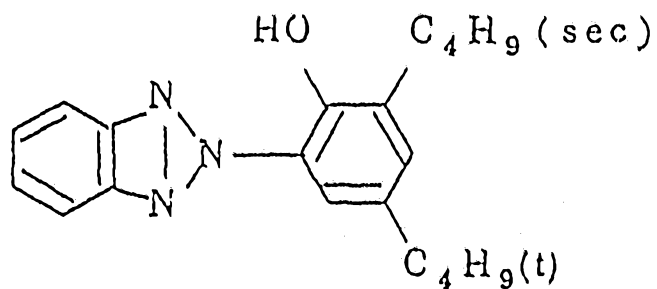


(q) Dye image stabilizer

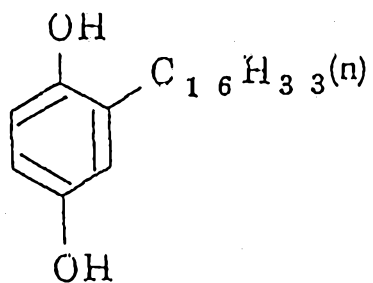
1:3:3 mixture (molar ratio) of



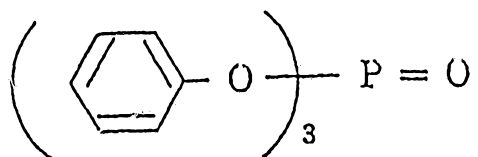
and



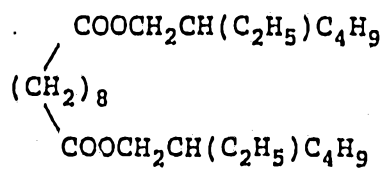
(s) Stabilizer



(t) Solvent



(u)



10 100 20595

Table 6

Layer	Specimen c-1 to c-4		Specimen d-1 to d-4	
3rd layer (green- sensitive layer)	Silver halide emulsion (see Table 7)	0.36 g/m ²	Silver halide emulsion (see Table 7)	0.14 g/m ²
	Magenta coupler (a)	0.32 g/m ²	Magenta coupler (v)	0.31 g/m ²
	Dye image stabilizer (b)	0.06 g/m ²	Dye image stabilizer (c)	0.19 g/m ²
	Dye image stabilizer (c)	0.13 g/m ²	Stain inhibitor (f)	0.04 g/m ²
	Solvent (d)	0.42 ml/m ²	Stain inhibitor (g)	0.03 g/m ²
	Gelatin	1.00 g/m ²	Solvent (h)	0.16 ml/m ²
			Solvent (i)	0.31 ml/m ²
			Gelatin	1.12 g/m ²

