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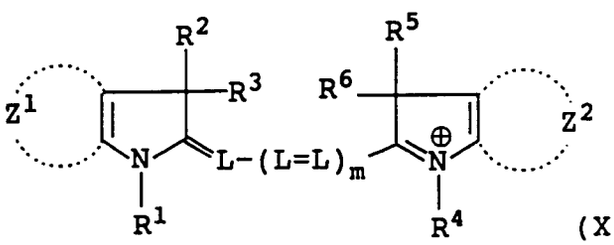
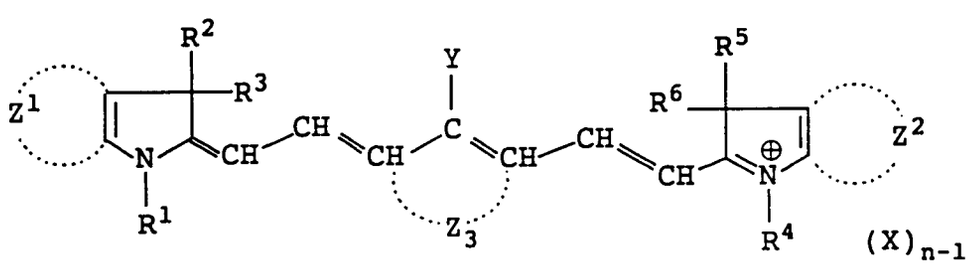
(54) Silver halide photographic material.

(57) Disclosed is a silver halide photographic material having a hydrophilic colloid layer containing at least one indolenine cyanine dye of formula (I) or (II):



(I)

where R^1, R^2, R^3, R^4, R^5 and R^6 may be same or different and each represents an alkyl group; Z^1 and Z^2 each represents a non-metallic atomic group necessary for forming a benzo-condensed ring or naphtho-condensed ring; L represents a methine group; m represents an integer of from 0 to 3; X represents an anion; n represents 1 or 2, provided that when the compound forms an internal salt, n is 1; and the compound has at least five acidic substituents, at least two of which contain a carboxylic acid group;



(II)

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where R^1, R^2, R^3, R^4, R^5 and R^6 may be same or different and each represents an alkyl group; Z^1 and Z^2 each represents a non-metallic atomic group necessary for forming a benzo-condensed ring or naphtho-condensed ring; Z^3 represents a non-metallic atomic group necessary for forming a 5-membered or 6-membered ring; Y represents a hydrogen atom or a monovalent group; X represents an anion; n represents 1 or 2, provided that when the compound forms an internal salt, n is 1; and the compound has at least four acidic substituents, at least one of which contains a carboxylic acid group. The dye is stable in the material during storage. After being processed, the dye is decolored well to give little color retention in the processed material.

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic material having a colored hydrophilic colloid layer and, more precisely, it relates to a silver halide photographic material having a hydrophilic colloid layer containing a dye which absorbs infrared rays, which exists stably in the material, which is photochemically inactive, and which is easily decolored in the step of photographic processing of the material.

BACKGROUND OF THE INVENTION

In preparing silver halide photographic materials, coloration of photographic emulsion layers or other layers is often effected for the purpose of absorbing light falling within a particular wavelength range.

If it is necessary to control the spectral composition of the light penetrating into photographic emulsion layers, a colored layer is provided on the support in a position more remote from the support than the photographic emulsion layers. A colored layer of this kind is called a filter layer. In the case of a multi-layered color photographic material having several photographic emulsion layers, the filter layer may be positioned between them.

For the purpose of preventing blurred images caused by re-penetration of the light as it is scattered during or after passing through photographic emulsion layers and reflected on the boundary between the emulsion layer and the support or on the surface of the photographic material opposite to the emulsion layer, into the photographic emulsion layers, or for the purpose of preventing such halation, a colored layer may be provided between the photographic emulsion layer and the support or on the surface of the support which is opposite to the photographic emulsion layer. The colored layer is called an anti-halation layer. In the case of a multi-layered color photographic material, the anti-halation layer may be provided between the respective layers.

For the purpose of preventing lowering of the image sharpness caused by scattering of light in photographic emulsion layers (the phenomenon is generally called "irradiation"), coloration of photographic emulsion layers is often effected.

The layers to be colored for this purpose are mostly hydrophilic colloid layers, and therefore, water-soluble dyes are generally incorporated into the layers so as to color them. The dyes needed to satisfy the following conditions.

(1) they have an appropriate spectral absorption in accordance with the use and the object;

(2) they are photochemically inactive. That is to say, they do not have any harmful influence on the chemical properties of silver halide photographic emulsion layers. For example, they do not lower the sensitivity of the emulsion layers, they do not cause latent image fading, and they do not cause fogging;

(3) they are decolored or dissolved out in the step of photographic processing so that they do not leave any harmful coloration on the processed photographic materials; and

(4) they have an excellent time-dependent storage stability in solutions or in photographic materials.

Many dyes have heretofore been known which satisfy these conditions and which absorb visible rays or ultraviolet rays. They are suitable for improving the images to be formed in conventional photographic elements which are sensitized to be sensitive to lights having a wavelength of 700 nm or less. In particular, triarylmethane and oxonole dyes have been used widely in relation to them.

On the other hand, there is a need for anti-halation and anti-irradiation dyes capable of absorbing light which falls within an infrared spectral range for near-infrared sensitized recording materials, for example, for photographic recording materials for recording outputs with near-infrared lasers.

For instance, as one means of exposing photographic materials of this kind, there is known an image forming method by a so-called scanner system. In that system, original is scanned and a silver halide photographic material is exposed on the basis of the resulting image signal so as to form a negative image or positive image corresponding to the image of the original thereon.

As recording light sources for such a scanner recording system, semiconductor lasers are used most favorably. Devices for semiconductor lasers are small-sized and low-priced, and may easily be modulated. In addition, semiconductor lasers have a longer life than other He-Ne lasers and argon lasers. Moreover, since they emit infrared rays, a light safelight may be used in handling infrared-sensitive photographic materials. Therefore, semiconductor lasers are advantageous with respect to handlability and operatability.

However, since no suitable dye is known which absorbs light falling within an infrared spectral range and which satisfies the preceding conditions (1), (2), (3) and (4), especially conditions (3) and (4), there are few photographic materials having a high light sensitivity in an infrared range and having excellent anti-halation and anti-irradiation properties. Therefore, in the current situation, the semiconductor lasers having

the above-mentioned excellent capacity can not fully be utilized.

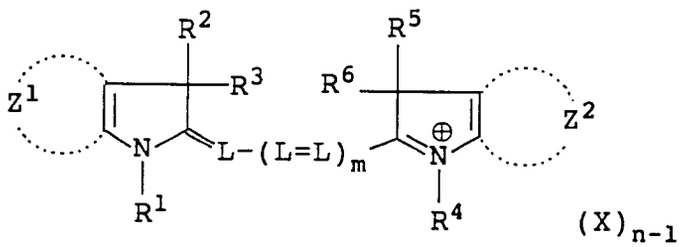
Until now, various efforts have been made to find dyes satisfying the preceding conditions, and many dyes have heretofore been proposed.

Examples of these dyes include indoaniline dyes described in JP-A-50-100116 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"); tricarbocyanine dyes described in JP-A-62-123454, JP-A-63-55544 and JP-A-64-33547; oxonole dyes described in JP-A-1-227148; and merocyanine dyes described in JP-A-1-234844. Also mentioned are tetra-aryl polymethine dyes described in JP-A-2-216140. However, there are few dyes which sufficiently satisfy all the preceding conditions.

SUMMARY OF THE INVENTION

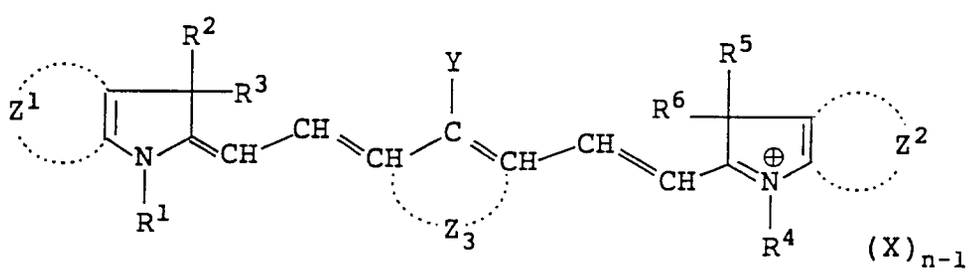
An object of the present invention is to provide dyes satisfying the preceding conditions (1), (2), (3) and (4). In particular, it is to provide a silver halide photographic material containing dye(s) which is(are) stable in the material during storage and which leave(s) little color therein after development of the material.

It has been found that this and other objects of the invention are attained by a silver halide photographic material having a hydrophilic colloid layer containing at least one compound (dye) of the following general formula (I) or (II):



(I)

where R^1, R^2, R^3, R^4, R^5 and R^6 may be same or different and each represents an alkyl group;
Z^1 and Z^2 each represents a non-metallic atomic group necessary for forming a benzo-condensed ring or naphtho-condensed ring;
L represents a methine group;
m represents an integer of from 0 to 3;
X represents an anion;
n represents 1 or 2, provided that when the compound forms an internal salt, n is 1; and
the compound has at least five acidic substituents, at least two of which contain a carboxylic acid group;



(II)

where R^1, R^2, R^3, R^4, R^5 and R^6 may be same or different and each represents an alkyl group;
Z^1 and Z^2 each represents a non-metallic atomic group necessary for forming a benzo-condensed ring or naphtho-condensed ring;
Z^3 represents a non-metallic atomic group necessary for forming a 5-membered or 6-membered ring;
Y represents a hydrogen atom or a monovalent group;
X represents an anion;
n represents 1 or 2, provided that when the compound forms an internal salt, n is 1; and
the compound has at least four acidic substituents, at least one of which contains a carboxylic acid group.

DETAILED DESCRIPTION OF THE INVENTION

Dyes of formula (I) are described in detail. In formula (I), R^1, R^2, R^3, R^4, R^5 and R^6 may be same or different and each represents a substituted or unsubstituted alkyl group, preferably a lower alkyl group having from 1 to 5 carbon atoms (e.g., methyl, ethyl, n-propyl, n-butyl, n-pentyl). They may optionally have substituent(s), such as a sulfonic acid group, a carboxylic acid group, a phosphonic acid group, SO_2NHSO_2R or $CONHSO_2R$ (where R is an alkyl group having from 1 to 5 carbon atoms, or a phenyl group as substituted by substituent(s) which will be referred to as Z^1 hereinafter), and a hydroxyl group. R^1 and R^4 each is preferably a lower alkyl group having from 1 to 5 carbon atoms and having a sulfonic acid group or a carboxylic acid group (e.g., 3-sulfopropyl, 4-sulfobutyl, 2-carboxyethyl). R^2 and R^3, and R^5 and R^6 may be bonded to each other to form a ring.

The acidic substituent as referred to herein indicates a sulfonic acid group, a carboxylic acid group, a phosphonic acid group, SO_2NHSO_2R or $CONHSO_2R$ (where R is an alkyl group having from 1 to 5 carbon atoms, or a phenyl group as substituted by substituent(s) which will be referred to as Z^1 hereinafter). The sulfonic acid group includes a sulfo group and its salts; the carboxylic acid group includes a carboxyl group and its salts; and the phosphonic acid group includes a phosphono group and its salts. SO_2NHSO_2R or $CONHSO_2R$ may be in the form of one of its salt. Examples of the salts include alkali metal salts with, for example, Na or K; ammonium salts, and organic ammonium salts of, for example, triethylammonium salts, tributylammonium salts, pyridinium salts and tetrabutylammonium salts.

