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(54) Silver halide photographic materials

Photographische Silberhalogenidmaterialien

Matériaux photographiques à l'halogénure d'argent

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23.10.1991 Bulletin 1991/43

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(56) References cited:
DE-A- 2 758 765
GB-A- 2 077 453
US-A- 4 734 353
US-A- 4 845 020

- **RESEARCH DISCLOSURE no. 184, August 1979, pages 433-441, Havant, Hampshire, GB; item 18431 "Radiographic films/materials"**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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EP 0 452 772 B1

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Description

FIELD OF THE INVENTION

The present invention concerns silver halide photographic materials and, in particular, it concerns sensitive materials which can be used in fields such as X-ray, photographic plate making, micro and general purpose amateur negative films, for example. The present invention concerns silver halide photographic materials which exhibit improved resistance to the slip-fogging and pressure sensitization which sometimes arise when films are rubbed together.

BACKGROUND OF THE INVENTION

In recent years, much progress has been made in the field of rapid processing of photosensitive materials. Increasingly rapid exposures have required shorter exposure times (higher photographic speeds) and greater toughness in transportation and handling inside the exposing apparatus (camera, scanner). Furthermore, high temperature rapid processing has been carried out in automatic processors to achieve more rapid processing; and photosensitive materials which have excellent developing properties and which can be dried in a short period of time after water-washing are required for use in such automatic processors.

Increased covering power (optical density per unit weight of silver) is essential to increase the speed of X-ray photosensitive materials, micro-photosensitive materials and general purpose amateur negative photosensitive materials, for example; and it is known that the covering power is increased by reducing the amount of gelatin using the methods disclosed, for example, in JP-A-61-116347 and JP-A-57-182732 (the term "JP-A" as used herein refers to a "published unexamined Japanese patent application"). However, blackening of abraded parts may occur when films are rubbed together if the amount of gelatin with respect to silver is reduced, and slip-fogging may occur as well.

In addition, when tabular silver halide grains with high aspect ratio are used to increase photographic speed, pressure sensitization may occur due to abrasion or kinking which takes place while handling the photosensitive material prior to development processing.

Furthermore, when the amount of binder is reduced to improve the processability (i.e., the rate of development) of the photosensitive material and to speed up the drying process, which occurs after water-washing, photographic performance, graininess, and pressure sensitisation on handling are adversely affected.

A method in which water-soluble polyesters are included in the photosensitive material has been suggested as a means of providing both abrasion resistance and covering power in JP-A-64-29834, but this technique does not resolve the problems completely; thus, there is a need for further improvement.

In the photographic plate making field, systems in which the instability of image formation in conventional lith development is eliminated, and in which a stable ultrahigh contrast image of gamma exceeding 10 is rapidly formed have been disclosed, for example, in US-A-4,166,742, 4,168,977, 4,221,857, 4,224,401, 4,243,739, 4,272,606 and 4,311,781. These systems are sensitized and provided with increased contrast by the use of hydrazine compounds, and much more rapid processing (development time 20 seconds to 30 seconds) than with lith development (development time 60 seconds to 100 seconds) has been realized. However, while achieving high photographic speeds and ultrahigh contrast, slip-fogging and pressure sensitization, for example, are also increased. The use of hydroquinone or substituted polyhydroxybenzene to improve pressure sensitization in these ultrahigh contrast image forming systems, in which hydrazine compounds are used, has been disclosed in JP-A-62-21143 and JP-A-56-1936.

Furthermore, the improved photographic speed and contrast resulting from the use of substituted hydroquinone and especially hydroquinone substituted with a thio group, has been disclosed in JP-A-54-40629.

Hydroquinone derivatives are used in JP-A-62-21143, JP-A-56-1936 and JP-A-54-40629, but these are different compounds from those represented by formula (I) of the present invention.

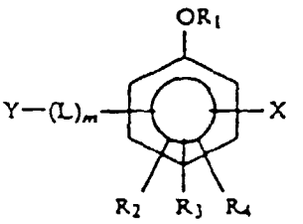
DE-A-2 758 765 discloses photographic materials comprising at least one hydrophilic layer containing a hydrazine derivative and a substituted hydroquinone derivative but does not disclose a benzotriazole which accelerates the adsorption on the surface of the silver halide grains.

GB-A-2 077 453 discloses photographic materials containing an indazole-substituted hydroquinone and hydrazine in the silver halide photographic emulsion layer. This prior art document discloses 6-methyl-2-(5-nitro-2-indazolyl)hydroquinone which however shows no effect on the abrasion and if further the addition amount of this compound is increased, the photographic speed is reduced.

SUMMARY OF THE INVENTION

The object of the present invention is to provide silver halide photographic materials with which the problems of the conventional technology outlined above are overcome. These materials exhibit improved resistance to abrasion during handling and blackening due to pressure, have high photographic speed and are suitable for rapid processing.

the above mentioned objects have been realized by means of a silver halide photographic material comprising a support having thereon at least one of a surface latent image silver halide emulsion layer and other hydrophilic colloid layers, wherein said at least one of an emulsion layer and other hydrophilic colloid layers contains a compound represented by formula (I):

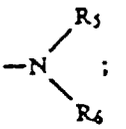


(I)

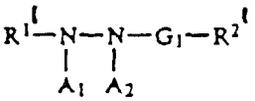
wherein X represents

$-OR_1$

or

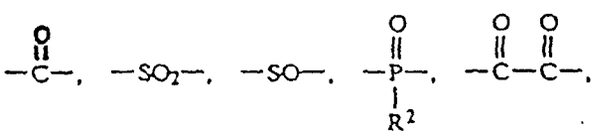


R_1 represents a hydrogen atom or a group capable of being converted to a hydrogen atom on hydrolysis; R_2, R_3 and R_4, which may be the same or different, each represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted oder unsubstituted aryl group, a substituted or unsubstituted alkylsulfonyl group, a substituted or unsubstituted arylsulfonyl group, a substituted or unsubstituted alkylcarbonyl group, a substituted or unsubstituted arylcarbonyl group, or a substituted or unsubstituted carbamoyl group; Y represents a 5- or 6-membered heterocyclic group having a mercapto group or a benzotriazole group having a > NH structure therein; L represents a member selected from the group consisting of a divalent alkylen group, a divalent alkenylen group, a divalent alkynylene group, a divalent arylene group, -NH-, -N=, -CO-, $-SO_2-$, and combinations thereof; and m represents 0 or 1;
and wherein said at least one emulsion layeror or other hydrophilic colloid layer containing a compound represented by formula (I) also contains a compound represented by formula (II) in an amount of from 1×10^{-6} to 5×10^{-2} mole per mole of the silver halide:



(II)

wherein $R^{1'}$ represents an aliphatic group or an aromatic group; R_2 represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryloxy group, a substituted or unsubstituted amino group, or a substituted or unsubstituted hydrazino group; G^1 represents

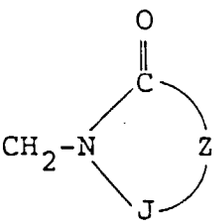


a thiocarbonyl group, or an iminomethylene group; and A_1 and A_2 each represents a hydrogen atom, a substituted of unsubstituted alkylsulfonyl group, a substituted or unsubstituted arylsulfonyl group, provided that at least one of A_1 and A_2 is a hydrogen atom and that R_1' or R_2' contains a ballast group or a group which accelerates adsorption of the compound of formula (II) onto the silver halide grain surface.

DETAILED DESCRIPTION OF THE INVENTION

The compounds of formula (I) which are used in the present invention will be further described below in detail.

The group which can become a hydrogen atom by hydrolysis, represented here by R_1, is, for example, a $-COR_7$ group (where R_7 represents a substituted or unsubstituted alkyl group having from 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having from 6 to 20 carbon atoms or a substituted or unsubstituted amino group having from 1 to 20 carbon atoms) or a



group (where J represents



or $-SO_2-$, and Z represents a plurality of atoms required to form at least one 5- or 6-membered heterocyclic ring).

The substitutable groups represented by R_2, R_3 and R_4 can be, for example, halogen atoms (fluorine, chlorine, bromine), alkyl groups (preferably having 1 to 20 carbon atoms), aryl groups (preferably having 6 to 20 carbon atoms), alkoxy groups (preferably having 1 to 20 carbon atoms), aryloxy groups (preferably having 6 to 20 carbon atoms), alkylthio groups (preferably having 1 to 20 carbon atoms), arylthio groups (preferably having 6 to 20 carbon atoms), acyl groups (preferably having 2 to 20 carbon atoms), acylamino groups (preferably alkanoylamino groups having 1 to 20 carbon atoms and benzoylamino groups having 6 to 20 carbon atoms), nitro groups, cyano groups, oxycarbonyl groups (preferably alkoxycarbonyl groups having 1 to 20 carbon atoms and aryloxycarbonyl groups having 6 to 20 carbon atoms), carboxyl groups, sulfo groups, ureido groups (preferably alkylureido groups having 1 to 20 carbon atoms and arylureido groups having 6 to 20 carbon atoms), sulfonamide groups (preferably alkylsulfonamide groups having 1 to 20 carbon atoms and arylsulfonamide groups having 6 to 20 carbon atoms), sulfamoyl groups (preferably alkylsulfamoyl groups having 1 to 20 carbon atoms and arylsulfamoyl groups which having 6 to 20 carbon atoms), carbamoyl groups (preferably alkylcarbamoyl groups having 1 to 20 carbon atoms and arylcarbamoyl groups having 6 to 20 carbon atoms), acyloxy groups (preferably having 1 to 20 carbon atoms), amino groups (unsubstituted amino, and preferably secondary or tertiary amino groups substituted with alkyl groups having 1 to 20 carbon atoms or aryl groups having 6 to 20 carbon atoms), carboxylic acid ester groups (preferably alkylcarboxylic acid ester groups having 1 to 20 carbon atoms and arylcarboxylic acid ester groups having 6 to 20 carbon atoms), sulfonyl groups (preferably alkylsulfonyl groups having 1 to 20 carbon atoms and arylsulfonyl groups having 6 to 20 carbon atoms), sulfinyl groups (preferably alkylsulfinyl groups having 1 to 20 carbon atoms and arylsulfinyl groups having 6 to 20 carbon atoms, hydroxyl groups, and $-(L)_m-Y$ groups.

R_2, R_3 and R_4 may be the same or different, or in cases where any two of R_2, R_3 and R_4 are substituted onto adjacent carbon atoms of the benzene ring, they may be joined together to form a 5- to 7-membered carbocyclic or heterocyclic ring, and these rings may be saturated or unsaturated. Examples of ring compounds formed include cyclopentane, cyclohexane, cycloheptane, cyclopentene, cyclohexadiene, cycloheptadiene, indane, norbornane, norbornene and pyridine, and the ring compounds may have further substituent groups. R_2, R_3 and R_4 each preferably contain from 1 to 10 carbon atoms in total.

R_5 and R_6 each represents hydrogen atoms, substituted or unsubstituted alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted alkylsulfonyl groups, substituted or unsubstituted arylsulfonyl groups, substi-

tuted or unsubstituted alkylcarbonyl groups, substituted or unsubstituted arylcarbonyl groups or substituted or unsubstituted carbamoyl groups, and R_5 and R_6 may be the same or different, and they may be joined together to form a nitrogen-containing heterocyclic ring (for example, a morpholine group, a piperidine group, a pyrrolidine group, an imidazolyl group, a piperazino group may be formed).

These groups indicated as substitutable groups for R_2, R_3 and R_4, and the $-(L)_m-Y$ group can be cited as substituent groups for R_5 and R_6, and further R_5 and R_6 each is most preferably hydrogen atoms.

X is preferably substituted in the ortho or para position with respect to the $-OR_1$ group and, of the groups which can be represented by X, the $-OR_1$ groups are preferred, and R_1 is most preferably a hydrogen atom.

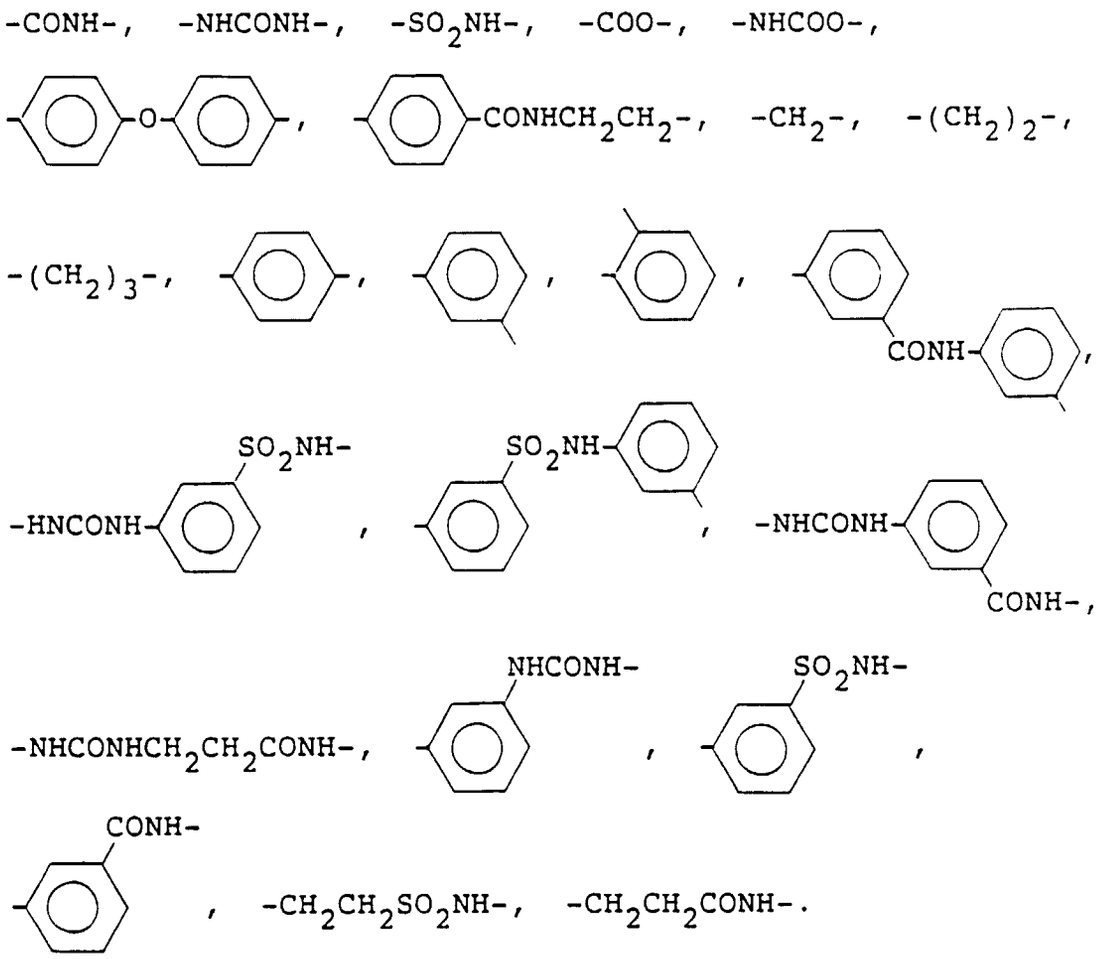
Y is a group which promotes adsorption on silver halide, and L is a divalent linking group. Moreover, m is 0 or 1. Preferred examples of groups which promote adsorption on silver halide, represented by Y, include the thioamido group, the mercapto group, groups which have a disulfide bond and nitrogen-containing heterocyclic groups.

