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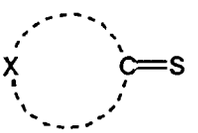
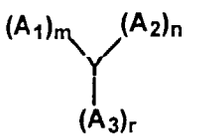
(54) Photographic silver halide emulsion

(57) A silver halide emulsion is disclosed, comprising reduction-sensitized silver halide grains and a compound represented by the following formula (1), (2) or (3); the silver halide grains having been further subjected to at least one chemical sensitization selected from the group consisting of sulfur sensitization, selenium sensitization and tellurium sensitization, in the presence of a spectral sensitizing dye represented by the following formula (4):

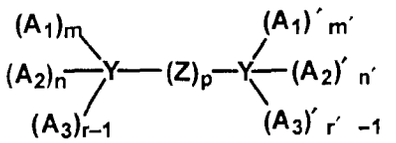
formula (1)



formula (2)



formula (3)



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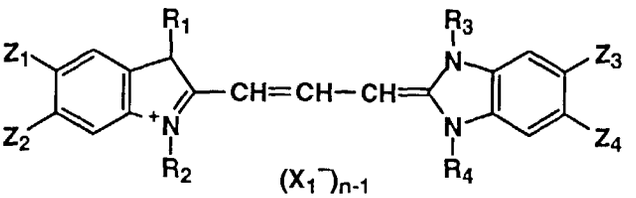
formula (4)



Description

FIELD OF THE INVENTION

[0001] The present invention relates to a silver halide emulsion, a method for processing a silver halide light sensitive photographic material having the emulsion and a photographing method by the use of the photographic material.

BACKGROUND OF THE INVENTION

[0002] Recently, with regard to processing of a silver halide photographic light sensitive material (hereinafter, simply referred to as photographic material), shortening of processing time has been demanded along with an increase of processing amounts. Especially, in the field of X-ray films for medical use, the amount of X-ray photographing is rapidly increasing due to increased use of X-rays for diagnosis and inspection in general medical examinations, as well as the increased tendency for periodical medical check-ups and clinical surveys. As a result, the desire for still faster processing is raised.

[0003] Shortening of processing time including developing, fixing, washing, drying, etc. is the key for faster processing of photographic materials. Shortening of the developing time alone, however, leads to a marked decrease of image density and sensitivity and deterioration of contrast. Shortening of only the fixing time leads to insufficient fixing, causing deterioration of image quality. Furthermore, shortening the time of each processing step results in incomplete dye leaching out of the processed material, causing stains due to residual dye. To overcome these problems, it is basically required to enhance developability and fixability of the photographic material, reduce the content of the dye and promote release or decoloring of the dye.

[0004] To reduce processing effluent for environmental protection, reduction of the amount of processing solutions and replenishing solutions or exhaustion of the processing solutions is required. In this case, however, various problems also occur similarly to the case of the above-described rapid-processing.

[0005] As techniques for solving these problems, for example, European Patent 0,506,584, and JP-A 5-88293 and 5-93975 (hereinafter, the term "JP-A" refers to unexamined and published Japanese Patent Application) disclose a technique of using, as a sensitizing dye, benzimidazolo-carbocyanines which are superior in decolorizability. JP-A 5-61148 discloses a technique in which a combination of an oxacarbocyanine and benzimidazolocarbocyanine is used in a specific proportion, in a silver halide emulsion containing 1 mol% or less iodide and the silver halide emulsion is further chemically sensitized with a selenium compound and/or tellurium compound.

[0006] The dye stain reduction and rapid-processability can be improved by these techniques, but it is not insufficient to satisfy other desired levels. Specifically, sensitivity and safelight safety characteristics are still insufficient. Furthermore, another defect is that when aged under high temperature and high humidity, the decrease in sensitivity is marked.

[0007] There have been made a variety of basic studies with regard to the relationship between silver halide grains and adsorption of sensitizing dyes. There have also been made studies for allowing the sensitizing dye to adsorb uniformly and selectively onto the grain or among the grains.

[0008] It is also known that when chemical sensitization is carried out in the presence of a sensitizing dye, the chemical sensitization is controllable and desensitization in intrinsic sensitivity can be reduced. However, these techniques are still insufficient for improving storage stability, pressure resistance, safelight safety characteristics and intensity reciprocity law failure.

[0009] There have been made attempts of reduction sensitization to enhance the sensitivity, as disclosed in U.S. Patents 2,487,850, 2,512,925, 2,518,698, and 3,930,867, and British Patent 789,823. However, these methods of reduction sensitization have not yet reached acceptable levels.

[0010] Also, in the field of photographic materials for medical use, simplification of overall processing are strongly desired, in addition to shortening of the processing time and reduction of processing effluents. With regard to processing chemicals, one conventional system is that a commercially available condensed processing solution is diluted to a given amount and the resulting solution is supplied as a replenisher to the processing tank of an automatic processor. As a result, the processing solution is massive in weight and volume, with the inherent disadvantages that enhancement in efficiency and safety of processing is difficult to achieve. Instead thereof, recently, there was proposed a system of solid processing chemicals, in which the processing chemicals are supplied in the form of a solid processing composition and diluent water. With this system, there have been achieved improvements in working efficiency as well as lowering of transportation cost and reduction of storage space. In addition, the amount of packaging material such as plastic resin, was advantageously reduced.

[0011] However, this system still has problems such that as processing chemicals are solid composition, its solubility (dissolution speed) is concerned and when subjected to ultrahigh speed processing, stable running performance can not be achieved.

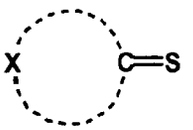
SUMMARY OF THE INVENTION

[0012] In view of the foregoing, an object of the present invention is to provide a photographic material superior in photographic characteristics, pressure resistance and storage stability, and without causing residual dye stain, even when continuously subjected to rapid processing at low effluents.

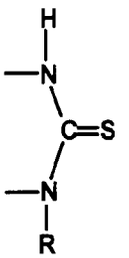
[0013] The object of the present invention can be accomplished by the following constitution:

[0014] 1. a silver halide emulsion comprising reduction-sensitized silver halide grains and a compound represented by formula (1), (2) or (3); the silver halide emulsion grains having been further subjected to at least one chemical sensitization selected from sulfur sensitization, selenium sensitization and tellurium sensitization, in the presence of a spectral sensitizing dye represented by formula (4):

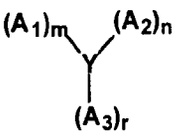
formula (1)



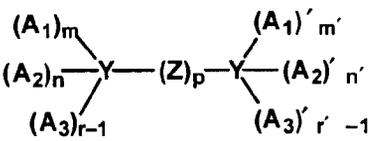
wherein X represents an atomic group necessary for forming a heterocyclic ring with a group selected from $-SO_3M$, -COOM and -OM, which is attached directly or indirectly to the ring; M represents a hydrogen atom, a metal atom, a quaternary ammonium group or a phosphonium group, provided that a compound having, in part, the following structure is excluded:



wherein R represents a hydrogen atom or a substituent, formula (2)

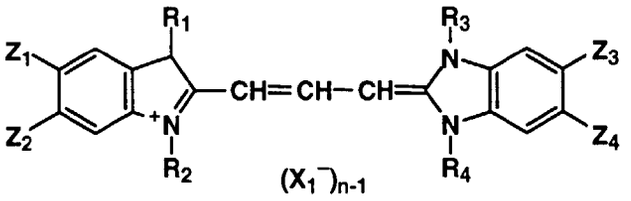


formula (3)



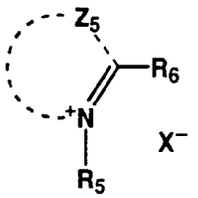
wherein (A_1) and $(A_1)'$ each represent $-SO_3M$, -COOM, -OM or a N-attached oxide group, in which M represents a hydrogen atom, a metal atom, quaternary ammonium group or a phosphonium group; and m and m' each are an integer of 1 to 10; (A_2) and $(A_2)'$ each represent an electron-withdrawing group; and n and n'each are an integer of 1 to 10; (A_3) and $(A_3)'$ represent a group containing a sulfur atom, selenium atom or a tellurium atom, which is capable of bonding to a silver ion; r and r' each are 1 or 2; Y represents an aliphatic hydrocarbon group, an aromatic hydrocarbon

group or a heterocyclic ring; Z represents a sulfur atom, selenium atom or a tellurium atom; and p is 1 or 2, formula (4)



wherein R_1 and R_3 each represent a substituted or unsubstituted alkyl group or a substituted or unsubstituted alkenyl group; R_2 and R_4 each represent an alkyl group, provided that at least one of R_2 and R_4 is an alkyl group substituted by a hydrophilic group; Z_1, Z_2, Z_3 and Z_4 each represent a hydrogen atom or a substituent; X_1^- represents an ion necessary for neutralizing an electric charge within the molecule; and n is 1 or 2, provided that when an intramolecular salt is formed, n is 1;

[0015] 2. the silver halide emulsion described above, wherein the chemical sensitization is performed further in the presence of a compound represented by the following formula (5): formula (5)



wherein Z_5 represents an atomic group necessary for forming a 5 or 6-membered heterocyclic ring; R_5 represents a hydrogen atom, an alkyl group or an alkenyl group; R_6 represents a hydrogen atom or a lower alkyl group; and x^- represents an anion; and

[0016] 3. the silver halide emulsion described above, wherein the silver halide grains have an aspect ratio of 2 to 20, and containing average iodide of 0 to 1.0 mol% and chloride content of 10 to 100 mol%.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The silver halide grains contained in the silver halide emulsion according to the invention may comprise silver chloride, silver iodochloride, silver iodochlorobromide, silver chlorobromide, silver bromide or silver iodobromide. Of these silver halides are preferred silver chloride, silver iodochloride silver bromochloride and silver bromide. A preferred embodiment of silver halide grains according to the invention is those containing 10 mol% or more, preferably 50 mol% or more and more preferably 90 mol% or more chloride In the case of silver iodochloride, the average overall iodide content is preferably 0.01 to 1.0 mol% and more preferably, 0.01 to 0.5 mol%. With regard to the form of silver halide grains used in the invention, it may be cube, octahedron, tetradecahedron, spherical form or tabular form. Of these are preferred tabular grains.

[0018] The iodide content of each grain and an average iodide content of overall grains can be determined by means of EPMA (Electron Probe Micro Analyzer). In this method, a sample which is prepared by dispersing silver halide grains so as not to be contact with each other, is exposed to an electron beam to conduct X-ray analysis by excitation with the electron beam. Thereby, elemental analysis of a minute portion can be done. Thus, halide composition of each grain can be determined by measuring intensities of characteristic X-ray emitted from each grain with respect to silver and iodide. At least 50 grains are subjected to the EPMA analysis to determine their iodide contents, from which the average iodide content can be determined.

[0019] It is preferred that the tabular silver halide grains contained in the silver halide emulsion according to the invention have uniformly iodide contents among grains. When the iodide content of grains is determined by the EPMA analysis, a relative standard deviation thereof (i.e., a variation coefficient of the iodide content of grains) is 35% or less, preferably, 20% or less.

[0020] In the tabular silver halide grains used in the invention, iodide contents among grains are preferably uniform. When the iodide contents among the grains are determined by the EPMA method, a relative standard deviation (i.e.,

coefficient of variation of the iodide content of grains) is preferably 35% or less and more preferably 20% or less.

[0021] In cases where the tabular silver halide grains contain iodide, the iodide is preferably, internally contained. In this case, the iodide is contained more preferably in the central portion of the grain. It is also preferable that the iodide is made present in the surface portion of the grain.

[0022] The halide composition within a silver halide grain can be determined by cutting ultra-thinly slices from the grain and making observation and analysis of the grain by a transmission electron microscope with cooling. Thus, after silver halide grains are taken out from an emulsion, the grains are buried in a resin, which is cut at a thickness of ca. 60 nm with a diamond knife to prepare a slice sample. With cooling with liquid nitrogen, the slice sample is observed and analyzed at various points with a transmission electron microscope provided with an energy-dispersion type X-ray analyzing apparatus to determine the halide composition within the grain (Inoue & Nagasawa, Abstracts of Annual Meeting of The Society of Photographic Science and Technology of Japan, 1987, page 62).

[0023] The iodide is present preferably in the outermost surface layer. In this case, the iodide content in the outermost surface layer is preferably between 1 mol% and 10 mol%. The iodide content in the outermost surface layer of the tabular silver halide grains refers to a silver iodide content of a portion in a depth from the surface of 50 nm, which can be determined by the XPS method (X-ray Photoelectron Spectroscopy). Thus, a sample is cooled to -110° C in super-vacuo of not more than $1x10^{-8}$ torr. and exposed to MgK α-line, as X-ray for probe, at 15 kV for the X-ray source voltage and 40 mA for the X-ray source current to make measurement with respect to Ag3d5/2, Br3d and I3d3/2 electrons. Measured integral intensity of each peak is corrected with a sensitivity factor and from their intensity ratio, the halide composition of the surface can be determined. By cooling the sample, measurement errors resulted from destruction of the sample (i.e., decomposition of silver halide and diffusion of halide, specifically, iodide) when exposed to X-ray at room temperature are minimized, resulting in enhanced measurement accuracy. When cooled down to -110° C, sample destruction is minimized to a level which prevents problems in measurement.

