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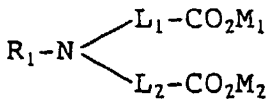
(54) **Method of processing silver halide color photographic material**

(57) Disclosed is a method for processing a silver halide color photographic material, which has excellent adaptability for rapid processing and bleaching ability preferred in view of environmental conservation, comprising color developing a photographic material comprising a support having thereon at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer, at least one blue-sensitive silver halide emulsion layer and at least one light-insensitive layer, at least one of the light-sensitive silver halide emulsion layers having a silver chloride content of 50 mol% or more, and then processing the photographic material with a processing solution having bleaching ability which contains at least one ferric complex salt of the compound represented by formula (I) :



$$R_1-N\begin{cases} L_1-CO_2M_1 \\ L_2-CO_2M_2 \end{cases} \qquad (I)$$

wherein R_1, L_1, L_2, and M_1 and M_2 are as defined in the specification

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to an image formation method of a silver halide photographic material (hereinafter, sometimes referred to simply as a "photographic material"), more specifically, it relates to an image formation method having excellent adaptability to rapid processing, ensuring superior photographic properties in the graininess and the aging stability, and providing excellent effects in view of environmental conservation.

BACKGROUND OF THE INVENTION

[0002] A variety of silver halide color photographic materials and image information methods using them are now available on the market and used in almost all kinds of fields. The halogen composition of the silver halide emulsion used in these photographic materials is in many cases silver iodobromide, silver chloroiodobromide or silver chlorobromide mainly comprising silver bromide for the purpose of achieving high sensitivity.

[0003] On the other hand, the processing of a silver halide color photographic material fundamentally comprises a color development step and a desilvering step, and it is conducted, including other auxiliary processing steps, in a processor called an automatic processor. In the desilvering step, silver generated at the color development step is oxidized by the action of an oxidizing agent called a bleaching agent contained in the processing solution having bleaching ability and then dissolved out and removed from the photographic material by a silver ion-solubilizing agent called a fixing agent contained in the processing solution having fixing ability.

[0004] In recent years, the demand for rapid processing of a color photographic material is increasing more and more and to cope with the demand, the use of a silver halide color photographic material using a silver halide emulsion mainly comprising silver chloride is effective. However, even if the above-described photographic material is used, the rapid bleaching property achieved by the ethylenediamine-N,N,N',N'-tetraacetato ferrate complex salt which has hitherto been widely used as the bleaching agent is insufficient and when a 1,3-propanediamine-N,N,N',N'-tetraacetato ferrate complex salt is used, color stains called bleach fogging may be generated or during continuous processing, the desilvering property is reduced as compared with that at the initial stage of the processing.

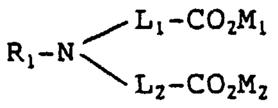
[0005] Further, in view of environmental protection of the globe advocated in recent years, the use of materials having excellent biodegradability is being demanded as an alternate of the materials sparingly biodegradable in the nature such as ethylenediamine-N,N,N',N'-tetraacetic acid and 1,3-propane-diamine-N,N,N',N'-tetraacetic acid which have been hitherto widely used as a bleaching agent.

SUMMARY OF THE INVENTION

[0006] Accordingly, the object of the present invention is to provide a processing method of a silver halide color photographic material using a processing solution having bleaching ability excellent in the adaptability to rapid processing and preferred in view of environmental conservation.

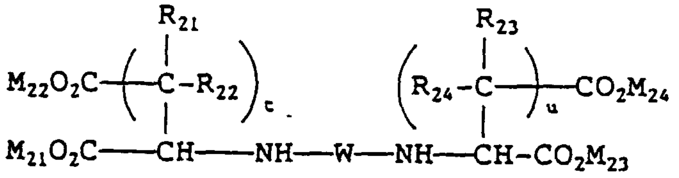
[0007] The above-described problem has been attained by the following method:

[0008] A method for processing a silver halide color photographic material comprising color developing a silver halide color photographic material comprising a support having thereon at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer, at least one blue-sensitive silver halide emulsion layer and at least one light-insensitive layer, wherein at least one of the light-sensitive silver halide emulsion layers comprises a silver halide emulsion comprising silver halide grains having a silver chloride content of 50 mol% or more, and then processing the silver halide color photographic material with a processing solution having bleaching ability containing at least one ferric complex salt of the compound represented by the following formula (I) or (II):



(I)

(wherein R_1 represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group, L_1 and L_2 each represents an alkylene group, and M_1 and M_2 each represents a hydrogen atom or a cation);



(II)

(wherein R_{21}, R_{22}, R_{23} and R_{24} each represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group, a heterocyclic group, a hydroxy group or a carboxy group, t and u each represents 0 or 1, W represents a divalent linking group containing a carbon atom, and M_{21}, M_{22}, M_{23} and M_{24} each represents a hydrogen atom or a cation).

DETAILED DESCRIPTION OF THE INVENTION

[0009] First, the preparation method of a high silver chloride content emulsion of the present invention is described below.

1) Nucleation Process

[0010] The tabular nucleus which grows into the nucleus of a tabular grain is produced at a high frequency under conditions such that lattice defects are readily introduced. An effective method for obtaining tabular nuclei at a good reproduction in a high production ratio uses halogen conversion of the nuclei produced. In this method, halogen nuclei are first produced and subsequently, halogen ions capable of forming more sparingly soluble silver halide are introduced to effect halogen conversion.

[0011] Stated more specifically, the halogen composition structure of the nucleus formed at the time of nucleation is, for example, ($AgX_1|AgX_2$) or ($AgX_1|AgX_4|AgX_3$). These structures may be formed by simultaneously mixing an aqueous silver salt solution (hereinafter referred to as an "Ag^+ solution") and an aqueous halide salt solution (hereinafter referred to as an "X^-solution") by a double jet method and discontinuously changing the halogen composition of the X^- solution at the gap interface. Also, an X^- solution is added to a dispersion medium solution, an Ag^+ solution is added thereto to form AgX_1, a separate X^- solution is added and then an Ag^+ solution is added to form an ($AgX_1|AgX_2$) structure. These methods may be used in combination.

[0012] AgX_1 and AgX_2, AgX_1 and AgX_4, or AgX_4 and AgX_3 are different in the Cl^- content or in the Br^- content by generally from 25 to 100 mol%, preferably from 50 to 100 mol%, more preferably from 75 to 100 mol%, or different in the I^- content by generally from 5 to 100 mol%, preferably from 10 to 100 mol%, more preferably from 30 to 100 mol%. In another embodiment, the difference in the Cl^- content or in the Br^-content falls in the above-described range and the difference in the I^- content is from 0 to 5 mol%. The size of the nucleus is preferably 0.15 µm or less, more preferably from 0.01 to 0.1 µm.

[0013] In the case of ($AgX_1|AgX_2$), the molar ratio of AgX_1:AgX_2 or in the case of ($AgX_1|AgX_4|AgX_3$), the molar ratio of AgX_1:AgX_2: AgX_3 may be changed variously and selected to give a most preferred embodiment of the present invention.

[0014] The atmosphere of the dispersion medium solution at the time of nucleation must be a {100} face-forming atmosphere. When the nucleation is conducted at an excessive concentration of Cl^-, almost all conditions (pCl: 0.8-3.0, pH: 2-9) are usually in a {100} face-forming atmosphere. The defect formation frequency is higher as the pH is higher within the range of pH being from 1 to 7, and also the defect formation frequency is higher as the pCl is higher. The pCl is expressed by the formula: $pCl = -\log (\text{mol/liter of } Cl^-)$.

[0015] At the time of nucleation, the dispersion medium concentration in the dispersion medium solution is preferably from 0.1 to 10 wt%, more preferably from 0.3 to 5 wt%. The pH is preferably from 1 to 10, more preferably from 2 to 8. The temperature is preferably from 10 to 80°C, more preferably from 30 to 60°C. The excessive Br^- concentration is preferably 10^{-2} mol/ℓ or less, more preferably $10^{-2.5}$ mol/ℓ or less. The excessive Cl^- concentration is preferably, in terms of pCl, 0.8 to 3.0, more preferably from 1.2 to 2.8.

[0016] In order to achieve uniform nucleation at the time of nucleation, the silver salt solution and/or the X^- salt solution may contain a dispersion medium. In this case, the dispersion medium concentration is preferably 0.1 wt% or more, more preferably from 0.1 to 2 wt%, most preferably from 0.2 to 1 wt%. A low molecular weight gelatin having a molecular weight of from 3,000 to 60,000, preferably from 8,000 to 40,000 is preferred. The Ag^+ solution and the X^- solution are preferably added directly to the solution through a porous material addition system having an addition pore number of from 3 to 10^{15}, preferably from 30 to 10^{15}. This addition system is described in detail in JP-A-3-21339 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-4-193336 and JP-A-6-86923. A gelatin having a low methionine content increases the defect formation frequency. A most preferred gelatin may be selected from gelatins having a methionine content of from 1 to 60 μmol/g depending on the case.

[0017] The mixing ratio of twin grains may be reduced by lowering the excessive X^- salt concentration or the excessive Ag^+ salt concentration at the time of nucleation.

[0018] An aqueous silver salt solution and a halide salt (hereinafter referred to as an "X^- salt") solution are added by a double jet method, while stirring, into a dispersion medium solution containing at least a dispersion medium and water to form nuclei. At the nucleation, the Cl^- concentration in the dispersion medium solution is preferably $10^{-1.5}$ mol/ℓ or less, Ag^+ concentration is preferably 10^{-2} mol/ℓ or less, the pH is preferably 2 or more, more preferably from 5 to 10, and the gelatin concentration is preferably from 0.1 to 3 wt%, more preferably from 0.2 to 2 wt%.

[0019] The temperature at the time of nucleation is not particularly restricted, but it is preferably 10°C or higher, more preferably from 20 to 70°C. The nucleation is followed by physical ripening to vanish non-tabular grains and to grow tabular grains. The addition rate of the aqueous silver salt solution is preferably from 0.5 to 20 g/min, more preferably from 1 to 15 g/min, per ℓ of the solution in the container. The pH of the solution in the container is not limited, however, usually, the pH is from 1 to 11, preferably from 3 to 10. A most preferred pH value may be selected according to the combination of the excessive silver salt concentration and the temperature.

2) Ripening Process

[0020] It is impossible to selectively form only tabular grain nuclei at the nucleation. Accordingly, tabular grains are grown and grains other than the tabular grains are caused to disappear by Ostwald ripening at the next ripening process. The ripening temperature is preferably 40°C or higher, more preferably from 45 to 90°C, most preferably from 50 to 80°C.

[0021] The ripening is preferably conducted in a {100} face formation atmosphere. The ripening conditions are preferably selected from the above-described condition range for the nucleation. The ripening rate increases as the pH becomes higher within the pH range of from 1 to 6, or as the Cl^-concentration becomes higher within the pCl range of from 1 to 3.