The heterocyclic mercapto groups which may be represented by Y may be the same as the cyclic thioamide groups to which they are related tautomerically in those cases where there is a nitrogen atom adjacent to the carbon atom to which the -SH group is bonded, and examples of these groups are 4-thiazolin-2-thione, 4-imidazolin-2-thione, 2-thiohydantoin, rhodanine, thiobarbituric acid, tetrazolin-5-thione, 1,2,4-triazolin-3-one, 1,3,4-thiadiazolin-2-thione, 1,3,4-oxadiazolin-2-thione, benzimidazolin-2-thione, benzoxazolin-2-thione and benzothiazolin-2-thione, and these may be further substituted with substituent groups.

The nitrogen-containing 5- or 6-membered heterocyclic rings represented by Y are comprised of combinations of nitrogen, oxygen, sulfur and carbon. From among these, preferred examples include benzotriazole, triazole, tetrazole, indazole, benzimidazole, imidazole, benzothiazole, thiazole, benzoxazole, oxazole, thiadiazole, oxadiazole and triazine. These mey be further substituted with appropriate substituent groups. Those listed as possible substituent groups for R_2, R_3 and R_4 can be cited as substituent groups for these nitrogen-containing compounds as well.

Of the groups which can be represented by Y, the cyclic thioamide groups (mercapto substituted nitrogen-containing heterocyclic groups, for example, 2-mercaptothiadiazole group, 3-mercapto-1,2,4-triazole group, 5-mercaptotetrazole group, 2-mercapto-1,3,4-oxadiazole group and 2-mercaptobenzoxazole group) or the benzotriazole group are preferred. Two or more $Y-(L)_m-$ groups may be substituted, and these groups may be the same or different.

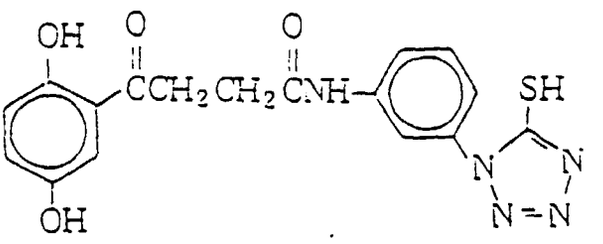
The divalent linking groups represented by L are atoms or groups of atoms containing at least one atom selected from C, N, S and O. Eexamples include alkylene groups, aralkylene groups, alkynylene groups, arylene groups, -O-, -S-, -NH-, -N=, -COO, $-SO_2-$ (these groups may have substituent groups) and these groups may be involved individually or in combination. Examples include the groups indicated below:



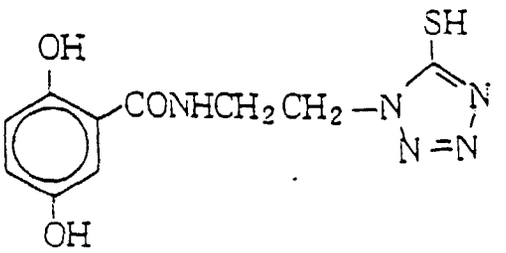
These groups may be substituted with appropriate substituent groups, such as those described above for R_2, R_3 and R_4.

Preferred examples of compounds which can be represented by formula (I) are indicated below, but the scope of the present invention is not limited by these examples.

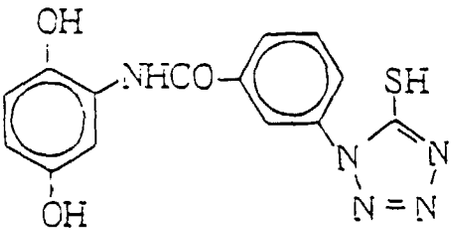
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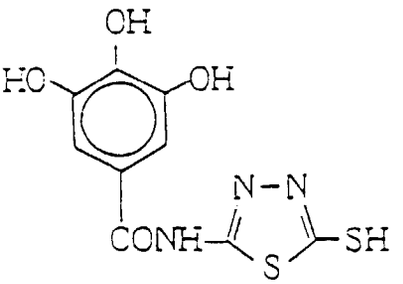
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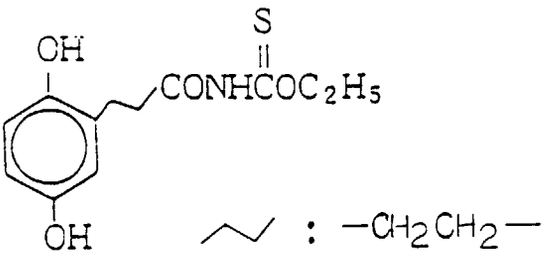
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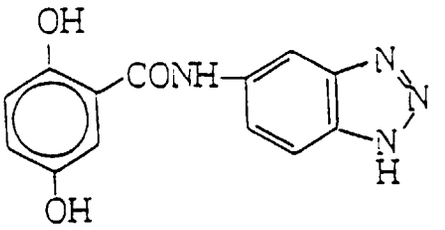
I-4



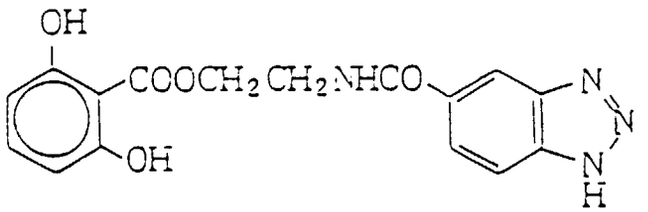
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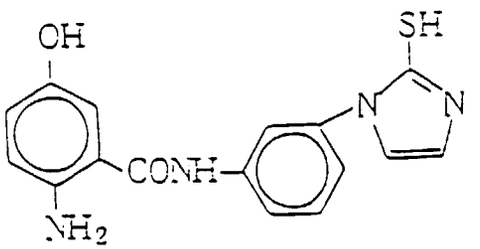
I-6



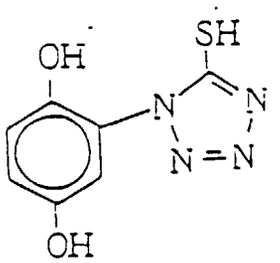
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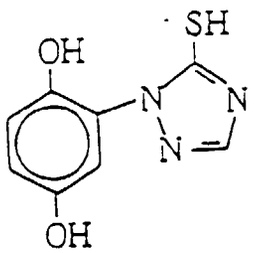
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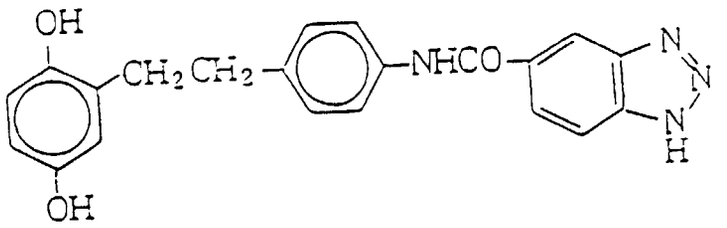
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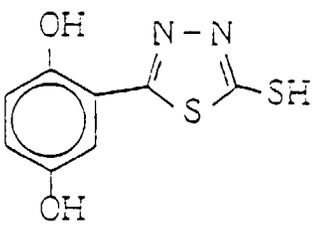
I-10



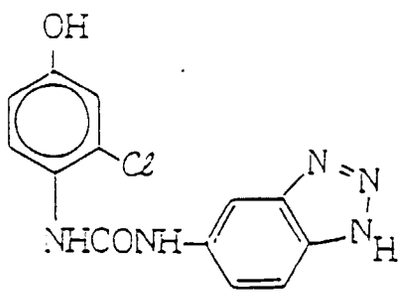
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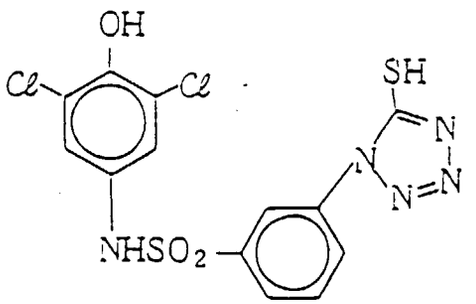
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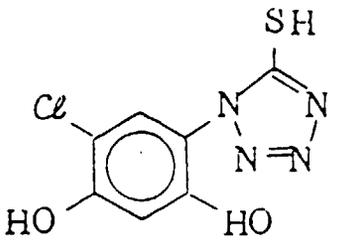
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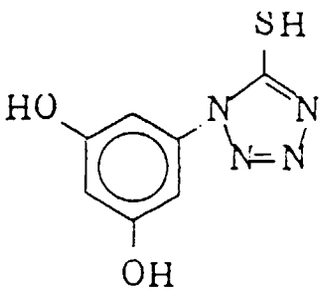
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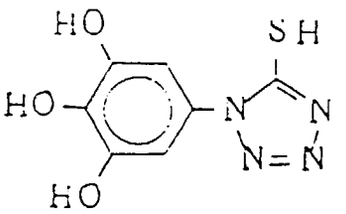
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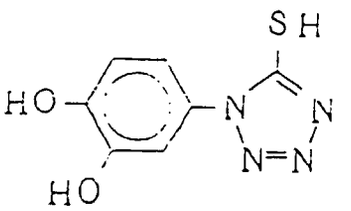
I-16



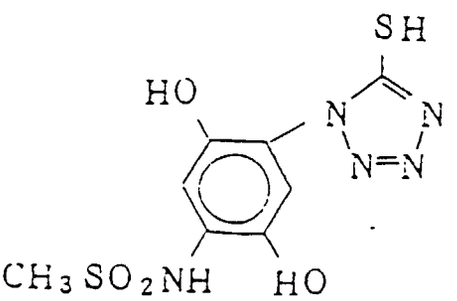
I-17



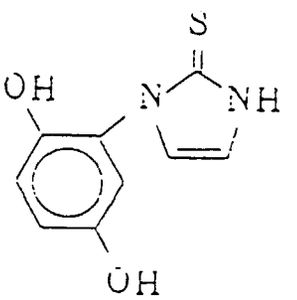
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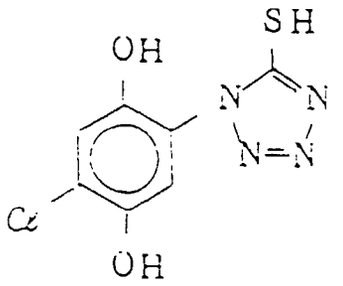
I-19



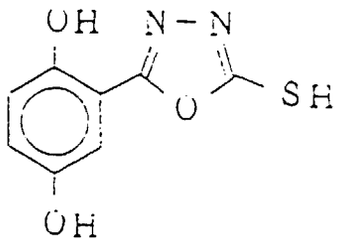
I-20



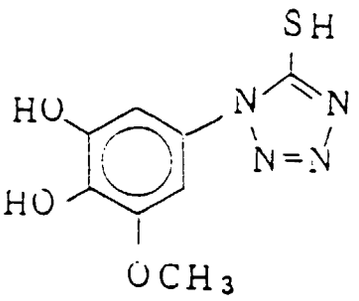
I-21



I-22



I-23



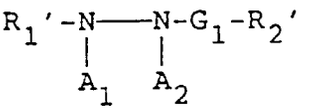
A typical example of synthesis for compounds represented by formula (I) is described below.

Example of Synthesis Preparation of Compound I-11

5-Phenylbenzotriazole carbonate (23.8 g, 0.1 mol), 25.2 g (0.11 mol) of 2-(4-aminophenyl)ethylhydroquinone and 100 ml of DMAC (dimethyl acetone) were heated together under nitrogen in an oil bath at 120°C (external temperature) for a period of 5 hours with stirring. The DMAC was then removed by distillation under reduced pressure, and on adding 200 ml of methanol, a trace of by-product in the form of black crystals remained as insoluble material. The insoluble material was removed by suction filtration, the methanol was removed by distillation under reduced pressure and the reaction mixture so obtained was refined using a silica gel column (chloroform/ methanol = 4/1). after washing with methanol, 14.4 g (38.5%) of the target compound I-11 was obtained. The melting point of the obtained compound was 256-257°C.

The compounds represented by formula (I) are included in photographic materials in amounts of preferably from 1×10^{-5} mol to 1×10^{-1} mol, and more preferably from 1×10^{-4} mol to 5×10^{-2} mol, per mol of silver halide.

Hydrazine compounds are also used in the present invention. The hydrazine derivatives which are used are those represented by formula (II) indicated below

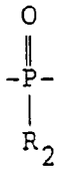


(II)

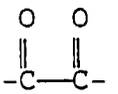
In this formula, R_1' represents an aliphatic group or an aromatic group; R_2' represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group or a hydrazino group; G_1 represents a



group, an $-SO_2-$ group, an -SO- group, a



group, a

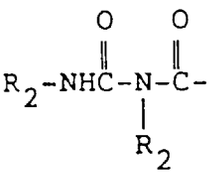


group, a thiocarbonyl group or an iminomethylene group; and A_1 and A_2 each represents hydrogen atoms, or one represents a hydrogen atom and the other represents a substituted or unsubstituted alkylsulfonyl group, or a substituted or unsubstituted arylsulfonyl group, or a substituted or unsubstituted acyl group.

The aliphatic groups represented by R_1' in formula (II) preferably have 1 to 30 carbon atoms, and they are most preferably linear chain, branched or cyclic alkyl groups which have 1 to 20 carbon atoms. The alkyl groups may also include substituent groups.

The aromatic groups represented by R_1' in formula (II) are single ring or double ring aryl groups or unsaturated heterocyclic groups. Here, the unsaturated heterocyclic groups may be condensed with aryl groups. Aryl groups are preferred for R_1', and those which contain a benzene ring are especially desirable.