The acidic substituent is preferably contained in any of R^1, R^2, R^3, R^4, R^5, R^6, Z^1 and/or Z^2, more preferably R^1 and R^4.

The benzo-condensed ring or naphtho-condensed ring formed by the non-metallic atomic group of Z^1 or Z^2 may optionally be substituted by a halogen atom (e.g., Cl, F, Br), a substituted amino group (e.g., dimethylamino, diethylamino, di-4-sulfobutylamino, di-2-carboxyethylamino), a hydroxyl group, a sulfonic acid group, a carboxylic acid group, a phosphonic acid group, SO_2NHSO_2R, $CONHSO_2R$ or by a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms which is bonded to the ring directly or via a divalent linking group. Examples of the alkyl group include methyl, ethyl and propyl groups; and the substituents of the alkyl group are preferably a sulfonic acid group, a carboxylic acid group and a hydroxyl group. The divalent linking group is preferably -O-, -NHCO-, -$NHSO_2$-, -$NHCO_2$-, -NHCONH-, -COO-, -CO- or -SO_2-.

The plurality L groups in formula (I) may be same or different.

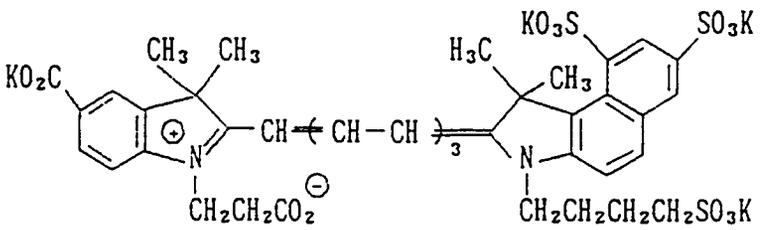
The methine group of L may optionally be substituted, for example, by a substituted or unsubstituted lower alkyl group having from 1 to 5 carbon atoms (e.g., methyl, ethyl, 3-hydroxypropyl, benzyl, 2-sulfoethyl), a halogen atom (e.g., F, Cl, Br), a substituted or unsubstituted aryl group having from 6 to 10 carbon atoms (e.g., phenyl, 4-chlorophenyl) and/or a lower alkoxy group having from 1 to 4 carbon atoms (e.g., methoxy, ethoxy). Substituents, if any, on the methine group may be bonded to each other to form a 5-membered or 6-membered ring (e.g., cyclopentene ring, cyclohexene ring, 4,4-dimethylcyclohexene ring) together with the three methine group in the formula. n is 1 or 2. When the dye forms an internal salt, n is 1.

The dye molecule of formula (I) has 5 or more acidic substituents, at least two of which contain a carboxylic acid group. Preferably, it has 6 or more acidic substituents, at least two of which contain a carboxylic acid group. Especially preferably, Z^1 or Z^2 contains a carboxylic acid group.

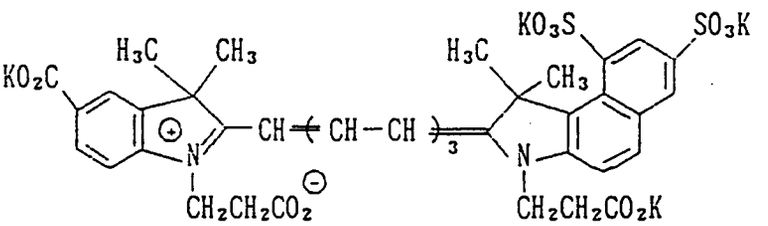
Compounds of formula (II) are described in detail. The alkyl groups represented by R^1, R^2, R^3, R^4, R^5 and R^6, the non-metallic atomic groups each necessary for forming a benzo-condensed ring or naphtho-condensed ring represented by Z^1 and Z^2, and X and n have the same meaning as those referred to in formula (I). Examples of the 5-membered or 6-membered ring to be represented by Z^3 include a cyclopentene ring, a cyclohexene ring and a 4,4-dimethylcyclohexene ring. Examples of the monovalent group represented by Y include a lower alkyl group having 1 to 3 carbon atoms such as a methyl group; a substituted or unsubstituted phenyl group; an aralkyl group having 7 to 9 carbon atoms such as a benzyl group; a lower alkoxy group having 1 to 3 carbon atoms such as a methoxy group; a di-substituted amino group such as a dimethylamino group, a diphenylamino group, a methylphenylamino group, a morpholino group, an imidazolidino group or an ethoxycarbonylpiperazino group; an alkylcarbonyloxy group having 2 to 4 carbon atoms such as an acetoxy group; an alkylthio group having 1 to 3 carbon atoms such as a methylthio group; a cyano group, a nitro group, and a halogen atom such as F, Cl or Br. The dye molecule has 4 or more acidic groups, at least one of which contains a carboxylic group. Preferably, it has 4 or more acidic groups, at least two of which contain a carboxylic group. Especially preferably, Z^1 or Z^2 contains a carboxylic acid group.

Specific examples of dyes of formula (I) and (II) for use in the present invention are shown below, which, however, are not limiting:

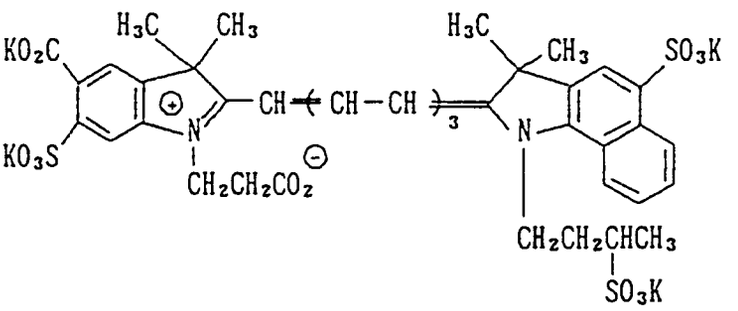
(I-1)



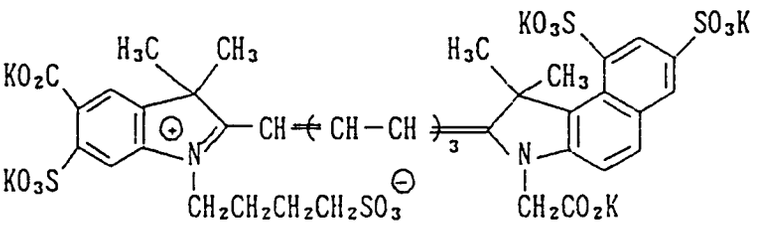
(I-2)



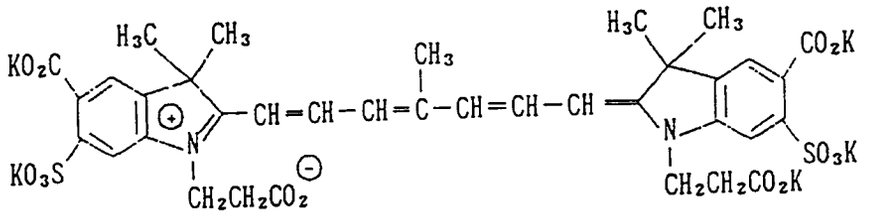
(I-3)



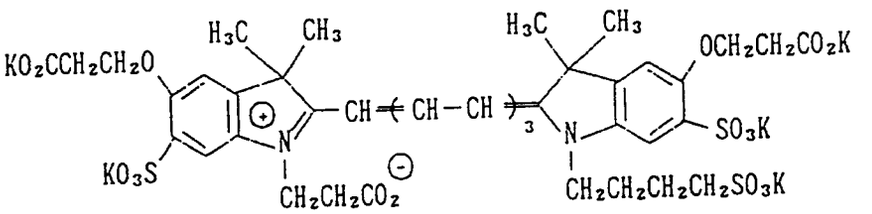
(I-4)



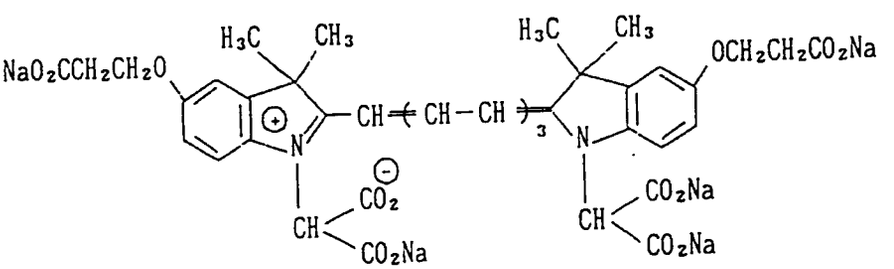
(I－5)



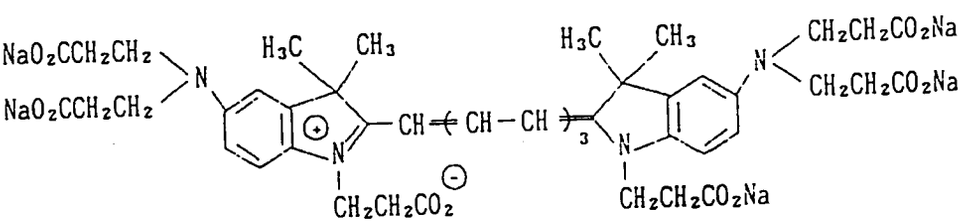
(I－6)



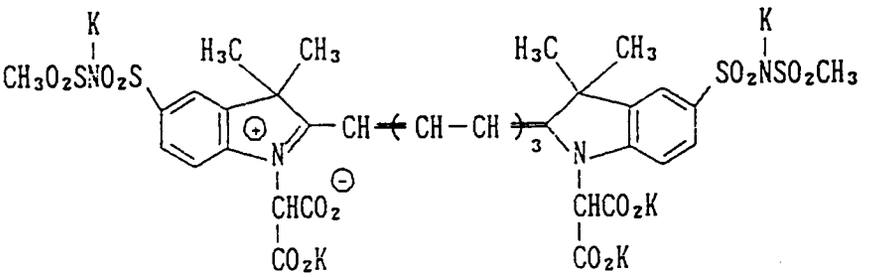
(I－7)



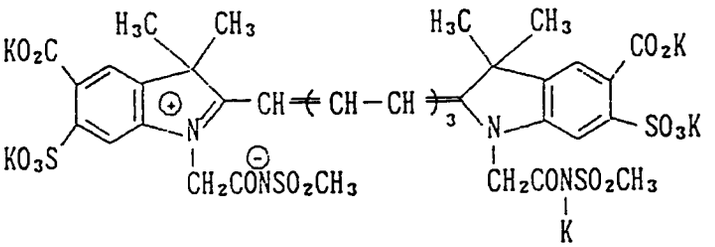
(I－8)