(v) Magenta coupler

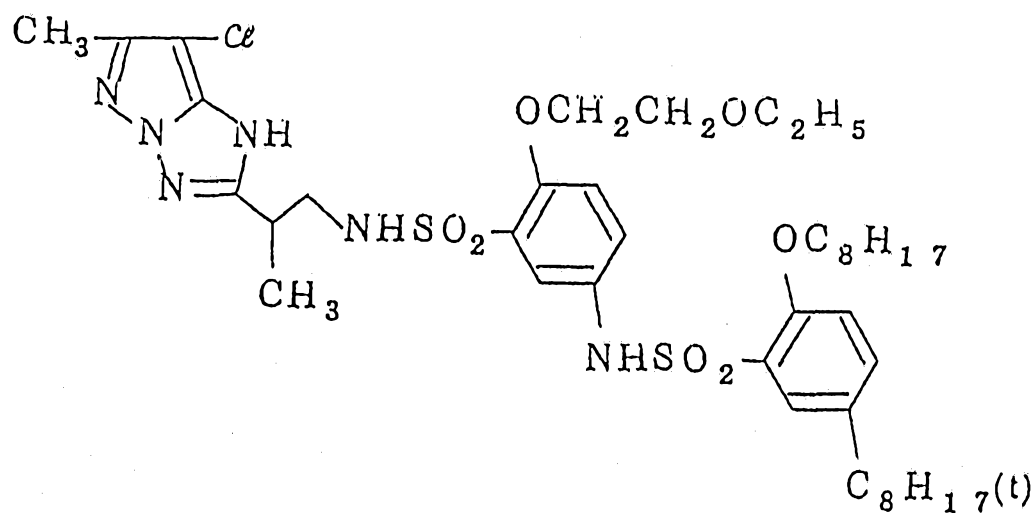


Table 7

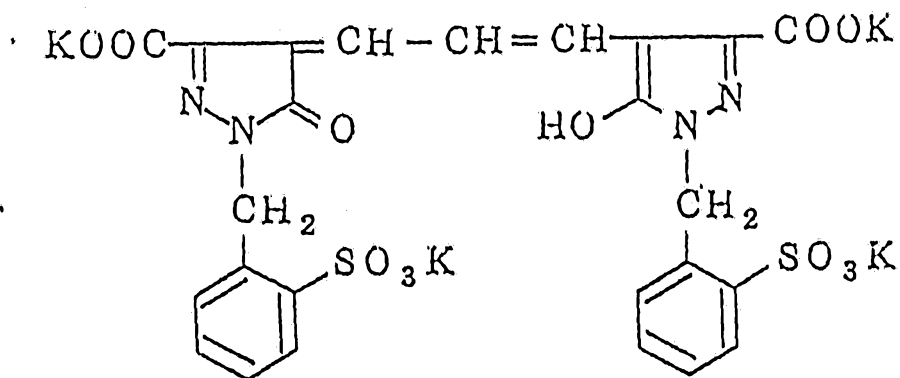
<u>Specimen</u>	<u>Green-sensitive Emulsion</u>	<u>Exemplary Compound (9)</u>
c-1	D-1	-
c-2	D-2	-
c-3	D-1	5×10^{-4}
c-4	D-2	5×10^{-4}
d-1	D-1	-
d-2	D-2	-
d-3	D-1	5×10^{-4}
d-4	D-2	5×10^{-4}

The figure in the 3rd column indicates the molar number of Exemplary Compound (9) to be added per 1 mol of silver halide.

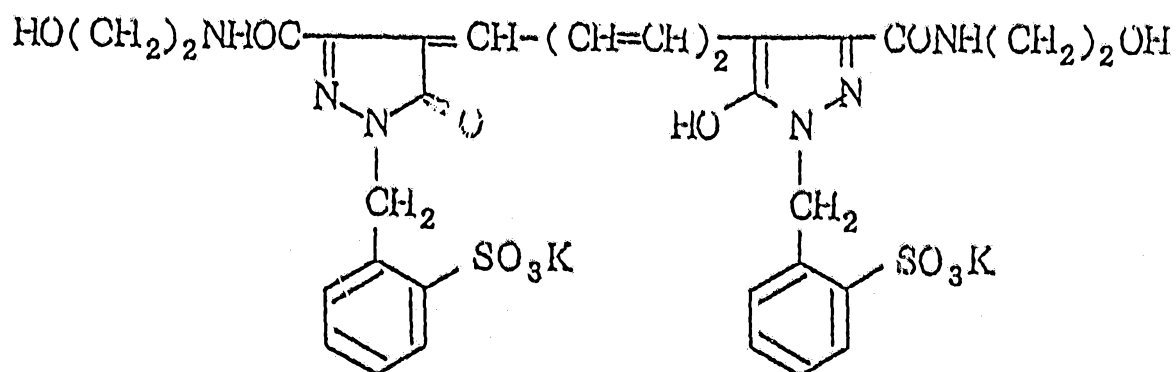
Exemplary Compound (9) was added in the form of a methanol solution during the preparation of green-sensitive emulsions D-1 and D-2.

As anti-irradiation dyes for each layer there were used the following compounds:

Anti-irradiation dye for green-sensitive emulsion layer



Anti-irradiation dye for red-sensitive emulsion layer



These eight coated specimens c-1 to d-4 were then examined for photographic properties in the same manner as in Example 1 (fluctuation in photographic properties due to aging of coating solution for green-sensitive emulsion layer, light discoloration of magenta dye, and fluctuation in photographic properties due to mixing of color developing solution with blix solution).

The results are shown in Table 8.

10 100 20505

Table 8

<u>Specimen</u>	<u>Coated with solution 30 minutes after preparation</u>		<u>Coated with solution 6 hours after preparation</u>		<u>Light discoloration ($\Delta D_{1.5}$) 100,000 lux, 8 days</u>	<u>Developing solution mixed with blix solution</u>		<u>Remarks</u>
	<u>Relative Sensitivity</u>	<u>Contrast</u>	<u>Relative Sensitivity</u>	<u>Contrast</u>		<u>Relative sensitivity</u>	<u>Contrast</u>	
c-1	100	1.39	96	1.38	0.39	122	1.59	Comparative
c-2	99	1.45	95	1.45	0.38	118	1.67	"
c-3	98	1.36	89	1.34	0.39	111	1.43	"
c-4	96	1.43	88	1.44	0.37	109	1.52	"
d-1	110	1.33	83	0.93	0.04	80	0.86	"
d-2	109	1.39	81	0.97	0.05	77	0.88	"
d-3	111	1.42	109	1.41	0.06	110	1.41	Present invention
d-4	111	1.48	110	1.48	0.05	111	1.47	"

The sensitivity is represented relative to that of Speciment c-1 (coated with a solution 30 mminutes after preparation) as 100. Since these specimens are multilayer light-sensitive materials comprising an ultraviolet absorbing layer, the period for light discoloration test was prolonged to 8 days.