The aliphatic groups or aromatic groups represented by R_1' may be substituted, and typical substituent groups include, for example, alkyl groups, aralkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, aryl groups, substituted amino groups, ureido groups, urethane groups, aryloxy groups, sulfamoyl groups, carbamoyl groups, alkyl- or arylthio groups, alkyl- or arylsulfonyl groups, alkyl- or arylsulfinyl groups, hydroxyl groups, halogen atoms, cyano groups, sulfo groups, aryloxycarbonyl groups, acyl groups, alkoxycarbonyl groups, acyloxy groups, carboxamido groups, sulfonamido groups, carboxyl groups, phosphonamido groups, diacylamino groups, imide groups and



groups. The preferred substituent groups are, for example, alkyl groups (preferably having 1 to 20 carbon atoms), aralkyl groups (preferably having 7 to 30 carbon atoms), alkoxy groups (preferably having 1 to 20 carbon atoms), substituted amino groups (preferably amino groups substituted with alkyl groups having 1 to 20 carbon atoms), acylamino groups (preferably having 2 to 30 carbon atoms), sulfonamido groups (preferably having 1 to 30 carbon atoms), ureido groups (preferably having 1 to 30 carbon atoms) and phosphonamido groups (preferably having 1 to 30 carbon atoms).

The alkyl groups represented by R_2' in formula (II) are preferably those having 1 to 4 carbon atoms, and the single ring and double ring aryl groups (for example, those which contain a benzene ring) are preferred as aryl groups.

In cases where G_1 is a



group, the preferred groups among those represented by R_2' are, for example, hydrogen atoms, alkyl groups (for

example, methyl, trifluoromethyl, 3-hydroxypropyl, 3-methanesulfonamidopropyl, phenylsulfonylmethyl), aralkyl groups (for example, o-hydroxybenzyl) and aryl groups (for example, phenyl, 3,5-dichlorophenyl, o-methanesulfonamidophenyl, 4-methanesulfonylphenyl, 2-hydroxymethylphenyl). The hydrogen atom is especially desirable.

R_2' may also be substituted, and the substituent groups may be substituent groups for on R_1.

G_1 in formula (II) is most preferably a



group.

R_2' may also be a group such that a cyclization reaction occurs, cleaving the G_1-R_2' portion from the rest of the molecule and forming a ring structure which contains the atoms of the -G_1-R_2' portion. Examples include those disclosed, for example, in JP-A-63-29751.

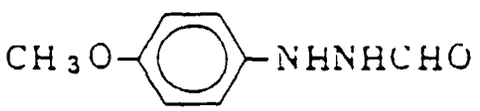
R_1' or R_2' in the formula (II) may have incorporated within them the ballast groups or polymers which are normally used in immobile photographically useful additives such as couplers. Ballast groups are comparatively inert groups with respect to photographic properties which have at least 8 carbon atoms; and examples of the ballast groups include alkyl groups, alkoxy groups, phenyl groups, alkylphenyl groups, phenoxy groups and alkylphenoxy groups. Furthermore, those disclosed, for example, in JP-A-1-100530 can be cited as the above polymers.

R_1' or R_2' in the formula (II) may have incorporated therein groups which intensify adsorption on silver halide grains. Examples of such absorbing groups include thiourea groups, heterocyclic thioamide groups, mercapto heterocyclic groups and triazole groups disclosed, for example, in US-A-4,385,108 and 4,459,347, JP-A-59-195233, JP-A-59-200231, JP-A-59-201045, JP-A-59-201046, JP-A-59-201047, JP-A-59-201048, JP-A-59-201049, JP-A-61-170733, JP-A-61-270744, JP-A-62-948, JP-A-63-234244, JP-A-63-234246 and JP-A-63-234245.

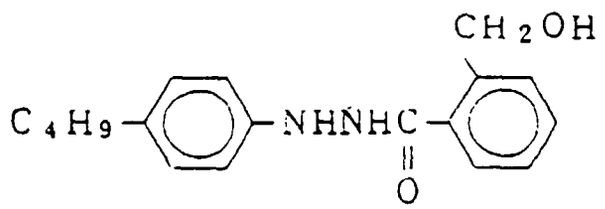
A_1 and A_2 are most preferably hydrogen atoms.

Examples of compounds which can be represented by formula (II) are indicated below, but the present invention is not limited by these compounds.

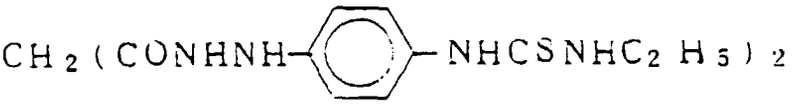
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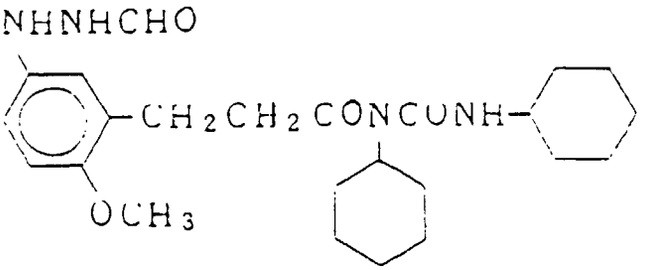
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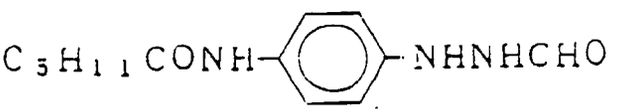
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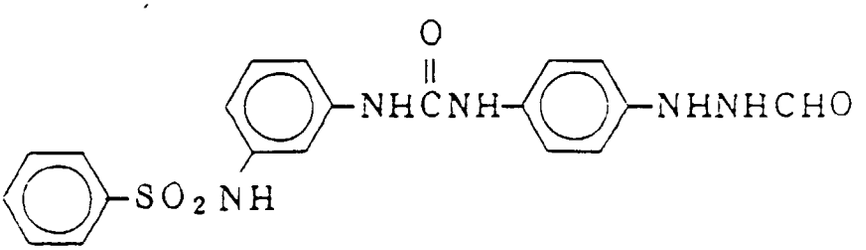
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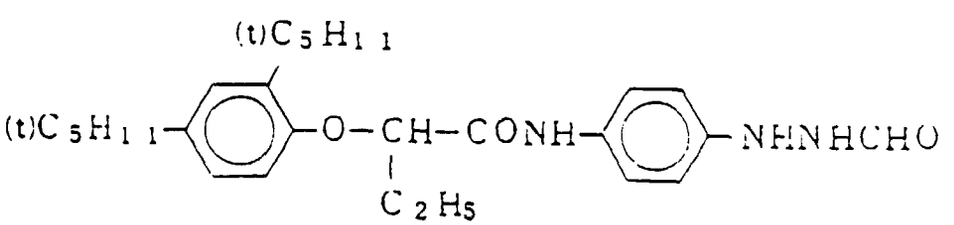
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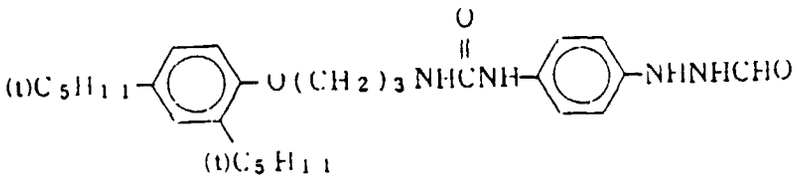
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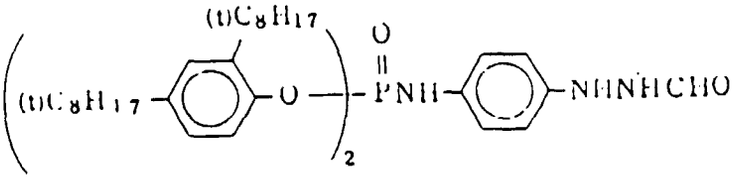
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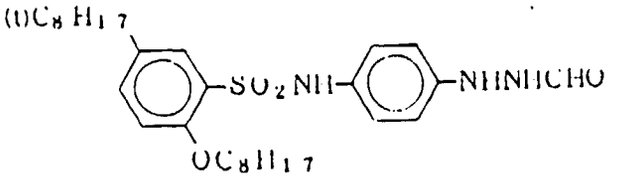
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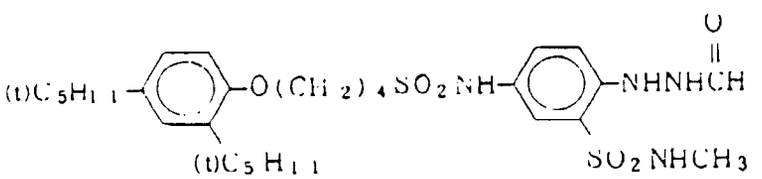
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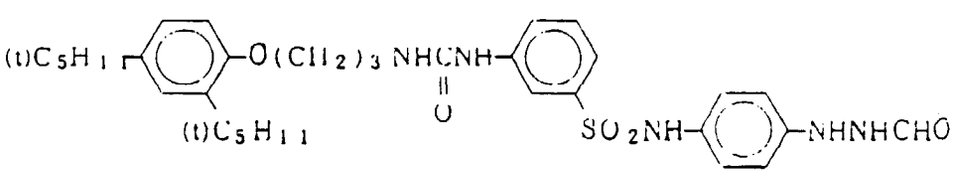
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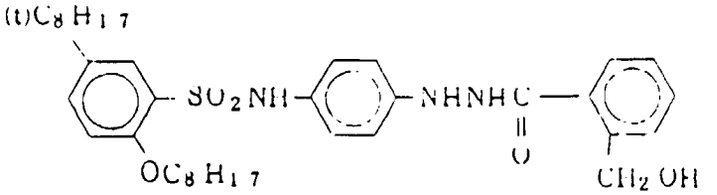
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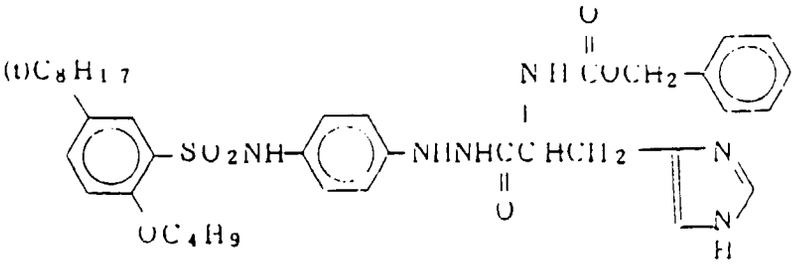
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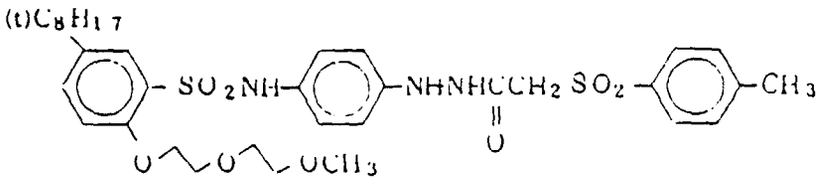
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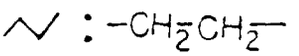


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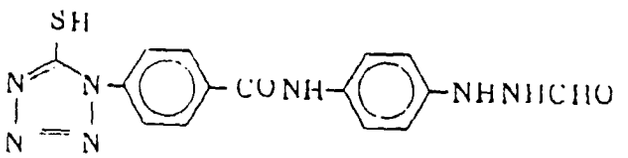


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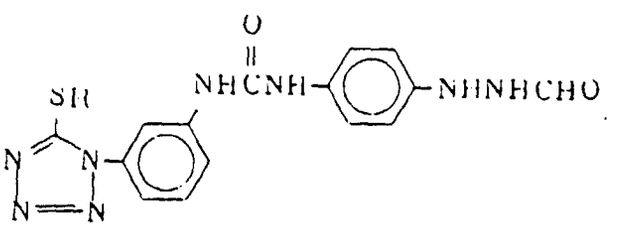