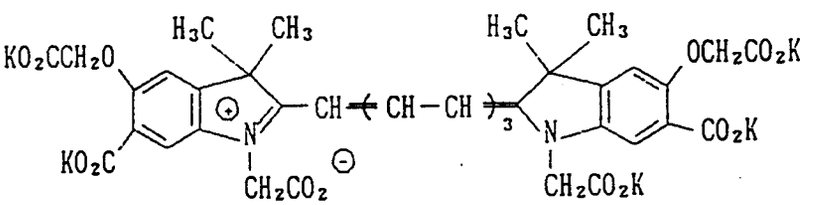
(I－9)



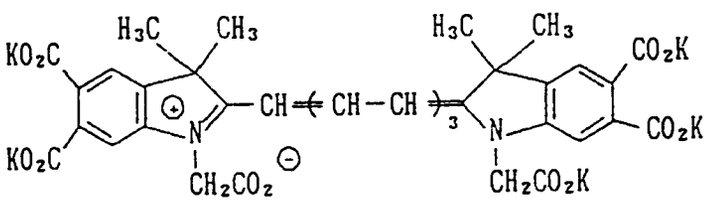
(I－10)



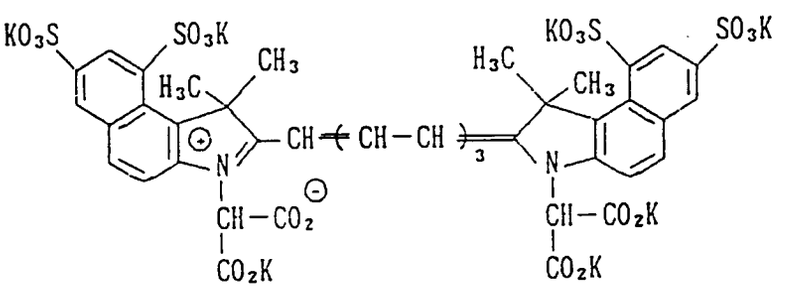
(I－11)

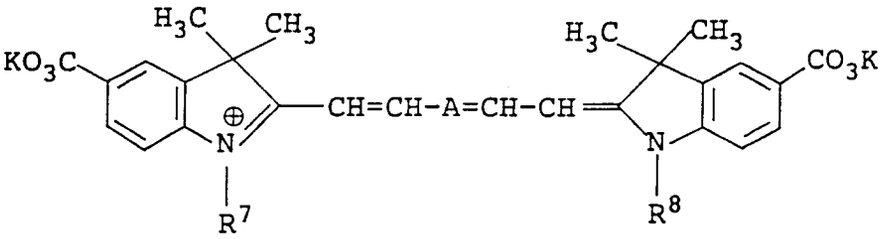


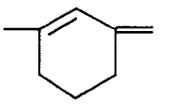
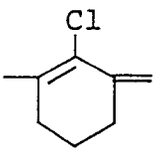
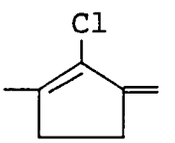
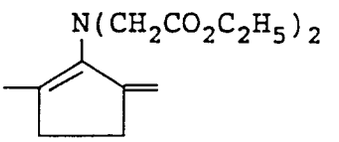
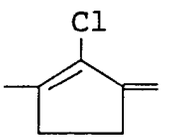
(I－12)

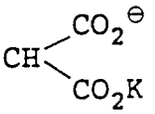
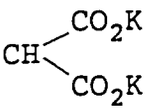
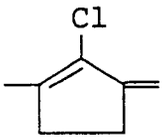
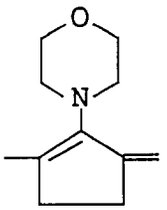
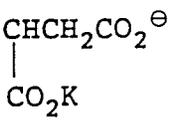
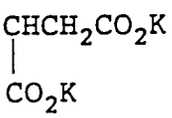
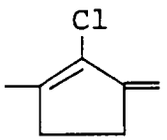


(I－13)





Compound	R^7	R^8	A
II-1	$CH_2CH_2CH_2CH_2SO_3^{\ominus}$	$CH_2CH_2CH_2CH_2SO_3K$	
II-2	"	"	
II-3	"	"	
II-4	"	"	
II-5	"	"	
II-6	$CH_2CO_2^{\ominus}$	CH_2CO_2K	

Compound	R^7	R^8	A
II-7			
II-8	"	"	
II-9			

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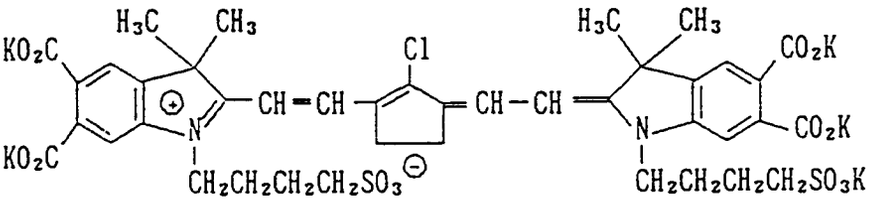

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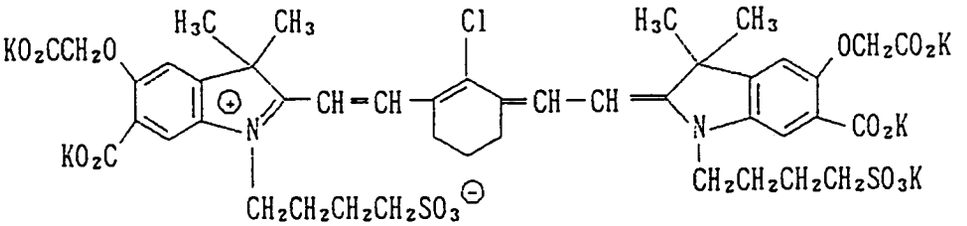

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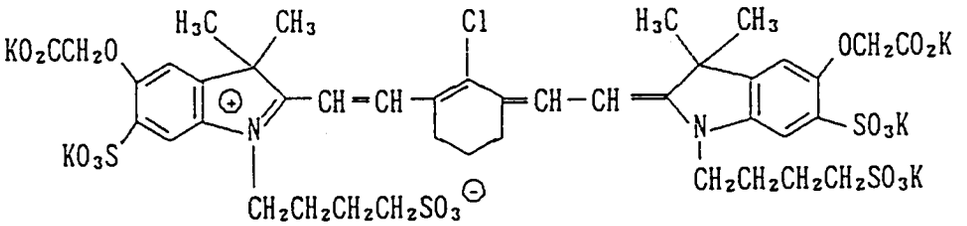

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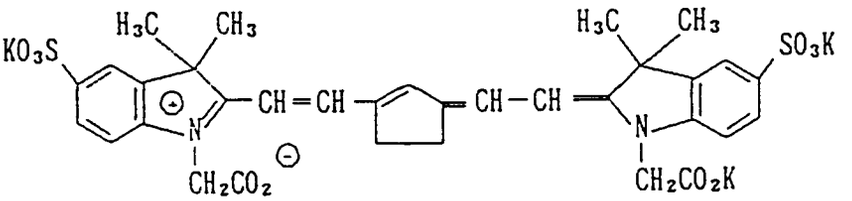

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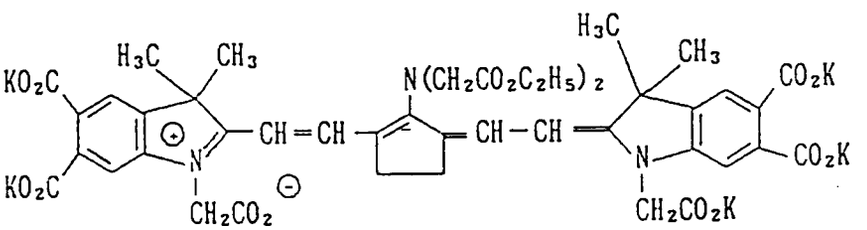

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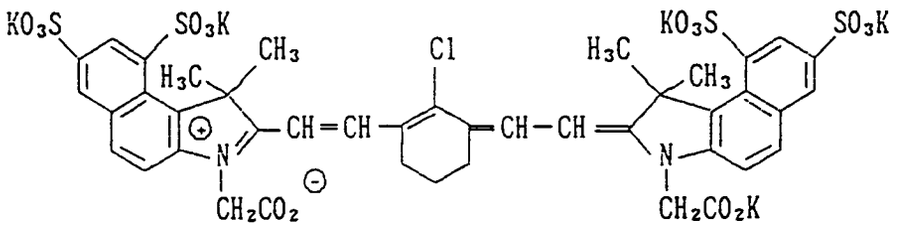

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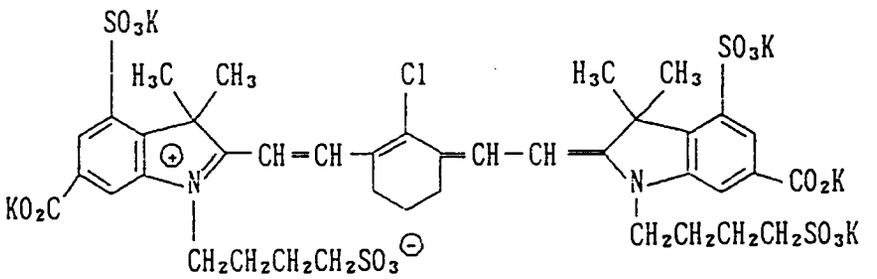

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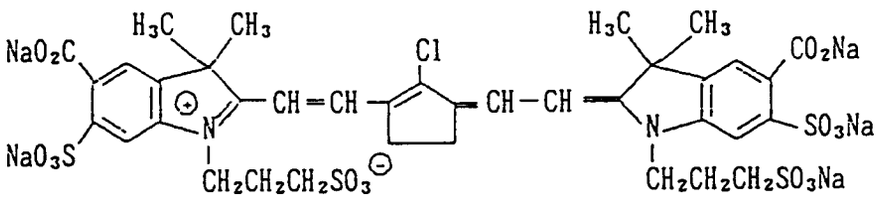

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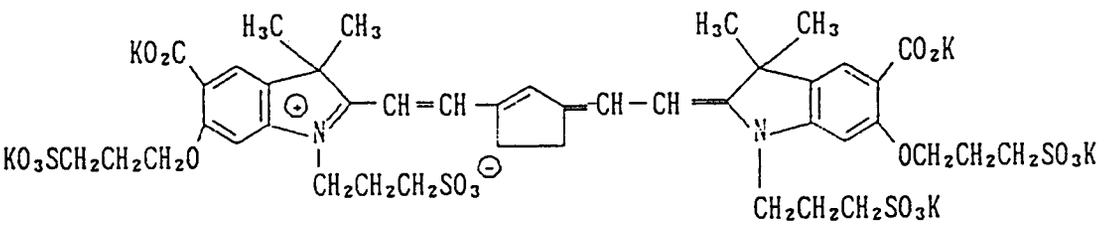

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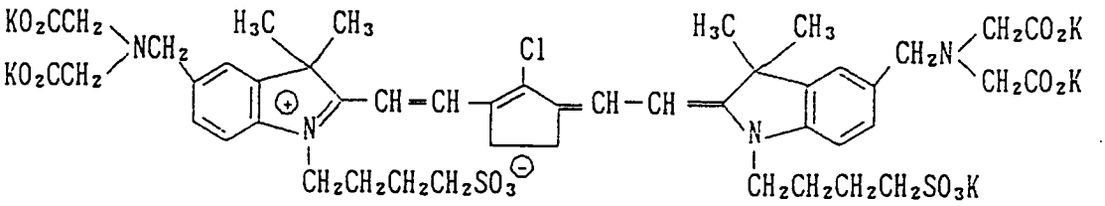