[0022] In the present invention, it is preferred that the silver halide solvent is substantially absent during ripening. The term "substantially absent" as used herein means that the silver halide solvent concentration d_0 satisfies preferably $d_0 \leqq 0.5$ mol/ℓ, more preferably $d_0 < 0.1$ mol/ℓ, still more preferably $d_0 < 0.02$ mol/ℓ.

[0023] The pH at the ripening is generally from 1 to 12, preferably from 2 to 8, more preferably from 2 to 6.

[0024] The dispersion medium for use in the nucleation, the ripening or the growth may be a conventionally known dispersion medium for silver halide emulsion, however, a gelatin having a methionine content of preferably from 0 to 50 μmol/g, more preferably from 0 to 30 μmol/g, is preferred. This gelatin is preferably used in the ripening or in the growth because thin tabular grains having a uniform diameter size distribution are formed. Also, synthetic high polymers described in JP-B-52-16365 (the term "JP-B" as used herein means an "examined Japanese patent publication"), Nippon Shashin Gakkai Shi, vol. 29 (1), 17, 22 (1966), ibid., vol. 30 (1), 10, 19 (1967), ibid., vol. 30 (2), 17 (1967), and ibid., vol. 33 (3), 24 (1967) may be preferably used as a dispersion medium. A crystal habit controlling agent described in European Patent 0534395A1 may be used in combination. The dispersion medium concentration is preferably from 0.1 to 10 wt%, and the controlling agent is used in an amount of preferably from 10^{-1} to 10^{-6} mol/ℓ, more preferably from 10^{-2} to 10^{-5} mol/ℓ. The dispersion medium and the controlling agent may be added at any stage between before the nucleation and after completion of the growth. They may be added in addition to the dispersion medium already present or after removing the dispersion medium already present by centrifugation.

3) Growth Process

[0025] The tabular grain ratio is increased by the ripening and then, the tabular grains are further grown by adding a solute. The solute may be added by 1) a solution addition method (a method of adding an aqueous silver salt solution and an aqueous halide salt solution), 2) a method of previously forming silver halide fine grains and adding the silver halide fine grains, or 3) a method using these two methods in combination. In order to preferentially grow tabular grains in the edge direction, the tabular grains must be grown at a low supersaturation concentration within the range that the tabular grains do not enter Ostwald ripening. In other words, the concentration must be precisely controlled to be a low supersaturation concentration. The method 2) above is preferred because the precise control can be achieved.

[0026] In the fine grain emulsion addition method, a silver halide fine grain emulsion having a size of 0.15 μm or less, preferably 0.1 μm or less, more preferably 0.06 μm or less is added and tabular grains are grown by Ostwald ripening. The fine grain emulsion may be added either continuously or intermittently. The fine grain emulsion may be continuously prepared in a mixer provided in the vicinity of the reaction vessel by supplying an aqueous silver salt solution and an aqueous halide salt solution into the mixer and at once continuously added to the reaction vessel, or it may be previously prepared batchwise in a separate vessel and then continuously or intermittently added. It is preferred that the fine grains contain substantially no twin grain. The term "contain substantially no twin grain" as used herein means that the twin grain number ratio is 5% or less, preferably 1% or less, more preferably 0.1% or less.

[0027] The halogen composition of the fine grain is silver chloride, silver bromide, silver iodide or a mixed crystals of two or more thereof.

[0028] The solution condition at the time of grain growth is the same as the above-described condition for the ripening. This is because, in either process, tabular grains are grown by Ostwald ripening and fine grains other than tabular grains are caused to disappear, thus, they are the same in mechanism. The fine grain emulsion addition method in general are described in detail in JP-A-4-34544, JP-A-5-281640 and JP-A-1-183417.

[0029] The fine grains containing substantially no twin plane may be formed by adding an aqueous silver salt solution and an aqueous halide salt solution by a double jet method at an excessive halogen ion concentration or excessive silver ion concentration, preferably of 10^{-2} mol/ℓ or less.

[0030] The fine grain formation temperature is preferably 50°C or lower, more preferably from 5 to 40°C, still more preferably from 10 to 30°C. The dispersion medium is preferably a gelatin where a low molecular gelatin having a molecular weight of preferably from 2,000 to 6×10^4, more preferably from 5,000 to 4×10^4, occupies preferably 30 wt% or more, more preferably 60 wt% or more, still more preferably 80 wt% or more. The dispersion medium concentration is preferably 0.2 wt% or more, more preferably from 0.5 to 5 wt%.

[0031] It is preferred that NH_3 is substantially absent at the nucleation process. The term "substantially absent" as used herein has the same meaning as defined above. It is also preferred that NH_3 is substantially absent at the growth. The term "substantially absent" as used herein means that the concentration Z_1 of NH_3 satisfies preferably $Z_1 \leqq 0.5$ mol/ℓ, more preferably $Z_1 < 0.1$ mol/ℓ, still more preferably $Z_1 < 0.02$ mol/ℓ. Furthermore, it is preferred that AgX solvent other than NH_3 is substantially absent at the nucleation and the growth. The term "substantially absent" as used herein has the same meaning as defined for the Z_1 concentration. Examples of the AgX solvent other than NH_3 include an antifoggant such as thioethers, thioureas, thiocyanates, organic amine-base compounds and tetraazaindenes, with thioethers, thioureas and thiocyanates being preferred.

[0032] A dislocation line may be introduced into the grain during the nucleation according to a halogen composition gap method, a halogen conversion method, an epitaxial growing method or a combination thereof. This is preferred because the pressure fogging property or the reciprocity law characteristic sensitization property is improved. These techniques are described in JP-A-63-220238, JP-A-64-26839, JP-A-2-127635, JP-A-3-189642, JP-A-3-175440, JP-A-2-123346, European Patent 0460656A1, and Journal of Imaging Science, vol. 32, 160-177 (1988).

[0033] The grain obtained may be used as a host grain for forming an epitaxial grain. Or, the grain may be used as a core grain to form a grain having dislocation lines in the inside thereof. In addition, the grain may be used as a substrate and a silver halide layer having a halogen composition different from that of the substrate is laminated thereon to form a grain having any of various known grain structures. These techniques are described in literatures described later.

[0034] The tabular grain may also be used as a core to form a shallow latent image-type emulsion. This technique is described in JP-A-59-133542, JP-A-63-151618, U.S. Patents 3,206,313, 3,317,322, 3,761,276, 4,269,927 and 3,367,778.

[0035] One of the most important parameters to finally obtain a silver halide grain having a high aspect ratio is the pAg at the time of ripening and growth. The aspect ratio of the tabular grain of the present invention is generally from 2 to 15, preferably from 3 to 13, more preferably from 4 to 10. The aspect ratio in the above-described range is preferred in view of the balance mainly between the sensitivity and the pressure property.

[0036] The adjacent edges length ratio of a main plane is 10 or less, more preferably 5 or less, still more preferably 2 or less. The projected area of tabular grains occupies generally 30% or more, more preferably 50% or more, still more preferably 70% or mote of the projected area of all grains. The thickness is generally 0.3 μm or less, preferably 0.2 μm or less.

[0037] The term "aspect ratio" as used herein means the ratio of the thickness between main planes to the average edge length of main planes of a grain. The "main plane" is defined as a pair of parallel planes having a largest area among crystal surfaces constituting a substantially rectangular parallelogram emulsion grain and whether the main plane is a {100} face can be verified by an electron beam diffraction method or an X-ray diffraction method. The term "substantially rectangular parallelogram" as used herein means that the main plane is a {100} face but from 1 to 8 {111} faces may be present. In other words, from 1 to 8 angles of a rectangular parallelogram may be missing. The "average edge length" is defined as a length of one side of a square having an area equal to the projected area of a grain observed on a microphotograph of an emulsion grain sample.

[0038] On the surface of a high silver chloride tabular grain having a {100} face as the main plane, a salt more sparingly soluble than silver chloride may be formed uniformly throughout grains so that a sensitizing dye can be adsorbed uniformly throughout grains, and this method is preferred.

[0039] Examples of the silver salt more sparingly soluble than silver chloride include silver bromide, silver iodide, silver iodobromide, silver thiocyanate, silver selenocyanate and a mixed crystal thereof, with silver bromide, silver iodide and silver iodobromide being preferred. The amount of the silver salt more sparingly soluble than silver chloride is 20 mol% or less, preferably 10 mol% or less, more preferably 5 mol% or less, still more preferably from 0.001 to 3 mol%, based on the entire grains.

[0040] Examples of the formation method of the silver salt more sparingly soluble than silver chloride on the surface of a tabular grain include a method of adding a water-soluble halide salt and an aqueous silver salt each having a corresponding composition by a double jet method, a method of adding fine grains, and a method using a gradually releasing agent of bromide ions or iodide ions.

[0041] According to a method of adding a water-soluble halide salt and a water-soluble silver salt by a double jet method, the halogen ions are in the free state upon addition even if the aqueous halide salt solution is added after dilution and accordingly, the reduction in locality among grains is limited. On the other hand, the method of adding them as fine grains or the method using a gradually releasing agent can form a salt more sparingly soluble than silver chloride on the surface of a grain uniformly throughout grains and these methods are preferred.

[0042] In the case of fine grain addition, the average sphere-corresponding diameter of fine grains is preferably 0.1 µm or less, more preferably 0.06 µm or less. The fine grain may be continuously prepared in a mixer provided in the vicinity of the reaction vessel by supplying an aqueous silver salt solution and an aqueous solution of a salt capable of forming a silver salt having solubility lower than the silver chloride into the mixer and at once continuously added to the reaction vessel, or it may be previously prepared batchwise in a separate vessel and then added. The method using a gradually releasing agent is disclosed in JP-B-1-285942 and JP-A-6-11780.

[0043] The preparation method of high silver chloride tabular grains comprising {111} faces, which are effectively used in the present invention, is not particularly limited.

[0044] In one specific example of the method, the grains are obtained by using adenine in combination during the grain formation.

[0045] The addition amount of adenine or a salt thereof is generally from 10^{-4} to 10^{-2} mol, preferably from 5×10^{-4} to 5×10^{-3} mol, per mol of silver halide.

[0046] The adenine or a salt thereof may be added so that it can be present at any stage between the nucleation of silver halide grains and after completion of the physical ripening during the grain formation in the production process of a silver halide emulsion, however, it is preferred that at least a part of adenine or a salt thereof is present from the initial stage of grain formation.

[0047] Once a high silver chloride tabular grain is formed, the adenine is no more needed, however, usually, at least a part thereof is still being adsorbed to the grain surface. The adenine can be taken the place of by a compound having a strong affinity for the silver halide grain surface such as a spectral sensitizing dye and thus, the adenine can be substantially washed out and removed from the emulsion.

[0048] The adenine is also known as an excellent antifoggant and the remaining of adenine in the emulsion is useful.