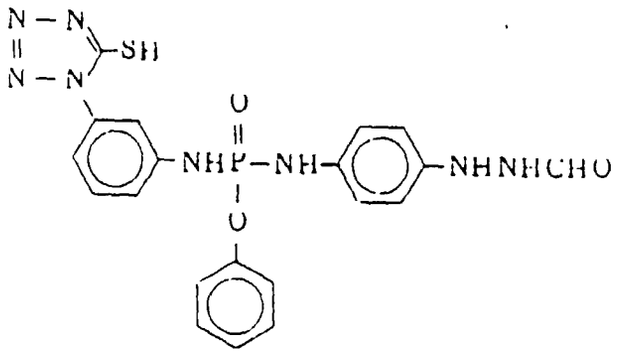
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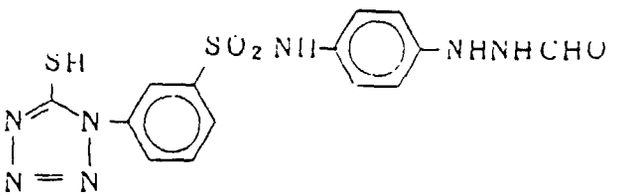
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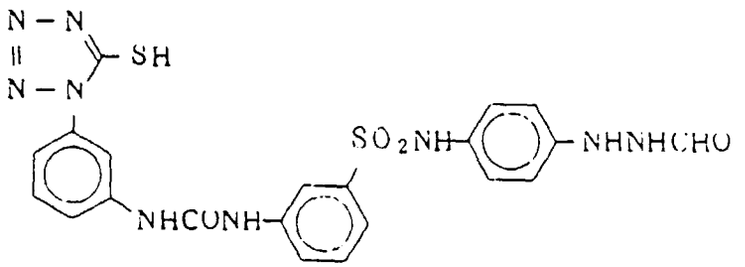
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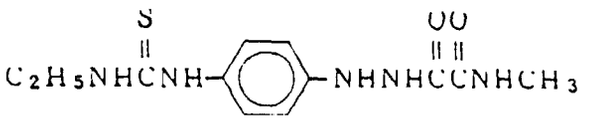
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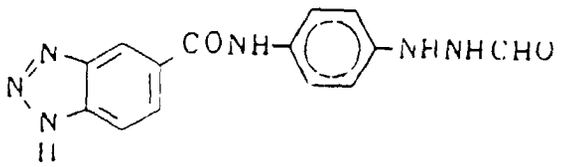
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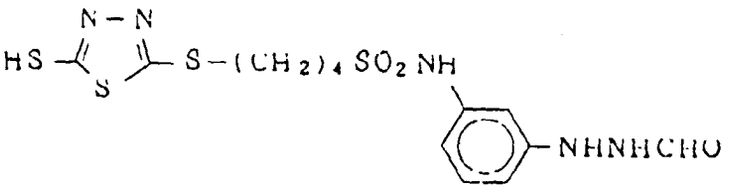
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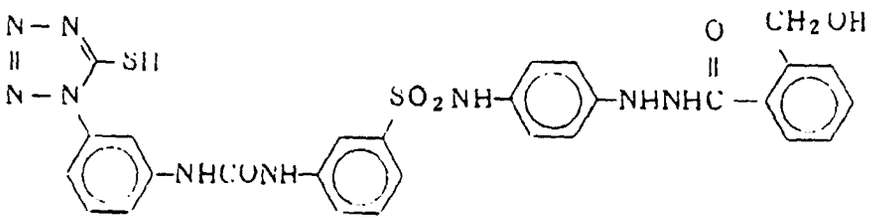
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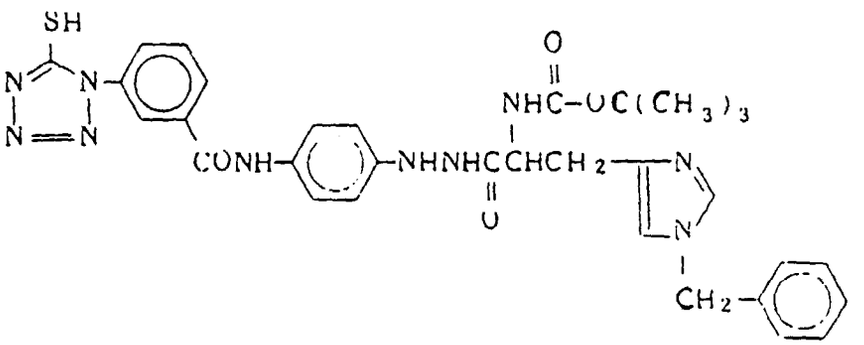
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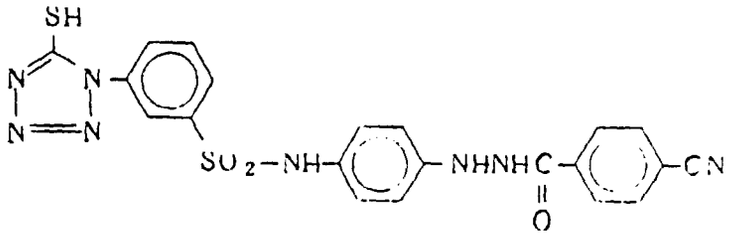
II-24



II-25



II-26



The hydrazine derivatives which can be used in the present invention include, as well as those indicated above, those disclosed in Research Disclosure, Item 23516 (November, 1983) page 346, and in the literature cited therein, and in US-A-4,080,207, 4,269,929, 4,276,364, 4,278,748, 4,385,108, 4,459,347, 4,560,638 and 4,478,928, GB-B-2,011,391B, JP-A-60-179734, JP-A-62-270948, JP-A-63-29751, JP-A-61-170733, JP-A-61-270744, JP-A-62-948, EP 217,310 or US-A-4,686,167, JP-A-62-178246, JP-A-63-32538, JP-A-63-104047, JP-A-63-121838, JP-A-63-129337, JP-A-63-223744, JP-A-63-234244, JP-A-63-234245, JP-A-63-234246, JP-A-63-294552, JP-A-63-306438, JP-A-1-100530, JP-A-1-105941, JP-A-1-105943, JP-A-64-10233, JP-A-1-90439, JP-A-1-276128, JP-A-1-283548, JP-A-1-280747, JP-A-1-283549, JP-A-2-2541, JP-A-2-77057, JP-A-1-285940 and JP-A-63-179760, 1-18377, 1-18378, 1-18379, 1-15755, 1-16814, 1-40792, 1-42615, 1-42616, 1-123693 and 1-126284.

In the present invention, the hydrazine derivatives are preferably added in amounts within the range from 1×10^{-6} mol to 5×10^{-2} mol, and most preferably from 1×10^{-5} mol to 2×10^{-2} mol, per mol of silver halide.

When these compounds of the formulae (I) and (II) are included in a photographic material, they can be added to a silver halide emulsion solution or to a hydrophilic colloid solution in the form of an aqueous solution if they are soluble in water; or in the form of a solution in an organic solvent which is miscible with water, such as an alcohol (for example, methanol, ethanol), an ester (for example, ethyl acetate) or a ketone (for example, acetone), in cases where the compounds are insoluble in water.

If the compounds are added to a silver halide emulsion solution, the addition can be made at any time from the start of chemical ripening until the solution is coated, but the addition is preferably made after the completion of chemical ripening, and addition to the coating liquid is especially desirable.

Methods for the preparation of the silver halide emulsions which can be used in the present invention include the methods described by P. Glafkides in Chimie et Physique Photographique (published by Paul Montel, 1967), by G.F. Duffin in Photographic Emulsion Chemistry (published by the Focal Press, 1966) and by V.L. Zelikman et al. in Making and Coating Photographic Emulsions (published by the Focal Press, 1964), the conversion methods disclosed, for example, in U.S. US-A-2,592,250 and 4,075,020, and the methods for the preparation of core/shell emulsions disclosed, for example, in GB-B-1,027,146.

The water-soluble silver salt (aqueous silver nitrate solution) is reacted with the water-soluble halogen salt solution using a single jet method, a double jet method or a combination of these methods. The method in which the pAg value in the liquid phase where the silver halide is formed is kept constant, that is, the controlled double jet method, can also be used as one type of a double jet method.

Furthermore, grain growth can also be carried out using "so-called silver halide solvents", such as ammonia, thioether and tetra-substituted thiourea, for example. Silver halide emulsions which have a regular crystalline form and a narrow grain size distribution can be prepared easily using the controlled double jet method and other grain growing methods in which silver halide solvents are used.

The silver halide grains in the photographic emulsions used in the present invention can have a comparatively wide grain size distribution, but emulsions which have a narrow grain size distribution are preferred, and those in which 90% of all the grains, either in terms of the weight or number of silver halide grains, are of a grain size within ±40% of the average grain size are most preferred (emulsions of this type are generally referred to as monodisperse emulsions).

The silver halide grains in the photographic emulsion may have a regular crystalline form, such as a cubic or octahedral form, or an irregular form, such as a spherical or plate-like form, or they may have a form which is a composite of these crystalline forms.

The silver halide grains may be such that the interior and surface layer are a uniform phase or different phases.

Mixtures of two or more silver halide emulsions which have been prepared separately may also be used.

Cadmium salts, sulfite, lead salts, thallium salts, iridium salts or complex salts thereof; and rhodium salts or complex salts thereof, for example, may also be present during the formation or physical ripening of the silver halide grains in a silver halide emulsion used in the present invention.

The silver halide emulsions used in the present invention may or may not be chemically sensitized. Gold sensiti-

zation, for example, can be used as a method of chemical sensitization, and combinations of gold sensitization with sulfur sensitization, reduction sensitization and noble metal sensitization methods, for example, can be used.

The gold sensitization method is typical of the noble metal sensitization methods. Gold compounds comprising principally gold complex salts are used for this purpose. Complex salts of noble metals other than gold, for example, platinum, palladium and iridium, can also be included. Examples have been disclosed, for example, in US-A-2,448,060 and GB-B-618,061.

In addition to the sulfur compounds which are contained in gelatin, various sulfur compounds, for example, thiosulfate, thioureas, thiazoles and rhodanines, can be used as sulfur sensitizing agents. Examples have been disclosed in US-A-1,574,944, 2,278,947, 2,410,689, 2,728,668, 3,501,313 and 3,656,955.

Stannous salts, amines, formamidinesulfinic acid and silane compounds, for example, can be used as reduction sensitizing agents, and examples have been disclosed in US-A-2,487,850, 2,518,698, 2,983,609, 2,983,610 and 2,694,637.

Moreover, the silver halide emulsions can be optically sensitized to increase the photographic speed and to provide photosensitivity to a prescribed wavelength region. Sensitizing dyes, such as cyanine dyes and merocyanine dyes, for example, can be used individually or together for optical sensitization purposes, and spectral sensitization and supersensitization can be achieved. These techniques have been disclosed, for example, in US-A-2,688,545, 2,912,329, 3,397,060, 3,615,635 and 3,628,964, JP-B-43-4936, JP-B-44-14030 (the term "JP-B" as used herein refers to an "examined Japanese patent publication") and JP-A-55-52050.

Various compounds can be included in the photographic emulsions used in the present invention to prevent the occurrence of fogging during the manufacture, storage or photographic processing of the photosensitive material, or to stabilize photographic performance. Many compounds, which are known as antifogging agents or stabilizers, such as azoles, for example, benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles (especially 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptotriazines; thioketo compounds such as oxazolinethione, for example; azaindenes, for example, triazaindenes, tetraazaindenes (especially 4-hydroxy substituted (1,3,3a,7)tetraazaindenes) and pentaazaindenes; benzenethiosulfonic acid, benzenesulfinic acid and benzenesulfonic acid amide, for example, can be used for this purpose. Among these materials, the benzotriazoles (for example, 5-methylbenzotriazole) and the nitroindazoles (for example, 5-nitroindazole) are especially desirable. These compounds may be included in a processing bath.

Inorganic or organic film hardening agents may be included in the photographic emulsion layers, and/or other hydrophilic colloid layers, of the photographic material of the present invention. For example, chromium salts (for example, chrome alum, chromium acetate), aldehydes (for example, formaldehyde, glyoxal, glutaraldehyde), N-methylol compounds (for example, dimethylolurea, methyloldimethylhydantoin), dioxane derivatives (for example, 2,3-dihydroxydioxane), active vinyl compounds (for example, 1,3,5-triacryloyl-hexahydro-s-triazine, 1,3-vinylsulfonyl-2-propanol), active halogen compounds (for example, 2,4-dichloro-6-hydroxy-s-triazine) and mucohalogen acids (for example, mucochloric acid, mucophenoxychloric acid), may be used either individually or in combinations.

Varioue surfactants can be included for various purposes in the photographic emulsion layers, and/or other hydrophilic layers, of a photosensitive material made using the present invention. These compounds may be used, for example, as coating aids or as antistatic agents, to improve slip properties, for emulsification and dispersion purposes, for the prevention of adhesion, and for improving photographic performance (for example, accelerating development, increasing contrast or increasing photographic speed).

For example, use can be made of nonionic surfactants, such as saponin (steroid based), alkylene oxide derivatives (for example, polyethylene glycol, polyethylene glycol/polypropylene glycol condensate, polyethylene glycol alkyl ethers or polyethylene glycol alkyl aryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyethylene glycol alkyl amines or amides, and poly(ethylene oxide) adducts of silicones), glycidol derivatives (for example, alkenylsuccinic acid polyglyceride, alkylphenol polyglyceride), fatty acid esters of polyhydric alcohols and sugar alkyl esters; anionic surfactants which include acidic groups, such as carboxylic acid groups, sulfo groups, phospho groups, sulfate ester groups and phosphate ester groups, for example, alkylcarboxylates, alkylsulfonates, alkylbenzenesulfonates, alkylnaphthalenesulfonates, alkylsulfate esters, alkylphosphate esters, N-acyl-N-alkyltaurines, sulfosuccinate esters, sulfoalkylpolyoxyethylene alkylphenyl ethers and polyoxyethylenealkylphosphate esters; amphoteric surfactants, such as amino acids, aminoalkylsulfonic acids, aminoalkyl sulfate or phosphate esters, alkylbetaines and amine oxides; and cationic surfactants such as alkylamine salts, aliphatic and aromatic quaternary ammonium salts, heterocyclic quaternary ammonium salts, for example, pyridinium and imidazolium, and phosphonium salts and sulfonium salts which contain aliphatic groups or heterocyclic rings. The polyalkylene oxides having a molecular weight of at least 600, disclosed in JP-B-58-9412, are the preferred surfactants for use in the present invention.

Dispersions of water-insoluble or sparingly soluble synthetic polymers can be included in a photographic emulsion layer and the other hydrophilic colloid layers of the photosensitive material used in the present invention to improve dimensional stability. For example, polymers in which alkyl (meth)acrylate, alkoxyalkyl (meth)acrylate, glycidyl (meth)

acrylate, (meth)acrylamide, vinyl esters (for example, vinyl acetate), acrylonitrile, olefin or styrene, for example, either individually or in combination, form the monomer units; or polymers in which combinations of these with acrylic acid or methacrylic acid, α,β-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylate, sulfoalkyl (meth)acrylate, or styrenesulfonic acid, for example, form the monomer units, can be used.

Processing baths which contain dihydroxybenzene based developing agents as the main developing agent, and p-aminophenol based developing agents or 3-pyrazolidone based developing agents as auxiliary developing agents, are preferably used in the present invention.

The dihydroxybenzene based developing agents which can be used in the present invention include hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, 2,3-dibromohydroquinone and 2,5-dimethylhydroquinone, for example, but the use of hydroquinone, among these compounds, is especially desirable.

Examples of l-phenyl-3-pyrazolidones and derivatives thereof which can be used as auxiliary developing agents include l-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-hydroxymethyl-3-pyrazolidone, 1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone, 1-p-aminophenyl-4,4-dimethyl-3-pyrazolidone and 1-p-tolyl-4,4-dimethyl-3-pyrazolidone.

The p-aminophenol based auxiliary developing agents which can be used in the present invention include N-methyl-p-aminophenol, p-aminophenol, N-(β-hydroxyethyl)-p-amino phenol, N-(4-hydroxyphenyl)glycine, 2-methyl-p-aminophenol and p-benzylaminophenol, for example; and, among these, N-methyl-p-aminophenol is preferred.

Generally, the use of a dihydroxybenzene based developing agent in an amount of from 0.05 to 0.8 mol/ liter is preferred. In cases where combinations of dihydroxybenzenes and 1-phenyl-3-pyrazolidones or p-aminophenols are used, the former are preferably used in amounts of from 0.05 to 0.5 mol/liter and the latter are preferably used in amounts of not more than 0.06 mol/ liter.

Sodium sulfite, potassium sulfite, lithium sulfite, sodium bisulfite, potassium metabisulfite and formaldehyde/sodium sulfite, for example, can be used as sulfite preservatives in the present invention. The sulfite is used in an amount of at least 0.3 mol/liter; but, if too large an amount is added, it precipitates in the developer and causes contamination of the liquid. So, an upper limit of 1.2 mol/liter is desirable.