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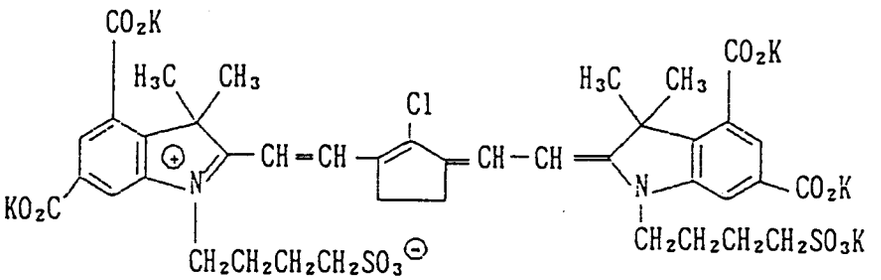

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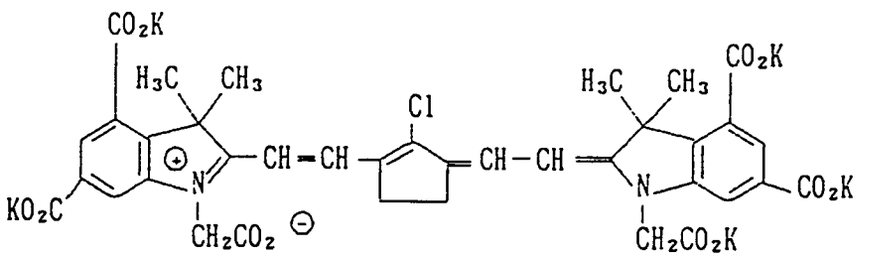

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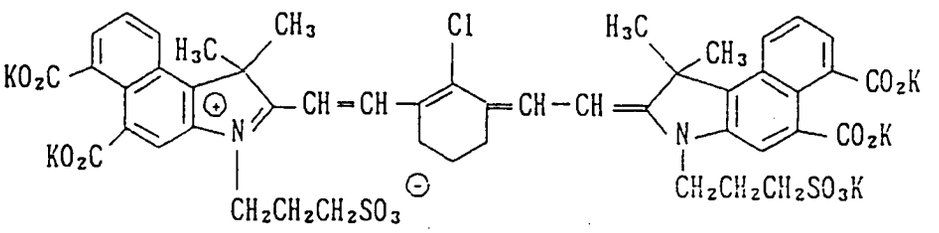


Compounds of formula (I) and (II) for use in the present invention can be produced according to the descriptions of JP-A-62-123454, JP-A-64-33547 and JP-A-3-171136.

The dye of formula (I) or (II) is dissolved in a suitable solvent (e.g., water, alcohols such as methanol or ethanol, methyl cellosolve) or a mixed solvent of these. The resulting solution is added preferably to a coating liquid for a light-sensitive or non-light-sensitive hydrophilic colloid layer, or an aqueous decomposate of the dye is added thereto. Two or more dyes may be combined in use depending or the purpose.

The amount of the dye to be added to the layer is generally from 10^{-3} g/m^2 to 2.5 g/m^2, especially preferably from 10^{-3} g/m^2 to 1.0 g/m^2.

The photographic dyes of formula (I) and (II) are effective especially for anti-irradiation. They are essentially added to emulsion layers of a photographic material, when used for this purpose.

The photographic dyes of formulae (I) and (II) are also effective especially for anti-halation. They are added to the layer on the back surface of a support of a photographic material or to the interlayer between the support and an emulsion layer of the material, when used for this purpose.

The photographic dyes of formulae (I) and (II) are also used advantageously as a filter dye.

The dyes of formulae (I) and (II) are preferably used along with a binder in the present invention.

The hydrophilic colloid materials to be used as a binder include, for example, gelatin and gelatin substituents; collodion, gum arabic; cellulose ester derivatives such as alkyl esters of carboxylated cellulose, hydroxyethyl cellulose or carboxymethylhydroxyethyl cellulose; amphoteric copolymers as described in Clavier et al's U.S. Patent 2,949,442 issued on August 16, 1960; polyvinyl alcohol and other various materials known in this technical field.

Examples of high polymer gelatin substituents usable in the present invention include copolymers of allylamine and methacrylic acid, copolymers of allylamine, acrylic acid and acrylamide, hydrolyzed copolymers of allylamine, methacrylic acid and vinyl acetate, copolymers of allylamine, acrylic acid and styrene, and copolymers of allylamine, methacrylic acid and acrylonitrile.

The photographic material of the present invention includes black-and-white and color photographic materials.

The concrete constitution of the photographic material of the present invention will be described below.

The silver halide emulsion to be used in the present invention may comprise any composition of silver bromide, silver chlorobromide or silver iodochlorobromide having a silver chloride content of 50 mol% or less. Preferably, it is silver chlorobromide having a silver chloride content of 50 mol% or less, especially preferably from 5 mol% to 40 mol%.

The reason is, as described in Japanese Patent Application No. 3-266934, because the silver chloride content in the emulsion is better when elevated so as to elevate the fixability of the emulsion, but if the content is too great, the sensitivity of the emulsion would lower.

Regarding the mean grain size of the silver halide grains for use in the present invention, the grains are desired to be fine grains, for example, having a mean grain size of 0.7 μ or less, especially preferably 0.5 μ or less.

Regarding the shape of the silver halide grains for use in the present invention, they may be any of cubic, octahedral, tetradecahedral, tabular or spherical ones, or they may be in the form of a mixture thereof. Preferred are cubic, octahedral and tabular grains.

The photographic emulsion for use in the present invention may be prepared by known methods, for example, those described in P. Glafkides, Chimie et Physique Photographique (published by Paul Montel, 1967), G.F. Duffin, Photographic Emulsion Chemistry (published by The Focal Press, 1966) and V.L. Zelikman et al, Making and Coating Photographic Emulsion (published by The Focal Press, 1964).

Briefly, the emulsion may be prepared by an acid method, a neutral method or an ammonia method. For forming the emulsion by reacting a soluble silver salt and soluble halide(s), a single jet method or a double jet method or combination thereof may be employed.

A so-called reversed jet method of forming silver halide grains in the presence of excess silver ions may also be employed. As one embodiment of a double jet method, a so-called controlled double jet method of keeping the pAg value in the liquid phase of the forming silver halide grains therein may be employed.

In accordance with the method, silver halide grains having a regular crystalline form and having nearly uniform grain sizes may be obtained.

For unifying the grain size of the silver halide grains to be formed, a method of varying the addition speed of silver halide and alkali halides in accordance with the growing speed of the grains to be formed, as described in British Patent 1,535,016 and JP-B-48-36890 and JP-B-52-16364, and a method of varying the concentrations of the aqueous solutions to be reacted, as described in U.S. Patent 4,242,445 and JP-A-55-158124, are preferably employed so as to rapidly grow the silver halide grains within a range not exceeding the critical saturation thereof.

The silver halide grains for use in the present invention may be so-called core/shell grains each having different halogen compositions in the inside (core) and the surface layer (shell).

Formation of the silver halide grains for use in the present invention is preferably effected in the presence of a silver halide solvent such as tetra-substituted thioureas or organic thioether compounds.

Preferred tetra-substituted thioureas of a silver halide solvent for use in the present invention are those described in JP-A-53-82408 and JP-A-55-77737.

Preferred organic thioethers of a silver halide solvent for use in the present invention are those containing at least one group having an oxygen atom and a sulfur atom interrupted by ethylene therebetween (e.g., -O-CH_2CH_2-S-), for example, as described in JP-B-47-11386 (corresponding to U.S. Patent 3,574,628), and chained thioether compounds having alkyl groups at both ends (the alkyl group each having at least two substituents selected from hydroxyl, amino, carboxyl, amido and sulfone groups), for example, as described in JP-A-54-155828 (corresponding to U.S. Patent 4,276,374).

The amount of the silver halide solvent to be added varies, depending upon the kind of compounds to be reacted and the grain size and halide composition of the silver halide grains to be formed. It is preferably from 10^{-5} to 10^{-2} mol per mol of the silver halide to be formed.

If silver halide grains having a larger grain size than that intended are formed due to addition of a silver halide solvent, the temperature in the step of forming silver halide grains and the time of adding the silver salt solution and halide solution(s) to be reacted may be varied so as to attain the intended grain size.

For forming the silver halide emulsion for use in the present invention, a water-soluble iridium compound may be added to the reaction system. For instance, examples of the compound include iridium(III) halides, iridium(IV) halides, as well as iridium complexes having halogens, amines or oxalato groups as the ligand, such as hexachloroiridium(III) or (IV) complex, hexamineiridium (III) or (IV) complex, and trioxalatoiridium(III) or (IV) complex. In the present invention, suitable iridium(III) and iridium(IV) compounds may be selected from these compounds and may be used in combination. The iridium compound may be used in the form of a solution dissolved in a suitable solvent. For instance, a method which is generally used for stabilizing an iridium compound solution or a method for adding an aqueous solution of a hydrogen halide (e.g., hydrochloric acid, hydrobromic acid, hydrofluoric acid) or an alkali halide (e.g., KCl, NaCl, KBr, NaBr) to the compound solution for the purpose may be employed in preparing the aqueous solution. In place of adding a water-soluble iridium compound, different iridium-doped silver halide grains may be added to the reaction system for forming silver halide grains.

The total amount of the iridium compound to be added for the preceding purpose may be 10^{-8} mol or more per mol of the silver halide to be formed, preferably from 1×10^{-8} to 1×10^{-5} mol, most preferably from 5×10^{-8} to 5×10^{-6} mol, per mol of the same.

Addition of the compound may suitably be effected at any stage during formation of the silver halide emulsions or before coating the formed emulsions. Especially preferably, it may be added during their formation so that the compound may be introduced into the silver halide grains formed. In place of using the iridium compound alone, any other compound containing a VIII group atom may be combined with the iridium compound for the same purpose.

The silver halide photographic emulsion of the present invention is chemically sensitized with a gold compound (gold sensitization) for the purpose of attaining high sensitivity and low fog. The gold sensitization is generally effected by adding a gold sensitizer to the emulsion followed by stirring it at a high temperature, preferably at 40 °C or higher, for a determined period of time.

The gold sensitizer for the gold sensitization is generally a gold compound having an oxidation number of gold of +1 or +3. Specific examples of the compound include chloroaurates, potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate and pyridyl trichlorogold.

The amount of the gold sensitizer to be added varies depending upon the various conditions for the sensitization, and it is generally preferably from 1×10^{-7} mol to 5×10^{-4} mol per mol of the silver halide to be sensitized therewith.

The silver halide photographic emulsion for use in the present invention may be sensitized also by sulfur sensitization so as to further elevate high sensitivity and lower fog.

The sulfur sensitization is generally effected by adding a sulfur sensitizer to the emulsion to be sensitized therewith followed by stirring it at a high temperature, preferably at 40 °C or higher, for a determined period of time.