[0024] The bromide is also present preferably in the outermost surface layer. The bromide content in the outermost surface layer is preferably between 1 mol% and 10 mol%.

[0025] The tabular silver halide grains used in the invention have an average aspect ratio of 2 to 20, preferably not more than 8, more preferably less than 7, and still more preferably less than 5. The tabular grains having (100) major faces account for preferably 50% or more, more preferably 70% or more, and still more preferably 90% or more of the total grain projected area of the emulsion layer. The (100) major faces can be identified by X-ray diffractometry.

[0026] The major faces of the tabular silver halide grains is in the form of a rectangle (i.e., right-angled parallelogram) or one with rounded corners. The edge ratio of the rectangle (i.e., ratio of the long edge length to the short edge length) is preferably less than 10, more preferably less than 5, and still more preferably less than 2. In cases where the corner is rounded, the edge length is defined as a distance between the intersection of an extended straight line of the edge and extended straight lines of adjacent edges.

[0027] An average grain diameter of the tabular silver halide grains of the invention is preferably 0.15 to 5.0 μm, more preferably 0.4 to 3.0 μ and furthermore preferably 0.4 to 2.0 μm. An average thickness of the tabular silver halide grains is preferably 0.01 to 1.0 μm, more preferably 0.02 to 0.40 μm and furthermore preferably 0.02 to 0.30 μm. The grain diameter and thickness can be optimized so as make best sensitivity and other photographic characteristics. The optimal grain diameter and thickness depend upon sensitivity and other factors affecting photographic characteristics (thickness of a hydrophilic colloidal layer, hardening degree, chemical ripening conditions, designed speed of a photographic material, silver coating amount, etc.).

[0028] The tabular silver halide grains used in the invention are preferably monodisperse grains having a narrow grain size distribution. Thus, a width of grain size (diameter) distribution, defined as below, is preferably 25% or less, more preferably 20% or less and furthermore preferably 15% or less:

Width of grain size distribution (%) = (standard deviation of grain size/average grain size)x100

[0029] The tabular silver halide grains used in the invention are preferably those having a narrow grain thickness distribution. Thus, a width of grain thickness distribution, defined as below, is preferably 25% or less, more preferably 20% or less and furthermore preferably 15% or less:

Width of grain size distribution (%) = (standard deviation of grain size/average grain size)x100.

[0030] The tabular silver halide grains used in the invention may have dislocation lines. The dislocation lines can be directly observed by use of a transmission type electron microscope at low temperature, as described in J. F. Hamilton, Phot. Sci. Eng., 57 (1967) and T. Shiozawa, J. Soc. Phot. Sci. Japan, 35, 213 (1972). Thus, silver halide grains, which are carefully taken out from an emulsion without applying pressure to an extent of causing dislocation, are placed on a mesh for electron microscopic observation and observed by the transmission method, while being cooled to avoid damage due to electron beam. In this case, the more is the grain thickness, the less the transmission of the electron

beam, so that clearer observation is achieved by use of a high voltage type electron microscope.

[0031] Reduction sensitization applicable to silver halide grains contained in the silver halide emulsion according to the invention will now be described. The process of preparing a silver halide emulsion is generally classified into grain formation, desalting, chemical sensitization and so on. The grain formation is further classified into nucleation, ripening, growth and so on. Steps of the process are not necessarily performed in this order, but may be reversed or repeated. Silver halide grains according to the invention are reduction sensitized. The reduction sensitization can be applied to any one of these steps. Thus, the reduction sensitization can be performed at the step of nucleation, physical ripening, or growth. The reduction sensitization can be performed prior to chemical sensitization other than the reduction sensitization or after the chemical sensitization. In cases where the chemical sensitization is applied in combination with gold sensitization, it is preferable to perform the reduction sensitization prior to the chemical sensitization so as not to cause unacceptable fog. It is more preferable to perform the reduction sensitization during the growth of silver halide grains. In this case, there are included a method of performing the reduction sensitization at the step of physical ripening or growing grains by adding an aqueous soluble silver salt and an aqueous soluble alkali halide, and a method in which during the course of grain growth, growing is stopped at a time, reduction sensitization is applied and then growing is further continued.

[0032] The reduction sensitization includes a method of adding a known reducing agent into a silver halide emulsion, a method of growing or ripening grains under environments at a low pAg of 1 to 7 (so-called silver ripening), and a method of growing or ripening grains under environments at a high pH of 8 to 11 (so-called high pH ripening).

[0033] These methods can be applied singly or in combination. The method of adding a reduction sensitizer is preferable in terms of delicate adjustment of the reduction sensitization level. Examples of the reduction sensitizer include stannous salts, amines or polyamines, hydrazine derivatives,
formamidinesulfinic acid, silane compounds and borane compounds. These compounds can be employed singly or in combination. Preferred reduction sensitizer includes stannous salts, thiourea dioxide, and dimethylamine borane. The adding amount of the reduction sensitizer, depending on conditions of emulsion preparation, is optimally between 10^{-7} and 10^{-3} mol per mol of silver halide.

[0034] Ascorbic acid and its derivatives can be employed as reduction sensitizer. Examples of ascorbic acid and its derivatives (hereinafter, also referred to as an ascorbic acid compound) are shown below.

(A-1) L-ascorbic acid
(A-2) Sodium L-ascorbate
(A-3) Potassium L-ascorbate
(A-4) DL-Ascorbic acid
(A-5) Sodium D-ascorbate
(A-6) L-Ascorbic acid-6-acetate
(A-7) L-Ascorbic acid-6-palmitate
(A-8) L-Ascorbic acid-6-benzoate
(A-9) L-ascorbic acid-5,6-diacetate
(A-10) L-Ascorbic acid-5,6-o-isopropylidene

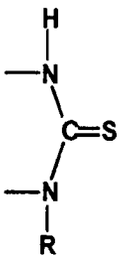
[0035] The addition amount of ascorbic acid compounds is desirably larger than that of conventionally used reduction sensitizers. JP-B 57-33572 (herein the term "JP-B" refers examined published Japanese patent) describes that the addition amount of a reducing agent conventionally does not exceed 0.75 milli-equivalent per lg of silver ion (8x10-4 mol/AgX mol); the amount of 1 to 10 mg per 1 kg of silver nitrate (ascorbic acid of 10^{-7} to 10^{-5} mol/AgX mol) is often effective. U.S. Patent 2,487,850 described that a tin compound is added, as a reduction sensitizer, in an amount of $1x10^{-7}$ to $44x10^{-6}$ mol. JP-A 57-179835 describes that the addition amount of thiourea dioxide or stannous chloride is optimally 0.01 to 2 mg or 0.01 to 3 mg per mol of silver halide, respectively. The addition amount of the ascorbic compound used in the invention, depending on the grain size and halide composition of an emulsion and the temperature, pH and pAg in emulsion making, is preferably $5x10^{-5}$ to $1x10^{-1}$, more preferably $5x10^{-4}$ to $1x10^{-2}$, and still more preferably $1x10^{-3}$ to $1x10^{2}$ mol/AgX mol.

[0036] The reduction sensitizer can be dissolved in water or a solvent such as alcohols, glycols, ketones ,esters and amides and added during grain formation, before or after chemical sensitization. Thus, the reduction sensitizer can be added at any step during the course of emulsion making and preferably added during the grain formation. The reduction sensitizer may be previously added into a reaction vessel and preferably added at any time during the grain formation. The reduction sensitizer is previously added to a silver salt or alkali halide aqueous solution, and the solution can be added during the grain formation. The sensitizer solution can be added separately or continuously during the grain formation.

[0037] The compound represented by formula (1) will now be described. In the formula (1), X represents an atomic group necessary for forming a heterocyclic ring having $-SO_3M$, -COOM or -OM, which may be attached directly or

indirectly, through a lincage group, to the ring. Thus, the heterocyclic ring contains at least one of $-SO_3M$, -COOM and -OM, or at least a group containing at least one of $-SO_3M$, -COOM or -OM. Examples of the heterocyclic ring include an oxazole ring, a thiazole ring, a imidazole ring, a selenazole ring, a triazole ring, a tetrazole ring, a thiadiazole ring, an oxadiazole ring, a pentazole ring, a pyrimidine ring, a thiazine ring, a triazine ring, a thiazine ring, or a heterocyclic ring condensed with another carbon ring or heterocyclic ring, such as a benzothiazole ring, a benzotriazole ring, a benzimidazole ring, a benzooxazole ring, a benzoselenazole ring, a naphthooxazole ring, a triazaindolidine ring, a diazaindolidine ring or a tetraazaindolidine ring. Of these are preferred an imidazole ring, a tetrazole ring, a thiazole ring, an oxazole ring, a benzimidazole ring, a benzthiazole ring, a benzoxazole ring and a triazole ring.

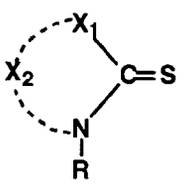
[0038] Further, the compound represented by formula (1) does not include a compound having, in part, the following structure:



wherein R represents a hydrogen atom or a substituent.

Furthermore, the compound represented by formula (1) is preferably represented by the following formula (1'):

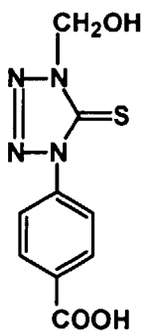
formula (1')



wherein X_1 represents NR', O or S, in which R' represents a substituent; R represents a hydrogen atom or substituent; and X_2 is the same as defined in X of formula (1) described above. The substituent represented by R or R' include an alkyl group or aryl group, each of which may be substituted.

[0039] Examples of the compound represented by formula (1) are

(1—1)



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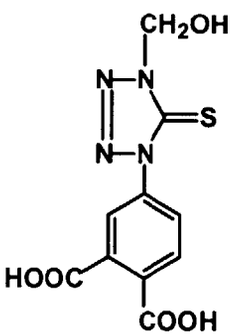

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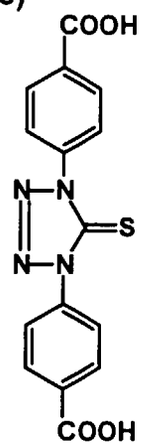

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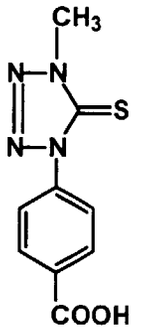

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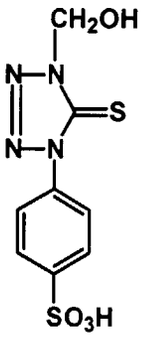
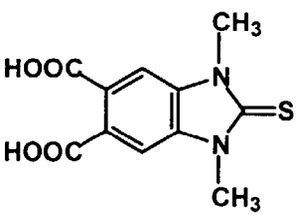


(1—6)



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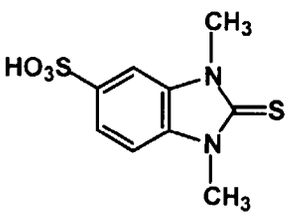

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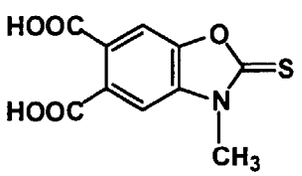

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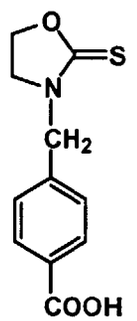

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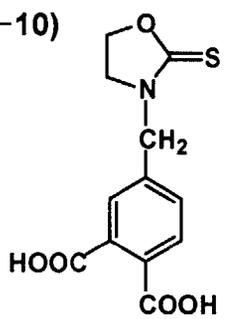

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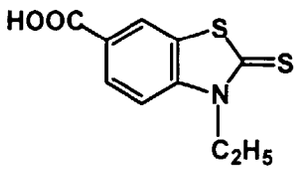

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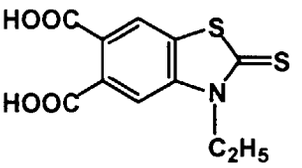

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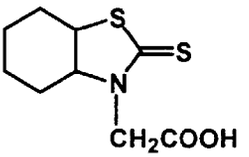
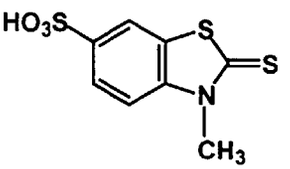


(1—14)

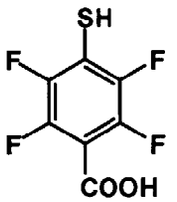


[0040] These compounds can be synthesized by referring to U.S. Patent 2,585,388 and 2,541,924; JP-B 42-21842; JP-A 53-50169; British patent 1,275,701; D.A. Berges et al., Journal of Heterocyclic Chemistry, 15, 981 (1978); "The Chemistry of Heterocyclic Compounds" Imidazole and Derivatives part I, p.336-339; Chemical Abstract, 58, 7921 (1963); E. Hoggarth, Journal of Chemical Society, p.1160-1167 (1949), S.R. Saudler, W. Karo "Organic Functional Group Preparation" Academic press, p.312-315 (1968); M. Chamdon, et al., Bulletin de la Societe Chimique de France, 723 (1954); D.A. Ahirley, D.W. Alley, J. Amer. Chem. Soc. 79, 4922 (1954); A. Wohl, W. Marchwald Ber., 22, 568 (1889); J. Amer. Chem. Soc. 44, p.1502-1510; U.S. Patent 3,017,270; British patent 940,169; JP-B 49-8334; JP-A 55-59463; "Advances in Heterocyclic Chemistry", West German patent 2,716,707; "The Chemistry of Heterocyclic Compounds Imidazole and Derivatives", 1, p.385; "Org. Synth." IV, 569 (1963); Ber., 9, 465 (1976); J. Amer. Chem. Soc. 45, 2390 (1923); JP-A 5089034; 53-28426 and 55-21007; and JP-B 40-28496. Next, the compound represented by formula (2) or (3) will be described. In the formula (2) or (3), (A_1) and (A_1)' represent-SO_3M, -COOM, -OM or a N-attached oxide group, in which M represents a metal, preferably, an alkali metal or a transition metal capable of bonding with sulfur, selenium or tellurium, such as silver, gold or palladium. The electron-withdrawing group represented by (A_2) and (A_2) is preferably a fluorine atom, trifluoromethyl group, cyano group, nitro group, -SO_2NH_2, or -SO_2CH_3. (A_3) and (A_3)' is a functional group containing a sulfur atom, selenium atom or tellurium atom, which is capable of bonding with a silver ion. Preferred examples of (A_3) and (A_3)'include a mercapto group (-SH), thione group (=S), -SeH and =Se. The aliphatic hydrocarbon carbon group represented by Y preferably has 4 to 10 carbon atoms, including buty and pentyl. The aromatic hydrocarbon ring grpup represented by Y is preferably a benzene ring or a naphthalene ring.