Tertiary amine compounds, and especially the compounds disclosed in US-A-4,269,929, can be included as development accelerators in the developer in the present invention.

pH buffers such as boric acid, borax, sodium triphosphate, potassium triphosphate, and the pH buffers disclosed in JP-A-60-93433 can also be used in the developer of the present invention.

Development inhibitors, such as potassium bromide and potassium iodide; organic solvents, such as ethylene glycol, diethylene glycol, triethylene glycol, dimethylformamide, methyl cellosolve, hexylene glycol, ethanol and methanol; indazole compounds such as 5-nitroindazole, antifogging agents and black spotting (black pepper) preventing agents, such as 2-mercaptobenzimidazole-5-sulfonic acid sodium salt, and 5-methylbenzotriazole may be included. When compounds such as 5-nitroimidazole are used, they are generally dissolved beforehand in the part of the solution which does not contain the dihydroxybenzene based developing agent and the sulfite preservative; then, both parts are mixed together, and water is added for use. Moreover, the solution in which the 5-nitroimidazole has been dissolved turns yellow under alkaline conditions; this is convenient for handling.

In addition, toners, surfactants, hard water softening agents and film hardening agents, for example, may be included, if desired.

Well known fixing agent compositions can be used in the present invention. As well as thiosulfate and thiocyanate, the organic sulfur compounds which are known to be effective as fixing agents can also be used. Water-soluble aluminum salts, such as aluminum sulfate and alum, for example, can be included in the fixing solution as film hardening agents. The amount of water-soluble aluminum salt used is generally from 0 to 3.0 g·Al/liter. Furthermore, ethylenediaminetetraacetic acid ferric complex salts may be used as oxidizing agents.

The processing temperature is generally selected within the range from 18°C to 50°C, but temperatures below 18°C and in excess of 50°C may be used.

The present invention is described in more detail below by means of illustrative examples.

EXAMPLE 1

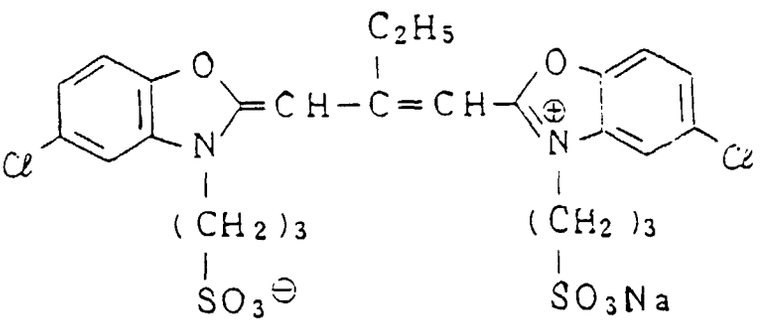
Preparation of the Emulsion

5 g of potassium bromide, 0.05 g of potassium iodide, 30 g of gelatin and 2.5 ml of a 5% aqueous solution of the thioether $HO(CH_2)_2S(CH_2)_2S(CH_2)_2OH$ were added to 1 liter of water. An aqueous solution containing 8.33 g of silver nitrate and an aqueous solution containing 5.94 g of potassium bromide and 0.726 g of potassium iodide were added using the double jet method, with stirring, over a period of 45 seconds, to this solution, which was being maintained at 73°C. Next, after adding 2.5 g of potassium bromide, an aqueous solution containing 8.33 g of silver nitrate was added

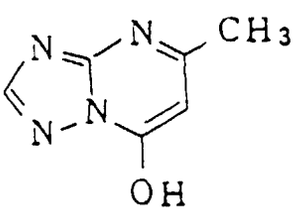
over a period of 26 minutes so the flow rate at the end of the addition was twice that at the start of the addition. Next, 20 ml of 25% ammonia solution and 10 ml of 50% NH_4NO_3 were added. 240 ml of 1 N sulfuric acid were added after physical ripening of 20 minutes duration, and the mixture was neutralized. Next, an aqueous solution containing 153.34 g of silver nitrate and an aqueous solution of potassium bromide were added over a period of 40 minutes using the controlled double jet method in such a way that the potential was maintained at a pAg value of 8.2. The flow rate at this time was accelerated so the flow rate at the end of the addition was nine times the flow rate at the start of the addition. After the addition had been completed, 15 ml of a 2 N solution of potassium thiocyanate were added and 25 ml of a 1% aqueous solution of potassium iodide were added over a period of 30 seconds. Subsequently, the temperature was reduced to 35°C and the soluble salts were removed using a sedimentation method. After the temperature was raised to 40°C, 30 g of gelatin and 2 g of phenol were added and the pH and pAg values were adjusted to 6.40 and 8.10, respectively, using caustic soda and potassium bromide.

After raising the temperature to 56°C, 600 mg of the sensitizing dye and 150 mg of the stabilizer indicated below were added. Ten minutes later, 2.4 mg of sodium thiosulfate pentahydrate, 140 mg of potassium thiocyanate and 2.1 mg of chloroauric acid were added, and the mixture was cooled rapidly and solidified after 80 minutes and an emulsion was obtained. In the emulsion obtained, 98% of the total projected area of all the grains were accounted for by grains having an aspect ratio of at least 3. The average projected area diameter for all the grains of aspect ratio 2 or more was 1.4 μm, the standard deviation was 15%, the average thickness was 0.187 μm and the aspect ratio was 7.5.

Sensitizing Dye



Stabilizer



Preparation of an Emulsion Coating Solution

A coating solution was prepared by adding the reagents indicated below to the emulsion per mol of silver halide.

Gelatin	
Gelatin was added so the Ag/binder ratio was 1.0. (binder = gelatin + polymer)	

(continued)

Gelatin	
Water-Soluble Polyester WD-SIZE made by the Eastman Chemical Co.	15.0 g
Polymer Latex (poly(ethyl acrylate/methacrylic acid) = 97/3)	25.0 g
Film Hardening Agent 1,2-Bis(sulfonylacetamido)ethane	8 mmol per 100 g of gelatin in the surface protective layer and emulsion layer
Compound of the Formula (I) of the Present Invention or Comparative Compound	Amounts added as shown in Table 1
2,6-Bis(hydroxyamino)-4-diethyl-amino-1,3,5-triazine	80 mg
Poly(sodium acrylate) (average molecular weight 41,000)	4.0 g
Poly(sodium styrenesulfonate) (average molecular weight 600,000)	1.0 g

The coating solution described above was coated onto a transparent PET support having a thickness of 175 μm at the same time as a surface protective layer coating solution.

The coated amount of silver was 2.0 g per square meter.

The surface protective layer was prepared using the amounts of each component indicated below. The photographic materials 1 to 13 (Table 1) were each obtained in this way.

Surface Protective Layer Content	Coated Amount
Gelatin	1.15 g/m^2
Polyacrylamide (average molecular weight 45,000)	0.25
Poly(sodium acrylate) (average molecular weight 400,000)	0.02
Sodium p-tert-octylphenoxydiglyceryl-sulfonate	0.02
Poly(degree of polymerization 10)oxy-ethylene cetyl ether	0.035
Poly(degree of polymerization 10)oxy-ethylene-poly(degree of polymerization 3)oxyglyceryl p-octylphenoxy ether	0.01
$C_8F_{17}SO_3K$	0.003
$C_8F_{17}SO_2N(C_3H_7)-(CH_2)_4-(CH_2)_4-SO_3Na$	0.001
$C_8F_{17}SO_2N(C_3H_7)-(CH_2CH_2O)_{10}-(CH_2CHCH_2O)_4-H$	0.003
Poly(methyl methacrylate) (average particle size: 3.5 μm)	0.025
Poly(methyl methacrylate/methacrylate) (mol ratio 7/3, average particle size: 2.5 μm)	0.020

Evaluation of Photographic Performance

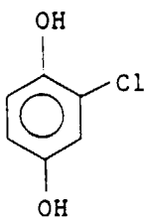
Photographic samples 1 to 13 were subjected to a 1/20th second exposure using green light which had a peak at 550 nm and then they were SP-processed at 35°C (dry to dry time: 45 seconds) using developer RD 7 and fixer Fuji F in an automatic processor FPM9000 made by the Fuji Photo Film Co., Ltd.

Photographic speed was expressed by means of the reciprocal of the exposure required to provide a density of fog + 1.0 and the results obtained, taking the speed of photographic material 1 to be 100, are summarized in Table 1.

Evaluation of Abrasion Resistance

Photographic materials 1 to 13 were equilibrated for 1 hour under conditions of 25°C, 25% RH and then they were rubbed at a speed of 1 cm per second with a commercial nylon brush under the same conditions with a loading of 100 g per 2 × 1 cm area. The samples were then processed in an unexposed condition in accordance with the automatic processing operation described above and the number of black abrasion lines was counted.

TABLE 1

Sample No.	Compound of Formula (I) Type	Compound of Formula (I) Amount Added (g/mol-Ag)	Photographic Speed	Number of Abrasion Lines	Remarks
1	—	—	100	55	Comparison
2	I- 1	0.5	107	23	Invention
3	"	1.0	100	17	"
4	I-13	0.5	110	26	"
5	"	1.0	105	20	"
6	I-15	0.5	100	24	"
7	"	1.0	98	21	"
8	I-20	0.5	102	25	"
9	"	1.0	98	18	"
10		2.0	93	49	Comparison
11	"	4.0	81	43	"
12		2.0	91	47	"
13	"	4.0	78	40	"

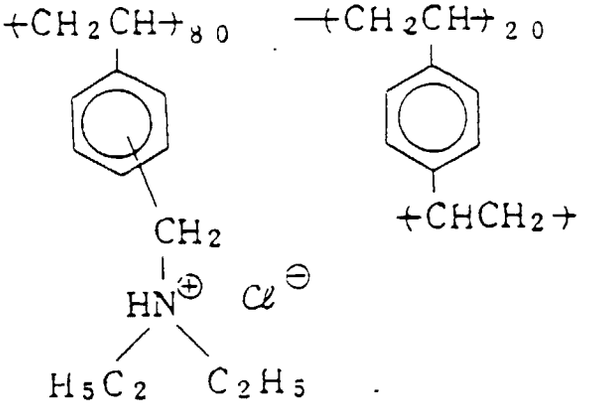
It is clearly seen from the results of Table 1 that the samples to which compounds of formula (I) of the present invention had been added had improved abrasion resistance without loss of photographic speed.

There was some improvement in respect of abrasion with sample Nos. 10 to 13 to which comparative compounds had been added, but this was accompanied by an undesirable loss of speed.

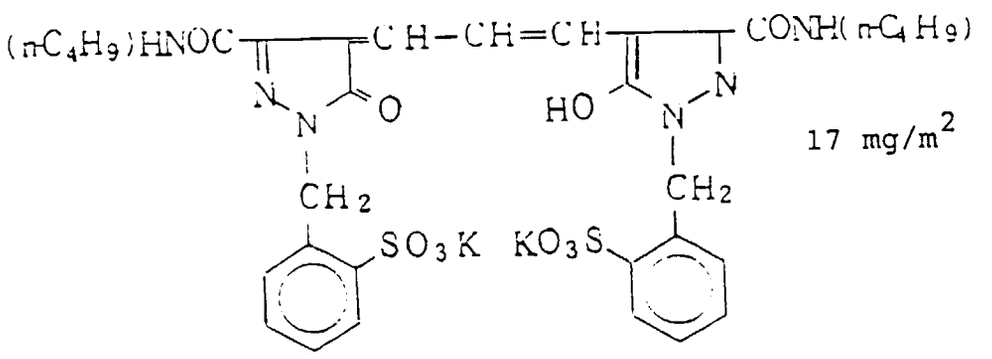
EXAMPLE 2

A base was prepared with an underlayer with the coated amounts indicated below established on both surfaces of a blue colored poly(ethylene terephthalate) support having a thickness of 175 µm.

Gelatin 84 mg/m^2



60 mg/m^2



17 mg/m^2

The emulsions described in Example 1 were coated onto both sides of this base in amounts of 1.9 g/ m^2 of coated silver per side. At this time, the compound of the formula (I), or the comparative compound, was added so the amount added per mol of silver was as shown in Table 2. Protective layers were obtained using the same coating solution as in Example 1. The amount of film hardening agent added was changed to 15 mmol per 100 g of gelatin. Photographic materials 1 to 13 were obtained in this way. Abrasion resistance was evaluated in the same way as described in Example 1. However, processing was modified to that described below for the evaluation of photographic performance.

Evaluation of Photographic Performance

The samples were exposed in the same way as in Example 1 from both sides and then processed in an automatic processor using the developer and fixer described below.

Developer Concentrate	
Potassium hydroxide	56.6 g
Sodium sulfite	200 g

(continued)

Developer Concentrate	
Diethylenetriaminepentaacetic acid	6.7 g
Potassium carbonate	16.7 g
Boric acid	10 g
Hydroquinone	83.3 g
Diethylene glycol	40 g
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	11.0 g
5-Methylbenzotriazole	2 g
Made up to 1 liter with water (pH adjusted to 10.60)	

Fixer Concentrate	
Ammonium thiosulfate	560 g
Sodium sulfite	60 g
Ethylenediaminetetraacetic acid disodium salt dihydrate	0.10 g
Sodium hydroxide	24 g
Made up to 1 liter with water (Adjusted to pH 5.10 with acetic acid)	

Automatic Processor		
Developing Tank	6.5 liters	35°C × 12.5 seconds
Fixing Tank	6.5 liters	35°C × 10 seconds
Water Washing Tank	6.5 liters	20°C × 7.5 seconds
Drying		50°C
Dry to Dry Processing Time		48 seconds

Each processing tank was filled with a processing solution as indicated below when starting development processing.

Developing Tank: The developer concentrated described above (333 ml), 667 ml of water and 10 ml of a starter which contained 2 g of potassium bromide and 1.8 g of acetic acid were added; and the pH was 10.15.

Fixing Tank: The fixer concentrate described above (250 ml) and 750 ml of water.

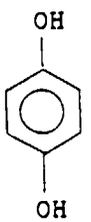
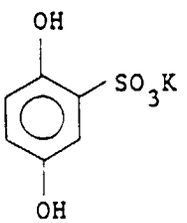
The results obtained are summarized in Table 2. The photographic speed of Sample No. 1 was taken to be 100.

Evaluation of Drying Properties

Automatic processor processing as described earlier was carried out using film samples measuring 24.5 × 30.5 cm and the drying conditions were investigated by touching the film emerging from the drying zone immediately with the fingers. The evaluation was made on the basis of the levels indicated below.