Any known sulfur sensitizer may be used for the sulfur sensitization. For instance, they include thiosulfates, thioureas, allyl isothiocyanate, cystine, p-toluenethiosulfonates and rhodanine. Also suitable are sulfur sensitizers described in U.S. Patents 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313, 3,656,955, German Patent 1,422,869, JP-B-56-24937 and JP-A-55-45016. The amount of the sulfur sensitizer to be added for the sensitization may be a sufficient amount for effectively increasing the sensitivity of the emulsion as sensitized therewith. The amount varies, depending upon various conditions of pH and temperature during the reaction and the size of the silver halide grains to be sensitized therewith. For instance, it is preferably 1×10^{-7} mol to 5×10^{-4} mol per mol of the silver halide to be sensitized therewith.

For chemical ripening the emulsions of the present invention, the time and order of adding the sulfur sensitizer and gold sensitizer thereto are not specifically limited. For instance, the compounds may be added simulaneously or separately to the emulsion, preferably at the start of the chemical ripening or during the chemical ripening thereof. For adding them, they may dissolved in water or a water-miscible organic solvent, such as methanol, ethanol or acetone, or a mixed solvent thereof and the resulting solutions may be added to the emulsions.

Combination of sulfur sensitization with thiosulfates, selenium sensitization with selenium compounds and gold sensitization with gold compounds is advantageously employed in the present invention for effectively displaying the effect of the present invention.

As effective selenium sensitizing agents for use in the present invention, any known selenium compound such as those described in various published patent specifications may be employed. In general, unstable selenium compounds and/or non-unstable selenium compounds may be added to the emulsions to be sensitized therewith and stirred at a high temperature, preferably at 40 °C or higher, for a determined period of time. As unstable selenium compounds for this purpose, preferred are those mentioned in JP-B-41-15748, JP-B-43-12489 JP-A-4-25832 and JP-A-4-109240. Specific examples of suitable unstable selenium sensitizers are isoselenocyanates (e.g., aliphatic isoselenocyanates such as allyl isocyanocyanate), selenoureas, selenoketones, selenoamides, selenocarboxylic acids (e.g., 2-selenopropionic acid, 2-selenobutyric acid), selenoesters, diacylselenides (e.g., bis(3-chloro-2,6-dimethoxybenzoyl)selenide), selenophosphates, phosphine selenides and colloidal metal selenium.

Preferred examples and analogues of unstable selenium compounds for use in the present invention are mentioned below, which, however, are not limiting. For those skilled in the art, the structures of unstable selenium compounds as sensitizers for photographic emulsions are not specifically important provided that the selenium in the compounds is unstable. Anyhow, it has generally be understood that the organic moiety in the selenium sensitizer molecule does not have any other role than that of carrying selenium therewith so as to release it in the emulsion as an unstable form thereof. In the present invention, any and every unstable selenium compound in this broad conceptual range may be employed.

Non-unstable selenium compounds for use in the present invention for sensitization of the emulsions may be those described in JP-B-46-4553, JP-B-52-34492 and JP-B-52-34491. Examples of suitable non-unstable selenium compounds include selenous acid, potassium selenocyanide, selenazoles, quaternary salts of selenazoles, diaryl selenides, diaryl diselenides, dialkyl selenides, dialkyl diselenides, 2-selenazolinedione, 2-selenoxazolidinethione and derivatives thereof.

Sensitizing dyes to be preferably applied to the silver halide emulsions of the present invention are those having a spectral sensitivity in 600 nm or more, such as those having an optimum spectral sensitivity to He-Ne lasers or semiconductor lasers. Preferred sensitizing dyes are those described in JP-A-3-15049, from page 12, left top column to page 21, left bottom column; JP-A-3-20730, from page 4, left bottom column to page 15, left bottom column; EP-0420011, from page 4, line 21 to page 6, line 54; EP-0420012, from page 4, line 12 to page 10, line 33; EP-0433466; U.S. Patent 4,975,362; JP-A-2-157749, pages 13 to 22; JP-A-3-171136, pages 8 to 12; and JP-A-62-215272, pages 22 to 38. Especially preferred are dyes of formulae (I), (II) or (III) as described in JP-A-3-171136, pages 8 to 12. However, where the sensitizing dyes are used singly, their spectral sensitizing effect is not sufficient. If the amount thereof to be added is increased, their intrinsic desensitization would increase. So as to overcome the problem, use of a super-color sensitizer along with them is known, for example, as described in JP-B-60-45414, JP-B-46-10473 and JP-A-59-192242.

The preceding sensitizing dyes may be used singly or may also be used as combination thereof. A combination thereof is often used for the purpose of super-color sensitization. Along with the sensitizing dyes, dyes which do not have a color sensitizing effect by themselves or substances which do not substantially absorb visible rays but show a super-color sensitizing activity may be incorporated into the emulsions.

Useful sensitizing dyes, a combination of super-color sensitizing dyes with such dyes, and super-color sensitizing substances are described in Research Disclosure, Vol. 176, No. 17643 (issued on December 1978), page 23, IV-J or in JP-B-49-25500, JP-B-43-4933, JP-A-59-19032, JP-A-59-192242.

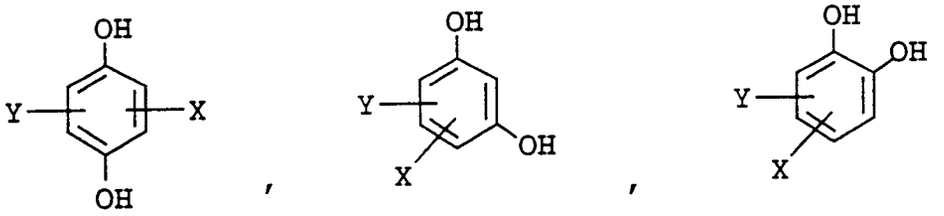
The optimum amount of the sensitizing dye having a spectral sensitivity in 600 nm or more to be added to the silver halide emulsion of the present invention may suitably be determined in accordance with the grain size and the halogen composition of the silver halide grains in the emulsion, the method and degree of chemical sensitization thereof, the relationship between the layer to which the compound (dye) is added and the silver halide emulsion therein, and the kind of antifoggant to be added to the emulsion. The test for the determination is well known by those skilled in the art. In general, the amount of the dye is from 10^{-7} mol to 1×10^{-2} mol, especially preferably from 10^{-6} mol to 5×10^{-3} mol, per mol of the silver halide in the

emulsion.

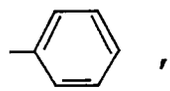
The preferred super-color sensitizers for use in the present invention are compounds as described in JP-A-3-15049, pages 22 to 25 and JP-A-62-123454, pages 15 to 20.

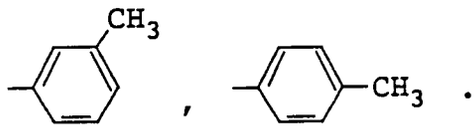
The photographic material of the present invention may contain various compounds for the purpose of preventing fogging of the material and stabilizing its photographic properties during manufacture, storage or processing. For instance, various compounds known as an antifoggant or stabilizer may be used for this purpose, including azoles such as benzothiazolium salts, nitroimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptothiadiazoles, aminotriazoles, benzothiazoles and nitrobenzotriazoles; mercaptopyrimidines; mercaptotriazines; thioketo compounds such as oxazolinethione; azaindenes such as triazaindenes, tetrazaindenes (especially, 4-hydroxy-substituted (1,3,3a,7)tetrazaindenes); and pentazaindenes; benzenethiosulfonic acids, benzenesulfinic acids and benzenesulfonic acid amides.

Polyhydroxybenzene compounds are especially preferred for the purpose, as improving the pressure resistance of photographic materials without lowering their sensitivity. In particular, polyhydroxybenzene compounds having any of the following structures are preferred:



In the formulae, X and Y each represents -H, -OH, a halogen atom, -OM (where M is an alkali metal ion), an alkyl group, a phenyl group, an amino group, a carbonyl group, a sulfone group, a sulfonated phenyl group, a sulfonated alkyl group, a sulfonated amino group, a sulfonated carbonyl group, a carboxyphenyl group, a carboxyalkyl group, a carboxyamino group, a hydroxyphenyl group, a hydroxyalkyl group, an alkyl-ether group, an alkylphenyl group, an alkyl-thioether group or a phenylthioether group. More preferably, they each are -H, -OH, -Cl, -Br, -COOH, $-CH_2CH_2COOH$, $-CH_3$, $-CH_2CH_3$, $-CH(CH_3)_2$, $-C(CH_3)_3$, $-OCH_3$, -CHO, $-SO_3Na$, $-SO_3H$, $-SCH_3$,





X and Y may be same as or different.

Polyhydroxybenzene compounds may be added either to the emulsion layers of photographic materials or to layers other than emulsion layers. The amount thereof to be added is effectively from 10^{-5} to 1 mol, especially preferably from 10^{-3} to 10^{-1} mol, per mol of silver halide in the material.

The photographic material of the present invention may contain water-soluble dyes in a hydrophilic colloid layer as a filter dye or for anti-irradiation and for various other purposes. Such dyes include, for example, oxonole dyes, hemioxonole dyes, styryl dyes, merocyanine dyes, cyanine dyes and azo dyes. Of them, especially useful are oxonole dyes, hemioxonole dyes, cyanine dyes and merocyanine dyes.

The photographic emulsion layers constituting the photographic material of the present invention may contain, for the purpose of elevation of sensitivity, contrast and developability of the material, a developing agent such as polyalkylene oxides or their ether, ester or amine derivatives, thioether compounds, thiomorpholines, quaternary ammonium compounds, urethane derivatives, urea derivatives, imidazole de-

rivatives, 3-pyrazolidones and aminophenols.

Of them, especially preferred are 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone). In general, the content of the developing agent in the material is 5 g/m^2 or less, especially preferably from 0.01 to 0.2 g/m^2.

The photographic emulsions or non-light-sensitive hydrophilic colloids constituting the photographic material of the present invention may contain an inorganic or organic hardening agent. For instance, suitable as the agent are active vinyl compounds (1,3,5-triacryloylhexahydro-s-triazine, bis(vinylsulfonyl)methylether, N,N-methylenebis-[β-(vinylsulfonyl)propionamide]), active halides (e.g., 2,4-dichloro-6-hydroxy-s-triazine), mucohalogenic acids (e.g., mucochloric acid), N-carbamoylpyridinium salts (e.g., 1-morpholinocarbonyl-3-pyridiniomethane sulfonate) and haloamidinium salts (e.g., 1-(1-chloro-1-pyridinomethylene)pyrrolidinium, 2-naphthalene-sulfonate), either singly or a combination thereof. In particular, the active vinyl compounds described in JP-A-53-41220, JP-A-53-57257, JP-A-59-162546 and JP-A-60-80846 and the active halides described in U.S. Patent 3,325,287 are preferred.

The photographic emulsion layers or other hydrophilic colloid layers constituting the photographic material of the present invention may contain various surfactants for the purposes of aiding coating, prevention of static charging, improvement of slide property, promotion of emulsification and dispersion, prevention of surface blocking and improvement of photographic characteristics (e.g., promotion of developability, elevation of contrast, elevation of sensitivity).