Table 8 shows that the effect of the present invention can be definitely recognized also in the multilayer color photographic light-sensitive materials. In other words, even when a pyrazoloazole magenta coupler is used in combination with a high silver chloride content emulsion, there can be recognized little or no drop in sensitivity and contrast due to the aging of coating solution or the mixing of the developing solution with the blix solution.

EXAMPLE 3

The same coated specimens as used in Example 2 were examined for photographic properties in the same manner as in Example 2 except that the development process and the processing solutions were replaced by those described later.

The results of the test show that the effect of the present invention can be definitely recognized as in Example 2.

<u>Processing Step</u>	<u>Temperature</u>	<u>Time</u>
Color development	35°C	45 seconds
Blix	30-36°C	45 seconds
Stabilizing 1	30-37°C	20 seconds
Stabilizing 2	30-37°C	20 seconds
Stabilizing 3	30-37°C	20 seconds
Stabilizing 4	30-37°C	30 seconds
Drying	70-85°C	60 seconds

(The stabilizing step was effected in a counter-current process in which the solution flew from the tank 4 to the tank 1 through the tank 3 and the tank 2.)

The composition of the various processing solutions used will be described hereinafter

Color Development Solution

Water	800 ml
Ethylenediaminetetraacetic acid	2.0 g
Triethanolamine	8.0 g
Sodium chloride	1.4 g
Potassium carbonate	25.0 g
N-ethyl-N-(β -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
N,N-diethylhydroxylamine	4.2 g
5,6-Dihydroxybenzene-1,2,4-trisulfonic acid	0.3 g
Brightening agent (4,4'-diaminostilbene series)	2.0 g

Water to make	1,000 ml
pH	10.10

Blix Solution

Water	400 ml
Ammonium thiosulfate (70%)	100 ml
Sodium sulfite	18 g
Ammonium ethylenediaminetetraacetato ferrate	55 g
Disodium ethylenediaminetetraacetate	3 g
Glacial acetic acid	8 g
Water to make	1,000 ml
pH	5.5

Stabilizing Solution

Formalin (37%)	0.1 g
Formalin-sulfurous acid addition product	0.7 g
5-Chloro-2-methyl-4-isothiazolin-3-one	0.02 g
2-Methyl-4-isothiazolin-3-one	0.01 g
Copper sulfate	0.005 g
Water to make	1,000 ml
pH	4.0

In accordance with the present invention, a silver halide color light-sensitive material suitable in a rapid color developing processing, excellent in a color reproducibility, excellent in a dye image fastness and having little or no drop in sensitivity and contrast due to the aging of coating solution or the mixing of

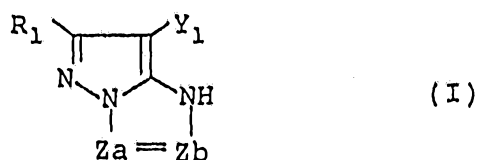
the developing solution with the blix solution can be obtained.

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.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

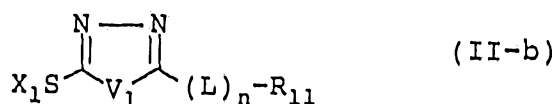
~~WHAT IS CLAIMED IS:~~

1. A silver halide color light-sensitive material comprising a support having provided thereon at least one light-sensitive emulsion layer containing surface latent image type silver halide grains, wherein said light-sensitive emulsion layer comprises a photographic emulsion containing silver bromochloride grains substantially free of silver iodide and having at least 90 mol% of average silver chloride content, said silver bromochloride grains having a localized silver bromide phase on the surface thereof in a discontinuous or isolated state, and at least one pyrazoloazole type coupler represented by formula (I) and said light-sensitive emulsion layer or at least one of other hydrophilic colloid layers comprises at least one compound represented by formula (II-a) or (II-b):