E: The emerging film was quite hot and thoroughly dry.
G: The emerging film was just warm and dry.
M: The emerging film had damp bands and drying was unsatisfactory.
B: The emerging film was wet and films stuck together.

TABLE 2

Sample No.	Compound of Formula (I) Type	Compound of Formula (I) Amount Added (g/mol-Ag)	Photographic Speed	Number of Abrasion Lines	Drying Properties	Remarks
1	—	—	100	48	E	Comparison
2	I- 5	0.3	105	12	E	"
3	"	0.6	110	7	G	"
4	I-11	0.3	107	15	E	Invention
5	"	0.6	115	11	E	"
6	I-16	0.3	110	13	E	"
7	"	0.6	107	6	G	"
8	I-22	0.3	105	10	E	"
9	"	0.6	100	8	E	"
10		1.5	95	39	M	Comparison
11	"	3.0	87	33	B	"
12		1.5	91	42	M	"
13	"	3.0	93	36	B	"

It is clearly seen from the results of Table 2 that the samples in which a compound of the formula (I) of the present invention had been used the drying properties were excellent in rapid processing. The samples also exhibited good abrasion resistance with a high photographic speed.

EXAMPLE 3

Emulsions A to E were prepared using the methods described below.

Preparation of a Regular Octahedral Silver Halide Emulsion

An aqueous solution of silver nitrate and an aqueous solution containing potassium bromide and potassium iodide were added, using the double jet method, to a container which contained potassium bromide and 25 g of gelatin in 1 liter of water, while maintaining a pAg value of 8.7. A regular octahedral silver iodobromide emulsion of average grain size 0.8 μm was obtained. This emulsion was chemically sensitized using sodium thiosulfate and chloroauric acid; a regular octahedral photosensitive silver iodobromide emulsion (A), which had an iodide content of 8 mol% at pAg 8.6, pH 6.4, was obtained.

Preparation of Irregular (twinned crystal thick plate) Silver Halide Emulsions

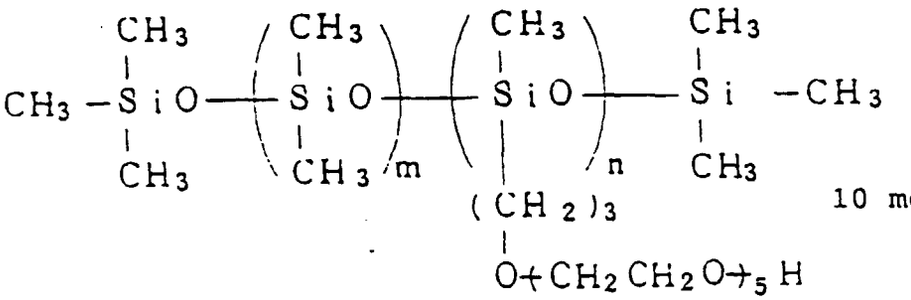
An aqueous solution of silver nitrate and an aqueous solution of potassium bromide were added using the double jet method, with the usual ammonia procedure, to a vessel which contained 25 g of potassium bromide, 4.5 g of potassium iodide, 9 ml of 2 N potassium thiocyanate and 24 g of gelatin in 1 liter of water. A silver chlorobromide emulsion with iodide content 3 mol% in the form of thick plates of a comparatively irregular form, average grain size 1.0 μm, was obtained. This emulsion was chemically sensitized using sodium thiosulfate and chloroauric acid; the photosensitive silver iodobromide emulsion (B) having pAg 8.6, pH 6.4 was obtained. Photosensitive silver iodobromide emulsion (C), average grain size 0.6 μm, which contained 6 mol% of iodide, was obtained by including 9 g of potassium iodide in the initial solution and carrying out grain formation and chemical sensitization in the same way as described for emulsion (B). The photosensitive silver iodobromide emulsion (D), average grain size 1.0 μm having silver iodide content 8 mol%, was obtained by adding 8 g of potassium iodide to the initial solution and 4 g of potassium iodide to the aqueous halogen solution using the double jet procedure.

Preparation of a Tabular Silver Halide Emulsion of Average Aspect Ratio 6.5

An aqueous solution of silver nitrate and a mixed aqueous solution of potassium bromide and potassium iodide were prepared. 5% of the volume of the aqueous solution of silver nitrate and the mixed aqueous solution were added to a vessel which contained 5 g of potassium bromide and 30 g of gelatin in 1 liter of water in such a way that the pAg value was maintained at 9.5. Then, 5% of the volume of the silver nitrate solution were added using the siagle jet method; and finally the remaining 90% of the aqueous silver nitrate solution and the mixed aqueous solution of potassium bromide and potassium iodide were added using the double jet method, maintaining a pAg value of 8.1. A tabular silver halide emulsion of average projected area diameter 1.3 μm, standard deviation 15% and average aspect ratio 6.5 was obtained. This emulsion was chemically sensitized using sodium thiosulfate and chloroauric acid; and the photosensitive silver iodobromide emulsion (E), which had an iodide content of 3 mol%, was obtained at pAg 8.6 and pH 6.4.

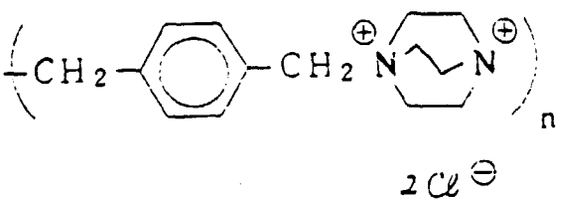
Preparation of Coated Samples

Coated samples were prepared by coating the emulsion layer formulation indicated below onto the emulsion layer coating side of a triacetyl cellulose support having a subbing layer on the emulsion coating side, and on the reverse side, a backing layer having the following formulation:



10 mg/m^2

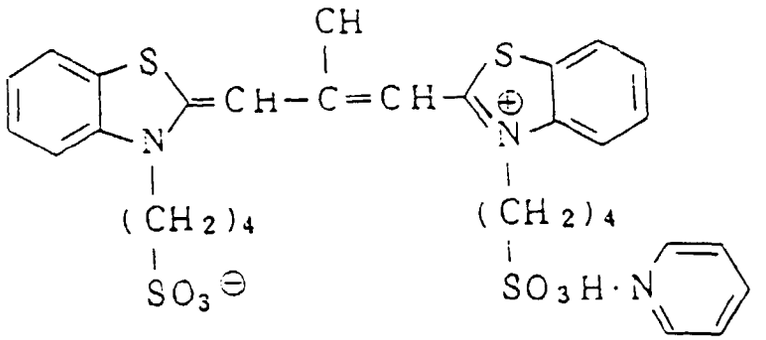
(m+n = 32)



60 mg/m^2

Diacetyl cellulose	143 mg/m^2
Silicon oxide	5 mg/m^2

Emulsion Layer Formulation	
Coated silver amount	3.5 g/m^2
Weight of gelatin	1.5 g/g-Ag
4-Hydroxy-6-methyl-1,3,3a,7-tetra-azaindene	10 mg/g-Ag
Poly(ethylene oxide)	8 mg/g-Ag
Poly(potassium p-vinylbenzenesulfonate)	20 mg/g-Ag
Sensitizing Dye	230 mg/mol-Ag



The compounds of the formula (I) and comparative compounds were added in the amounts shown in Table 3. Hard films were prepared after storing the coated samples for 7 days at 25°C, 65% RH by means of bis(vinylsulfonylacetamido)ethane so the film thickness on immersion for 3 minutes in distilled water at 25°C was 200 ±10% of the dry film thickness.

Surface Protecting Layer	
Amount of gelatin	0.8 g/m^2
Poly(potassium p-vinylbenzenesulfonate)	1 mg/m^2
Fine poly(methyl methacrylate)particles (average size: 3 μm)	0.13 mg/m^2

Developer Formulation	
Metol	2 g
Anhydrous sodium sulfite	100 g
Hydroquinone	5 g
Boric acid	2 g
Water to make (pH adjusted to 8.7)	1 liter

Fixer Formulation	
Sodium thiosulfate	240 g
Anhydrous sodium sulfite	15 g
28 wt% Acetic acid	48 ml
Boric acid	7.5 g
Potassium alum	15 g
Water to make	1 liter

Sensitometric Evaluation

Coated samples 1 to 25 were stored for 7 days under conditions of 25°C, 65% RH. The samples were then exposed for 1/100 second using a filter which had a wavelength distribution corresponding to sunlight, after which they were developed for 7 minutes at 20°C with the developer; then, after fixation with the fixer, the samples were washed with water and dried. The photographic speeds were measured at fog + 0.3 density using the processed samples.

The photographic speeds of each of the emulsions A to E were compared as relative value obtained by taking the speed of the blank in each case to be 100.

Evaluation of Abrasion Resistance

Abrasion was carried out with a nylon brush using the same method as described in Example 1. The sample was developed and processed in the same way, with sensitometry. Then, the number of blackened abrasion lines was

counted in the same way as described in Example 1.

Evaluation of Aging Storage Properties (Aging Fog)

Coated samples stored under conditions of 25°C, 65% RH and samples stored under conditions of 40°C, 75% RH were subjected to sensitometric measurements and the fog densities were compared. The difference between the fog values in the former and latter cases was measured as the aging fog; the results are shown in Table 3 below.

TABLE 3

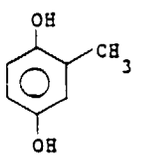
Sample No.	Emulsion Used	Compound of Formula (I) Type	Compound of Formula (I) Amount Added (g/mol-Ag)	Photographic Speed	Number of Abrasion Lines	Aged Fogging	Remarks
1	A	—	—	100	61	0.045	Comparison
2	B	—	—	100	75	0.037	"
3	C	—	—	100	53	0.050	"
4	D	—	—	100	66	0.055	"
5	E	—	—	100	77	0.058	"
6	A		1.7	83	53	0.040	"
7	B	"	"	85	64	0.035	"
8	C	"	"	79	48	0.048	"
9	D	"	"	87	59	0.050	"
10	E	"	"	85	61	0.052	"
11	A	I- 3	0.2	102	22	0.018	Invention
12	B	"	"	100	23	0.015	"
13	C	"	"	107	18	0.020	"
14	D	"	"	98	19	0.021	"
15	E	"	"	102	20	0.018	"
16	A	I- 7	0.3	107	20	0.015	"
17	B	"	"	110	18	0.017	"
18	C	"	"	105	17	0.016	"

TABLE 3 (cont'd)

Sample No.	Emulsion Used	Compound of Formula (I) Type	Compound of Formula (I) Amount Added (g/mol-Ag)	Photographic Speed	Number of Abrasion Lines	Aged Fogging	Remarks
19	D	I- 7	0.3	100	15	0.015	Invention
20	E	"	"	102	18	0.018	"
21	A	I-17	0.25	100	22	0.014	"
22	B	"	"	98	17	0.013	"
23	C	"	"	100	15	0.015	"
24	D	"	"	102	18	0.017	"
25	E	"	"	105	16	0.016	"

It is clearly seen from the results of Table 3 that Sample Nos. 11 to 25, in which a compound of the formula (I) of the present invention had been used, exhibited no loss of photographic speed, had improved abrasion resistance and exhibited little increase in fog level due to aging.

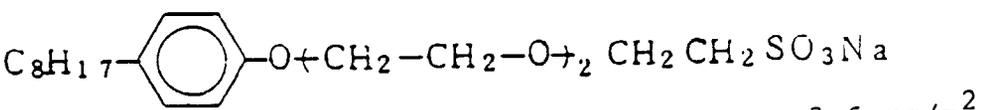
Furthermore, the samples of the present invention exhibited increased contrast in the toe part (so-called toe cutting) in the sensitometry; and a development accelerating effect was also observed when the development time was short.

EXAMPLE 4

Coated samples 1 to 11 were prepared with the layer constitution indicated below.

First Layer from the Support

Gelatin 0.6 g/m^2

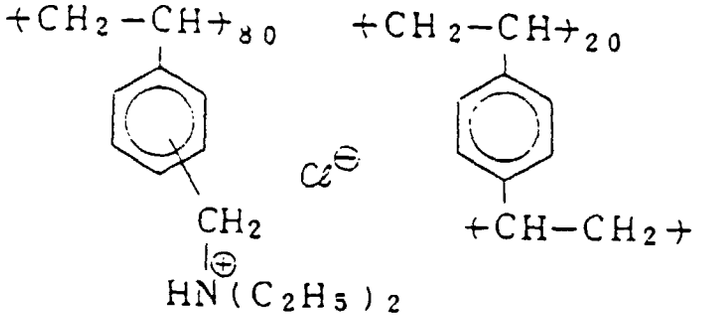


3.6 mg/m^2

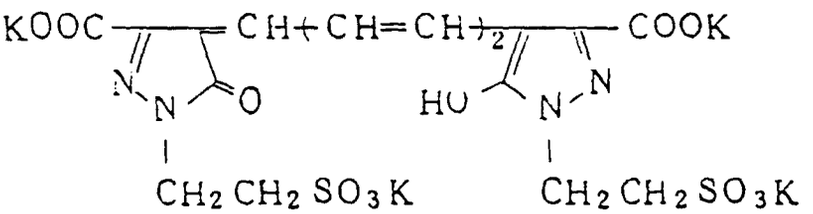
Poly(potassium p-vinylbenzene-sulfonate) 9 mg/m^2

Second Layer

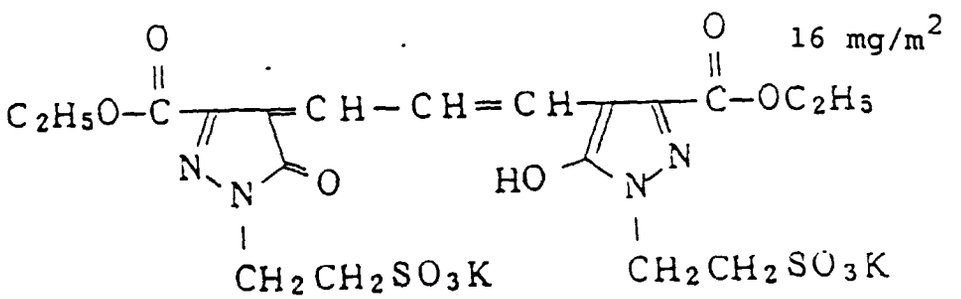
Gelatin 1.0 g/m^2



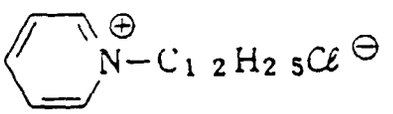
175 mg/m^2



26 mg/m^2



16 mg/m^2

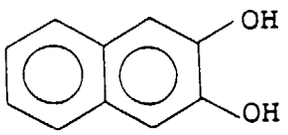


15 mg/m^2

HCl 0.11 mg/m^2

Third Layer	
Gelatin	0.4 g/m^2
Poly(potassium p-vinylbenzenesulfonate)	5 mg/m^2

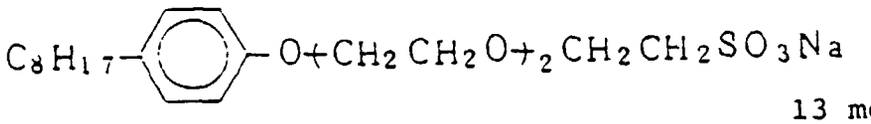
Fourth Layer (using Emulsion C)