For instance, suitable for these purposes are nonionic surfactants such as saponins (steroid type), alkylene oxide derivatives (e.g., polyethylene glycol, polyethylene glycol/polypropylene glycol condensates, polyethylene glycol alkyl ethers, polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or amides, silicone-polyethylene oxide adducts), glycidol derivatives (e.g., alkenylsuccinic acid polyglycerides, alkylphenol polyglycerides), fatty acid esters of polyalcohols, and alkyl esters of saccharides; anionic surfactants containing acid groups, for instance a carboxyl group, a sulfo group, a phospho group, a sulfate group or a phosphate group, such as alkylcarboxylic acid salts, alkylsulfonic acid salts, alkylbenzenesulfonic acid salts, alkylnaphthalenesulfonic acid salts, alkylsulfate esters, alkylphosphate esters, N-acyl-N-alkyltaurins, sulfosuccinate esters, sulfoalkylpolyoxyethylene alkylphenyl ethers, and polyoxyethylene alkylphosphate esters; amphoteric surfactants such as amino acid salts, aminoalkylsulfonic acids, aminoalkylsulfate or phosphate esters, alkyl-betains, and amineoxides; and cationic surfactants such as alkylamine salts, aliphatic or aromatic quaternary ammonium salts, heterocyclic quaternary ammonium salts (e.g., pyridinium or imidazolium salts), and aliphatic or heterocyclic phosphonium or sulfonium salts.

As an antistatic agent for this purpose, preferably used are fluorine-containing surfactants such as those described in JP-A-60-80849.

The photographic material of the present invention may contain a mat agent such as silica, magnesium oxide or polymethyl methacrylate in the photographic emulsion layers or other hydrophilic colloid layers constituting the material, for the purpose of prevention of surface blocking of the material.

The photographic material of the present invention may also contain a dispersion of a water-insoluble or hardly soluble synthetic polymer for the purpose of improving the dimensional stability of the material. For instance, suitable are homopolymers or copolymers composed of alkyl (meth)acrylates, alkoxyacryl (meth)-acrylates and glycidyl (meth)acrylates, optionally with acrylic acid and methacrylic acid.

As a binder for the photographic emulsion or as a protective colloid, advantageously used is gelatin. Any other hydrophilic colloid may also be used in addition to gelatin. For instance, suitable are proteins such as gelatin derivatives, graft polymers of gelatin and high polymers, albumin and casein; saccharide derivatives such as cellulose derivatives (e.g., hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulfates), sodium alginate and starch derivatives; and various other synthetic hydrophilic high polymer substances of homopolymers or copolymers such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole and polyvinyl pyrazole.

As gelatin, suitable are, for example, a lime-processed gelatin and an acid-processed gelatin, as well as hydrolysates of gelatin and enzyme-decomposed products of gelatin.

The silver halide emulsion layer constituting the photographic material of the present invention may contain a polymer latex such as an alkyl acrylate latex.

The support for the photographic material of the present invention may, for example, be cellulose triacetate, cellulose diacetate, nitrocellulose, polystyrene or polyethylene terephthalate paper, baryta-coated paper, or polyolefin-coated paper.

The developing agent in the developer for use in development of the photographic material of the present invention is preferably selected from dihydroxybenzenes and 3-pyrazolidones for attaining the high

sensitivity of the material. Especially preferred are hydroquinone, 1-phenyl-3-pyrazolidone and 1-phenyl-4-mehtyl-4-hydroxymehtyl-3-pyrazolidone.

The sulfites to be used in the present invention as a preservative in the developer include, for example, sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite, potassium metabisulfite, and formaldehyde-sodium bisulfite. The content of the sulfite in the developer is preferably 0.25 mol/liter or more, especially preferably 0.4 mol/liter or more. The uppermost limit is preferably up to 2.5 mol/liter, especially preferably 1.2 mol/liter.

For adjusting the pH value of the developer, an alkali agent may be incorporated therein. It includes, for example, a pH adjusting agent or a buffer, such as potassium hydroxide, sodium carbonate or potassium carbonate.

Various other additives may be in the developer, which include, for example, a development inhibitor such as boric acid, borax and like compounds as well as sodium bromide, potassium bromide and potassium iodide; an organic solvent such as ethylene glycol, diethylene glycol, triethylene glycol, dimethylformamide, methyl cellosolve, hexylene glycol, ethanol and methanol; and an antifoggant or a black pepper inhibitor such as mercapto compounds (e.g., 1-phenyl-5-mercaptotetrazole, sodium 2-mercaptobenzimidazole-5-sulfonate), indazole compounds (e.g., 5-nitroindazole), and benzotriazole compounds (e.g., 5-methylbenzotriazole). In addition, the developer may further contain, if desired, a color toning agent, a surfactant, a defoaming agent, a water softener, a hardening agent, and the amino compounds described in JP-A-56-106244, JP-A-61-267759 and JP-A-2-208652.

The developer for use in the present invention may also contain the compounds described in JP-A-56-24347 as a silver stain inhibitor; the compounds described in JP-A-62-212651 as a development unevenness inhibitor, and the compounds described in JP-A-61-267759 as a dissolution aid.

The developer for use in the present invention may also contain, as a buffer, boric acid as described in JP-A-62-186259, saccharides (e.g., saccharose), oximes (e.g., acetoxime) and phenols (e.g., 5-sulfosalicylic acid) as described in JP-A-60-93433.

The photographic material of the present invention may be processed in the presence of a polyalkylene oxide. In order to incorporate a polyalkylene oxide into the developer with which the material is processed, the polymer is desired to be a polyethylene glycol having a mean molecular weight of from 1000 to 6000; and the content of the polymer in the developer is desired to be from 0.1 to 10 g/liter.

The fixer to be applied to the photographic material of the present invention may contain, in addition to a fixing agent, a water-soluble aluminum compound as a hardening agent. If desired, it may further contain acetic acid or a dibasic acid (e.g., tartaric acid, citric acid or their salts) to be an acidic aqueous solution having pH of 3.8 or more, preferably from 4.0 to 6.5.

The fixing agent to be in the fixer may be sodium thiosulfate and ammonium thiosulfate. In view of the fixing rate, ammonium thiosulfate is especially preferred. The amount of the fixing agent in the fixer may suitably be varied and is, in general, approximately 0.1 to 5 mol/liter.

The water-soluble aluminum salt which acts essentially as a hardening agent in the fixer is a compound which is generally known as a hardening agent for an acidic hardening fixer, and it includes, for example, aluminum chloride, aluminum sulfate and potassium alum.

As the preceding dibasic acid, suitable are tartaric acid and its derivatives, and citric acid and its derivatives. They may be used either singly or in combination of two or more. The content of the compound in the fixer is effectively 0.005 mol/liter or more, especially effectively from 0.01 mol/liter to 0.03 mol/liter.

Specifically mentioned are tartaric acid, potassium tartarate, sodium tartarate, sodium potassium tartarate, ammonium tartarate, and potassium ammonium tartarate.

Effective examples of citric acid and its derivatives for use in the present invention are citric acid, sodium citrate and potassium citrate.

The fixer for use in the present invention may further contain, if desired, a preservative (e.g., sulfites, bisulfites), a pH buffer (e.g., acetic acid, boric acid), a pH adjusting agent (e.g., ammonia, sulfuric acid), an image storability improving agent (e.g., potassium iodide), and a chelating agent. The content of the pH buffer may be approximately from 10 to 40 g/liter, more preferably from 18 to 25 g/liter, since the pH value of the developer is high.

The rinsing water to be applied to the processed photographic material of the present invention may contain, if desired, a microbicide (e.g., compounds described in Horiguchi, Bactericidal and Fungicidal Chemistry, and JP-A-62-115154), a rinsing promoter (e.g., sulfites), and a chelating agent.

The developed and fixed photographic material of the present invention is rinsed in water and then dried. The rinsing is effected for the purpose of almost completely removing the silver salts which have been dissolved by the previous fixation, and it is preferably conducted at about 20 °C to about 50 °C for 10 seconds to 3 minutes. The drying is conducted at about 40 °C to about 100 °C. The drying time may

suitably be varied in accordance with ambient conditions, and it is generally approximately 5 seconds to 3 minutes and 30 seconds.

The photographic material of the present invention may be processed with a roller-conveying type automatic developing machine which is described in, for example, U.S. Patents 3,025,779 and 3,545,971. The machine is referred to herein as a roller-conveying type processor. The roller-conveying type processor comprises the four steps of development, fixation, rinsing and drying. Most preferably for processing the photographic material of the present invention, all four steps are applied, of course not excluding other steps (e.g., stopping step).

In the rinsing step, the amount of the replenisher going to the rinsing tank may be 1200 ml/m^2 or less (including 0 ml/m^2).

The case where the amount of the replenisher to the rinsing or stabilization tank is 0 (zero) means that the rinsing is effected by a so-called stagnant water rinsing system. As a means of reducing the amount of the replenisher going to the tank, a multi-stage countercurrent system (for example, comprising two stage or three stages) is known.

Various problems would result from reduction of the amount of the replenisher going to the rinsing or stabilization tank, which could be solved by combination of the techniques mentioned below whereby a favorable result could be obtained.

For instance, the rinsing bath or stabilization bath may contain, as a microbicide, the isothiazoline compounds described in R.T. Kreiman, J. Image. Tech., Vol. 10, No. 6, 242 (1984); the isothiazolidine compounds described in Research Disclosure (R.D.), Vol. 205, No. 20526 (May, 1981); the isothiazoline compounds described in ibid., Vol. 228, No. 22845 (April, 1983); and the compounds described in JP-A-61-115154 and JP-A-62-209532. In addition, it may also contain various compounds described in H. Horiguchi, Bactericidal and Fungicidal Chemistry (published by Sankyo Publishing Co.); Handbook of Bactericidal and Fungicidal Technology (edited by the Bactericidal and Fungicidal Society of Japan and published by Hakuho-do Publishing Co., 1986); L.E. West, "Water Quality Criteria", Photo. Sci. & Eng., Vol. 9, No. 6 (1965); M.W. Beach, "Microbiological Growths in Motion Picture Processing", SMPTE Journal, Vol. 85 (1976); and R.O. Deegan, "Photo Processing Wash Water Biocides", J. Imaging Tech., Vol. 10, No. 6 (1984).

When the processed photographic material of the present invention is rinsed with a reduced small amount of rinsing water, squeeze rollers and crossover lack washing tanks are more preferred.

Water which has previously been processed to be microbicidal may be replenished to the rinsing or stabilization bath in accordance with the degree of processing of the photographic material of the invention, whereupon a part or all of the overflow from the rinsing or stabilization bath may be recirculated back to the previous step for fixation, as described in JP-A-60-235133 and JP-A-63-129343. In addition, for the purpose of preventing scummy unevenness which would often result from rinsing with a reduced small amount of water and/or preventing transference of the processing components adhered to squeeze rollers to the processed film, a water-soluble surfactant or defoaming agent may be added to the rinsing water.

For the purpose of preventing the processed material from being stained with the dye liberated from the material, a dye adsorbing agent may be provided in the rinsing tank as described in JP-A-63-163456.

The photographic material of the present invention is suitable for rapid processing with an automatic developing machine for which the total processing time is from 15 seconds to 60 seconds. In such rapid processing, the material displays an extremely excellent capacity.

For rapid processing of the photographic material of the present invention, the temperature and time for development and fixation are approximately from 25 °C to 50 °C and each 25 seconds or less, preferably from 30 °C to 40 °C and each from 4 to 15 seconds.

The developed and fixed photographic material of the present invention is then rinsed in water or stabilized. The rinsing step may be effected by a counter-current rinsing system comprising 2 to 3 stages so as to save the rinsing water. When the material is rinsed with a reduced small amount of water, a squeeze roller-equipped rinsing tank is preferably used. If desired, a part or all of the overflow from the rinsing bath or stabilization bath may be recirculated back to the previous fixation bath as so described in JP-A-60-235133. Accordingly, the amount of the waste from the process may be reduced preferably.