[0049] In order to selectively form regular crystal (from octahedral to tetradecahedral) grains, nontabular grains or tabular grains using adenine or a salt thereof, it is preferred to control the pH particularly at the initial stage (so-called at the time of nucleation) of the grain formation. The pH at the nucleation for obtaining tabular grains is generally from 4.5 to 8.5, preferably from 4.8 to 8.0, more preferably from 5.0 to 7.0. At a pH of 8.5 or more, regular crystals are formed and at a pH of 4.5 or less, non-tabular grains having a non-parallel twin plane are formed.

[0050] The chloride concentration at the nucleation is preferably from 0.05 to 0.12 mol. If it is less than 0.05 mol, regular crystals are liable to be formed, whereas if it exceeds 0.12 mol, non-tabular grains are predominantly formed.

[0051] The pH at the time of grain growth is not particularly limited, however, it is preferably kept at from 4.5 to 8.5.

[0052] The chloride concentration at the grain growth is preferably 5 mol or less, more preferably from 0.07 to 3 mol. In the present invention, the temperature at the grain formation is from 10 to 95°C, preferably from 35 to 90°C.

[0053] An adenine derivative other than adenine may also be effectively used to form {111} tabular grains.

[0054] Examples thereof include compounds described in claim 1 of U.S. Patent 5,178,997, xanthines described in U.S. Patent 5,178,998, pyrimidines described in U.S. Patents 5,185,239 and 5,252,452, and quaternary ammonium compounds described in U.S. Patent 4,983,508.

[0055] The {111} tabular grain has the same preferred range with respect to the aspect ratio, the main plane adjacent edges length ratio, the thickness and the projected area ratio in the total projected area of all grains, as those of the {100} tabular grain.

[0056] The developing agent which can be used in the present invention is described below. A developing agent which is used in a silver halide color photographic material, in general, imagewise reduces silver halide directly or via other electron transfer agents and produces the oxidation product of a developing agent corresponding to exposure amount. The oxidation product of a developing agent further reacts with a coupler to form a dye. In usual color photographic systems in recent years, a developing agent is contained in a developing solution and the developing agent is permeated into a photographic material during development processing and the development proceeds. That is, a high reactive developing agent is always supplied as a fresh one during development processing (a developing agent easily decomposes by air oxidation as it is a reducing agent).

[0057] In the image-forming method of the present invention, a developing agent can be incorporated into a developer as in the conventional processing method, but is preferably incorporated into a photographic material in terms of rapid processing aptitude. As the developing agent which can be incorporated into the photographic material, preferred are compounds represented by the following formula (D-1):

$$(L)_n\text{-}D \qquad \text{(D-1)}$$

wherein L represents an electron attractive group releasable during development processing; D represents a compound residue obtained by removing n hydrogen atoms from a compound H_nD having developing activity; and n represents an integer of from 1 to 3.

[0058] The developing agent represented by formula (D-1) preferably has the structure represented by the following formula (D-2):

$$L^{d1}L^{d2}N\text{-}(NH)_p\text{-}(X{=}Y)_q\text{-}Z \qquad \text{(D-2)}$$

wherein L^{d1} and L^{d2} each represents a hydrogen atom or an electron attractive group releasable during color development processing, and L^{d1} and L^{d2} do not represent hydrogen atoms at the same time; X and Y independently represent methine or azomethine; Z represents a hydrogen atom, a hydroxyl group, an amino group or $-NHL^{d3}$; L^{d3} represents an electron attractive group; p represents 0 or an integer of 1; q represents an integer of from 1 to 3; and arbitrary two of L^{d1}, L^{d2}, X, Y and Z may be linked to form a ring.

[0059] The preferred range of the developing agent represented by formula (D-2) is described in detail below. Preferred examples of the electron attractive group represented by L^{d1} and L^{d2} in formula (D-2) include a formyl group, an acyl group, a sulfinyl group, a sulfonyl group and a phosphonyl group, and particularly preferred are an acyl group and a sulfonyl group. L^{d1} and L^{d2} are released in color development processing and they may be released either after or before the developing agent represented by formula (D-2) is oxidized. However, the constitution in which the developing agent for use in the present invention imagewise develops silver halide under a basic condition, the oxidation product of the developing agent produced at that time coupling reacts with a coupler, then L^{d1} and L^{d2} are released to form a dye is preferred from the viewpoint that the development is preferred not to exceed at an unexposed part (prevention of fog) and the viewpoint of preventing a coloring material from being formed by the unreacted development activating seed, which has been produced in development processing, remaining in the photographic material (prevention of stain). L^{d1} and L^{d2} may be released in the form of an anion or a radical, or may be decomposed and released by nucleophilic attack by the nucleophilic seed in a developing solution (water, hydroxide ion, hydrogen peroxide, sulfite ion, hydroxylamine), and particularly in the latter case, the release of L^{d1} and L^{d2} can be accelerated by adding positively a nucleophilic seed to the developing solution, or when a compound accelerating silver development (particularly preferably hydrogen peroxide) is added, the release of L^{d1} and L^{d2} can be accelerated making use of the nucleophilicity thereof.

[0060] In formula (D-2), $(X{=}Y)_q$ represents a π electron conjugated system by a carbon atom or a nitrogen atom, X and Y are particularly preferably linked to form a ring, q is preferably 2 or 3, and the number of the nitrogen atom contained is preferably from 0 to 3. When $(X{=}Y)_q$ forms a ring, a 5- or 6-membered ring is preferred, and a hetero atom may be contained as an atom constituting the ring, with a preferred hetero atom being a nitrogen atom, an oxygen atom and a sulfur atom, particularly preferably a nitrogen atom. Further, $(X{=}Y)_q$ may have a condensed ring, and a benzene ring is preferred as the condensed ring.

[0061] When p represents 0, X bonding to $L^{d1}L^{d2}N$ may be either of a carbon atom or a nitrogen atom, but when p represents 1, X bonding to NH is preferably a carbon atom.

[0062] In formula (D-2), when p represents 0, Z is preferably a hydroxyl group, an amino group or NHL^{d3}, and when p represents 1, Z is preferably a hydrogen atom or NHL^{d3}. When Z is represented by NHL^{d3}, L^{d3} is preferably a formyl group, an acyl group, a sulfinyl group, a sulfonyl group or a phosphonyl group, and particularly preferably an acyl group or a sulfonyl group.

[0063] The developing agent represented by formula (D-2) is preferably introduced into a photographic material by a method of dissolving in a high boiling point organic solvent, followed by emulsion dispersing, a so-called oil-protecting method. Accordingly, the developing agent for use in the present invention preferably has a comparatively large lipophilic group generally called a ballast group for easily dissolving in a high boiling point organic solvent and maintaining a stability in a photographic material. Therefore, it is preferred that this ballast group contain straight chain or branched alkyl group(s) of a certain degree of a bulk, and the total carbon atom number of these alkyl groups is preferably from 8 to 32, more preferably from 12 to 22, and particularly preferably from 12 to 18. The substitution position of the ballast group may be L^{d1}, L^{d2}, (X=Y) or Z, but L^{d1} or L^{d2} is preferred.

[0064] The developing agent represented by formula (D-2) may have substituents for acquiring suitable pKa (acid dissociation constant) corresponding to pH of a developing solution to be used, and for adjusting the absorption wavelength of a dye to be formed, releasing rate of L^{d1} and L^{d2}, coupling rate with a coupler, and an oxidation potential to objective ranges. Examples of the substituent include a halogen atom, a cyano group, a nitro group, an amino group, a carboxyl group, a sulfo group, an acyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonylamino group, a sulfamoyl group, an alkyl group, an aryl group, an alkoxy group and an aryloxy group. An electron attractive group is preferred, and a halogen atom, a cyano group, an acyl group, a carbamoyl group, a sulfonyl group and a sulfamoyl group are particularly preferred.

[0065] The developing agents represented by formula (D-2) are particularly preferably represented by the following formulae (D-3) to (D-10):

$$R^{d1}SO_2NH\text{-}\phi^1\text{-}NR^{d2}R^{d3} \qquad \text{(D-3)}$$

$$R^{d4}SO_2NH\text{-}\phi^2\text{-}OH \qquad \text{(D-4)}$$

$$R^{d5}CONH\text{-}\phi^3\text{-}NR^{d6}R^{d7} \qquad \text{(D-5)}$$

$$R^{d8}CONH\text{-}\phi^4\text{-}OH \qquad \text{(D-6)}$$

$$R^{d9}SO_2NHNHR^{d10} \qquad \text{(D-7)}$$

$$R^{d11}CONHNHR^{d12} \qquad \text{(D-8)}$$

$$R^{d13}SO_2NHN{=}\phi^5 \qquad \text{(D-9)}$$

$$R^{d14}CONHN{=}\phi^6 \qquad \text{(D-10)}$$

[0066] In formulae (D-3) to (D-10), R^{d1} to R^{d4}, R^{d6}, R^{d7}, R^{d9}, R^{d10}, R^{d12} and R^{d13} represent an alkyl group, an aryl group or a heterocyclic group; R^{d5}, R^{d8}, R^{d11} and R^{d14} represent a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group or an amino group; ϕ^1 to ϕ^4 represent an arylene group or a heteroarylene group; and ϕ^5 and ϕ^6 represent a hydrocarbon ring group or a heterocyclic group bonded to a nitrogen atom by a double bond.

[0067] In formulae (D-3) to (D-10), the alkyl group represented by R^{d1} to R^{d14} is preferably a straight chain or branched, or acyclic or cyclic alkyl group having from 1 to 30 carbon atoms, and particularly preferred is a straight chain alkyl group having from 1 to 22 carbon atoms such as methyl, ethyl, propyl, butyl, dodecyl, tetradecyl, hexadecyl, and octadecyl.

[0068] In formulae (D-3) to (D-10), the aryl group represented by R^{d1} to R^{d14} is preferably an aryl group having from 6 to 20 carbon atoms, more preferably an aryl group having from 6 to 10 carbon atoms such as phenyl, naphthyl, anthrathenyl, and most preferably phenyl.

[0069] In formulae (D-3) to (D-10), the heterocyclic group represented by R^{d1} to R^{d14} is preferably a 5- to 7-membered heterocyclic group, the hetero atom is preferably a nitrogen atom, an oxygen atom or a sulfur atom, and the number of the carbon atom is preferably from 1 to 10. Particularly preferred examples include a nitrogen-containing 5- or 6-membered heterocyclic group such as 2-imidazolyl, 1,3-oxazol-2-yl, 1,3-thiazol-2-yl, 5-tetrazolyl, 3-indolinyl, 1,3,4-thiadiazol-2-yl, 1,3-benzoxazol-2-yl, 1,3-benzothiazol-2-yl, 1,3-benzimidazol-2-yl, 1,2,4-triazol-5-yl, 3-pyrazolyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-pyrimidyl, and 3-pyrimidyl. Further, they may have a condensed ring, and a benzene ring is preferred as the condensed ring.