Amount of silver	1.36 g/m^2
Gelatin	2.0 g/m^2
4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	30 mg/m^2
Poly(ethylene oxide)	7 mg/m^2
	1.5 mg/m^2
Poly(potassium p-vinylbenzene-sulfonate)	50 mg/m^2

Fifth Layer (using Emulsion D)	
Amount of silver	4.6 g/m^2
Amount of gelatin	7.0 g/m^2
4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	41 mg/m^2
Poly(ethylene oxide)	23 mg/m^2
Poly(potassium p-vinylbenzenesulfonate)	88 mg/m^2

Uppermost Layer

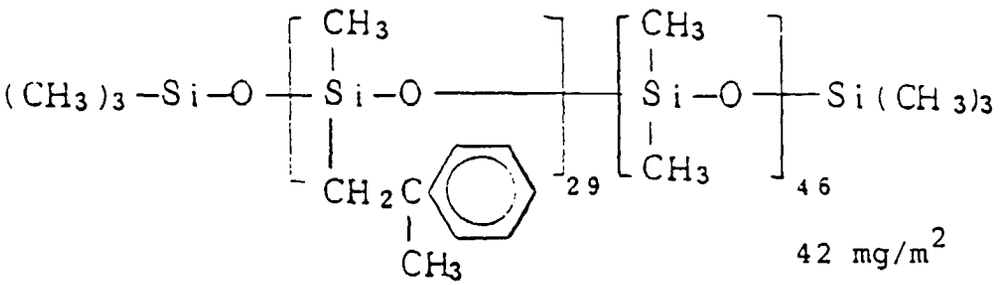
Gelatin 0.8 g/m^2



13 mg/m^2

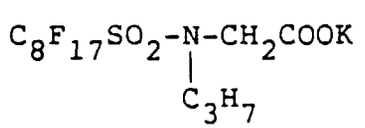
Fine poly(methyl methacrylate) particles (average particle size: 3 μm) 0.13 mg/m^2

Poly(potassium p-vinylbenzene-sulfonate) 6 mg/m^2



42 mg/m^2

$C_{15}H_{31}COOC_{16}H_{33}$ 50 mg/m^2



1.8 mg/m^2

Hard films were prepared after storing the coated samples for 7 days at 25°C, 65% RH. Bis(vinylsulfonylacetamido) ethane was used to ensure that the film thickness, after immersion for 3 minutes in distilled water at 25°C, was 300 ± 10% with respect to the dry film thickness.

Emulsions (C) and (D) had 230 mg/mol-Ag of the same dye as in Example 3 added before post ripening.

The amount of the compound of the formula (I) of the present invention added and the layer to which it was added are shown in Table 4.

Sensitometry, abrasion resistance and aging fog were evaluated using the same methods as described in Example 3, and the results obtained are shown in Table 4.

TABLE 4

Sample No.	Compound of Formula (I)			Photographic Speed	Number of Abrasion Lines	Aged Fogging	Remarks
	Layer to Be Added	Type	Amount Added				
			(g/mol-Ag)				
1	-	-	-	100	58	0.053	Comparison
2	1st Layer	Hydroquinone	1.5	85	47	0.050	"
3	2nd Layer	"	"	87	45	0.048	"
4	3rd Layer	"	"	85	48	0.047	"
5	4th Layer	"	"	85	43	0.051	"
6	5th Layer	"	"	83	46	0.049	"
7	1st Layer	I-2	0.2	107	17	0.017	Invention
8	2nd Layer	"	"	105	15	0.020	"
9	3rd Layer	"	"	105	18	0.018	"
10	4th Layer	"	"	102	18	0.018	"
11	5th Layer	"	"	107	15	0.019	"

It is clearly seen from the results of Table 4 that samples 7 to 11 of the present invention exhibited good abrasion resistance and aging fog level irrespective of the layer to which the addition was made.

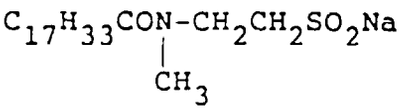
EXAMPLE 5

An aqueous solution of silver nitrate and an aqueous solution containing potassium bromide and potassium iodide were mixed using the double jet method in the presence of ammonia while maintaining a pAg value of 7.9. A monodisperse cubic silver iodobromide emulsion was prepared, having average grain size of 0.2 μm (silver iodide 2.0 mol%, silver bromide 98.0 mol%).

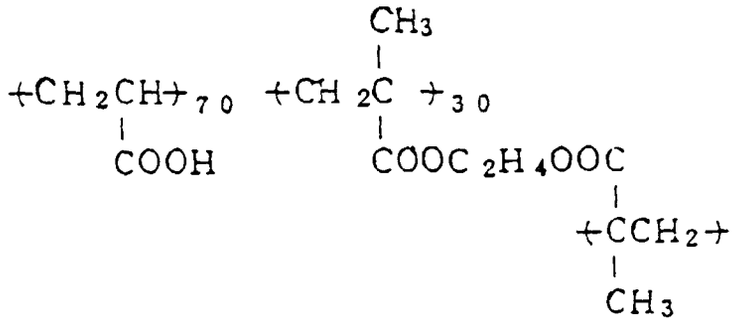
Sodium thiosulfate (3×10^{-5} mol/mol-Ag) was added to the silver iodobromide emulsion for chemical ripening, and sulfur sensitization was carried out.

The sensitizing dye 5,5'-dichloro-3,3'-di(3-sulfopropyl)-9-ethyl-oxacarbocyanine sodium salt was added in an amount of 6×10^{-4} mol per mol of silver to spectrally sensitize the emulsion.

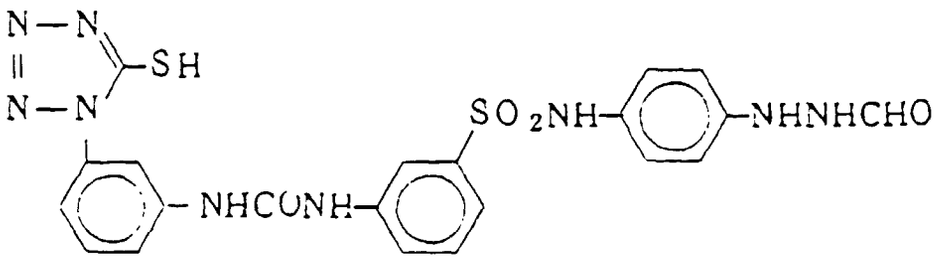
Moreover, 4-hydroxy-6-methyl-1,3,3a,7-tetra-azaindene was added as stabilizer. The compound indicated below and saponin were added as coating aids:



Moreover, $CH_2=CHSO_2CH_2CONH(CH_2)_nNHCOCH_2SO_2CH=CH_2$ (n = 2, 3) was added as a vinyl sulfone based hardening agent, poly(sodium styrenesulfonate) was added as a thickener, and a dispersion of poly(styrene acrylate) was added as a latex polymer in an amount of 0.30 g/m^2; and the compound indicated below was added in an amount of 0.40 g/m^2.



In addition, 0.1 g per mol of silver of 1-phenylmercaptotetrazole was added as an antifoggant, after which 6.0×10^{-4} mol/mol-Ag of the compound indicated below was added as a hydrazine compound.



Compounds of the formula (I) were added in the amounts indicated in Table 5.

Furthermore, emulsions to which hydroquinone was added, instead of a compound of the formula (I), were also prepared as comparative samples.

An aqueous gelatin solution comprised of gelatin, sodium dodecylbenzenesulfonate, silicone oil, fluorine based surfactant, colloidal silica, poly(ethyl acrylate) dispersion, poly(methyl methacrylate) (particle size: 2.5 μm) matting agent and poly(sodium styrenesulfonate) thickener was coated as a protective layer to provide a coated gelatin amount of 1.6 g/m^2. The emulsion layer and the protective layer were coated simultaneously in such a way that the emulsion provided a coated silver amount of 3.6 g/m^2.

Two of each of these samples were prepared and a sapphire needle having a diameter of 0.025 mm was applied to one sample with loadings of 2, 4, 6, 8 and 10 g in order to carry out a pressure sensitization test. The other sample was prepared without abrasion for the measurement of photographic speed and gamma value in sensitometric tests.

The two samples were exposed for 5 seconds through an optical wedge for sensitometric purposes using tungsten light (color temperature: 3,200K). Then, they were developed for 30 seconds at 38°C in a developer having the composition indicated below, fixed, washed with water and dried. (An automatic processor, model FG-660F, made by the Fuji Photo Film Co., Ltd. was used for development processing.)

The results obtained are shown in Table 5.

Developer Formulation	
Hydroquinone	50.0 g
N-Methyl-p-aminophenol 1/2-sulfate	0.3 g
Sodium hydroxide	18.0 g
5-Sulfosalicylic acid	45.0 g
Potassium sulfite	110.0 g
Ethylenediaminetetraacetic acid disodium salt	1.0 g
Potassium bromide	10.0 g
5-Methylbenzotriazole	0.4 g
2-Mercaptobenzimidazole-5-sulfonic acid	0.3 g
3-(5-Mercaptotetrazole)benzene -sulfonic acid sodium salt	0.2 g

(continued)

Developer Formulation	
N-n-Butyl diethanolamine	15.0 g
Sodium toluenesulfonate	8.0 g
Water to make	1 liter
pH to 11.6 (potassium hydroxide added)	11.6

Method of Evaluating Photographic Speed

The photographic speed was read off from the exposure at the point of fog + density 1.5 on the characteristic curve.

Method of Evaluating Gamma

The gamma value was obtained as the gradient of the straight line drawn between the point of fog + density 0.3 and the point of fog + density 3.0 on the characteristic curve. Hence:

$$\text{Gamma} = \frac{3.0 - 0.3}{[\log(\text{exposure at the point of fog + density 3.0})] - [\log(\text{exposure at the point of fog + density 0.3})]}$$

A gamma value of at least 10 is desirable to ensure adequate image quality.

Method of Evaluating Abrasion Sensitization

The extent of abrasion sensitization was evaluated visually in the part which had little background density, corresponding to the toe part in sensitometry.

The loading on the needle used for abrasion was increased; and the load at which abrasion sensitization was observed to occur was recorded. The resistance to abrasion is strong when this value is high, and a value of at least 6 g is desirable.

TABLE 5

Sample No.	Compound of Formula (I)		Photographic Speed	Gamma Value	Abrasion	Remarks
	Type	Amount Added				
		(mol/mol-Ag)				
1	-	-	100	16	2	Comparison
2	I- 1	7×10^{-4}	102	16	8	Invention
3	I- 1	2×10^{-3}	98	15	10 or more	"
4	I- 3	7×10^{-4}	100	17	10	"
5	I- 3	2 x 10-3	95	16	10 or more	"
6	I- 7	7×10^{-4}	98	16	10	"
7	I- 7	2×10^{-3}	95	16	10 or more	"
8	I- 8	7×10^{-4}	102	16	8	"
9	I- 8	2×10^{-3}	95	14	10	"
10	I-13	7×10^{-4}	100	17	9	"
11	I-13	2×10^{-3}	98	16	10	"
12	Hydroquinone	2×10^{-3}	81	14	3	Comparison
13	Hydroquinone	8×10^{-3}	69	13	5	"

It is clearly seen from the results of Table 5 that the samples in which a compound of the present invention had been used had virtually no loss of photographic speed or reduction in gamma. They also exhibited greatly improved abrasion sensitization.

Furthermore, the samples in which hydroquinone was used as a comparative compound, instead of a compound of the formula (I), exhibited a smaller improvement in abrasion sensitization and lower photographic speed than the samples of the present invention; thus, the compounds used in the present invention were superior.

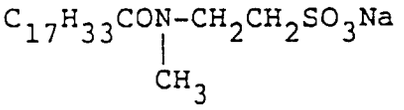
EXAMPLE 6

A silver chloroiodobromide emulsion (silver iodide content: 0.1 mol%, silver bromide content: 30 mol%) was prepared using the double jet method. $(NH_4)_3RhCl_6$ was added as a rhodium salt to the aqueous halogen solution in an amount of 1×10^{-7} mol/mol-Ag in the silver chloroiodobromide emulsion. K_3IrCl_6, an iridium salt, was also added to the aqueous halogen salt at the same time in an amount of 4×10^{-7} mol/mol-Ag. The aqueous halogen solution and the aqueous silver nitrate solution were mixed at 45°C over a period of 60 minutes and a monodisperse cubic emulsion having an average grain size of 0.25 μm was obtained.

After washing with water and desalting, 5×10^{-5} mol/mol-Ag of sodium thiosulfate were added to the emulsion and sulfur sensitization was carried out. Then, 4×10 mol/mol-Ag of potassium chloroaurate were added and gold sensitization was carried out.

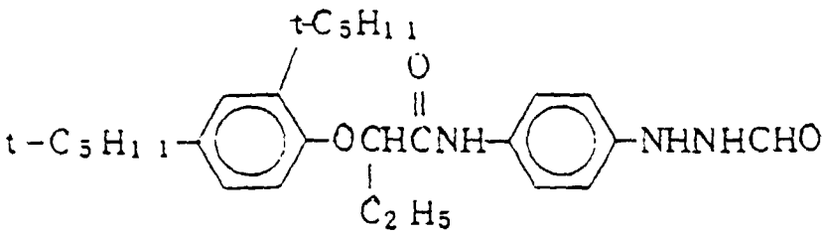
3×10^{-4} mol/mol-Ag of 1-(2-hydroxyethoxyethyl)-3-(pyridin-2-yl)-5-[(3-sulfobutyl-5-chloro-2-benzoxazolinidene) ethylidene]-2-thiohydantoin, potassium salt, as sensitizing dye; 0.1 g of 1-phenyl-5-mercaptotetrazole, 2 g of resorcin aldoxime, and 1.5 g of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, per mol of silver, as stabilizer, were added to the emulsion.