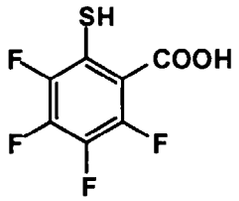
[0041] The compound represented by formula (2) or (3) may be substituted by a substituent ,such as a halogen atom except for fluorine, hydroxy, amino, acylamino, alkylamino, alkyl, alkenyl, cycloalkyl, aryl, alkoxy, aryloxy, alkylthio, alkoxycarbonyl, carbamoyl, alkoxyalkyl, aminoalkyl, acylaminoalkyl, hydroxyalkyl, carboxyalkyl, sulfoalkyl or alkylsulfonamido. These compounds can be synthesized by reference to J. Chem. Soc. Sect. C, p.626 (1965) & p.1347 (1971); J. Org. Chem. 34 534 (1969); JP-A 60-184057 and 60-204742, and is also commercially available.

[0042] The compound represented by formula (2) or (3) is exemplarily shown below, but is nor limited to these examples.

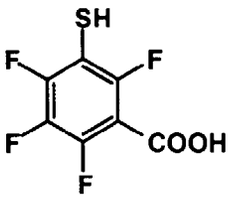
(2—1)



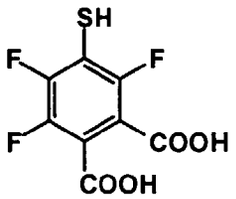
(2—2)



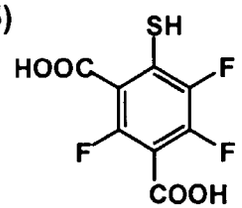
(2—3)



(2—4)



(2—5)



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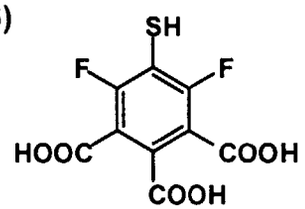
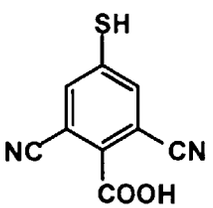
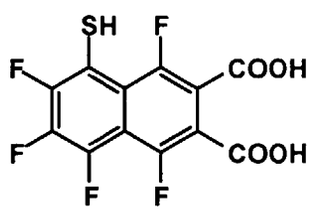


(2—7)



(2—8)



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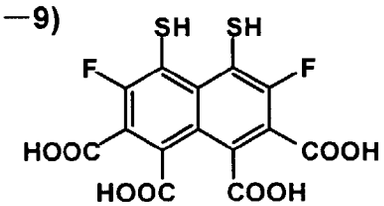
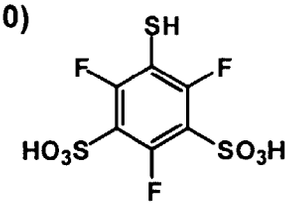
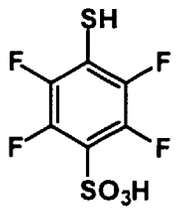


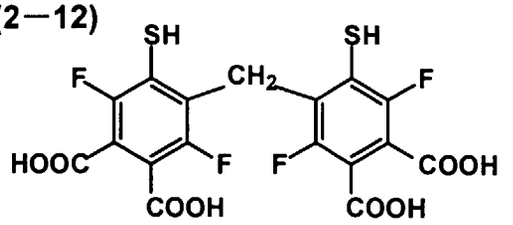
(2—10)



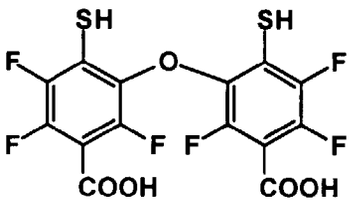
(2—11)



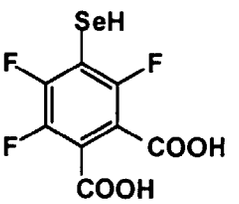
(2—12)



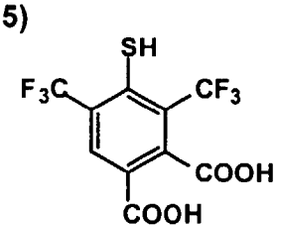
(2—13)



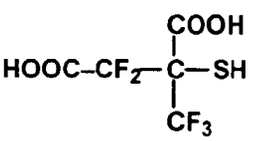
(2—14)



(2—15)



(2–16)



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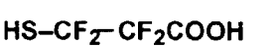

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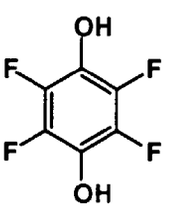
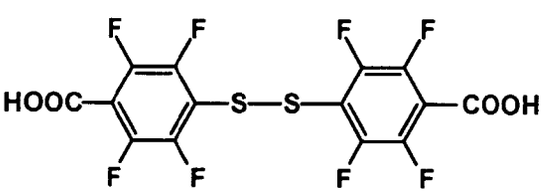
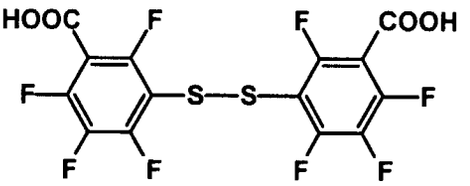


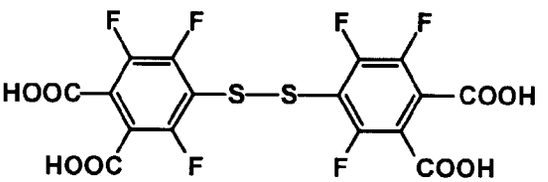
(3—1)



(3—2)



(3—3)



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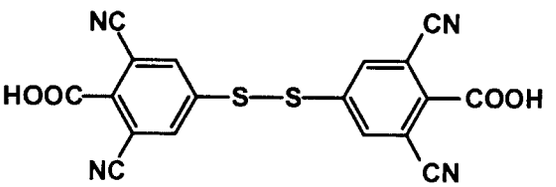
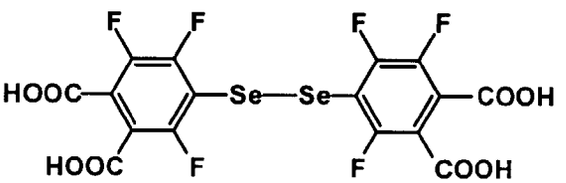
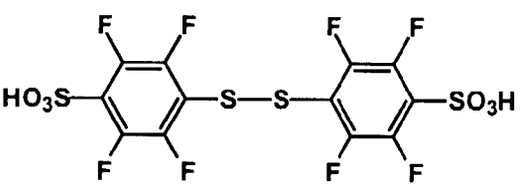


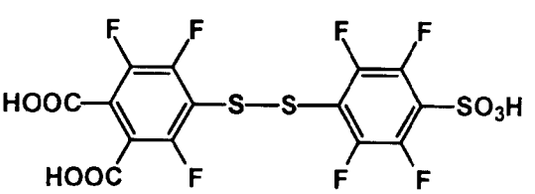
(3—5)



(3—6)



(3—7)



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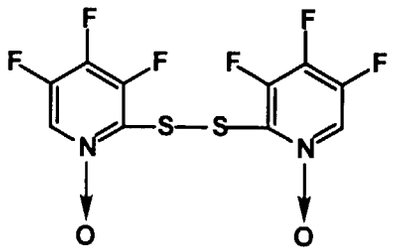
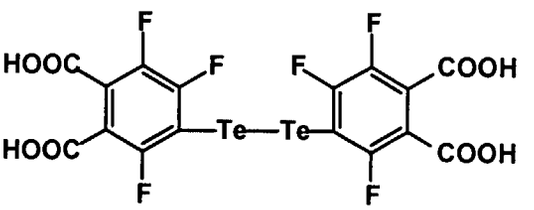


(3—9)



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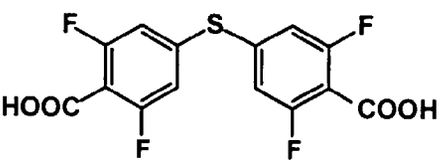

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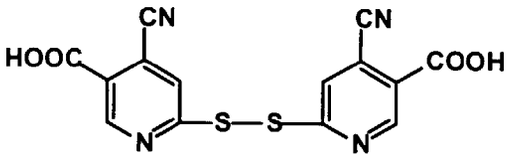

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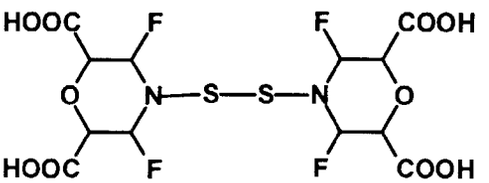

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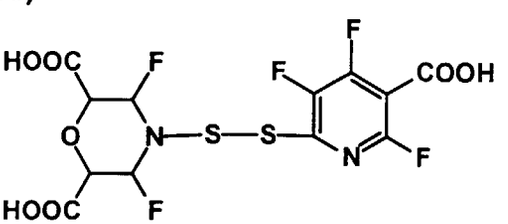
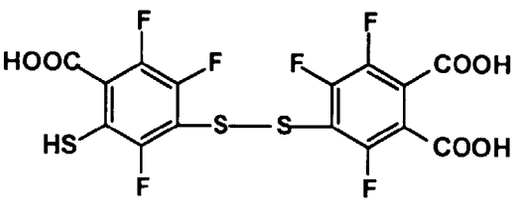


(3—14)



[0043] The compound represented by formula (1), (2) or (3) can be added before, during or after chemical sensitization. When added before completion of chemical sensitization, enhanced effects can be obtained, and when added separately before and after completion of chemical sensitization, further enhanced effects can be obtained. Each of the compound can be added, singly or in combination, and can also be added in combination with other inhibitors. The compound can be added in the form of powder or through solution in water, a low boiling solvent such as methanol, ethanol or ethyl acetate, or a mixture of water and the low boiling solvent. To enhance solubility, a pH adjusting agent may be optionally added. In some cases, the compound is added in the form of a dispersion of fine solid particles, resulting in enhanced effects. In any cases, the addition amount is preferably 0.01 to 0.5 g, and more preferably 0.02 to 0.2 g per mol of silver halide.

[0044] The silver halide emulsion according to the invention is subjected to at least one of sulfur sensitization, selenium sensitization and tellurium sensitization, in the presence of a spectral sensitizing dye represented by formula (4).

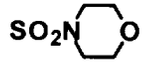
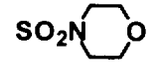
[0045] A spectral sensitizing dye is adsorbed to silver halide grains and contributes to sensitization. It is preferred that when the sensitizing dye represented by formula (4) is allowed to adsorbed to silver halide emulsion grains and its reflection spectrum is measured, the maximum absorption wavelength of J-band is not more than 550 nm. In application of the spectral sensitizing dye relating to the invention to X-ray photographic materials for medical use which employ a phosphor emitting green light, when the dye is allowed to adsorbed to silver halide emulsion grains and its reflection spectrum is measured, J-band is formed preferably in the same wavelength region as the green light emitted from the phosphor. Thus, it is necessary to select a spectral sensitizing dye so as to form the J-band having an absorption maximum in a range of 520 to 555 nm, preferably 530 to 553 nm and more preferably, 540 to 550 nm.