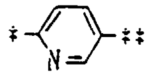
[0070] In formulae (D-5), (D-6), (D-8) and (D-10), the alkoxy group represented by R^{d5}, R^{d8}, R^{d11} and R^{d14} is preferably a straight chain or branched, or acyclic or cyclic alkoxy group having from 1 to 30 carbon atoms, and particularly preferred is a straight chain alkoxy group having from 1 to 22 carbon atoms such as methoxy, ethoxy, propyloxy, butyloxy, dodecyloxy, tetradecyloxy, hexadecyloxy, and octadecyloxy.

[0071] In formulae (D-5), (D-6), (D-8) and (D-10), the aryloxy group represented by R^{d5}, R^{d8}, R^{d11} and R^{d14} is preferably an aryloxy group having from 6 to 20 carbon atoms, more preferably an aryloxy group having from 6 to 10 carbon atoms such as phenoxy, naphthoxy, and anthrathenoxy, and most preferably a phenoxy group.

[0072] In formulae (D-5), (D-6), (D-8) and (D-10), the amino group represented by R^{d5}, R^{d8}, R^{d11} and R^{d14} is preferably an alkylamino group, a dialkylamino group, an arylamino group, a diarylamino group and an alkylarylamino group, each having from 2 to 40 carbon atoms, more preferably an alkylamino group, a dialkylamino group and an arylamino group, each having from 1 to 20 carbon atoms, such as methylamino, ethylamino, diethylamino, di-n-octylamino, and phenylamino.

[0073] In formulae (D-3) to (D-6), the arylene group represented by ϕ^1 to ϕ^4 is preferably an arylene group having from 6 to 20 carbon atoms, more preferably an arylene group having from 6 to 10 carbon atoms such as phenylene, naphthylene, and anthrathenylene, and most preferably a phenylene group. In addition, they may have a condensed ring, and a benzene ring is preferred as the condensed ring.

[0074] In formulae (D-3) to (D-6), the hetero atom contained in the heteroarylene group represented by ϕ^1 to ϕ^4 is preferably a nitrogen atom, an oxygen atom and a sulfur atom, the number of the hetero atom is preferably from 1 to 3, more preferably 1 or 2, the number of the carbon atom is preferably from 2 to 8, more preferably from 3 to 5, the number of the ring member is preferably 5 or 6, they may have a condensed ring, and a benzene ring is preferred as the condensed ring. Specific examples of the heteroarylene groups represented by ϕ^1 to ϕ^4 include the following (HA-1) to (HA-24), and particularly preferred of them are (HA-1), (HA-2), (HA-6), (HA-22) and (HA-23).



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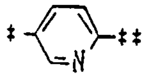

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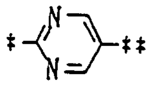

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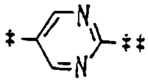

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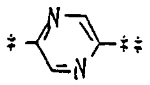
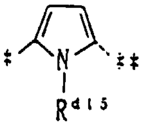
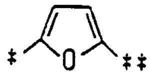


(HA-5)



(HA-6)



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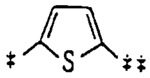

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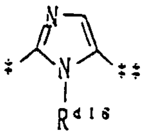

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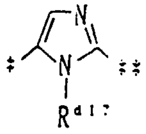

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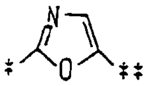

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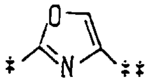

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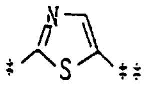

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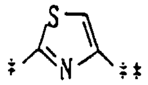

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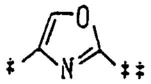

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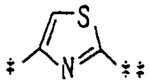

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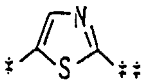

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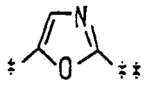

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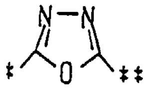

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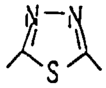

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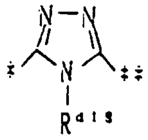
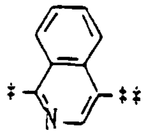


(HA-21)



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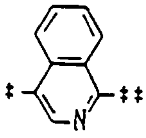
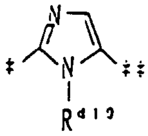


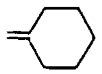
(HA-23)



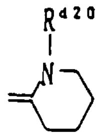
(HA-24)

[0075] In formulae (HA-1) to (HA-24), * indicates the bonding position with NH in formulae (D-3) to (D-6), ** indicates the bonding position with $NR^{d2}R^{d3}$, OH or $NR^{d6}R^{d7}$, R^{d15} to R^{d19} represent an alkyl group or an aryl group, and these alkyl and aryl groups have the same meaning as the alkyl and aryl groups represented by R^{d1} to R^{d14} in formulae (D-3) to (D-10).

[0076] In formulae (D-9) and (D-10), the hydrocarbon ring group or a heterocyclic group bonded to a nitrogen atom by a double bond represented by ϕ^5 and ϕ^6 is preferably a 5- to 7-membered hydrocarbon ring group or heterocyclic group, the preferred hetero atom is nitrogen, oxygen, and sulfur, the number of the hetero atom contained is preferably from 0 to 3, more preferably from 0 to 2, the number of the carbon atom is preferably from 2 to 8, more preferably from 3 to 6, and particularly preferred of them is a 5- or 6-membered nitrogen-containing unsaturated heterocyclic ring. It is preferred that the carbon atoms in the rings of these hydrocarbon ring and heterocyclic ring in formulae (D-9) and (D-10) form double bonds with $R^{d13}SO_2NHN$ or $R^{d14}CONHN$, and they may have a condensed ring, and a benzene ring is preferred as the condensed ring. Examples of the hydrocarbon ring group or a heterocyclic group bonded to a nitrogen atom by a double bond represented by ϕ^5 and ϕ^6 include the following (CH-1) to (CH-18), and preferred of them are (CH-5), (CH-6), (CH-9), (CH-10), (CH-11), (CH-15) and (CH-17).



(CH-1)



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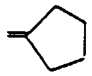
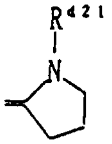


(CH-3)



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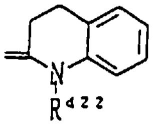

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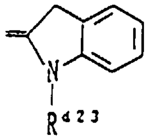

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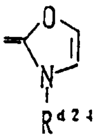

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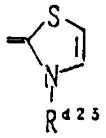

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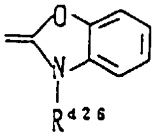

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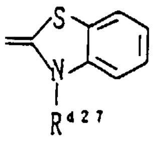

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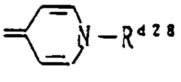

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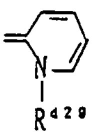

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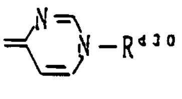

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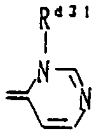

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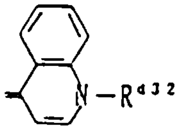

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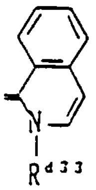

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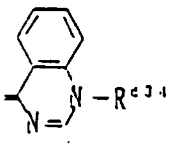

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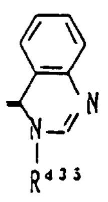


(CH-18)

[0077] In formulae (CH-1) to (CH-18), R^{d21} to R^{d35} represent an alkyl group or an aryl group, and these alkyl and aryl groups have the same meaning as the alkyl and aryl groups represented by R^{d1} to R^{d14} in formulae (D-3) to (D-10).

[0078] In formulae (D-3) and (D-5), R^{d2} and R^{d3}, ϕ^1 and R^{d2}, ϕ^1 and R^{d3}, R^{d6} and R^{d7}, ϕ^3 and R^{d6}, ϕ^3 and R^{d7} may be linked to form a ring, and the number of the ring member is preferably 5 or 6, a hetero atom may be contained as an atom constituting the ring, and an oxygen atom is preferred as the hetero atom.

[0079] The preferred range of the developing agent represented by formulae (D-3) to (D-10) is described in detail below.

[0080] In formulae (D-3), (D-4), (D-7) and (D-9), R^{d1}, R^{d4}, R^{d9} and R^{d13} preferably represent a phenyl group, and the preferred substituents therefor include a halogen atom (fluorine, chlorine, bromine), an alkyl group (having from 1 to 22 carbon atoms), an acyl group (having from 1 to 18 carbon atoms), a sulfonyl group (having from 1 to 18 carbon atoms), an alkoxy group (having from 1 to 22 carbon atoms), an alkoxycarbonyl group (having from 2 to 23 carbon atoms), a carbamoyl group (having from 1 to 23 carbon atoms), a sulfamoyl group (having from 0 to 22 carbon atoms), an acylamino group (having from 1 to 22 carbon atoms), a sulfonylamino group (having from 1 to 22 carbon atoms), a cyano group, and a nitro group.

[0081] In formulae (D-3) and (D-5), R^{d2}, R^{d3} , R^{d6} and R^{d7} preferably represent an alkyl group having from 1 to 8 carbon atoms, and the preferred substituents therefor include a hydroxyl group, an alkoxy group (having from 1 to 12 carbon atoms), an acylamino group (having from 1 to 12 carbon atoms), and a sulfonylamino group (having from 1 to 12 carbon atoms).

[0082] In formulae (D-5), (D-6), (D-8) and (D-10), R^{d5}, R^{d8}, R^{d11} and R^{d14} preferably represent an alkyl group having from 1 to 22 carbon atoms, an alkoxy group having from 1 to 22 carbon atoms, or a phenyl group. When R^{d5}, R^{d8}, R^{d11} and R^{d14} represent an alkyl group, the preferred substituents include a halogen atom (fluorine, chlorine, bromine), an acyl group (having from 1 to 18 carbon atoms), a sulfonyl group (having from 1 to 18 carbon atoms), a carbamoyl group (having from 1 to 23 carbon atoms), a sulfamoyl group (having from 0 to 22 carbon atoms), and a cyano group. When R^{d5}, R^{d8}, R^{d11} and R^{d14} represent an alkoxy group, the preferred substituents include a halogen atom (fluorine, chlorine, bromine), an aryl group (particularly preferably phenyl), an acyl group (having from 1 to 18 carbon atoms), a sulfonyl group (having from 1 to 18 carbon atoms), a carbamoyl group (having from 1 to 23 carbon atoms), a sulfamoyl group (having from 0 to 22 carbon atoms), a cyano group, and a nitro group. When R^{d5}, R^{d8}, R^{d11} and R^{d14} represent a phenyl group, the preferred substituents include a halogen atom (fluorine, chlorine, bromine), an alkyl group (having from 1 to 22 carbon atoms), an acyl group (having from 1 to 18 carbon atoms), a sulfonyl group (having from 1 to 18 carbon atoms), an alkoxy group (having from 1 to 22 carbon atoms), an alkoxycarbonyl group (having from 2 to 23 carbon atoms), a carbamoyl group (having from 1 to 23 carbon atoms), a sulfamoyl group (having from 0 to 22 carbon atoms), an acylamino group (having from 1 to 22 carbon atoms), a sulfonylamino group (having from 1 to 22 carbon atoms), a cyano group and a nitro group.