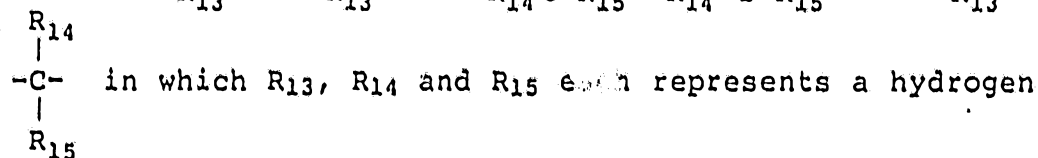
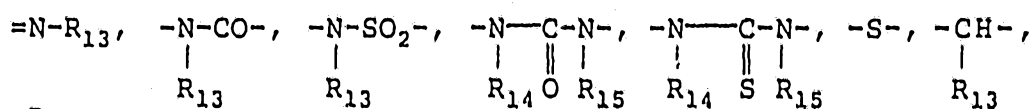


wherein Z_a and Z_b each represents a methine group, a substituted methine group or $-N=$; R_1 represents a hydrogen atom or a substituent; and Y_1 represents a halogen atom or a group which can be released upon

coupling reaction with an oxidation product of an aromatic primary amine developing agent (release group), with the proviso that a dimer or higher polymer may be formed via R_1 , Z_a , Z_b or Y_1 :



wherein R_{11} represents an alkyl group, an alkenyl group, a heterocyclic group or an aryl group; X_1 represents a hydrogen atom, an alkaline metal atom, an ammonium group or the precursor thereof; V_1 represents an oxygen atom, a sulfur atom, $=\text{NH}$, $=\text{N}-(\text{L})_n-\text{R}_{12}$ in which R_{12} has the same meaning as R_{11} ; L represents a divalent linking group such as



atom, an alkyl group, or an aralkyl group; and n and n' each represents an integer 0 or 1.

2. The silver halide color light-sensitive material as claimed in claim 1, wherein 95 to 99.9 mol% of all silver halide content constituting each of said silver halide grains is silver chloride.

3. The silver halide color light-sensitive material as claimed in claim 1 or claim 2, wherein said light-sensitive emulsion layer contains the photographic emulsion in an amount of at least 70% by weight of the total silver halide emulsion therein.

4. The silver halide color light-sensitive material as claimed in claim 3, wherein the amount of said emulsion is at least 90% by weight.

5. The silver halide color light-sensitive material as claimed in any one of claims 1-4, wherein the silver bromide content in said localized silver bromide phases is 5 mol% or more.

6. The silver halide color light-sensitive material as claimed in claim 5, wherein said silver bromide content is 20 mol% or more.

7. The silver halide color light-sensitive material as claimed in claim 6, wherein said silver bromide content is 20 mol% to less than 70 mol%.

8. The silver halide color light-sensitive material as claimed in any one of claims 1-7, wherein the amount of the compound represented by formula (II-a) or (II-b) to be incorporated is in the range of 1×10^{-5} to 5×10^{-2} mol per 1 mol of silver halide.

9. The silver halide color light-sensitive material as claimed in claim 8, wherein the amount of the compound represented by formula (II-a) or (II-b) is in the range of 1×10^{-4} to 1×10^{-2} mol per 1 mol of silver halide.

10. The silver halide color light-sensitive material as claimed in any one of claims 1-9, wherein the pyrazoloazole type coupler represented by formula (I) is a pyrazolo[5,1-c][1,2,4]triazole.



11. The silver halide color light-sensitive material as claimed in any one of claims 1-9, wherein the pyrazoloazole type coupler represented by formula(I) is an imidazo[1,2-b]pyrazole.

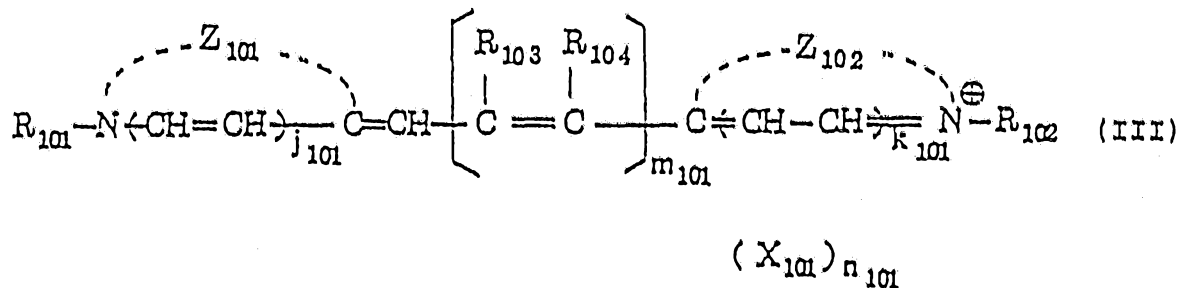
12. The silver halide color light-sensitive material as claimed in any one of claims 1-9, wherein said pyrazoloazole type coupler is a pyrazolo[1,5-b][1,2,4]-triazole.