[0046] In the formula (4), the alkyl group represented by R_1 and R_3 includes straight-chained or branched one (preferably, a lower alkyl group having 1 to 6 carbon atoms), such as ethyl, butyl or 3-methylbutyl. Examples of the substituted alkyl group include 2-hydroxyethyl, 2-methoxyethyl, 2-ethoxyethyl, ethoxycarbonylethyl, phenethyl, methanesulfonylethyl and 3-oxobutyl. Examples of the alkenyl group include vinyl and allyl. The alkyl group represented by R_2 and R_4 includes straight-chained or branched one, such as methyl, ethyl, butyl or isobutyl. The hydrophilic group contained in the alkyl group include sulfo group, carboxy group, methanesulfonylaminocarbonyl group, methanesulfonylamino-sulfonyl group, acetylaminosulfonyl group, sulfoamino group, trifluoroacetylaminosulfonyl group, acetylaminocarbonyl group, and N-methylsulfamoyl group. Examples thereof include 2-sulfoethyl, 3-sulfopropyl, 3-sulfobutyl, 5-sulfopentyl, 2-N-ethyl-N-sulfoaminoethyl, carboxymethyl, carboxyethyl, 3-sulfoaminopropyl, 6-sulfo-3-oxahexyl, 10-sulfo-3,6-dioxadecyl, 6-sulfo-3-thiahexyl, o-sulfobenzyl, p-carboxybenzyl, methnesulfonylaminocarbonylmethyl and acetylaminosulfonyl-methyl.

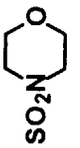
[0047] Z_1, Z_2, Z_3 and Z_4 independently represent a hydrogen atom or a substituent. Examples of the substituent include a halogen atom, an alkyl group (e.g., a lower alkyl having 1 to 5 carbon atoms, such as methyl, ethyl propyl), an alkoxy group (e.g., methoxy, ethoxy proxy), a halogen-substituted alkoxy group (e.g., fluoromethyl, trifluoromethyloxy, 2,2,2-trifluoroethyloxy), an aryloxy group (e.g., phenoxy, p-bromophenoxy), an acyl group (e.g., acetyl, benzoyl), an acyloxy (e.g., acetyloxy, propionyloxy), an alkylthio group (e.g., methylthio, ethylthio), a halogen-substituted alkylthio group (e.g., trifluoromethylthio, difluoromethylthio), an alkoxycarbonyl group (e.g., methylcarbonyl, ethoxycarbonyl), a carbamoyl group (e.g.,carbamoyl, N-methylcarbamoyl, N,N-dimethylcarbamoyl, N,N-diethylcarbamoyl, N,N-3-oxapentamethylenecarbamoyl, N-phenylcarbamoyl), a sulfamoyl group (e.g., N-methylsulfamoyl, N,N-tetramethylenesulfamoyl, N,N-3-oxapentamethylensulfamoyl, N-phenylsulfamoyl, N,N-diethylsulfamoyl), a halo-alkyl group (e.g., monofluoromethyl, difluoromethyl, trifluoromethyl, monochloromethyl), a sulfonyl group (e.g., methanesulfonyl, ethanesulfonyl, trifluoromethanesulfonyl, fluorosulfonyl, benzenesulfonyl, p-toluenesulfonyl), an acylamino group (e.g., N-acetylamino, N-trifluoroacetylamino), substituted or unsubstituted aryl group (e.g., phenyl, o-fluorophenyl, p-cyanophenyl, m-chlorophenyl), a heterocyclic group (e.g., 1-pyrrolyl, 2-furyl, 2-benzooxazolyl).

[0048] X_1^- represents an ion necessary for neutralizing the charge within the spectral sensitizing dye, including an anion and a cation. Examples of the anion include a halide ion, perchlorate, ethylsulfatethiocyanate, p-toluenesulfonate and perfluoroborate. Examples of the cation include a hydrogen ion, an alkali metal ion (e.g., lithium, sodium and potassium ions), alkali earth metal ion (e.g., magnesium and calcium ions), ammonium ion and an organic ammonium ion (e.g., triethylammonium, triethanolammonium, and tetramethylammonium ions).

[0049] Exemplary examples of the spectral sensitizing dye represented by formula (4) are shown below, but the dye is not limited to these examples.

No.	R_1	R_2	R_3	R_4	Z_1	Z_2	Z_3	Z_4	X_1
4—1	CH_3	$(CH_2)_4SO_3^-$	CH_3	C_2H_5	H	SCH_3	H	SCH_3	—
4—2	CH_3	CH_3	CH_3	$(CH_2)_3SO_3^-$	CH_3	CH_3	H	CF_3	—
4—3	C_2H_5	$(CH_2)_3SO_3^-$	CH_3	C_2H_5	H	CF_3	H	CF_3	—
4—4	CH_3	$(CH_2)_4SO_3^-$	CH_3	C_2H_5	SCH_3	CF_3	SCH_3	CF_3	—
4—5	CH_3	C_2H_5	CH_3	$(CH_2)_3SO_3^-$	SCH_3	CF_3	SCH_3	CF_3	—
4—6	CH_3	CH_2COOCH_3	C_2H_5	$(CH_2)_3SO_3^-$	H	CF_3	H	CF_3	—
4—7	C_2H_5	$(CH_2)_3SO_3Na$	C_2H_5	$(CH_2)_3SO_3^-$	H	$COOC_4H_9$	H	$COOC_4H_9$	—
4—8	CH_3	$(CH_2)_4SO_3^-$	C_2H_5	CH_2CF_3	CH_3	CF_3	CH_3	CF_3	—
4—9	CH_3	CH_2CF_3	CH_3	$(CH_2)_4SO_3^-$	H	CF_3	H	CF_3	—
4—10	CH_3	CH_2CF_3	CH_2	$CH_2-CHC_2H_5$ (with SO_3^-)	H	CF_3	H	CF_3	—
4—11	CH_3	$(CH_2)_3SO_3^-$	C_2H_5	CH_2CF_3	H	CF_3	H	CF_3	—
4—12	CH_3	$(CH_2)_3SO_3Na$	C_2H_5	$(CH_2)_3SO_3^-$	H	CF_3	H	CF_3	—
4—13	CH_3	$(CH_2)_3SO_3Na$	CH_3	$(CH_2)_3SO_3^-$	H	CF_3	H	CF_3	—
4—14	C_2H_5	$(CH_2)_4SO_3Na$	CH_3	$(CH_2)_4SO_3^-$	H		H		—
4—15	CH_3	$(CH_2)_3SO_3^-$	$CH_2CH=CH_2$	CH_2COOH	H	CF_3	H	CF_3	$HN^+(C_2H_5)_3$
4—16	CH_3	$(CH_2)_3SO_3^-$	C_2H_5	C_2H_5	H	CF_3	H	CF_3	—
4—17	CH_3	$(CH_2)_3SO_3^-$	C_2H_4OH	CH_2COOH	H	CF_3	H	CF_3	$HN^+(C_2H_5)_3$

No.	R_1	R_2	R_3	R_4	Z_1	Z_2	Z_3	Z_4	X_1
4—18	$CH=CH_2$	$(CH_2)_3SO_3^-$	CH_3	$(CH_2)_3SO_3Na$	H	CF_3	H	CF_3	—
4—19	$CH=CH_2$	$(CH_2)_3SO_3^-$	$CH=CH_2$	$(CH_2)_3SO_3Na$	Cl	CF_3	H	CF_3	—
4—20	$CH=CH_2$	$(CH_2)_3SO_3^-$	C_2H_5	$(CH_2)_3SO_3Na$	H	CF_3	H	CF_3	—
4—21	CH_3	$(CH_2)_3SO_3^-$	C_2H_5	$(CH_2)_3SO_3Na$	H	Cl	H	SO_2N	—
4—22	C_2H_5	$(CH_2)_3SO_3^-$	C_2H_5	$(CH_2)_3SO_3Na$	Cl	Cl	H	SO_2N	—
4—23	CH_3	$(CH_2)_3SO_3^-$	C_2H_5	CH_2CF_3	Cl	H	Cl	SO_2N	—
4—24	C_2H_5	$(CH_2)_3SO_3^-$	CH_3	CH_2CF_3	CF_3	CF_3	CF_3	SO_2N	—
4—25	CH_3	$(CH_2)_3SO_3^-$	C_2H_5	$(CH_2)_3SO_3Na$	CF_3	SO_2CF_3	CF_3	H	—
4—26	$CH=CH_2$	$(CH_2)_3SO_3^-$	CH_3	$(CH_2)_3SO_3Na$		H	H	CF_3	—
4—27	$CH=CH_2$	$(CH_2)_3SO_3^-$	CH_3	$(CH_2)_3SO_3Na$	Cl	CF_3	H	SO_2CF_3	—

No.	R_1	R_2	R_3	R_4	Z_1	Z_2	Z_3	Z_4	X_1
4—28	$CH=CH_2$	CH_2CF_3	C_2H_5	$(CH_2)_3SO_3^-$	Cl	Cl	H	CF_3	—
4—29	CH_3	$(CH_2)_3SO_3^-$	C_2H_5	$(CH_2)_3SO_3Na$	Cl	Cl	H		—
4—30	$CH_2CH=CH_2$	$(CH_2)_2CF_3$	CH_3	$(CH_2)_3SO_3^-$	CF_3	CF_3	H		—
4—31	$CH=CH_2$	$(CH_2)_3SO_3^-$	$C_2H_4OCH_3$	$(CH_2)_2CF_3$	H	Cl	H	CF_3	—
4—32	$CH=CH_2$	$(CH_2)_3SO_3^-$	CH_3	C_2H_5	H	CF_3	H	CF_3	—
4—33	CH_3	$(CH_2)_3SO_3^-$	C_2H_5	$(CH_2)_3SO_3Na$	CF_3	SO_2CF_3	CF_3	SO_2CF_3	—
4—34	$CH=CH_2$	$(CH_2)_3SO_3^-$	CH_3	$(CH_2)_3SO_3Na$	Cl	H	CF_3	SO_2CF_3	—
4—35	$CH=CH_2$	$(CH_2)_4SO_3^-$	CH_3	$(CH_2)_3SO_3Na$	Cl	CF_3	H	CF_3	—

[0050] These spectral sensitizing dyes each can be employed in combination with other spectral sensitizing dyes. Examples of the due employed in combination include a cyanine dye, a merocyanine dye, a complex cyanine dye, a complex merocyanine dye, a holopolar cyanine dye, a hemi-cyanine dye, a styryl dye and a hemioxonol dye. Of these dyes are useful a cyanine dye, merocyanine dye and a complex merocyanine dye. To these dyes are applicable any one of nuclei conventionally used, including a pyrroline nucleus, a oxazoline nucleus, a pyrrol nucleus, a an oxazole

nucleus, a thiazole nucleus, a selenazole nucleus, imidazole nucleus, tetrazole nucleus and pyridine nucleus. There are also applicable nuclei in which the nucleus described above is condensed with an aliphatic hydrocarbon ring, including an indolenine, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthooxazole nucleus, a benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus, benzimidazole nucleus and quinoline nucleus. These nuclei may be substituted. In the merocyanine dye and complex merocyanine dye, a nucleus having a ketomethine structure is applicable, including 5 or 6-membered heterocyclic nucleus such as a pyrazoline-5-one nucleus, a thiohydantoin nucleus, a 2-thiooxazolidine-2,4-dione nucleus, a thiazoline-2,4-dione nucleus, a rhodanine nucleus and a thiobarbituric acid nucleus. The dyes are described in German Patent 929,080; U.S. Patent 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 3,655,394, 3,656,959, 3,672,897 and 3,649,217; British Patent 1,242,588 and JP-B 44-14030.

[0051] The adding amount of the spectral sensitizing dye, depending on the kind of the dye, and structure, composition, ripening conditions, objectives and uses of silver halide, is preferably in such an amount as to be 30 to 90% of monomolecular layer coverage, and more preferably, 40 to 80%. The monomolecular layer coverage refers to a relative value, based on that, when absorption isotherm at 50° C is prepared, a saturated absorbing amount is 100% of the coverage. The optimal amount of the spectral sensitizing dye, which is variable, depending on the total surface area of silver halide grains contained in an emulsion, is less than 600 mg and preferably less than 450 mg per mol of silver halide. Furthermore, the proportion of the dye represented by formula (4) is preferably not less than 30% of the total dye to enhance sensitivity and improve residual dye stain.

[0052] As a solvent for the sensitizing dye are usable conventionally employed water-miscible organic solvents, including alcohols, ketones, nitriles, and alkoxyalcohols. examples thereof include methanol, ethanol, n-propyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol, 1,3-propanediol, acetone, acetonitrile, 2-methoxyethanol and 2-ethoxyethanol.

[0053] Surfactants have been conventionally employed as a dispersing agent. In the invention is also usable any type of surfactants, including an anionic type, cationic type, nonionic type and amphoteric type.

[0054] According to the invention, advantageous effects are enhanced by adding the sensitizing dye in the form of an acidic solution or a solid fine particle dispersion rather than in the form of an organic solvent solution. At least one sensitizing dye is preferably added in the form of scarcely water-soluble, solid fine particles dispersed in water substantially free from an organic solvent and/or surfactant, allowing the dye to be adsorbed uniformly and effectively onto the surface of silver halide grains.. The expression, "water substantially free from an organic solvent and/or surfactant" refers to water containing impurities less than an extent of not exerting an unfavorable influence upon a silver halide emulsion. It is preferably deionized water or distilled water.

[0055] Solubility in water of the sensitizing dye used in the invention is preferably $2x10^{-4}$ to $4x10^{-2}$, and more preferably $1x10^{-3}$ to $4x10^{-2}$. When the solubility is less than this range, sizes of dispersed particles become larger and inhomogeneous, leading to formation of precipitate of a dispersing material or to interference with adsorption of the sensitizing dye to silver halide, when the dispersion is added into a silver halide emulsion. When the solubility is larger than this range, on the other hand, viscosity of the dispersion becomes larger than that needed and bubbles are incorporated, resulting in interference with dispersion, and when the solubility is still larger, the dispersion becomes impossible. The solubility of the sensitizing dye can be determined in accordance with the following procedure.