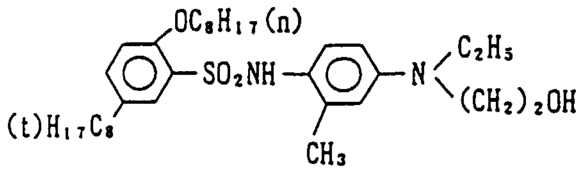
[0083] In formulae (D-7) and (D-8), R^{d10} and R^{d12} preferably represent an aryl group or a heterocyclic group. When R^{d10} and R^{d12} represent an aryl group, particularly preferred is a phenyl group. When R^{d10} and R^{d12} represent a heterocyclic group, particularly preferred is a 6-membered nitrogen-containing heteroaryl group, and the number of the nitrogen atom contained in the ring in this case is preferably 1 or 2. An electron attractive group is preferred as the substituent for R^{d10} and R^{d12}, and particularly preferred substituents include a halogen atom (fluorine, chlorine, bromine), a halogenoalkyl group (trifluoromethyl, trichloromethyl), an acyl group (having from 1 to 18 carbon atoms), a sulfonyl group (having from 1 to 18 carbon atoms), an alkoxycarbonyl group (having from 2 to 23 carbon atoms), a carbamoyl group (having from 1 to 23 carbon atoms), a sulfamoyl group (having from 0 to 22 carbon atoms), a cyano group and a nitro group.

[0084] In formulae (D-3) to (D-6), ϕ^1 to ϕ^4 preferably represent a phenylene group, and the preferred substituents therefor include a halogen atom (fluorine, chlorine, bromine), an alkyl group (having from 1 to 22 carbon atoms), an alkoxy group (having from 1 to 22 carbon atoms), an acyl group (having from 1 to 18 carbon atoms), a sulfonyl group (having from 1 to 18 carbon atoms), an alkoxycarbonyl group (having from 2 to 23 carbon atoms), a carbamoyl group (having from 1 to 23 carbon atoms), a sulfamoyl group (having from 0 to 22 carbon atoms), an acylamino group (having from 1 to 22 carbon atoms), a sulfonylamino group (having from 1 to 22 carbon atoms), and a cyano group.

[0085] In formulae (D-9) and (D-10), ϕ^5 and ϕ^6 preferably represent a 5- or 6-membered nitrogen-containing heterocyclic group bonded to a nitrogen atom by a double bond, the number of the nitrogen atom contained is preferably 1 or 2, a sulfur atom is preferred as the hetero atom other than the nitrogen atom, and the number of the sulfur atom contained in the ring in this case is preferably 1. ϕ^5 and ϕ^6 particularly preferably represent (CH-10), (CH-11), (CH-15) and (CH-17).

[0086] Specific examples of the developing agent for use in the present invention are shown below, but the present invention is not limited thereto.

D−(1)



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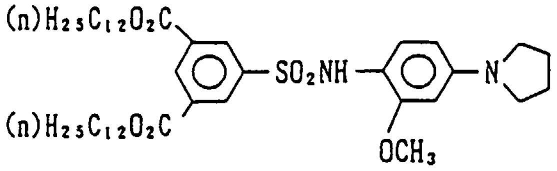

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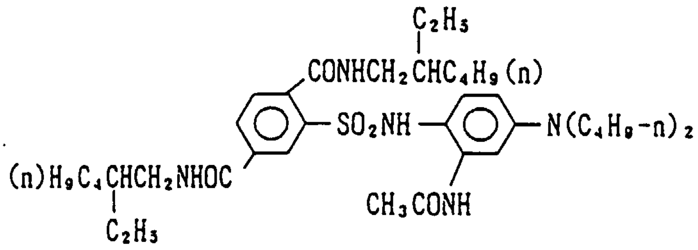

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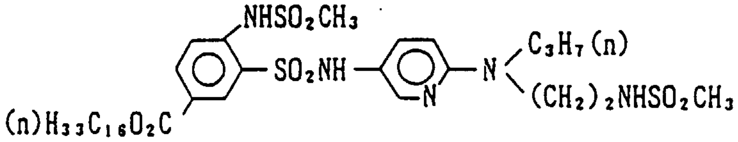

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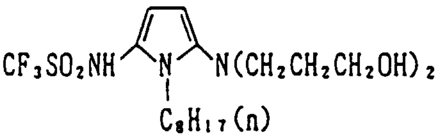

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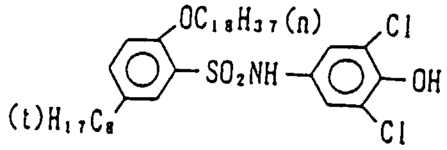

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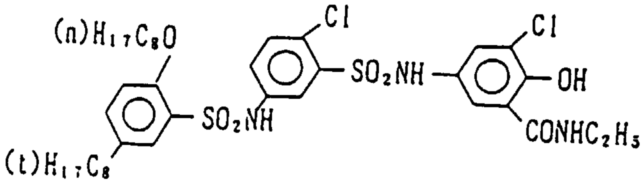

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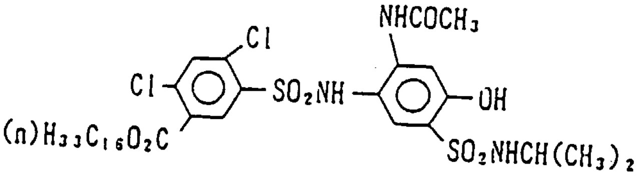

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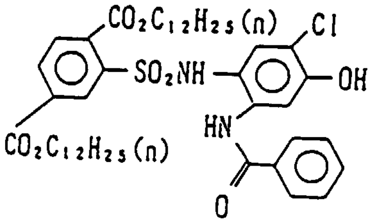

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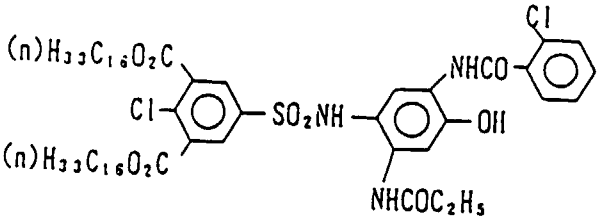
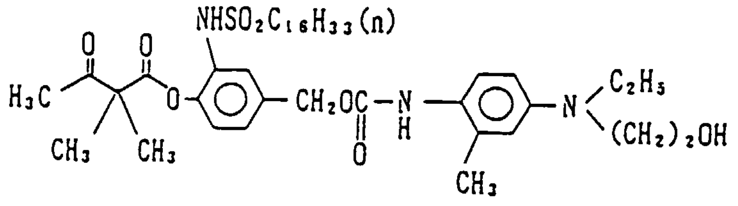


D-(11)



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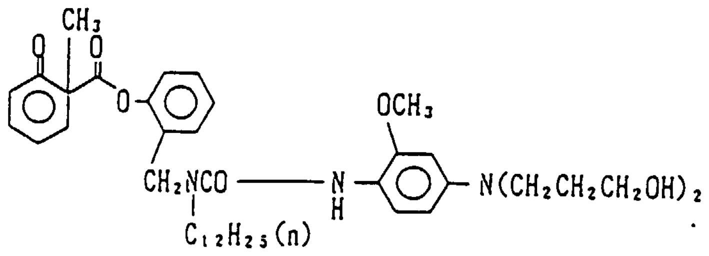

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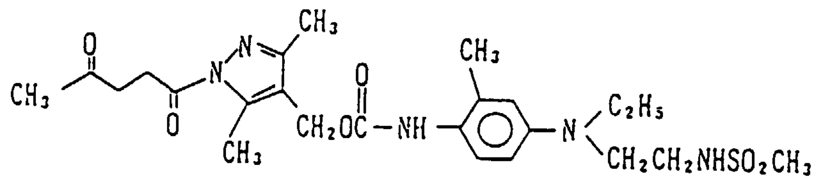

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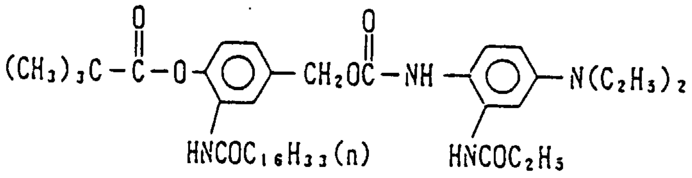

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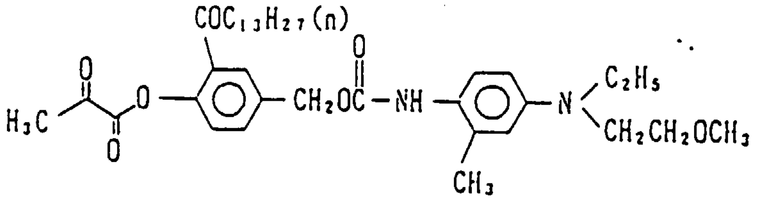

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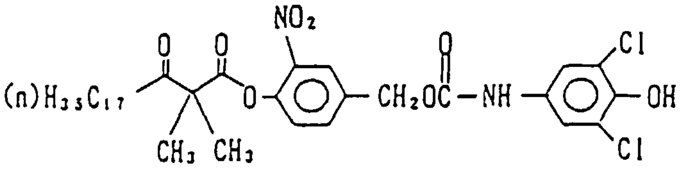

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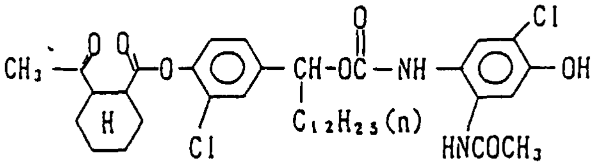

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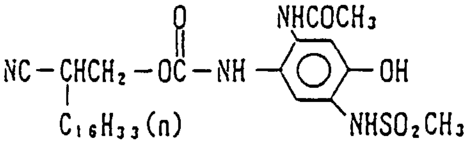

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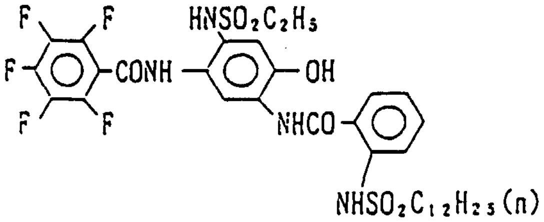

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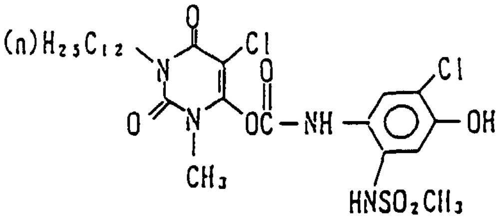

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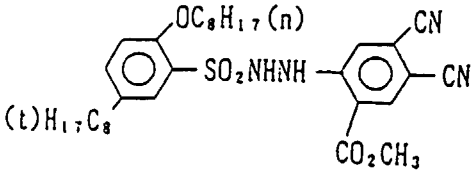