The developed, fixed and rinsed photographic material of the present invention is then dried via squeeze rollers. Drying of the material is effected at 40 to 80 °C for 4 seconds to 30 seconds.

The total processing time referred to herein means the time from insertion of the top of the film to be processed into the inlet of the automatic developing machine to the taking-out of the processed film from the outlet of the drying zone, via the development tank, the connecting passage, the fixation tank, the connecting passage, the rinsing tank, the connecting passage and the drying zone.

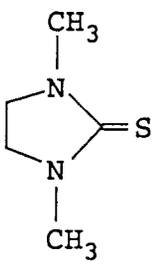
When the photographic material of the present invention is a color photographic material, it preferably contains cyan couplers, magenta couplers and yellow couplers as described in JP-A-2-285345, pages 100 to 129. Regarding the dispersion media for couplers and their dispersing method, the disclosure of JP-A-2-285345, pages 129 to 132 may be referred to. For processing such a color photographic material, the disclosure of JP-A-2-285345, from page 144, line 8 to page 168, line 11 is referred to. For scanning exposure of the photographic material of the present invention, the disclosure of JP-A-2-285345, from page 168, line 12 to page 170, line 9 is referred to. For the layer constitution of the photographic material of the invention, when it is a color photographic material, the disclosure of JP-A-2-285345, from page 171, line 1 to page 172 is referred to.

The present invention will be explained in more detail by way of the following examples, which, however, are not intended to restrict the scope of the present invention.

EXAMPLE 1

1. Preparation of Silver Halide Emulsion:

Forty g of gelatin was dissolved in one liter of water and heated up to 53 °C in a container. To this were added 5 g of sodium chloride, 0.4 g of potassium bromide and 60 mg of compound (A):



(A)

Next, 1000 ml of an aqueous solution containing 200 g of silver nitrate and 1080 ml of an aqueous solution containing potassium hexachloroiridate(III) in a molar ratio of 10^{-7} to the finished silver halide along with 21 g of sodium chloride and 100 g of potassium bromide were added thereto by a double jet method. Thus, monodispersed cubic silver chlorobromide grains having a mean grain size of 0.35 μm were prepared. The emulsion was de-salted and 40 g of gelatin was added thereto. After it was adjusted to have pH of 6.0 and pAg of 8.5, 2.5 mg of sodium thiosulfate and 4 mg of chloroauric acid were added thereto for chemical sensitization at 60 °C. Then, 0.2 g of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added thereto and rapidly cooled for solidification.

2. Preparation of Emulsion Coating Liquid:

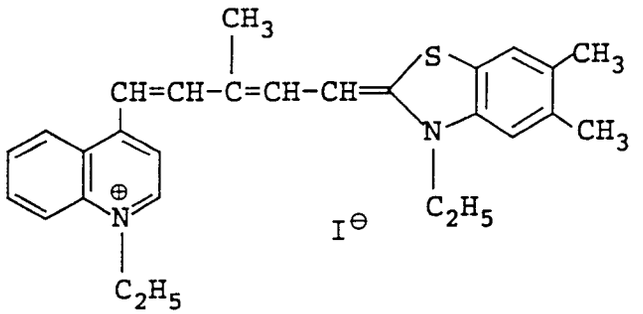
Ove thousand g of the emulsion prepared above was put into a container and heated up to 40 °C. The following additives were added to prepare an emulsion coating liquid.

Formulation of Emulsion Coating Liquid:

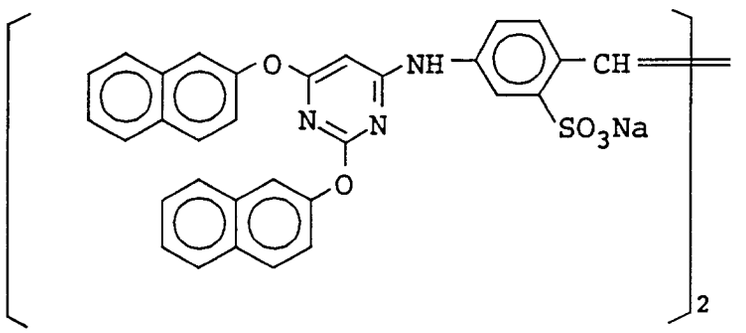
a. Emulsion	1000 g
b. Color Sensitizing Dye (2)	1.2×10^{-4} mol
c. Super-color Sensitizer (3)	0.8×10^{-3} mol
d. Storability Improving Agent (4)	1×10^{-3} mol
e. Polyacrylamide (molecular weight: 40,000)	7.5 g
f. Trimethylol Propane	1.6 g
g. Sodium Polystyrenesulfonate	1.2 g
h. Latex of Poly(ethyl acrylate/methacrylic acid)	12 g
i. N,N'-ethylenebis-(vinylsulfonacetamide)	3.0 g
j. 1-Phenyl-5-mercaptotetrazole	50 mg

The compounds identified above are shown below.

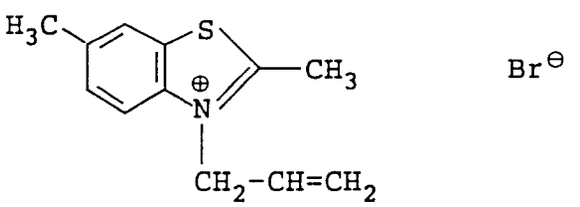
Color Sensitizing Dye (2):



Super-color Sensitizer (3):



Storability Improving Agent (4):



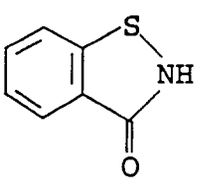
3. Preparation of Coating Liquid for Surface Protecting Layer of Emulsion Layer:

A container was heated up to 40 °C, and the components mentioned below were put therein and formed into a coating liquid.

Formulation of Coating Liquid for Surface Protecting Layer of Emulsion Layer:

a.	Gelatin	100 g
b.	Polyacrylamide (molecular weight, 40,000)	12 g
c.	Sodium Polystyrenesulfonate (molecular weight, 600,000)	0.6 g
d.	N,N'-ethylenebis-(vinylsulfonacetamide)	2.2 g
e.	Fine Grains of Polymethyl Methacrylate (mean grain size 2.0 μm)	2.7 g
f.	Sodium t-Octylphenoxyethoxyethanesulfonate	1.8 g
g.	$C_{16}H_{33}O-(CH_2CH_2O)_{10}-H$	4.0 g
h.	Sodium Polyacrylate	6.0 g
i.	$C_8F_{17}SO_3K$	70 mg
j.	$C_8F_{17}SO_2N(C_3H_7)(CH_2CH_2O)_4(CH_2)_4-SO_3Na$	70 mg
k.	NaOH (1 N)	6 ml
ℓ.	Methanol	90 ml
m.	Compound (5)	0.06 g

Compound (5):



4. Preparation of Coating Liquid for Backing Layer:

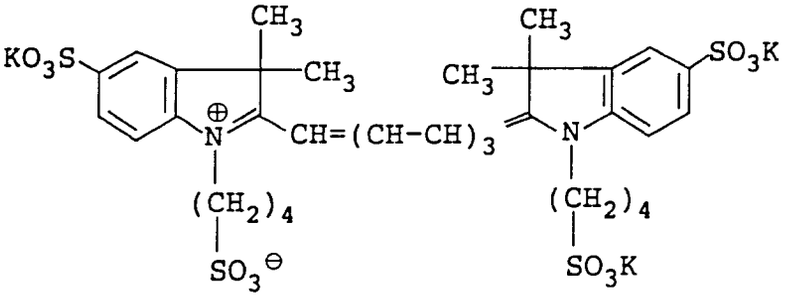
A container was heated up to 40 °C, and the components mentioned below were put therein and formed into a coating liquid for backing layer.

Formulation of Coating Liquid for Backing Layer:

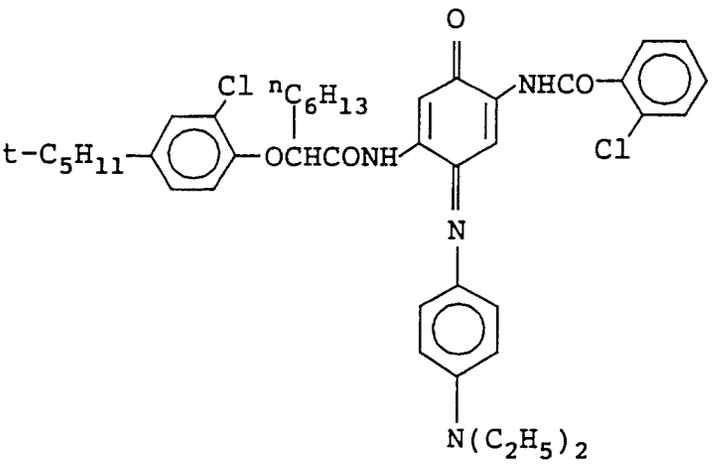
a. Gelatin	100 g
b. Dye (1)	4.2 g
c. Sodium Polystyrenesulfonate	1.2 g
d. Poly(ethyl acrylate/methacrylic acid) Latex	5 g
f. N,N'-ethylenebis-(vinylsulfonacetamide)	4.8 g
g. Compound (5) (above)	0.06 g
h. Dye (2)	0.3 g
i. Dye (3)	0.05 g

The compounds identified above are as follows:

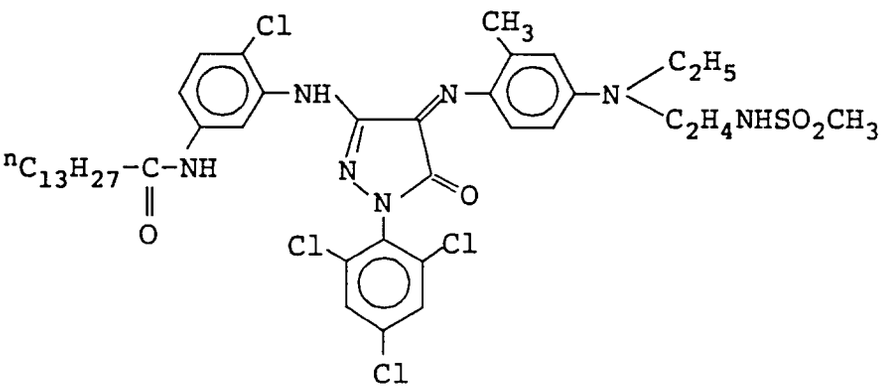
Dye (1):



Dye (2):



Dye (3):



5. Preparation of Coating Liquid for Back Surface Protecting Layer:

A container was heated up to 40 °C, and the components mentioned below were put therein and formed into a coating liquid.