[0056] To a conical flask with a volume of 50 ml was added deionized water of 30 ml, a dye was added thereto in excess of soluble amounts and stirred with a magnetic stirrer for 10 min., while maintaining a temperature of 27° C in a thermostat. The suspension was filtered through filter paper No. 2 (available from Toyo Corp.), and the filtrate was optimally diluted and the absorbance thereof was measured by a spectrophotometer. From the measurement result, the solution concentration was determined in accordance with Beer-Lambert law to determine the solubility, as follows:

$$D = \varepsilon$$

where D is absorbance, ε is extinction coefficient, l is a length of an absorption measuring cell, and c is a concentration (mol/l).

[0057] The sensitizing dye used in the invention can be added in the process of chemical sensitization, preferably at the start of chemical sensitization. Addition of the dye during the course of nucleation of a silver halide emulsion to completion of washing results in a sensitive silver halide emulsion with enhanced spectral sensitization efficiency.

[0058] Sulfur sensitizers usable in the invention include those as described in U.S. Patent 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313 and 3,656,955; German patent (OLS)1,422,869; JP-A 56-24937 and 55-45016. Preferred examples thereof include thiourea derivatives such as 3-diphenylthiourea, triethylthiourea and 1-ethyl-3-(2-thiazolyl)thiourea; rhodanine derivatives, dithiacarbamates, polysulfide organic compounds and sulfur single body. The sulfur single body is preferably rhombic α-sulfur. The amount of the sulfur sensitizer to be added, depending on the kind of a silver halide emulsion, the kind of the compound and ripening conditions, is $1x10^{-9}$ to $1x10^{-4}$ mol, and preferably

$1x10^{-8}$ to $1x10^{-5}$ mol per mol of silver halide.

[0059] Selenium sensitizers usable in the selenium sensitization include a variety of selenium compounds, as described in U.S. Patent 1,574,944, 1,602,592 and 1,623,499; and JP-A 60-150046, 4-25832, 4-109240 and 4-147250. Examples thereof include colloidal selenium metal, isoselenocyanates (e.g., allylisoselenocyanate), selenoureas (e.g., N,N-dimethylselenourea, N,N,N'-triethylselenourea, N,N,N'-trimethyl-N'-heptafluoroselenourea, N,N,N'-trimethyl-N'-heptafluoropropylcarbonylselenourea, N,N,N'-trimethyl-N'-4-nitrophenylcarbonylselenourea), selenoketones (e.g., selenoacetone, selenoacetophenone), selenoamides (e.g., selenoacetoamide, N,N-dimethylselenobenzamide), selenocarboxylic acids and selenoesters (e.g., 2-selenopropionic acid, methyl-3-selenobutylate), selenophosphates (tri-p-triselenophosphate), and selenides (e.g., triphenylphosphine selenide, diethyl selenide, diethyl diselenide). Of these sensitizers, selenoureas, selenoamides and selenoketones are preferred. The amount of the selenium sensitizer to be used, depending on a selenium compound, silver halide grains and chemical ripening conditions, is generally 10^{-8} to 10^{-4} mol per mol of silver halide. The temperature of chemical sensitization with the selenium sensitizer is preferably 40 to 90° C and more preferably 45 to 80° C. The pH and pAg is preferably 4 to 9 and 6 to 9.5, respectively.

[0060] Tellurium sensitizer and its sensitization method is disclosed in U.S. Patents 1,623,499, 3,320,069, 3,772,031, 3,531,289 and 3,655,394; British Patents 235,211, 1,121,496, 1,295,462 and 1,396,696; Canadian patent 800,958; and JP-A 4-204640 and 4-333043. Examples of useful tellurium sensitizers include tellurureas (e.g., N,N-dimethyltellurourea, tetramethyltellurourea, N-carboxyethyl-N,N'-dimethyltellurourea, N,N'-dimethyl-N'-phenyltellurourea), phosphine tellurides (e.g., tributylphosphine telluride, tricyclohexylphosphine telluride, triisopropylphosphine telluride, butyl-diisopropylphosphine telluride, dibutylphenylphosphine telluride), telluroamides (e.g., telluroacetoamide, N,N-dimethyltellurobenzamide), telluroketones, telluroesters and isotellurocyanates.

[0061] Chemical sensitization other than the sulfur sensitization, selenium sensitization and tellurium sensitization can be employed in combination. There is no limitation with respect to the condition in the process of chemical sensitization, such as pH, pAg, temperature and time, and chemical sensitization is performed under conditions employed in the art. The combined chemical sensitization includes reduction sensitization by the use of a reducing material and noble metal sensitization by the use of gold or other noble metals. Of these, gold sensitization and reduction sensitization are preferable. Examples of gold sensitizers include chloroauric acid, gold thiosulfate, gold thiocyanate, and gold complexes of various compounds such as thioureas and rhodanines. The amount of the gold sensitizer to be used is the same as that of the sulfur sensitizer.

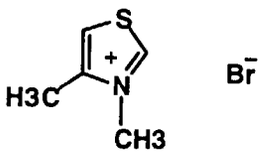
[0062] The sensitizer described above can be incorporated through solution in water, alcohols, or organic or inorganic solvents, or incorporated in the form of a dispersion employing water-insoluble solvents or a medium such as gelatin. Sensitization can be simultaneously applied, or separately and stepwise applied. It is also preferable to subject the grain surface to reduction sensitization by allowing to be stood under optimal reducing conditions. Examples of preferable reducing agents include thiourea dioxide, ascorbic acid and its derivatives, polyamines such as hydrazine and diethylenetriamine, dimethylamine boranes and sulfites.

[0063] The silver halide emulsion according to the invention is chemically sensitized preferably in the presence of the compound represented by formula (5). In the formula (5), Z_5 represents an atomic group necessary for forming a 5- or 6-membered nitrogen-containing heterocyclic ring, including thiazoliums {e.g., thiazolium, 4-methylthiazolium, benzothiazolium, 5-methylbenzothiazolium, 5-chlorobenzothiazolium, 5-methoxybenzothiazolium, 6-methylbenzothiazolium, 6-methoxybenzothiazolium, naphtho[1,2-d]thiazolium, naphtho[2,1-d]thiazolium}, oxazoliums {e.g., oxazolium, 4-methyloxazolium, benzooxazolium, 5-chlorobenzooxazolium, 5-phenylbenzooxazolium, 5-methylbenzooxazolium, naphtho[1,2-d]oxazolium}, imidazoliums (e.g., 1-methylbenzimidazolium, 1-propyl-5-chlorobenzimidazolium, 1-ethyl-5,6-dichlorobenzimidazolium, 1-allyl-5-trichloromethyl-6-chloro-benzimidazolium), selenazoliums {e.g., benzopselenazolium, 5-chlorobenzoselenazolium, 5-methylbenzoselenazolium, 5-methoxybenzoselenazolium, naphtho [1,2-d]selenazolium}. Of these are preferred thiazoliums, especially, benzoselenazolium and naphthothiazolium.

[0064] The alkyl group represented by R_5 is preferably a lower alkyl group having 1 to 5 carbon atoms. The alkenyl group represented by R_5 is preferably vinyl or allyl. The lower alkyl group represented by R_6 is one having 1 to 5 carbon atoms. The anion represented by X is preferably an acid anion, such as a hydrohalogenic acid anion (e.g., Cl^-, Br^-, I^-).

[0065] Exemplary examples of the compound represented by formula (5) are shown below, but the compound is not limited to these examples.

(5–1)



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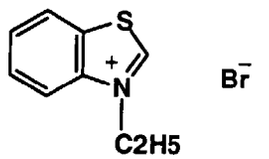

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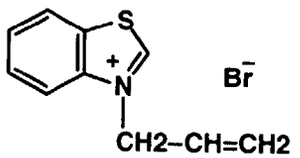

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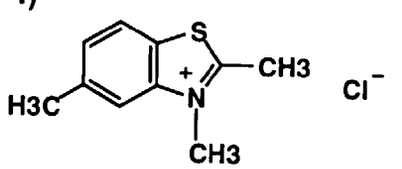

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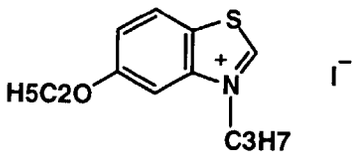

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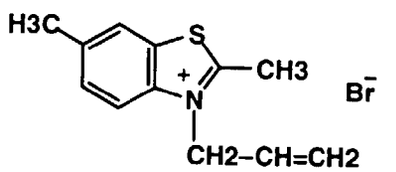

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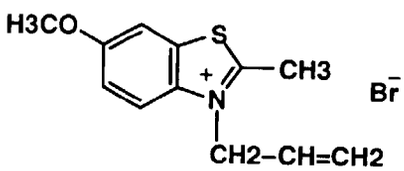

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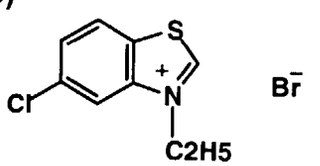

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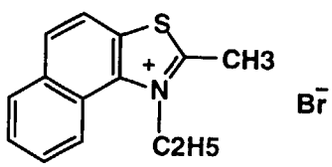

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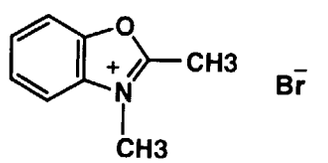

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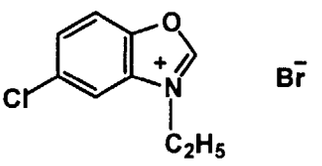

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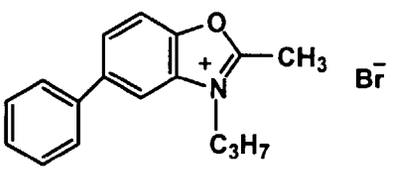

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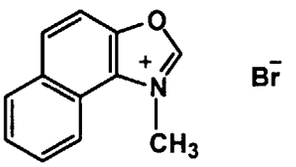

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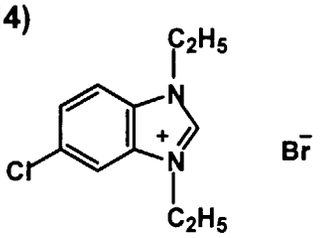

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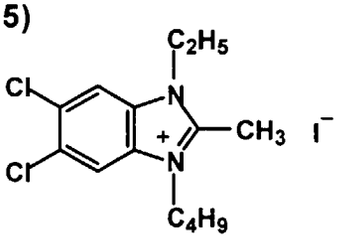

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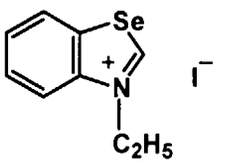

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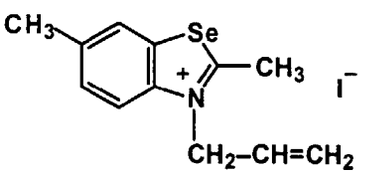

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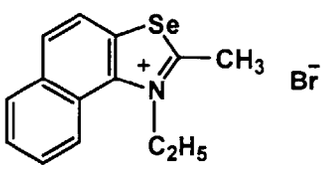

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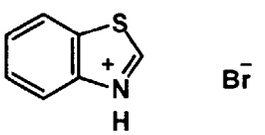
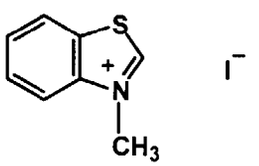


(5–20)



[0066] These compounds each can be employed in an amount of 10 to 5 g per mol of silver halide, and incorporated by directly dispersing in the emulsion or through solution in an appropriate solvent (e.g., water, methanol, ethanol,

propanol, methyl cellosolve, acetone). Further the compound can also be incorporated in a manner similar to the sensitizing dye.

[0067] Dyes usable in the photographic material according to the invention are preferably those which are substantially water-insoluble at a pH of 7 or less and water-soluble at a pH of not less than 8. The addition amount, which is variable according to aided sharpness, is preferable 0.2 to 20 mg/m^2, and more preferably 0.8 to 15 mg/m^2. Examples thereof are described in German patent 616,007; British Patents 584,609 and 1,177,429; JP-B 26-7777, 39-22969 and 54-38129; JP-A 48-85130, 49-99620, 49-114420, 49-129537, 50-28827, 52-108115, 57-185038, 2-282244 and 4-307539; U.S. Patents 1,878,961, 1,884,035, 1,912,797, 2,098,891, 2,150,695, 2,274,782, 2,298,731, 2,409,612, 2,461,484, 2,527,583, 2,533,472, 2,865,752, 2,956,879, 3094,418, 3,125,448, 3,148,187, 3,177,078, 3,247,127, 3,260,601, 3,282,699, 3,409,433, 3,549,887, 3,575,704,3,653905, 3,718,472, 3,865,817, 4,070,352 and 4,071,312; PB Report No. 74175; and PHOTO. ABS. 1, 28 (721).