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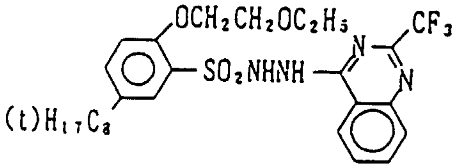

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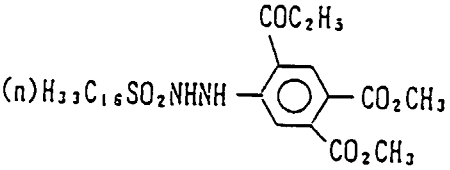

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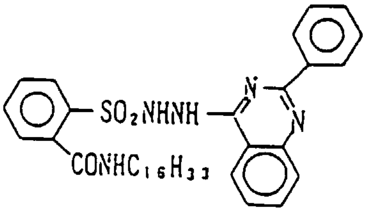

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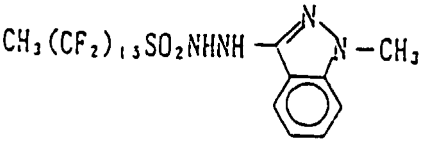

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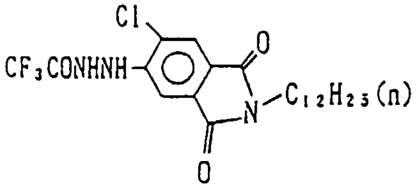

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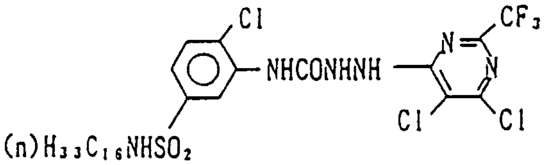

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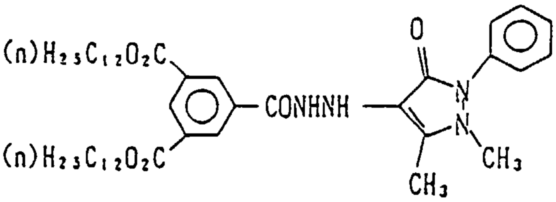

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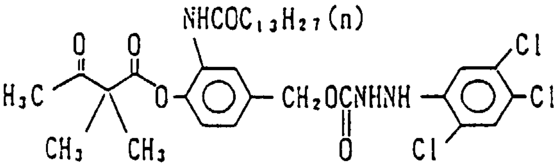

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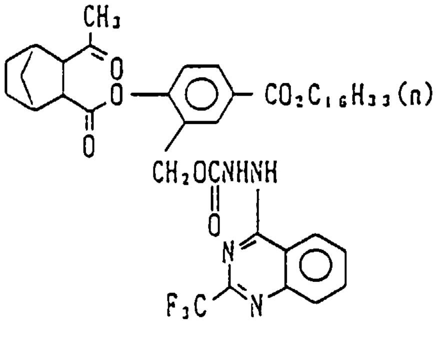
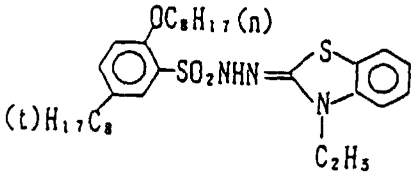
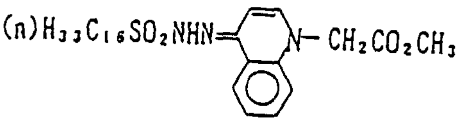


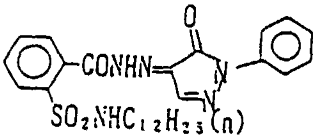
D-(31)



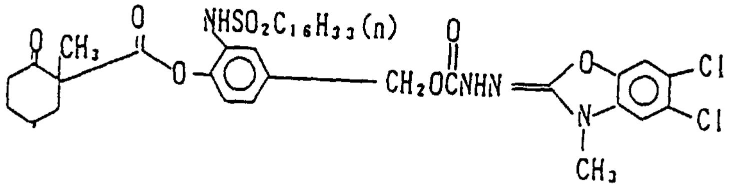
D-(32)



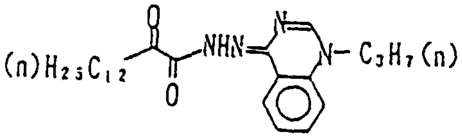
D-(33)



D-(34)



D-(35)



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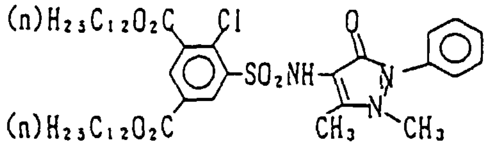

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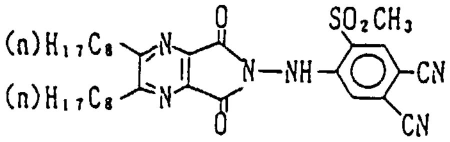

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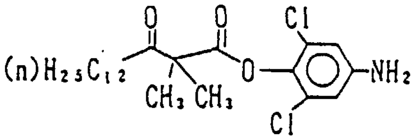

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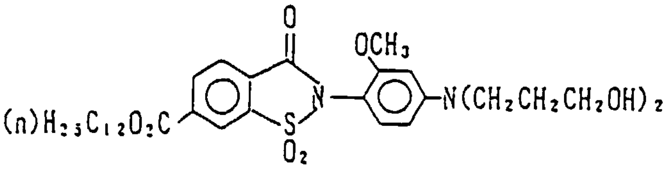
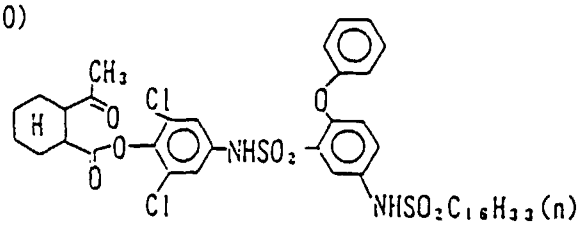


D－(40)

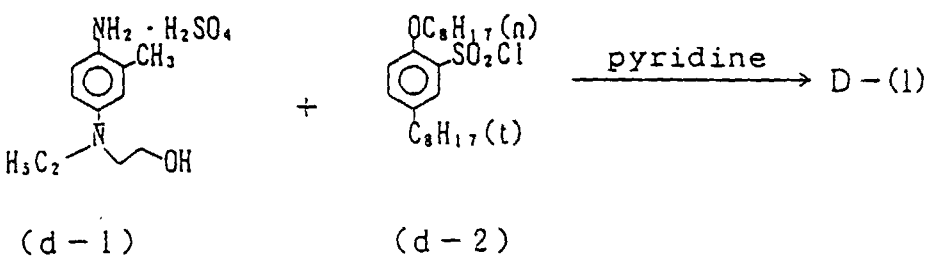


[0087] The synthesis examples of the developing agents for use in the present invention are described below. Other developing agents can also be synthesized by the similar methods.

SYNTHESIS EXAMPLE 1

Synthesis of Developing Agent D-(1)

[0088] Developing agent D-(1) was synthesized according to the following synthesis scheme.

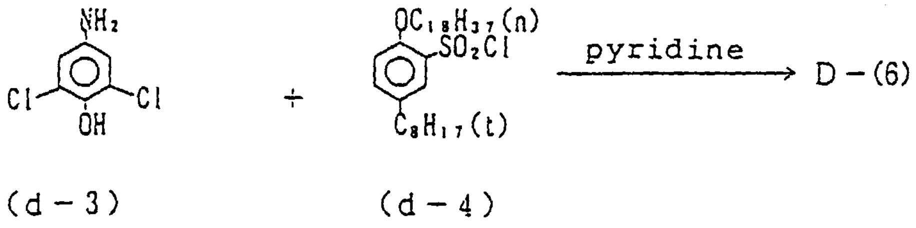


[0089] 20 g of Compound (d-1) and 20 ml of pyridine were dissolved in 100 ml of a distilled water, and a solution of 29 g of Compound (d-2) dissolved in 100 ml of ethyl acetate was dropwise added thereto over 30 minutes while stirring at room temperature. The reaction mixture was further stirred at room temperature for 1 hour, then an organic phase was separated and washed with dilute hydrochloric acid and water and dried over magnesium sulfate. The desiccant was filtered off, the solvent was distilled off, and the obtained brown oily product was subjected to purification through a silica gel column chromatography to obtain 32 g of the objective Developing Agent D-(1) as a pale yellow vitreous solid.

SYNTHESIS EXAMPLE 2

Synthesis of Developing Agent D-(6)

[0090] Developing agent D-(6) was synthesized according to the following synthesis scheme.

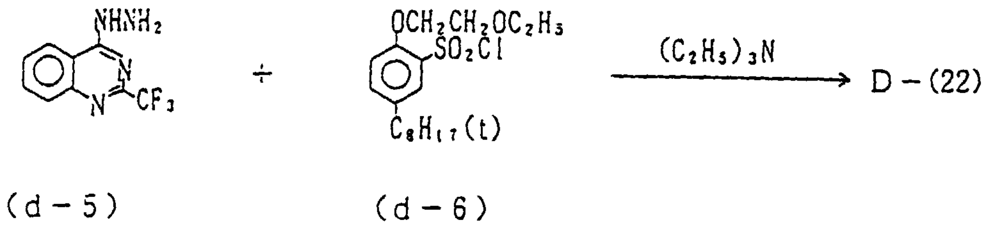


[0091] 30 g of Compound (d-3) and 30 ml of pyridine were dissolved in 150 ml of N,N-dimethylformamide, and a solution of 94 g of Compound (d-4) dissolved in 100 ml of ethyl acetate was dropwise added thereto over 40 minutes while stirring at room temperature. The reaction mixture was further stirred at room temperature for 2 hours, then poured into water, and extracted with ethyl acetate. An organic phase was separated and washed with dilute hydrochloric acid and water and dried over magnesium sulfate. The desiccant was filtered off, the solvent was distilled off, and the obtained brown oily product was subjected to purification through a silica gel column chromatography to obtain 115 g of the objective Developing Agent D-(6) as a colorless vitreous solid.

SYNTHESIS EXAMPLE 3

Synthesis of Developing Agent D-(22)

[0092] Developing agent D-(22) was synthesized according to the following synthesis scheme.



[0093] 30 g of Compound (d-5) and 20 ml of triethylamine were dissolved in 150 ml of N,N-dimethylformamide, and a solution of 54 g of Compound (d-6) dissolved in 40 ml of tetrahydrofuran was dropwise added thereto over 100 minutes while stirring at room temperature. The reaction mixture was further stirred at room temperature for 2 hours, then poured into water, and extracted with ethyl acetate. An organic phase was separated and washed with dilute hydrochloric acid and water and dried over magnesium sulfate. The desiccant was filtered off, the solvent was distilled off to obtain a yellow oily product. The oily product was crystallized from the mixed solvent of n-hexane/ethyl acetate to obtain 42 g of the objective Developing Agent D-(22) as colorless crystals. Melting point: 96-100°C.