Formulation of Coating Liquid for Back Surface Protecting Layer:

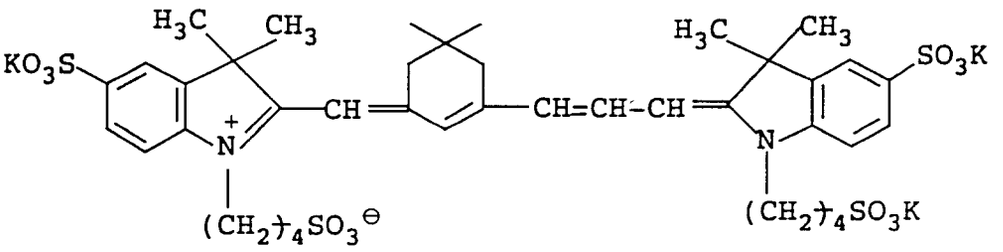
a. Gelatin	100 g
b. Sodium Polystyrenesulfonate	0.5 g
c. N,N'-ethylenebis-(vinylsulfonacetamide)	1.9 g
d. Fine Grains of Polymethyl Methacrylate (mean grain size 4.0 μm)	4 g
e. Sodium t-Octylphenoxyethoxyethanesulfonate	2.0 g
f. NaOH (1 N)	6 ml
g. Sodium Polyacrylate	2.4 g
h. $C_{16}H_{33}O$-$(CH_2CH_2O)_{10}$-H	4.0 g
i. $C_8F_{17}SO_3K$	70 mg
j. $C_8F_{17}SO_2N(C_3H_7)(CH_2CH_2O)_4(CH_2)_4$-$SO_3Na$	70 mg
k. Methanol	150 ml
ℓ. Compound (5) (above)	0.06 g

6. Formation of Photographic Materials:

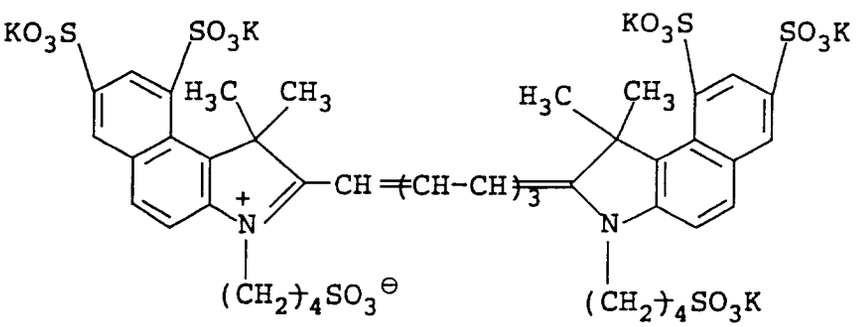
The preceding coating liquid for the backing layer was coated on a polyethylene- terephthalate support along with the preceding coating liquid for the protecting layer for protecting the backing layer, the total gelatin amount coated being 3 g/m^2. Subsequently, the preceding emulsion coating liquid and the preceding coating liquid for protecting layer for protecting the surface of the emulsion layer were coated on the opposite surface of the support, the silver amount coated being 2.5 g/m^2 and the gelatin amount coated in the surface protecting layer being 1 g/m^2. Thus, photographic material Sample No. 1 was formed.

Photographic material Sample Nos. 2 to 9 were formed in the same manner as above, except that the same amount of Comparative Dye (4) or (5) shown below or Dye (I-2), (I-6), (II-3), (II-9), (II-17) or (II-21) of the present invention was used in place of Dye (1).

Comparative Dye (4):



Comparative Dye (5):



7. Evaluation of Storage Stability:

Photographic material Sample Nos. 1 to 9 as formed in the manner mentioned above and shown in Table 1 below were stored under a humidity of 70% and a temperature of 50 °C for 3 days. The reflection spectrum of each sample stored was then measured. From the data, the variation of the light absorption at the absorption peak wavelength of each dye was obtained for each sample and is shown in Table 1. The variation is represented by the following equation.

Variation of Light Absorption = (absorption of sample as stored under 50 °C and 70%)/(absorption of fresh sample before stored under 50 °C and 70%)

8. Evaluation of Decolorability:

Each photographic material sample identified in Table 1 was processed for forming an image thereon, and the reflection spectrum of the white background area of the processed sample was measured. The light absorption of the dye at the absorption peak thereof in each sample before and after the image forming processing was measured, and the color retention percentage in each sample was calculated out from the data and is shown in Table 1.

For the image forming processing, each of photographic material Sample Nos. 1 to 9 was stored under a temperature of 25 °C and a humidity of 60 % for 7 days and then exposed to a semiconductor laser of 780 nm for 10^{-7} second at room temperature for scanning exposure. The exposed samples were then processed with the following Developer (1) and Fixer (1). The development time was 7 seconds, the fixation time was 7 seconds, the rinsing time was 4 seconds, and the water-removing and drying time was 11 seconds.

Composition of Developer (1):	
Potassium Hydroxide	29 g
Sodium Sulfite	31 g
Potassium Sulfite	44 g
Ethylenetriaminetetraacetic Acid	1.7 g
Boric Acid	1 g
Hydroquinone	30 g
Diethylene Glycol	29 g
1-Phenyl-3-pyrazolidone	1.5 g
Glutaraldehyde	4.9 g
5-Methylbenzotriazole	60 mg
5-Nitroindazole	0.25 g
Potassium Bromide	7.9 g
Acetic Acid	18 g
Water to make	1000 ml
pH	10.3

Composition of Fixer (1):	
Ammonium Thiosulfate	140 g
Sodium Sulfite	15 g
Disodium Ethylenediaminetetraacetate Dihydrate	20 mg
Sodium Hydroxide	7 g
Aluminum Sulfate	10 g
Boric Acid	10 g
Sulfuric Acid	3.9 g
Acetic Acid	15 g
Water to make	1000 ml
pH	4.30

The results obtained are shown in Table 1 below.

TABLE 1

Photographic Material Sample No.	Dye Contained	Percentage of Dye Kept in Stored Sample (%)	Percentage of Color in Processed Sample (%)
1*	(1)	92	6
2*	(4)	93	7
3*	(5)	93	10
4	(I-2)	96	2
5	(I-6)	97	3
6	(II-3)	94	2
7	(II-9)	95	1
8	(II-17)	97	3
9	(II-21)	98	2

* Comparative

From the results in Table 1 above, it is apparent that the dyes of the present invention were stable in the stored samples and that they were well decolored in the processed samples.

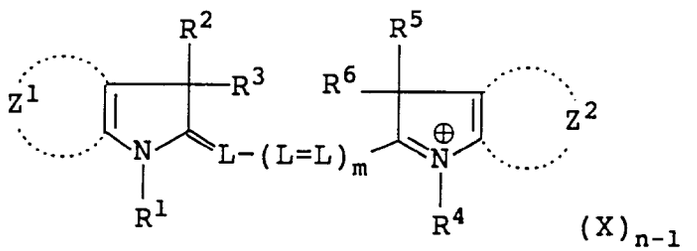
Specifically, the photographic material of the present invention is stable during storage, especially with respect to the dye contained therein. That is, the dye contained in the material does not decompose during storage of the material. After the photographic material has been processed, the dye decomposes well to give little color retention in the processed material. Thus, the dye in the photographic material of the

present invention is stable in the material during storage, while it is decolored well in the processed sample.

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

Claims

1. A silver halide photographic material having a hydrophilic colloid layer containing at least one compound of formula (I):

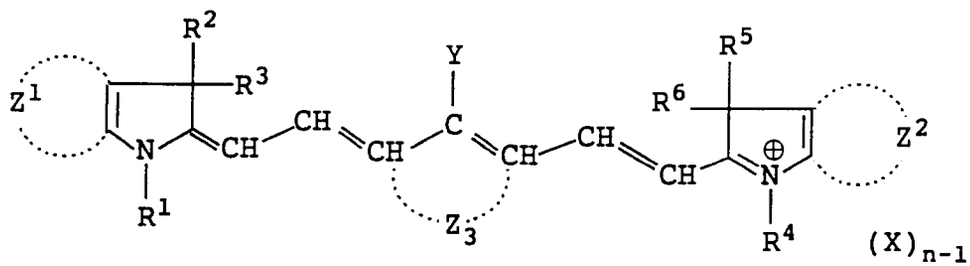


(I)

where R^1, R^2, R^3, R^4, R^5 and R^6 may be same or different and each represents an alkyl group;
Z^1 and Z^2 each represents a non-metallic atomic group necessary for forming a benzo-condensed ring or naphtho-condensed ring;
L represents a methine group;
m represents an integer of from 0 to 3;
X represents an anion;
n represents 1 or 2, provided that when the compound forms an internal salt, n is 1; and
the compound has at least five acidic substituents, at least two of which contain a carboxylic acid group.

2. The silver halide photographic material as claimed in claim 1, in which the compound of formula (I) contains at least two carboxylic acid groups in Z^1 and Z^2.

3. A silver halide photographic material having a hydrophilic colloid layer containing at least one compound of formula (II):



(II)

where R^1, R^2, R^3, R^4, R^5 and R^6 may be same or different and each represents an alkyl group;
Z^1 and Z^2 each represents a non-metallic atomic group necessary for forming a benzo-condensed ring or naphtho-condensed ring;
Z^3 represents a non-metallic atomic group necessary for forming a 5-membered or 6-membered ring;
Y represents a hydrogen atom or a monovalent group;
X represents an anion;
n represents 1 or 2, provided that when the compound forms an internal salt, n is 1; and
the compound has at least four acidic substituents, at least one of which contains a carboxylic acid group.

4. The silver halide photographic material as claimed in claim 3, in which the compound of formula (II) contains at least four acidic substituents, at least two of which are carboxylic acid groups.

5. The silver halide photographic material as claimed in claim 3, in which the compound of formula (II) contains at least two carboxylic acid groups in Z^1 and Z^2.

6. The silver halide photographic material as claimed in claim 1 or 3, in which the dye of formula (I) or (II) is an anti-irradiation dye.

7. The silver halide photographic material as claimed in claim 1 or 3, in which the dye of formula (I) or (II) is an anti-halation dye.

8. The silver halide photographic material as claimed in claim 1 or 3, in which the dye of formula (I) or (II) is a filter dye.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 6833

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,X	EP-A-0 430 244 (FUJI PHOTO FILM CO., LTD.) * page 6, compound 9 * * page 7, formulas 11-13 * * page 10, formulas 22-24 * * abstract *	3-8	G03C1/83
D,Y	US-A-4 839 265 (SHIGERU OHNO ET AL.) * column 3, formula I-3 * * column 5, formulas I-4 and I-6 * * column 9, formulas I-20 and I-23 *	1,2,6-8	
D,A	* column 11, formula I-28 * * column 13, line 14 - line 30 *	3-5	
Y	EP-A-0 445 627 (FUJI PHOTO FILM CO., LTD.) * page 44, formula F-I-29 * * page 45, formulas F-I-30 and F-I-31 * * page 46, formula F-I-32 * * page 49, formula F-I-39 * * page 3, line 16 - line 26 *	1,2,6-8	
Y	EP-A-0 342 939 (KONICA CORPORATION) * page 4, formula 4 * * page 5, formula 6 * * page 9, line 34 - line 36 *	1,2,6-8	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03C
Y	EP-A-0 428 112 (KONICA CORPORATION) * page 8, formula 11 * * page 9, formula 16 * * page 16, line 14 - line 25 *	1,2,6-8	
Y	EP-A-0 341 958 (KONICA CORPORATION) * page 6, formulas 7 and 10 * * page 7, formula 11 * * page 8, formula 16 *	1,2,6-8	
A	* page 10, formula 27 * * page 14, line 52 - line 54 *	3-5	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 AUGUST 1993	HINDIAS E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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