The compound indicated below and saponin were added as coating aids:



$CH_2=CHSO_2CH_2CONH(CH_2)_nNHCOCH_2SO_2CH=CH_2$ (n 2, 3) was added as a vinylsulfone based hardening agent, poly(sodium styrenesulfonate) was added as a thickener, and a dispersion of poly(ethyl acrylate) was added as a latex polymer.

The compound indicated below was added in an amount of 1.2×10^{-3} mol/mol-Ag as a hydrazine compound.



The compound of the formula (I) or hydroquinone was added in the amount shown in Table 6.

An aqueous gelatin solution comprised of gelatin, sodium dodecylbenzenesulfonate, silicone oil, fluorine based surfactant, colloidal silica, a dispersion of poly(ethyl acrylate), polyacrylamide (molecular weight: 5,000), poly(methyl methacrylate) (particle size: 2.5μm), matting agent and poly(sodium styrenesulfonate), thickener, was coated as a protective layer so that the coated amount of gelatin was 1.6 g/m^2. The emulsion was coated so that the coated amount of silver was 3.6 g/m^2. The emulsion layer and the protective layer were coated simultaneously.

These samples were abraded using the method described in Example 5, exposed and developed, and then evaluated in the same way as in Example 5. The results obtained are shown in Table 6.

TABLE 6

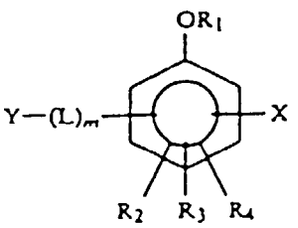
Sample No.	Compound of Formula (I)		Photographic Speed	Gamma Value	Abrasion	Remarks
	Type	Amount Added				
		(mol/mol-Ag)				
1	-	-	100	14	2	Comparison
2	I- 2	7×10^{-4}	108	15	10	Invention
3	I- 2	2×10^{-3}	105	15	10 or more	"
4	I- 5	7×10^{-4}	102	16	10	"
5	I- 5	2×10^{-3}	98	14	10 or more	"
6	I- 9	7×10^{-4}	100	14	10	"
7	I- 9	2×10^{-3}	98	13	10 or more	"
8	I-11	7×10^{-4}	100	15	8	"
9	I-11	2×10^{-3}	95	14	10	"
10	I-14	7×10^{-4}	102	14	9	"
11	I-14	2×10^{-3}	98	13	10	"
12	Hydroquinone	2×10^{-3}	72	11	3	Comparison
13	Hydroquinone	8×10^{-3}	59	9	4	"

It is clearly seen from the results of Table 6 that the samples in which compounds of the present invention had been used showed no loss of photographic speed or reduction in gamma. These samples exhibited very good abrasion sensitization even though a gold/sulfur sensitized silver chloroiodobromide emulsion had been used.

Furthermore, the compounds of the formula (I) used in the present invention performed better with respect to loss of photographic speed, decrease in gamma and abrasion than the comparative compound hydroquinone.

Claims

1. A silver halide photographic material comprising a support having thereon at least one of a surface latent image silver halide emulsion layer and other hydrophilic colloid layers, wherein said at least one of an emulsion layer and other hydrophilic colloid layers contains a compound represented by formula (I):

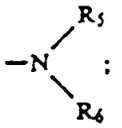


(I)

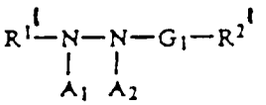
wherein X represents



or

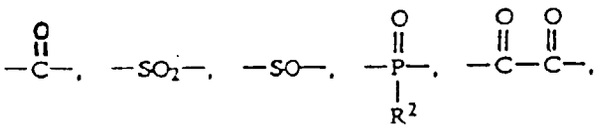


R_1 represents a hydrogen atom or a group capable of being converted to a hydrogen atom on hydrolysis; R_2, R_3 and R_4, which may be the same or different, each represents a hydrogen atom or a substituent group, R_5 and R_6, which may be the same or different, each represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkylsulfonyl group, a substituted or unsubstituted arylsulfonyl group, a substituted or unsubstituted alkylcarbonyl group, a substituted or unsubstituted arylcarbonyl group, or a substituted or unsubstituted carbamoyl group; Y represents a 5- or 6-membered heterocyclic group having a mercapto group or a benzotriazole group having a > NH structure therein; L represents a member selected from the group consisting of a divalent alkylene group, a divalent alkenylene group, a divalent alkynylene group, a divalent arylene group, -NH-, -N=, -CO-, $-SO_2-$, and combinations thereof; and m represents 0 or 1;
and wherein said at least one emulsion layer or other hydrophilic colloid layer containing a compound represented by formula (I) also contains a compound represented by formula (II) in an amount of from 1×10^{-6} to 5×10^{-2} mol per mol of the silver halide:



(II)

wherein R_1' represents an aliphatic group or an aromatic group; R_2' represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryloxy group, a substituted or unsubstituted amino group, or a substituted or unsubstituted hydrazino group; G_1 represents



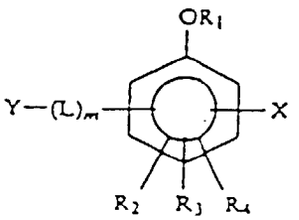
a thiocarbonyl group, or an iminomethylene group; and A_1 and A_2 each represents a hydrogen atom, a substituted or unsubstituted alkylsulfonyl group, a substituted or unsubstituted arylsulfonyl group, or a substituted or unsubstituted acyl group, provided that at least one of A_1 and A_2 is a hydrogen atom and that R_1' or R_2' contains a ballast group or a group which accelerates adsorption of the compound of formula (II) onto the silver halide grain surface.

2. A silver halide photographic material as claimed in claim 1, wherein said compound represented by formula (I) is added in an amount of 1×10^{-5} to 1×10^{-1} mol per mol of silver halide.

3. A silver halide photographic material as claimed in claim 1, wherein said compound represented by formula (II) is added in an amount of 1×10^{-6} to 5×10^{-2} mol per mol of silver halide.

Patentansprüche

1. Photographisches Silberhalogenidmaterial, umfassend einen Träger mit darauf wenigstens einem aus Silberhalogenidemulsionsschicht mit latentem Oberflächenbild und anderen hydrophilen Kolloidschichten, worin wenigstens eines aus einer Emulsionsschicht und anderen hydrophilen Kolloidschichten eine durch Formel (I) dargestellte Verbindung enthält:

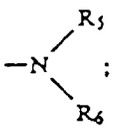


(I)

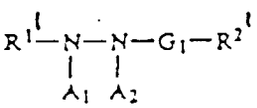
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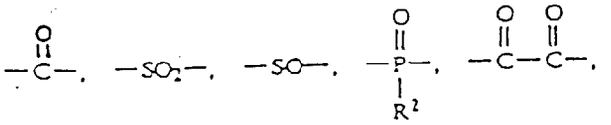


bedeutet;
R_1 bedeutet ein Wasserstoffatom oder eine Gruppe, die fähig ist zu einem Wasserstoffatom bei Hydrolyse umgewandelt zu werden; R_2, R_3 und R_4, die gleich oder verschieden sein können, bedeuten jeweils ein Wasserstoffatom oder eine Substituentengruppe, R_5 und R_6, die gleich oder verschieden sein können, bedeuten jeweils ein Wasserstoffatom, eine substituierte oder nicht substituierte Alkylgruppe, eine substituierte oder nicht substituierte Arylgruppe, eine substituierte oder nicht substituierte Alkylsulfonylgruppe, eine substituierte oder nicht substituierte Arylsulfonylgruppe, eine substituierte oder nicht substituierte Alkylcarbonylgruppe, eine substituierte oder nicht substituierte Arylcarbonylgruppe oder eine substituierte oder nicht substituierte Carbamoylgruppe; Y bedeutet eine 5- oder 6-gliedrige heterocyclische Gruppe mit einer Mercaptogruppe oder einer Benzotriazolgruppe mit einer >NH-Struktur darin; L bedeutet ein Mitglied, ausgewählt aus der Gruppe bestehend aus einer zweiwertigen Alkylengruppe, einer zweiwertigen Alkenylengruppe, einer zweiwertigen Alkinylengruppe, einer zweiwertigen Arylengruppe, -NH-, -N=, -CO-, $-SO_2-$ und Kombinationen davon; und m bedeutet 0 oder 1;
und worin diese wenigstens eine Emulsionsschicht oder andere hydrophile Kolloidschicht, die eine durch Formel (I) dargestellte Verbindung enthält, auch eine durch Formel (II) dargestellte Verbindung in einer Menge von 1 x 10^{-6} bis 5 x 10^{-2} Mol pro Mol Silberhalogenid enthält:



(II)

worin $R^{1'}$ eine aliphatische Gruppe oder eine aromatische Gruppe bedeutet; $R^{2'}$ bedeutet ein Wasserstoffatom, eine substituierte oder nicht substituierte Alkylgruppe, eine substituierte oder nicht substituierte Arylgruppe, eine substituierte oder nicht substituierte Alkoxygruppe, eine substituierte oder nicht substituierte Aryloxygruppe, eine substituierte oder nicht substituierte Aminogruppe oder eine eine substituierte oder nicht substituierte Hydrazinogruppe; G1 bedeutet



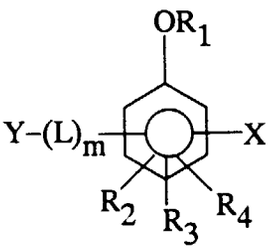
eine Thiocarbonylgruppe oder eine Iminomethylengruppe; und A_1 und A_2 bedeuten jeweils ein Wasserstoffatom, eine substituierte oder nicht substituierte Alkylsulfonylgruppe, eine substituierte oder nicht substituierte Arylsulfonylgruppe oder eine substituierte oder nicht substituierte Acylgruppe, mit der Maßgabe, daß wenigstens eines von A_1 und A_2 ein Wasserstoffatom ist, und daß $R^{1'}$ oder $R^{2'}$ eine Ballastgruppe oder eine Gruppe enthält, welche die Adsorption der Verbindung der Formel (II) auf die Silberhalogenidkornoberfläche beschleunigt.

2. Photographisches Silberhalogenidmaterial nach Anspruch 1, worin die durch Formel (I) dargestellte Verbindung in einer Menge von 1×10^{-5} bis 1×10^{-1} Mol pro Mol Silberhalogenid zugegeben wird.

3. Photographisches Silberhalogenidmaterial nach Anspruch 1, worin die durch Formel (II) dargestellte Verbindung in einer Menge von 1×10^{-6} bis 5×10^{-2} Mol pro Mol Silberhalogenid zugegeben wird.

Revendications

1. Matériau photographique à l'halogénure d'argent comprenant un support sur lequel se trouve au moins une couche parmi une couche d'émulsion d'halogénure d'argent à image latente de surface et d'autres couches de colloïdes hydrophiles, dans lequel ladite ou lesdites couches parmi une couche d'émulsion et d'autres couches de colloïdes hydrophiles contiennent un composé représenté par la formule (I) :

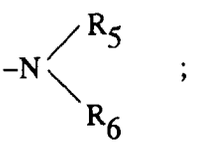


(I)

dans laquelle X représente



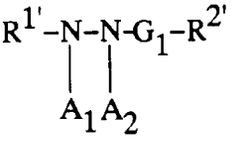
ou



;

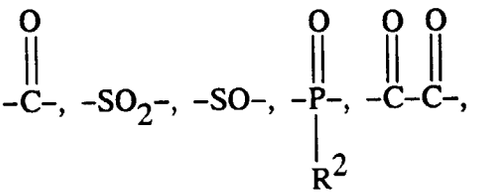
R_1 représente un atome d'hydrogène ou un groupe capable d'être converti en un atome d'hydrogène par hydrolyse; R_2, R_3 et R_4, qui peuvent être identiques ou différents, représentent chacun un atome d'hydrogène ou un groupe substituant, R_5 et R_6, qui peuvent être identiques ou différents, représentent chacun un atome d'hydrogène, un groupe alkyle substitué ou non substitué, un groupe aryle substitué ou non substitué, un groupe alkylsulfonyle substitué ou non substitué, un groupe arylsulfonyle substitué ou non substitué, un groupe alkylcarbonyle substitué ou non substitué, un groupe arylcarbonyle substitué ou non substitué ou un groupe carbamoyle substitué ou non substitué ; Y représente un groupe hétérocyclique à 5 ou 6 chaînons ayant un groupe mercapto ou un groupe

benzotriazole contenant une structure > NH; L représente un élément choisi dans le groupe consistant en un groupe alkylène divalent, un groupe alcénylène divalent, un groupe alcynylène divalent, un groupe arylène divalent, -NH-, -N=, -CO-, -SO_2-, et des combinaisons de ceux-ci ; et m représente 0 ou 1 ;
et dans lequel ladite ou lesdites couches d'émulsion ou autres couches de colloïdes hydrophiles contenant un composé représenté par la formule (I) contiennent aussi un composé représenté par la formule (II) en une quantité de $1x10^{-6}$ à 5×10^{-2} mol/mol d'halogénure d'argent :



(II)

où $R^{1'}$ représente un groupe aliphatique ou un groupe aromatique, $R^{2'}$ représente un atome d'hydrogène, un groupe alkyle substitué ou non substitué, un groupe aryle substitué ou non substitué, un groupe alcoxy substitué ou non substitué, un groupe aryloxy substitué ou non substitué, un groupe amino substitué ou non substitué ou un groupe hydrazino substitué ou non substitué ; G_1 représente



un groupe thiocarbonyle ou un groupe iminométhylène, et A_1 et A_2 représentent chacun un atome d'hydrogène, un groupe alkylsulfonyle substitué ou non substitué, un groupe arylsulfonyle substitué ou non substitué ou un groupe acyle substitué ou non substitué, à condition qu'au moins l'un des symboles A_1 et A_2 représente un atome d'hydrogène et que $R^{1'}$ ou $R^{2'}$ contienne un groupe ballast ou un groupe qui accélère l'adsorption du composé de formule (II) sur la surface des grains d'halogénure d'argent.

2. Matériau photographique à l'halogénure d'argent selon la revendication 1, dans lequel ledit composé représenté par la formule (I) est ajouté en une quantité de 1×10^{-5} à 1×10^{-1} mol/mol d'halogénure d'argent.

3. Matériau photographique à l'halogénure d'argent selon la revendication 1, dans lequel ledit composé représenté par la formule (II) est ajouté en une quantité de 1×10^{-6} à 5×10^{-2} mol/mol d'halogénure d'argent.