[0068] A variety of photographic adjuvants can be employed in the photographic material relating to the invention. The known adjuvants include compounds described in Research Disclosure No. 17643 (1978, December), ibid No. 18716 (1979, November), and ibid No. 308119 (1089, December). The photographic material can contain, in an emulsion layer or other layers, a developing agent such as aminophenol, ascorbic acid, pyrocatechol, hydroquinone, phenylenediamine or 3-pyrazolidone. Supports usable in the photographic material include those described in above-described RD-17643 at page 28, and RD-308119 at page 1009. The surface of the support may be provided with a sub-layer or be subjected to corona discharge or UV exposure to improve adhesion property of coating layers. The sub-layer preferably contain an antistatic agent such as a colloidal tin oxide sol.

[0069] When the photographic material relating to the invention is employed for the use in X-ray photographing, enhanced sensitivity and sharpness and superior processability can be achieved by providing, on both sides of the support, a silver halide emulsion layer and a cross-over light cutting layer. The total amount of gelatin used in the silver halide emulsion layer, a surface protective later and other layer(s), per one side, is preferably 0.5 to 3.5 g/m^2, and more preferably 1.5 to 3.0 g/m^2. There are preferably employed photographic latexes comprised of photographically inert surfaces having no interaction with various kinds of photographic additives, that is, the surfaces do not adsorb any dye or dyestuff, resulting in no stain and do not also adsorb any development accelerator or inhibitor, leading to no adverse effects on sensitivity or fog.

[0070] The silver halide photographic material relating to the invention can be processed by the use of a solid processing composition, such as powdered processing composition or solid processing compositions in the form of a tablet, a pellet or granules. The powder is referred to an aggregate comprised of fine crystal particles. The granules is referred to granular material prepared by subjecting the powder to granulating process, having particle sizes of 50-5000 μm. The tablet is one prepared by subjecting the powder or granules to compression-molding to a given form.

[0071] The processing composition can be solidified in such a manner that the processing composition, in the form of a concentrated solution, fine powder or granules, is mixed with a water soluble bonding agent and then the mixture is molded, or the water soluble bonding agent is sprayed on the surface of temporarily-molded processing composition to form a covering layer. Further, the solid processing composition is preferably in the form of a tablet. A preferred tablet-making process is to form a tablet by compression-molding after granulating powdery processing composition. Granulation can be performed by the known method, such as rolling granulation, extrusion granulation, compression granulation, grinding granulation, stirring granulation, fluidized bed granulation and spray-drying granulation.

[0072] It is preferred that the average grain size of the granules is 100 to 800 μm and preferably 200 to 750 μm. In particular, 60% or more of the granules is with a deviation of ± 100 to 150 μm.

[0073] As hydraulic press machine, any conventional compression molding machine, such as a single-engine compression molding machine, rotary-type compression machine, briquetting machine, etc. may be employed to form a tablet. Compression-molded (compression-tableted) solid processing composition may take any form and is preferably in a cylindrical form from the point of productivity, handleability and problems of powder dust in cases when used in user-side. It is further preferred to granulate separately each component, such as an alkali agent, reducing agent and preservative in the above process.

[0074] The solid processing composition can be used as not only a developer or fixer but also a photographic processing chemicals such as a rinsing agent. Particularly when used as a developer, effects of stabilizing photographic performance are marked.

[0075] As for the means for supplying a solid processing composition to a processing tank in the invention, and in the case where the solid processing chemical is of the tablet type, for example, there are such a well-known means as described in Japanese Utility Model OPI Publication Nos. 63-137783/1988, 63-97522/1988 and 1-85732/1989, wherein, in short, any means may be used, provided that at least a function for supplying a tableted chemical to a processing tank can be performed. And, in the case where the solid processing chemical is of the granulated or powdered type, there are such a well-known means such as the gravity dropping systems described in JP OPI Publication Nos. 62-81964/1987, 63-84151/1988 and 1-292375/1989, and the screw system described in JP OPI Publication Nos. 63-105159/1987 and 63-84151/1988. A solid processing composition of the invention may be added to any position

inside a processing tank and, preferably, to a position communicated with a section for processing a light-sensitive material and circulating a processing solution between the processing tank and the processing section. It is also preferable to have such a structure that a certain amount of processing solution can be circulated therebetween so that a dissolved component can be moved to the processing section. It is further preferable that a solid processing chemical is added to a thermostatically controlled processing solution.

[0076] A X-ray photographic material prepared by the use of the silver halide emulsion according to the invention is advantageously employed in combination with an intensifying screen with a phosphor filling ratio of 68 to 90%.

EXAMPLES

[0077] The present invention will be explained based on examples, but embodiments of the invention is not limited thereto.

Example 1	
Preparation of Emulsion Em-1	
Solution A1	
Ossein gelatin 10% Ethanol solution of Compound (A) described below Potassium bromide Water to make	56.6 g 0.36 ml 48.2 g 8083 ml
Solution B1	
2.0 N Aqueous silver nitrate solution	1791 ml
Solution C1	
3.5 N Aqueous silver nitrate solution	11505 ml
Solution D1	
4.0 N Aqueous potassium bromide solution	10962 ml
Solution E1	
2.0 N Aqueous potassium bromide solution used for controlling the silver potential	
Solution F1	
Ossein gelatin 10% Ethanol solution of Compound (A) described below Water	245 g 14.12 ml 2264 ml
Solution G1	
Thiosulfonic acid Water to make	1.556 g 156 ml
Solution H1	
Fine grain emulsion comprised of 3 wt.% gelatin and fine silver iodide grains (av. grain size 0.05 μm)* 0.088 mol equivalent	
Solution I1	
Thiourea dioxide Water to make	0.171 g 170 ml
Solution J1	
2,2'-dithio-bis- (pyridine)-N-oxide Water to make	1.556 g 156 ml

[0078] Compound (A):

$$HO(CH_2CH_2O)_n\text{-}[CH(CH_3)CH_l]\text{-}(CH_2CH_2O)_mH \qquad m+n=5\text{-}7$$

[0079] * The silver iodide fine grain emulsion (H1) was prepared in the following manner. To 6.64 1 of 5.0 wt.% gelatin aqueous solution containing 0.06 mol of potassium iodide were added 2.0 l of a solution containing 7.06 mol of silver nitrate and 2.0 l of a solution containing 7.06 mol of potassium iodide over a period of 10 min, while the pH and temperature were maintained at 2.0 and 40° C. After completing addition, the pH was adjusted to 6.0.

[0080] To solution A1 were added the total amount of solution B1 and 895 ml of solution D1 by the double jet precipitation method for a period of 3 min. 5 sec. to form nucleus grains, with stirring at 55° C by using a mixing stirrer as shown in JP-B 58-58288 and 58-58289. After completing addition of solutions B1 and D1, solution F1 was added thereto and the temperature was raised to 70° C in 30 min. and ripening was carried out. Further, solution C1 of 907 ml was added in 11 min., then 28 % ammonium aqueous solution was added and ripening was further carried out at a pH of 8.2 for 10 min. After completing the ripening, the pH was adjusted with acetic acid so as to be neutral and the total amount of solution I1 was added. Solution C1 and the remainder of solution EI were simultaneously added at an accelerated flow rate (23 ml/min from start to finish at 154 ml/min.) in 134 min., while being maintained at a pAg of 7.8. When the remainder of solution C1 reached 6360 ml, 56% aqueous acetic acid solution was added to adjust the pH to 4.4. At 122 min. after adding solution C1, solution H1 was added in 12 min. so that addition of solutions H1 and C1 completed at the same time. After being stirred for 10 min., the total amount of solution J1 was added at 50° C. Then the temperature was lowered to 40° C and the emulsion was desalted by the flocculation process to remove soluble salts.

[0081] According to electron microscopic observation, it was proved that not less than 90% of the projected area of silver halide grains of the resulting emulsion was accounted for by hexagonal tabular grains having a maximum adjacent edge ratio of 1.0 to 2.0, the average thickness and average diameter (equivalent circle diameter of the hexagonal tabular grains) being 0.18 μm and 0.81 μm, respectively, and the average aspect ratio of 4.5. The width of equivalent circle diameter distribution was 15%.

Preparation of Emulsion Em-2

[0082] Emulsion Em-2 was prepared in the same manner as Em-1, except that solutions I1 and J1 were not added.

Chemical Sensitization

[0083] Subsequently, the emulsions were each divided to a given amount, the temperature was raised to 55° C and fine silver iodide grains of 0.5 mol% was added. Thereafter, the compound represented formula (1), (2) or (3) as shown in Table 1, and spectral sensitizing dyes according to the invention and comparative dye (as shown in Table 1) in the form of solid particle dispersion were added thereto. Further, 10 mg of sodium thiosulfate and 2 mg of triphenylphosphine selenide in the form of fine solid particle dispersion were added, then 105 mg of ammonium thiocyanate and 12.5 mg of chloroauric acid were added and subsequently, ripening was carried out for 2 hr. in total. After completing the ripening, 5 mg of 1-phenyl-5-mercaptotetrazole (PMT) and 200 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (TAI) were added. The addition amount was expressed as per mol of silver halide.

Preparation of tabular iodochloride grains

[0084] Preparation of Emulsion Em-3

Solution A2	
Ossein gelatin	75.0 g
KI	1.25 g
NaCl	33.0 g
Distilled water to make	15000 ml
Solution B2	
Silver nitrate	410 g
Distilled water to make	684 ml
Solution C2	
Silver nitrate	11590 g
Distilled water	19316 ml
Solution D2	
KI	4 g
NaCl	140 g
Distilled water to make	684 ml
Solution E2	
NaCl	3980 g
Potassium hexachloroiridate (IV)	$8x10^{-6}$ mol
Distilled water to make	19274 ml

[0085] To solution A2 were added solutions B2 and D2 at 40° C in 1 min. with stirring by a mixing stirrer described in JP-B 58-58288. The EAg was adjusted to 149 mV, and after ripening for 20 min., solution C2 and E2 were added in 320 min., while the EAg was maintained at 149 mV. After completing addition, the emulsion was washed to remove soluble salts. From microscopic observation, it was proved that the thus prepared emulsion Em-3 was comprised of tabular grains with (100) major faces, accounting for 65% of the total grain projected area and having the average grain thickness of 0.14 μm, the average grain diameter of 1.0 μm and a coefficient of variation of grain diameter of 25%.

Chemical Sensitization

[0086] Subsequently, the emulsion was divided to a given amount, the temperature was raised to 55° C and thiourea dioxide of 4.25 mg was added as a reduction sensitizer. Then, fine silver iodide grains of 0.5 mol% was further added. Thereafter, 2,2'-dithiobis-(pyridine)-N-oxide was added and spectral sensitizing dye (as shown in Table 2) was added in the form of solid particle dispersion. Further, 15 mg of sodium thiosulfate and 3 mg of triphenylphosphine selenide in the form of fine solid particle dispersion were added, then 145 mg of ammonium thiocyanate, 18.5 mg of chloroauric acid and compound represented by formula (1), (2) or (3) were added and subsequently, ripening was carried out for 2 hr. in total. After completing the ripening, PMT of 5 mg and TAI of 100 mg were added. The addition amount was expressed as per mol of silver halide.

[0087] The solid particle dispersion of the sensitizing dyes were prepared according to the method described in JP-A 5-297496. Thus, a given amount of the sensitizing dyes was added into water previously adjusted at 27° C and stirred by means of a high-speed stirrer (dissolver) at 3,500 rpm for 30 to 120 min. to obtain the dispersion.

[0088] Preparation of photographic material sample

[0089] To the emulsion were added the following additives to prepare a coating solution of an emulsion layer. Coating solutions of a protective layer were also prepared, as below. Using these coating solutions, simultaneous double side coating was conducted by two slide-hopper type coating machines at a speed of 80 m/min. so that silver and gelatin coating amounts were respectively 1.6 g/m^2 and 2.5 g/m^2 of one side of a support, and coated web was dried over a period of 2 min. 20 sec. to obtain samples. As a support was employed a blue-tinted polyethylene terephthalate (PET) film base for use in radiography, with a density of 0.13 and a thickness of 175 μm and having thereon a layer mainly comprising glicidylmethaacrylate-methyl methaacrylate-butyl methaacrylate copolymer (50:10:40 by wt.%) and a layer mainly comprised of cross-linked gelatin.

[0090] Additives used in each layer are as follows, provided that the coating amount was expressed as per 1 m^2 of one side of the photographic material.

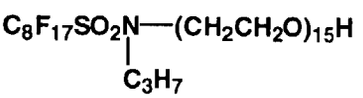
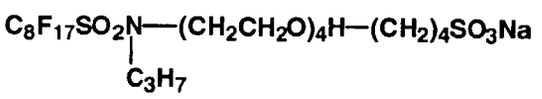
First layer (Dye layer)	
Solid particle dispersion of dye (AHD)	180 mg/m^2
Gelatin	0.2 mg/^{2}
Sodium dodecylbenzenesulfonate	5 mg/m^2
Compound (I)	5 mg/m^2
Sodium 2,4-dichloro-6-hydroxy-1,3,5-triazine	5 mg/m^2
Colloidal silica (av. size 0.014 μm)	10 mg/m^2

Second layer (Emulsion layer)

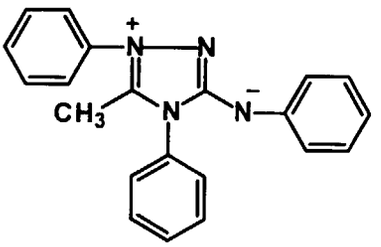
[0091] (The following additives were added to the emulsion above-described.)