[0094] The developing agent can be preferably incorporated into a light-sensitive silver halide layer in an amount of from 0.5 to 40 mol%, more preferably from 0.5 to 30 mol%, based on the amount of the light-sensitive silver halide contained in the light-sensitive silver halide layer.

[0095] Known dispersion methods can be used for incorporation of the developing agent as well as couplers described later.

[0096] The developing agent can be incorporated into a light-insensitive layer or a light-sensitive emulsion layer, but is preferably incorporated into a light-sensitive emulsion layer.

[0097] It is preferred that at least one of the light-sensitive layers comprises a high-sensitive layer and a low-sensitive layer each containing a color developing agent and the ratio of the color developing agent to the silver halide of the high-sensitive layer is smaller than the ratio of the low-sensitive layer.

[0098] The total film thickness of the hydrophilic colloid layers on the emulsion layer side of the silver halide color photographic material of the present invention is preferably 17 μm or less, more preferably 15 μm or less.

[0099] The tabular grains of the present invention can be doped with an ion of metal such as group VIII metals, In, Cd, Zn, Tl, Pb, Bi, Hg, Cu, Cr, Mo and Re. Preferred metal ions to be doped are ions of Pb, Fe, Cr, Rh, Ir and Ru.

[0100] It is preferred that the silver halide emulsion is subjected to gold sensitization and selenium sensitization.

[0101] The selenium compounds disclosed in the patents conventionally well-known can be used as a selenium sensitizer in the present invention. That is, an unstable type selenium compound and/or a non-unstable type selenium compound are usually added and used by stirring an emulsion at a high temperature of preferably 40°C or more for a certain period of time. The compounds disclosed in JP-B-44-15748, JP-B-43-13489, JP-A-4-25832 and JP-A-4-109240 are preferably used as the unstable selenium compounds. Specific examples of the unstable selenium sensitizers include isoselenocyanates (e.g., aliphatic isoselenocyanates such as allyl isoselenocyanate), selenoureas, selenoketones, selenoamides, selenocarboxylic acids (e.g., 2-selenopropionic acid, 2-selenobutyric acid), selenoesters, diacylselenides (e.g., bis(3-chloro-2,6-dimethoxybenzoyl)selenide), selenophosphates, phosphine-selenides, and colloidal metal selenium.

[0102] The preferred types of the unstable selenium compounds are described above but they are not limitative. In the unstable type selenium compound as the sensitizer for a photographic emulsion, the structure of the compound is not important as long as the selenium is unstable. It is generally understood that an organic moiety of a selenium sensitizer molecule has no role except for carrying selenium and allowing it to be present in an emulsion in an unstable form. The unstable selenium compounds having such a broad idea are advantageously used in the present invention.

[0103] The compounds disclosed in JP-B-46-4553, JP-B-52-34492 and JP-B-52-34491 are used as the non-unstable selenium compound in the present invention. Examples of the non-unstable selenium compounds include, for example, selenious acid, potassium selenocyanide, selenazoles, quaternary salts of selenazoles, diaryl selenide, diaryl diselenide, dialkyl selenide, dialkyl diselenide, 2-selenazolidinedione, 2-selenoxazolidinethione, and derivatives thereof.

[0104] The selenium sensitization method is disclosed in the following patents and literature: U.S. Patents 1,574,944, 1,602,592, 1,623,499, 3,297,446, 3,297,447, 3,320,069, 3,408,196, 3,408,197, 3,442,653, 3,420,670, 3,591,385, French Patents 2,693,038, 2,093,209, JP-B-52-34491, JP-B-52-34492, JP-B-53-295, JP-B-57-22090, JP-A-59-180536, JP-A-59-185330, JP-A-59-181337, JP-A-59-187338, JP-A-59-192241, JP-A-60-150046, JP-A-60-151637, JP-A-61-246738, JP-A-3-4221, JP-A-3-148648, JP-A-3-111838, JP-A-3-116132, JP-A-3-237450, JP-A-4-25832, JP-A-4-32831, JP-A-4-109240, Japanese Patent Application No. 2-110558, British Patents 255,846, 861,984, and H.E. Spencer et al., Journal of Photographic Science, Vol. 31, pages 158 to 169 (1983).

[0105] The silver halide photographic emulsion of the present invention can achieve higher sensitivity and lower fog by the combined use with sulfur sensitization and/or gold sensitization in the chemical sensitization. Particularly, in the silver halide emulsion of the present invention, it is the most preferred mode to carry out the gold sensitization and the sulfur sensitization in combination with the selenium sensitization.

[0106] The sulfur sensitization is usually carried out by adding a sulfur sensitizer and stirring an emulsion at a high temperature, preferably 40°C or more, for a certain period of time.

[0107] The gold sensitization is usually carried out by adding a gold sensitizer and stirring an emulsion at a high temperature, preferably 40°C or more, for a certain period of time.

[0108] Conventionally known sensitizers can be used as sulfur sensitizers for the above sulfur sensitization. They include, for example, thiosulfate, thioureas, allyl isothiacyanate, cystine, p-toluenesulfonate, and rhodanine. In addition thereto, the sulfur sensitizers described in U.S. Patents 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313, and 3,656,955, German Patent 1,422,869, JP-B-56-24937 and JP-A-55-45016 can also be used. The addition amount of the sulfur sensitizers may be an amount which is sufficient for effectively increasing the sensitivity of an emulsion. This amount is varied over a considerably wide range under various conditions such as pH, temperature and a size of a silver halide grain, but is preferably from 1×10^{-7} mol to 5×10^{-4} mol per mol of the silver halide.

[0109] The oxidation number of the gold in the gold sensitizer for the above gold sensitization may be either +1 valent or +3 valent, and gold compounds which are usually used as the gold sensitizer can be used. The representative examples thereof include chloroaurate, potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiocyanate, and pyridyl trichlorogold.

[0110] The addition amount of the gold sensitizer is varied according to various conditions, and the standard therefor is preferably from 1×10^{-7} mol to 5×10^{-4} mol per mol of the silver halide.

[0111] In a chemical ripening, no limit is required to put on the addition time and the addition order of a silver halide solvent, the selenium sensitizer, and the sulfur sensitizer and/or the gold sensitizer which can be used in combination with the selenium sensitizer, and the above compounds can be added at the same time or at a different addition time, for example, at an initial stage of the chemical ripening (preferably) or during the chemical ripening. The above compounds may be added by dissolving in water or a single solution or a mixed solution of an organic solvent which is miscible with water, for example, methanol, ethanol and acetone.

[0112] The light-sensitive material of the present invention can comprise at least one blue-sensitive layer, at least one green-sensitive layer and at least one red-sensitive layer on a support. The number of silver halide emulsion layers and light-insensitive layers and the order of the arrangement of the layers are not specifically limited. In a typical embodiment, the silver halide photographic material of the present invention comprises at least one light-sensitive layer consisting of a plurality of silver halide emulsion layers having substantially the same color sensitivity but different degrees of sensitivity on a support. The light-sensitive layer is a unit light-sensitive layer having a color sensitivity to any of blue light, green light and red light. In the multilayer silver halide color photographic material, these unit light-sensitive layers are generally arranged in the order of red-sensitive layer, green-sensitive layer and blue-sensitive layer from the support side. However, the order of arrangement can be reversed depending on the purpose, alternatively, the light-sensitive layers may be arranged in such a way that a layer having a different color sensitivity is interposed between layers having the same color sensitivity.

[0113] Light-insensitive layers such as various interlayers may be provided between the above-described silver halide light-sensitive layers, and as an uppermost layer or a lowermost layer.

[0114] These interlayers can contain couplers and DIR compounds as described in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037 and JP-A-61-20038, and they can further contain a color mixing inhibitor as generally used.

[0115] As the plurality of silver halide emulsion layers constituting each unit light-sensitive layer, a two-layer structure of a high-sensitive emulsion layer and a low-sensitive emulsion layer can be preferably used as disclosed in West German Patent 1,121,470 and British Patent 923,045. It is usually preferred that the emulsion layers are arranged so as to decrease in sensitivity toward a support in turn. Further, a light-insensitive layer can be provided between these silver halide emulsion layers. In addition, a low sensitivity emulsion layer may be provided farther from the support and a high sensitivity emulsion layer may be provided nearer to the support as disclosed in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541 and JP-A-62-206543.

[0116] In one specific example, a low sensitivity blue-sensitive layer (BL)/a high sensitivity blue-sensitive layer (BH)/a high sensitivity green-sensitive layer (GH)/a low sensitivity green-sensitive layer (GL)/a high sensitivity red-sensitive layer (RH)/a low sensitivity red-sensitive layer (RL), or BH/BL/GL/GH/RH/RL, or BH/BL/GH/GL/RL/RH can be arranged in this order from the side farthest from the support.

[0117] A blue-sensitive layer/GH/RH/GL/RL can be arranged in this order from the side farthest from the support as disclosed in JP-B-55-34932. Further, a blue-sensitive layer/GL/RL/GH/RH can be arranged in this order from the side farthest from the support as disclosed in JP-A-56-25738 and JP-A-62-63936.

[0118] Further, useful arrangements include the arrangement in which there are three layers having different degrees of sensitivities with the sensitivity being lower towards the support such that the uppermost layer is a silver halide emulsion layer having the highest sensitivity, the middle layer is a silver halide emulsion layer having a lower sensitivity than that of the uppermost layer, and the lowermost layer is a silver halide emulsion layer having a lower sensitivity than that of the middle layer, as disclosed in JP-B-49-15495. In the case of the structure of this type comprising three layers having different degrees of sensitivity, the layers in the unit layer of the same color sensitivity may be arranged in the order of a middle sensitivity emulsion layer/a high sensitivity emulsion layer/a low sensitivity emulsion layer, from the side farthest from the support, as disclosed in JP-A-59-202464.

[0119] Alternatively, the layers can be arranged in the order of a high sensitivity emulsion layer/a low sensitivity emulsion layer/a middle sensitivity emulsion layer, or a low sensitivity emulsion layer/a middle sensitivity emulsion layer/a high sensitivity emulsion layer.

[0120] Moreover, the arrangement may be varied as indicated above in the case where there are four or more layers.

[0121] As described above, various layer structures and arrangements can be selected depending on the purpose of the light-sensitive material.

[0122] The silver halide grains in the photographic emulsion other than the silver halide of the present invention may have a regular crystal form such as a cubic, octahedral or tetradecahedral form, an irregular crystal form such as a spherical or plate form, a form which has crystal defects such as twin crystal planes, or a form which is a composite of these forms.

[0123] The silver halide grains other than the silver halide of the present invention may be a fine grain having a projected area diameter of about 0.2 μm or less or a large grain having a projected area diameter of up to about 10 μm, and the emulsion may be polydispersed or monodispersed.

[0124] The silver halide emulsions for use in the present invention have been usually subjected to physical ripening, chemical ripening and spectral sensitization.

[0125] There are cases that a method in which the chalcogen compounds as disclosed in U.S. Patent 3,772,031 are added during the emulsion formation is useful. Cyanide, thiocyanide, selenocyanic acid, carbonate, phosphate and acetate can be present in addition to S, Se and Te.