13. The silver halide color light-sensitive material as claimed in any one of claims 1-12, wherein the amount of the pyrazoloazole type coupler represented by formula (I) to be used is in the range of 0.001 to 1 mol per 1 mol of light-sensitive silver halide.

14. The silver halide color light-sensitive material as claimed in any one of claims 1-13, wherein said silver bromochloride grains are grains having (100) plane and having localized silver bromide phases on the corners of the surface thereof or tabular grains having localized silver bromide phases on the corners or edges of the surface thereof.

15. The silver halide color light-sensitive material as claimed in any one of claims 1-14, wherein said photographic emulsion containing the silver bromochloride grains is a monodisperse emulsion.

16. The silver halide color light-sensitive material as claimed in any one of claims 1-15, wherein said silver bromochloride grains are formed by adding a cyanine dye represented by formula (III) after the formation of host grains, of before or during the chemical sensitization,



wherein Z_{101} and Z_{102} each represents an atomic group needed to form a heterocyclic nucleus; R_{101} and R_{102} each represents an alkyl group, an alkenyl group, an alkynyl group or an aralkyl group; m_{101} represents 0 or an integer of 1 to 3; when m_{101} represents 1, R_{103} represents a hydrogen atom, a lower alkyl group, an aralkyl group or an aryl group; when m_{101} represents 1, R_{104} represents a hydrogen atom; when m_{101} represents 2 or 3, R_{103} represents a hydrogen atom, and R_{104} represents a hydrogen atom, a lower alkyl group, or an aralkyl group and may be connected to R_{102} to form a 5- or 6-membered ring; when m_{101} represents 2 or 3, and R_{104} represents a hydrogen atom, R_{103} may be connected to another R_{103} to form a hydrocarbon ring or heterocyclic ring; j_{101} and k_{101} each represents 0 or 1; X_{101} represents an acid anion; and n_{101} represents 0 or 1.

17. The silver halide color light-sensitive material as claimed in claim 16, wherein said cyanine dye represented by formula (III) has a reduction potential of -1.27 or more negative (V. vs. SCE).

18. The silver halide color light-sensitive material as claimed in ^{claim 16 or} claim 17, wherein said cyanine dye is a pentamethine cyanine dye containing a benzothiazole nucleus, a pentamethine cyanine dye



containing a benzoselenazole nucleus or a trimethine cyanine dye containing 4-quinoline nucleus.

19. The silver halide color light-sensitive material as claimed in any one of claims 16-18 wherein
5 m_{101} in formula (III) represents 2 and R_{103} in formula (III) is connected to another R_{103} to form a 6-membered hydrocarbon ring.

20. The silver halide color light-sensitive material as claimed in any one of claims 1-19, wherein said
10 localized silver bromide phases or its substrate contain metal ions selected from the group VIII metal ions or its complex ions.

21. The silver halide color light-sensitive material as claimed in claim 20, wherein said localized
15 silver bromide phases contain an iridium ion or its complex ion.

22. The silver halide color light-sensitive material as claimed in claim 20 or 21, wherein said
20 substrate contains at least one ion selected from osmium, iridium, platinum, ruthenium, rhodium, palladium, iron, cobalt and nickel ions and its complex ions.

23. The silver halide color light-sensitive material as claimed in any one of claims 20-22, wherein the
25 amount of said metal ions or its complex ions to be added is in the range of 10^{-8} to 10^{-5} mol per mol of silver halide.

24. The silver halide color light-sensitive material as claimed in any one of claims 1-23, wherein said
30 silver halide color light-sensitive material contains a dye having, in a gelatin film, a maximum absorption wavelength of 570 to 660 nm in a gelatin-containing light-sensitive silver halide emulsion layer or a gelatin-containing light-insensitive hydrophilic colloid layer.

25. The silver halide color light-sensitive
35 material as claimed in any one of claims 1-24, wherein said silver halide color light-sensitive material contains at least one of a compound (A) which is chemically bonded to an



aromatic amine developing agent left after the color development to produce a chemically inert and substantially colorless compound and a compound (B) which is chemically bonded to an oxidation product of an aromatic amine color developing agent left after the color development to produce a chemically inert and substantially colorless compound in at least one of a light-sensitive silver halide emulsion layer and a light-insensitive hydrophilic colloid layer.

26. A silver halide color light-sensitive material, substantially as herein described with reference to any one of the examples.

Dated this 25th February, 1991

FUJI PHOTO FILM CO., LTD
By their Patent Attorney
GRIFFITH HACK & CO.



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