Compound (G)	0.5 mg
2,6-Bis (hydroxyamino)-4-diethylamino -1,3,5-triazine	5 mg/m^2
t-Butyl-catechol	130 mg/m^2
Polyvinyl pyrrolidone (M.W. 10,000)	35 mg/m^2
Styrene-anhydrous maleic acid copolymer	80 mg/m^2
Sodium polystyrenesulfonate	80 mg/m^2
Trimethylolpropane	350 mg/m^2
Diethylene glycol	50 mg/m^2
Nitrophenyl-triphenyl-phosphonium chloride	20 mg/m^2
Ammonium 1,3-dihydroxybenzene-4-sulfonate	500 mg/m^2
Sodium 2-mercaptobenzimidazole-5-sulfonate	5 mg/m^2
Compound (H)	0.5 mg/m^2
n-$C_4H_9OCH_2CH(OH)CH_2N(CH_2COOH)_2$	350 mg/m^2
COMPOUND (M)	5 mg/m^2
Compound (N)	5 mg/m^2
Colloidal silica	0.5 g/m^2
Latex (L)	0.2 g/m^2
Dextran (av. M.W. 1000)	0.2 g/m^2
Gelatin	1.5 g/m^2
Compound (1), (2) or (3) as shown in Table 1	

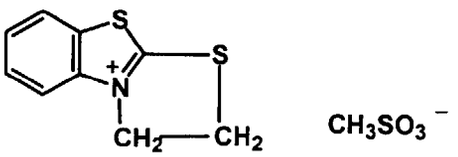
Third layer (Protective layer)

Gelatin	0.8 g/m^2
Matting agent of polymethyl methaacrylate (area-averaged particle size 7.0 μm)	50 mg/m^2
Formaldehyde	20 mg/m^2
Sodium 2,4-dichloro-6-hydroxy-1,3,5-triazine	10 mg/m^2
Bis-vinylsulfonylmethyl ether	36 mg/m^2
Latex (L)	0.2 g/m^2
Polyacrylamide (av. M.W. 10000)	0.1 g/m^2
Polyacrylic acid sodium salt	30 mg/m^2
Polysiloxane (SI)	20 mg/m^2
Compound (I)	12 mg/m^2
Compound (J)	2 mg/m^2
Compound (S-1)	7 mg/m^2
Compound (K)	15 mg/m^2
Compound (O)	50 mg/m^2
Compound (S-2)	5 mg/m^2
C_9F_{19}-O-$(CH_2CH_2O)_{11}$-H	3 mg/m^2
	2 mg/m^2
	1 mg/m^2

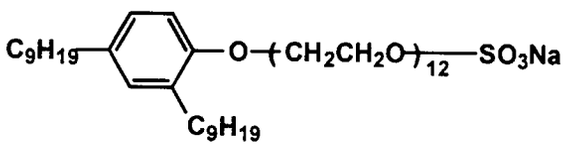
Compound (G)



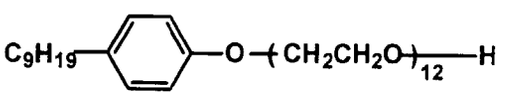
Compound (H)



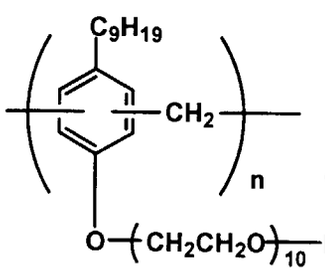
Compound (I)



Compound (J)

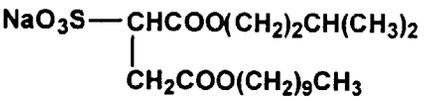


Compound (K)

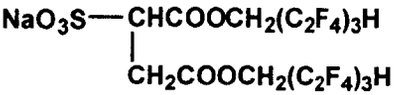


(Mixture of n=2-5)

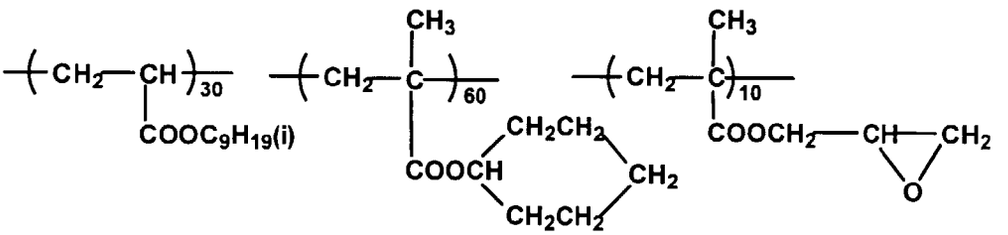
Compound (S-1)



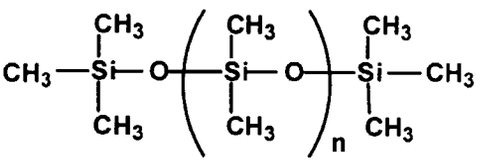
Compound (S-2)



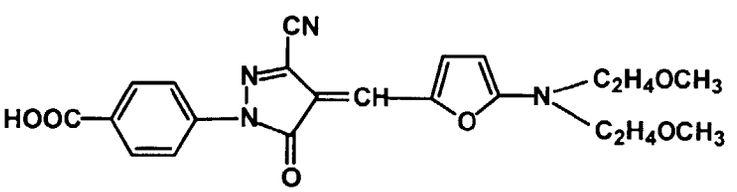
Latex (L)



Polysiloxane (SI)



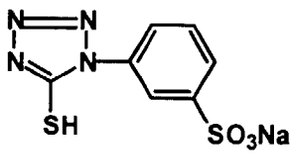
Dye(AH) in the form of fine particle dispersion



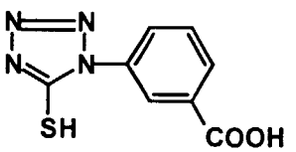
Compound (M)

$C_{11}H_{23}CONH(CH_2CH_2O)_5H$

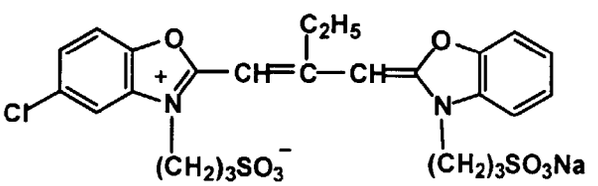
Compound (N)



Compound (O)



Comparative Dye D-1



[0092] Samples were allowed to stand under the condition, A (23° C, 40% RH, 3 days) or B (55° C, 80% RH, 3 days), and thereafter, each was evaluated with respect to photographic characteristics. Thus, each sample was sandwiched between intensifying screens (high sensitive screen as described below), exposed to X-ray, through an aluminum wedge, to X-ray at tube voltage of 80 kVp and tube current of 100 mA for 0.05 sec.

[0093] Solid developer composition used for 100 liters of a developing solution was prepared according to the following procedure.

Granules (A)

[0094] Hydroquinone of 3,000 g, 1-phenyl-3-pyrazolidone of 400 g, N-actyl-D,L-penicillamine of 10 g and sodium glutaraldehyde bissulfite of 500 g each were pulverized up in a commercially available mill so as to have an average particle size of 10 μm. To the resulting fine particles, sodium sulfite of 700 g and D-sorbit of 200 g were added and stirred in the mill for 30 min.. In stirring granulator commercially available, the resulting mixture was granulated for 5 min. at room temperature by adding 30 ml of water. The resulting granules were dried up at 40° C for 2 hr. in a fluidized

bed drier so that the moisture content of the granules was almost completely removed off.

Preparation solid developer composition A

[0095] Thus prepared granules (A) was mixed with sodium 1-octanesulfonate of 100 g for 10 min. by making use of a mixer in a room controlled to be not higher than 25° C and 40% RH. The resulting mixture was compression-tableted so as to have a filling amount of 10 g per tablet, by making use of a tableting machine that was modified model of Tough Press Collect 1527HU manufactured by Kikusui Mfg. Works, Inc. Thereby, hydroquinone type developing composition tablets with 30 mm in diameter were prepared.

Granules (B)

[0096] Potassium carbonate was added in such an amount as to have buffering capability of 0.16. In this case, the buffering capability indicates pH variation when acetic acid of 0.1 mol/Lwp was added to a developing solution, the pH of which was adjusted to 10.0. Further, sodium bicarbonate of 1,000 g and KBr of 200 g each were pulverized up in a commercially available mill so as to have an average particle size of 10 μm. To the resulting fine particles, were added LiOH H_2O of 200 g, DTPA. 5Na of 250 g, 1-phenyl-5-mercaptotetrazole of 5 g, sodium sulfite of 4,000 g, Compound (M) of 40 g, Compound (N) of 5 g and D-mannit of 1,000 g. In stirring granulator commercially available, the resulting mixture was granulated for 5 min. at room temperature by adding 30 ml of water. The resulting granules were dried up at 40° C for 2 hr. in a fluidized bed drier so that the moisture content of the granules was almost completely removed off to obtain granules (B).

Preparation solid developer composition B

[0097] Thus prepared granules (B) was mixed with sodium 1-octanesulfonate of 200 g for 10 min. by making use of a mixer in a room controlled to be not higher than 25° C and 40% RH. The resulting mixture was compression-tableted so as to have a filling amount of 10 g per tablet, by making use of a tableting machine that was modified model of Tough Press Collect 1527HU manufactured by Kikusui Mfg. Works, Inc. Thereby, alkaline developing composition tablets with 30 mm in diameter were prepared. The thus prepared developer composition A and B The thus-prepared developing compositions in the form of a tablet A and B were packaged into a pillow bag containing aluminum for moisture-proof, in an amount of 4.0 liters of the developing solution.

[0098] Solid fixer composition used for 100 liters of a fixing solution was prepared according to the following procedure. Granules (C)

[0099] Ammonium thiosulfate/sodium thiosulfate (90/10 by weight) of 15,000 g was pulverized up in a commercially available mill so as to have an average particle size of 10 μm. To the resulting fine powder, were added sodium sulfite of 500 g, $Na_2S_2O_5$ of 750 g and binder Pineflow of 1,300 g and the mixture was mixed in the mill for 3 min. In stirring granulator commercially available, the resulting mixture was granulated by adding 50 ml of water. The resulting granules were dried up at 40° C in a fluidized bed drier so that the moisture content of the granules was almost completely removed off.

Granules (D)

[0100] Boric acid of 400 g, aluminum sulfate octahydrate of 1,200 g, cinnamic acid of 1200 g and tartaric acid of 300 g were pulverized up in a commercially available mill so as to have an average particle size of 10 μm. To the resulting fine particles was added D-mannit of 250 g, D-sorbit of 120 g and PEG #4000 of 160 g and the resulting mixture was granulated by adding 30 ml of water. The resulting granules were dried up at 40° C in a fluidized bed drier so that the moisture content of the granules was almost completely removed off.

Solid fixer composition

[0101] To the thus prepared granules (C) were added β-alanine of 3400 g, sodium acetate of 4330 g and sodium 1-octanesulfonate in an amount so as to be 1.5% of the total weight, to granule (D) were added sodium metabisulfite of 750 g and sodium 1-octanesulfonate in an amount so as to be 1.0% of the total weight, and each mixed for 10 min. by making use of a mixer in a room controlled to be not higher than 25° C and 40% RH. Each of the mixture was compression-tableted so as to have a filling amount of 10.2 g per tablet (C) and 11.2 g per tablet (D), by making use of a tableting machine that was modified model of Tough Press Collect 1527HU manufactured by Kikusui Mfg. Works, Inc. Thus prepared fixing compositions C and D in the form of a tablet were each packaged into a pillow bag containing aluminum for moisture-proof, in an amount for 4 liters of the fixing solution.

[0102] There was employed an automatic processor, modified SRX-201 (available from Konica Corp.). A starting developer solution in a developing tank was prepared so as to dissolve packaged tablets of developer composition-tablet in water using a modified chemical mixer. In this case, the tablets were completely dissolved and no precipitate was observed. Thus prepared developing solution of 7.8 l was introduced into the processor, modified SRX-201 and a starter having the composition as below was added thereto in amount of 33 ml/l to prepare a starting developing solution. A fixing solution for use in the processor was prepared so as to dissolve packaged fixing composition-tablets C and D in water using the chemical mixer. In the thus prepared fixing solution, the tablets were completely dissolved and no precipitate was observed. The fixing solution of 5.6 liters was introduced into a processor SRX-201 as a starting fixer solution.

Starter	
KBr	5.5 g
$HO(CH_2)_2S(CH_2)_2S(CH_2)_2OH$	0.05 g
N-acetyl-D, L-penicilamine	0.10 g
Sodium metabisulfite for pH-adjustment Water to make	35 ml

[0103] In SRX-201, an inlets of a modified chemical mixer for supplying each of the developing and fixing solid compositions was provided and a built-in chemical mixer was modified for dissolving the solid processing composition.

[0104] An opened package of solid developing or fixing composition tablets was set at the inlet of modified chemical mixer and at the same time when the tablets was supplied into the tank, warm water (25 to 30° C) was also introduced to prepare the processing solution of 4.0 liter, with stirring and dissolving for 25 min. The resulting solution was used as a replenishing solution for developing or fixing solution. The pH of the developing solution and fixing solution was respectively adjusted to 10.55 and 4.80 with acetic acid or potassium hydroxide. The built-in chemical mixer was comprised of a supplying tank and an auxiliary tank, each having a volume of 4 liters. The auxiliary tank was provided so as to supply a replenishing solution, without no supply of the replenishing solution, during the time a replenishing solution prepared in the supplying tank was exhausted during the running process and the solid processing compositions were being dissolved for a period of 25 min. The starter was added and the pH of the developer stating solution was adjusted to 10.45.

[0105] Photographic material samples each were subjected to exposure giving a density of 1.0 and running process. In the running process, developer and fixer were replenished at a rate of 90 ml/m^2 and 90 ml/m^2, respectively.

Developing	39° C	5.0 sec.
Fixing	36° C	3.5 sec.
Washing	35° C	2.5 sec.
Squeezing		1.5 sec.
Drying	50° C	2.5 sec.
Total		15 sec.

[0106] When reached the stationary state in the running process, the following evaluation was made. Processed samples each were subjected to sensitometry and the spectral absorption density at 500 nm was also measured with a spectrophotometer to evaluate residual color. Further, unprocessed samples each were scratched with a needle of a scratch- meter with applying a load of 5 g. and then, processed in the same manner as above. The pressure fog density was measured with a microdensitometer. Results of samples are shown as a relative value in Table 2, based on those of Sample 1 being 100.

Table 1

Sample No.	Emulsion	Dye (mg/Ag·mol)		Compound (1),(2),(3)			Remarks
				(mg/Ag·mol) *		(mg/Ag·mol)**	
1	Em-2	D-1	(450)	-			Comp.
2-1	Em-2	D-1 4-11	(225) (225)	-			Comp.

*:Amount added at the time of chemical sensitization.

**:Amount added to an emulsion layer coating solution.

Table 1 (continued)

Sample No.	Emulsion	Dye (mg/Ag·mol)		Compound (1),(2),(3)			Remarks
				(mg/Ag·mol) *		(mg/Ag·mol)**	
2-2	Em-2	D-1 4-11	(225) (225)	1-11	(4)	250	Comp.
3	Em-1	D-1 4-11	(225) (225)	1-11	(4)	250	Inv.
4	Em-1	D-1 4-23	(135) (315)	2-4	(4)	280	Inv.
5	Em-1	4-18	(450)	2-4	(5)	300	Inv.
6	Em-1	D-1 4-18	(45) (405)	3-12	(5)	300	Inv.
7	Em-1	D-1 4-12	(405) (45)	3-3	(8)	300	Inv.
8	Em-3	D-1	(450)	-			Comp.
9	Em-3	D-1 4-24	(135) (315)	1-12	(5)	300	Inv.
10	Em-3	D-1 4-18	(90) (360)	2-9	(8)	320	Inv.
11	Em-3	4-23	(450)	3-5	(10)	350	Inv.

*:Amount added at the time of chemical sensitization.

**:Amount added to an emulsion layer coating solution.

Table 2

Sample No.	Condition A		Pressure resistance	Residual color	Dmax	Condition B		Remarks
	Fog	Sensitivity				Fog	Sensitivity	
1	100	100	100	100	100	126	67	Comp.
2	108	108	105	80	100	124	69	Comp.
3	50	127	84	80	120	54	119	Inv.
4	45	129	82	61	122	50	125	Inv.
5	34	132	76	32	124	37	131	Inv.
6	36	130	80	43	123	40	129	Inv.
7	41	112	89	90	122	38	108	Inv.
8	100	100	100	100	100	127	65	Comp.
9	49	128	85	62	119	55	122	Inv.
10	36	130	81	61	123	49	125	Inv.
11	33	125	75	31	125	36	121	Inv.

[0107] As can be seen from Table 2, samples according to the invention exhibited enhanced sensitivity, improved pressure resistance and residual color and reduced variation in photographic performance even when aged at high temperature and high humidity. When developed for a short period of 15 sec. using solid processing compositions, there was no deterioration in sensitivity and no problem in practice.

Example 2

[0108] The emulsion, Em-1 was chemically sensitized in the same manner as in Example 1, except that after adding a spectral sensitizing dye, a compound represented by formula (5) was added, as shown in Table 3. Photographic

material samples were also prepared in the same manner as in Example 1, except that a compound represented by formula (1), (2) or (3) of 300 mg/ mol·Ag was added to the Emulsion layer coating solution, as shown in Table 3. Samples prepared by the use of Em-2 were prepared in the same manner as in Example 1. Samples by the use of Em-3 were prepared in the same manner as in Example 1, except that a compound represented by formula (1), (2) or (3) of 350 mg/ mol·Ag was added to the Emulsion layer coating solution, as shown in Table 3.

[0109] Each sample was sandwiched between intensifying screens, exposed to X-ray, through an aluminum wedge, to X-ray at tube voltage of 60 kVp and tube current of 200 mA for 0.05 sec. The intensifying screen described below was employed.

[0110] Preparation of high sensitive intensifying screen (S-1)

Phosphor Gd_2O_2S:Tb (average particle size, 1.8 μm)	200 g
Polyurethane type thermoplastic elastomer Deluxe TPKL-5-2625, solid component of 40% (product by Sumitomo Bayer Corp.)	20 g
Nitrocellulose (nitration degree of 11.5%)	2 g

[0111] To the above was added methylethylketone as a solvent and the mixture was dispersed with a propeller type mixer to obtain a coating solution for a phosphor layer with a viscosity of 25 ps at 25° C (binder/fluorescent substance = 1/22).

[0112] Separately, 90 g of soft type acryl resin, 50 g of nitrocellulose were added to methylethylketone to be dispersed to obtain a dispersion with a viscosity of 3 to 6 ps at 25° C, as a coating solution to form a sublayer.

[0113] A polyethylene terephthalate base (support) compounded with titanium dioxide and with a thickness of 250 μm was horizontally placed on a glass plate and thereon was uniformly coated the coating solution of the sublayer above-described by using a doctor blade. Thereafter, the coated layer was dried with slowly increasing a temperature from 25 to 100° C to form the sublayer on the support. A thickness of the sublayer was 15 μm.

[0114] Further thereon, the coating solution of the phosphor layer was coated in a thickness of 240 μm by using a doctor blade and dried, and subjected to compression. The compression was conducted by means of a calendar roll at a pressure of 300 kgw/cm^2 and a temperature of 80° C. After compression, a transparent protective layer was formed in accordance with the method described in Example 1 of JP-A 6-75097. There was thus obtained an intensifying screen with a thickness of 160 mm and a filling ratio of 68% and exhibiting sharpness (CTF) of 48%. Preparation of comparative intensifying screen (S-2)

[0115] A screen (S-2) comprising a support, sublayer, phosphor layer and transparent protective layer was prepared in the same manner as the S-1 described above, except that the coating solution of the phosphor was coated in a thickness of 150 μm and the compression was not applied. There was thus obtained an intensifying screen with a thickness of 105 mm and a filling ratio of 65%.

[0116] Processed samples were each subjected to sensitometry and also evaluated with respect to sharpness. Portions with a density of 1.0 of each sample was measured with an aperture of 30 μm x 500 μm and a MTF value at a spatial frequency of 1.0 cycle/mm was denoted as the sharpness. Results obtained are shown as a relative value in Table 4, based on those of Sample 12 by the use of S-2 being 100.

Table 3

Sample No.	Emul-sion	Dye (mg/Ag·mol)		Compound (1),(2),(3) (mg/Ag·mol)		Compound (5) (mg/ Ag·mol)		Remarks
12	Em-2	D-1 4-11	(225) (225)	-		-		Comp.
13	Em-2	D-1	(450)	1-7	(12)	-		Comp.
14	Em-1	D-1 4-12	(45) (405)	2-12	(4)	5-20	(3)	Inv.
15	Em-1	4-18	(450)	3-5	(5)	5-2	(3)	Inv.
16	Em-3	D-1 4-3	(400) (50)	-		-		Inv.
17	Em-3	4-18	(450)	2-10	(4)	5-5	(3)	Inv.
18	Em-3	D-1 4-24	(90) (360)	3-14	(4)	5-12	(3)	Inv.

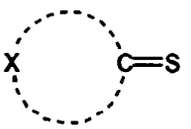
Table 4

Sample No.	Fog	Sensitivity		Sharpness		Remarks
		S-2	S-1	S-2	S-1	
12	100	100	114	100	80	Comp.
13	30	69	78	79	65	Comp.
14	39	119	136	78	64	Inv.
15	35	122	139	78	65	Inv.
16	100	100	115	100	79	Comp.
17	34	122	139	76	61	Inv.
18	38	120	137	79	64	Inv.

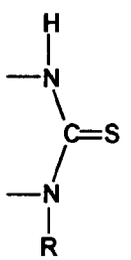
[0117] As can be seen from Table 4, when developed by the use of the solid developer composition, samples according to the invention exhibited enhanced sensitivity. Specifically, when exposed through the high sensitive screen, further enhanced sensitivity and superior sharpness were achieved.

Claims

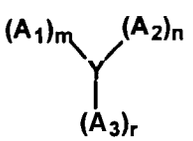
1. A silver halide emulsion, wherein said silver halid emulsion comprises silver halide grains which have been subjected to reduction sensitization, and a compound represented by the following formula (1), (2) or (3); said silver halide grains having been further subjected to at lea one chemical sensitization selected from the group consistin of sulfur sensitization, selenium sensitization and tellurium sensitization, in the presence of a spectral sensitizing dye represented by the following formula (4): formula (1)



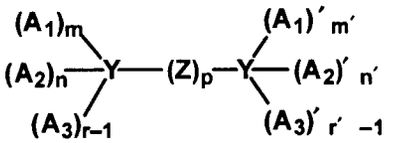
wherein X represents an atomic group necessary for forming a heterocyclic ring having $-SO_3M$, -COOM or -OM, or a group containing $-SO_3M$, -COOM or -OM, in which M represents a hydrogen atom, a metal atom, quaternary ammonium group or a phosphonium group, provided that a compound having, in part, the following structure is excluded:



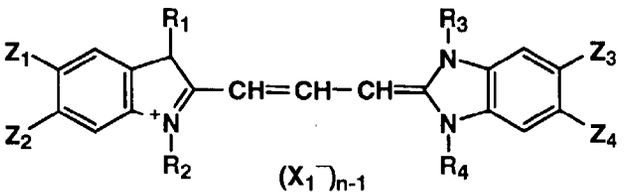
wherein R represents a hydrogen atom or a substituent; formula (2)



formula (3)

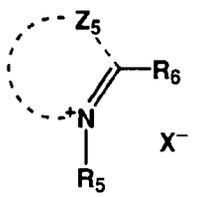


wherein (A_1) and $(A_1)'$ each represent $-SO_3M$, -COOM or -OM; M represents a hydrogen atom, a metal atom, a quaternary ammonium group or a phosphonium group; m and m' each are an integer of 1 to 10; (A_2) and $(A_2)'$ each represent an electron-withdrawing group; n and n' each are an integer of 1 to 10; (A_3) and $(A_3)'$ each represent a group containing a sulfur atom, selenium atom or a tellurium atom; r and r' each are 1 or 2; Y represents an aliphatic hydrocarbon group, an aromatic hydrocarbon group or a heterocyclic ring group; Z represents a sulfur atom, selenium atom or a tellurium atom; and p is 1 or 2; formula (4)



wherein R_1 and R_3 each represent an alkyl group or an alkenyl group; R_2 and R_4 each represent an alkyl group, provided that at least one of R_2 and R_4 is an alkyl group substituted by a hydrophilic group; Z_1, Z_2, Z_3 and Z_4 each represent a hydrogen atom or a substituent; X_1- represents an ion; and n is 1 or 2.

2. The silver halide emulsion of claim 1, wherein said chemical sensitization is performed further in the presence of a compound represented by the following formula (5): formula (5)



wherein Z_5 represents an atomic group necessary for forming a 5 or 6-membered heterocyclic ring; R_5 represents a hydrogen atom, an alkyl group or an alkenyl group; R_6 represents a hydrogen atom or a lower alkyl group; and X^- represents an anion.

3. The silver halide emulsion of claim 1, wherein at least 50% of the total grain projected area is accounted for by tabular silver halide grains having an aspect ratio of not less than 2.

4. The silver halide emulsion of claim 3, wherein said tabular grains have an average iodide content of 0 to 1.0 mol% and an average chloride content of not less than 10 mol%.

5. The silver halide emulsion of claim 4, wherein said tabulat grains each have (100) major faces.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 7192

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 768 568 A (KONICA CORPORATION) 16 April 1997 * page 2, line 5 - line 7 * * page 2, line 29 - line 37 * * page 3, line 33 - page 5, line 20 * * page 30, line 8 - line 24 * * page 35, line 6 - line 18 * * page 36, line 1 - page 37, line 18 * * page 37, line 55 - page 38, line 24 * * claims 1,2,4,5,11 *	1-5	G03C1/10 G03C1/18 G03C1/34 G03C1/005
A	US 5 565 315 A (YAMASHITA) 15 October 1996 * column 1, line 6 - line 13 * * column 2, line 9 - line 18 * * column 5, line 43 - column 7, line 24 * * column 8, line 1 - line 27 * * column 9, line 50 - column 15, line 38 * * claims 1,2,4-8 *	1-5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	11 December 1998	BINDER, R

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 98 30 7192

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11-12-1998

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82