[0126] The silver halide grains for use in the present invention can be subjected to at least one of sulfur sensitization, selenium sensitization, gold sensitization, palladium sensitization, other noble metal sensitization and reduction sensitization at an arbitrary stage during silver halide emulsion formation. As described above, a combined use of gold sensitization, sulfur sensitization and selenium sensitization is most preferred. Various types of emulsions can be prepared depending upon the stages when the chemical sensitization is carried out. There are a type in which a chemically sensitized nucleus is buried in the internal part of a grain, a type in which a chemically sensitized nucleus is buried in the shallow part from the surface of a grain, or a type in which a chemically sensitized nucleus is formed on the surface of a grain. The emulsion of the present invention can select the place of a chemically sensitized nucleus according to the purpose, but it is generally preferred to have at least one chemically sensitized nucleus in the vicinity of the surface of a grain.

[0127] The silver halide emulsion for use in the present invention is preferably reduction sensitized during grain formation, after grain formation and before chemical sensitization or during chemical sensitization, or after chemical sensitization.

[0128] The method of the reduction sensitization can be selected from a method in which a reduction sensitizer is added to a silver halide emulsion, a method in which grains are grown or ripened in the atmosphere of low pAg of from 1 to 7 which is called silver ripening, or a method in which grains are grown or ripened in the atmosphere of high pH of from 8 to 11 which is called high pH ripening. Further, two or more of these methods can be used in combination.

[0129] A method of adding a reduction sensitizer is preferred from the point of capable of delicately controlling the level of the reduction sensitization.

[0130] Stannous salt, ascorbic acid and derivatives thereof, amines and polyamines, hydrazine derivatives, formamidine-sulfinic acid, silane compounds and borane compounds are well known as a reduction sensitizer. These known reduction sensitizers can be selected and used in the present invention, and two or more of these compounds can also be used in combination. Stannous chloride, thiourea dioxide, dimethylamineborane, ascorbic acid and derivatives thereof are preferred compounds as a reduction sensitizer. As the addition amount of the reduction sensitizer depends upon the production conditions of the emulsion, the addition amount needs to be selected, but 10^{-7} to 10^{-3} mol per mol of the silver halide is preferred.

[0131] The reduction sensitizers are dissolved in water or a solvent such as alcohols, glycols, ketones, esters or amides and added during grain growth. They may be previously added to a reaction vessel but is more preferably added at an appropriate stage during grain growth. Further, the reduction sensitizers have been previously added to an aqueous solution of water-soluble silver salt or an aqueous solution of water-soluble alkali halide and silver halide grains can be precipitated using these aqueous solutions. In addition, the solution of the reduction sensitizers may be divided to several parts and added in several times or may be added continuously over a long period of time with the degree of the grain growth.

[0132] It is preferred to use an oxidizing agent for silver during the production process of the emulsion of the present invention. An oxidizing agent for silver is a compound having a function of acting on metal silver and converting it to a silver ion. In particular, a compound which can convert superminute silver grains by-produced in the course of the formation of silver halide grains and chemical sensitization to a silver ion is effective. The silver ion converted may form slightly water-soluble silver salt such as silver halide, silver sulfide or silver selenide, or may form easily water-soluble silver salt such as silver nitrate. An oxidizing agent for silver may be inorganic or organic. Examples of inorganic oxidizing agents include oxyacid salt, such as ozone, hydrogen peroxide and addition products thereof (e.g., $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$, $2NaCO_3 \cdot 3H_2O_2$, $Na_4P_2O_7 \cdot 2H_2O_2$, $2Na_2SO_4 \cdot H_2O_2 \cdot 2H_2O$), peroxyacid salt (e.g., $K_2S_2O_8$, $K_2C_2O_6$, $K_2P_2O_8$), peroxy complex compound (e.g., $K_2[Ti(O_2)C_2O_4] \cdot 3H_2O$, $4K_2SO_4 \cdot Ti(O_2)OH \cdot SO_4 \cdot 2H_2O$, $Na_3[VO(O_2)(C_2H_4)_2] \cdot 6H_2O$), permanganate (e.g., $KMnO_4$), and chromate (e.g., $K_2Cr_2O_7$), halogen element such as iodine and bromine, perhalogen acid salt (e.g., potassium periodate), salt of metal of high valency (e.g., potassium hexacyanoferrate(III)), and thiosulfonate.

[0133] Further, examples of organic oxidizing agents include quinones such as p-quinone, organic peroxide such as peracetic acid and perbenzoic acid, a compound which releases active halogen (e.g., N-bromosuccinimide, chloramine T, chloramine B).

[0134] The oxidizing agents which are preferably used in the present invention are inorganic oxidizing agents such as ozone, hydrogen peroxide and addition products thereof, halogen element, thiosulfonate, and organic oxidizing agents such as quinones. It is preferred to use the above described reduction sensitization in combination with an oxidizing agent for silver. The method of usage can be selected from a method in which an oxidizing agent is used and then reduction sensitization is carried out, an inverse method thereof, or a method in which both are concurred with. These methods can be used either in grain formation process or in chemical sensitization process selectively.

[0135] The silver halide light-sensitive material of the present invention is a material having two or more light-sensitive layers of different spectral sensitivities, and these spectral sensitivities are not limited to blue sensitivity, green sensitivity and red sensitivity.

[0136] The silver halide emulsion has been generally subjected to physical ripening, chemical ripening and spectral sensitization and used. The additives which are used in these processes are disclosed in Research Disclosure, No. 17643, No. 18716 and No. 307105 the the locations related thereto are indicated in the table below.

	Kinds of Additives	RD17643 (Dec. 1978)	RD18716 (Nov. 1979)	RD307105 (Nov. 1989)
1.	Chemical sensitizer	p. 23	p. 648, right col.	p. 866
2.	Sensitivity increasing agent		p. 648, right col.	
3.	Spectral sensitizer, supersensitizer	pp. 23-24	p. 648, right col.-p. 649, right col.	pp. 866-868
4.	Brightening agent	p. 24	p. 647, right col.	p. 868
5.	Antifoggant, stabilizer	pp. 24-25	p. 649, right col.	pp. 868-870
6.	Light absorbent, filter dye, UV absorbent	pp. 25-26	p. 649, right col.-p. 650, left col.	p. 873
7.	Stain inhibitor	p. 25, right col.	p. 650, left to right cols.	p. 872
8.	Dye Image Stabilizer	p. 25	p. 650, left col.	p. 872
9.	Hardening agent	p. 26	p. 651, left col.	pp. 874-875
10.	Binder	p. 26	p. 651, left col.	p. 873-874

(continued)

	Kinds of Additives	RD17643 (Dec. 1978)	RD18716 (Nov. 1979)	RD307105 (Nov. 1989)
11.	Plasticizer, lubricant	p. 27	p. 650, right col.	p. 876
12.	Coating aid, surface active agent	pp. 26-27	p. 650, right col.	pp. 875-876
13.	Antistatic agent	p. 27	p. 650, right col.	pp. 876-877
14.	Matting agent			pp. 878-879

[0137] Other techniques and inorganic/organic materials which can be used in the color photographic material of the present invention are described in European Patent 436,938A2 at the portion described below and in the patents referred to in the following.

1.	Layer structure:	from page 146, line 34 to page 147, line 25
2.	Yellow coupler:	from page 137, line 35 to page 146, line 33, page 149, lines 21 to 23
3.	Magenta coupler:	page 149, lines 24 to 28; European Patent 421,453A1, from page 3, line 5 to page 25, line 55
4.	Cyan coupler:	page 149, lines 29 to 33; European Patent 432,804A2, from page 3, line 28 to page 40, line 2
5.	Polymer coupler:	page 149, lines 34 to 38; European Patent 435,342A2, from page 113, line 39 to page 123, line 37
6.	Colored coupler:	from page 53, line 42 to page 137 line 34 and page 149, lines 39 to 45
7.	Other functional couplers:	from page 7, line 1 to page 53, line 41 and from page 149, line 46 to page 150, line 3; European Patent 435,334A2, from page 3, line 1 to page 29, line 50
8.	Antiseptic/antimold:	page 150, lines 25 to 28
9.	Formalin scavenger:	page 149, lines 15 to 27
10.	Other additives:	page 153, lines 38 to 47; European Patent 421,453A1, from page 75, line 21 to page 84, line 56 and from page 27, line 40 to page 37, line 40
11.	Dispersion method:	page 150, lines 4 to 24
12.	Support:	page 150, lines 32 to 34
13.	Film thickness, physical property:	page 150, lines 35 to 49
14.	Desilvering:	from page 151, line 48 to page 152, line 53
15.	Automatic processor:	from page 152, line 54 to page 153, line 2
16.	Water washing/stabilization	page 153, lines 3 to 37

[0138] The processing method of the present invention is described in detail below.

[0139] In the present invention, the photographic material is processed with a color developer, desilvered and then processed with washing water and/or stabilizing solution.

[0140] In the desilverization process, the photographic material is fundamentally bleach-fixed with a processing solution having bleaching ability and then fixed with a processing solution having fixing ability. The bleaching and the fixing may be conducted individually or may be conducted simultaneously using a bleach-fixing solution having both bleaching ability and fixing ability (bleach-fixing). The bleaching, the fixing or the bleach-fixing may comprise one tank or two or more tanks.

[0141] The processing solution having bleaching ability of the present invention means, out of processing solutions used in the desilverizing step, a processing solution containing a bleaching agent, more specifically, it includes a bleaching solution and a bleach-fixing solution. Specific embodiments of the desilvering of the present invention are set forth below but the present invention is by no means limited thereto.

1. Bleaching - Fixing
2. Bleach-fixing
3. Bleaching - Bleach-fixing
4. Bleach-fixing - Bleach-fixing
5. Bleaching - Bleach-fixing - Fixing
6. Bleaching - Bleach-fixing - Bleach-fixing
7. Bleaching - Fixing - Fixing
8. Bleaching - Fixing - Bleach-fixing
9. Bleach-fixing - Fixing
10. Bleach-fixing - Bleaching

[0142] Between these processings, a water washing step may be freely provided.

[0143] The compound represented by formula (I) is described in detail. The carbon number referred to in the following indicates the carbon number exclusive of the substituent moiety.

[0144] The aliphatic hydrocarbon group represented by R_1 is a linear, branched or cyclic alkyl group (preferably having from 1 to 12 carbon atoms, more preferably from 1 to 10 carbon atoms, still more preferably having from 1 to 8 carbon atoms), an alkenyl group (preferably having from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, still more preferably from 2 to 7 carbon atoms) or an alkynyl group (preferably having from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, still more preferably from 2 to 7 carbon atoms), which may have a substituent.

[0145] Examples of the substituent include an aryl group (having preferably from 6 to 12 carbon atoms, more preferably from 6 to 10 carbon atoms, still more preferably from 6 to 8 carbon atoms, e.g., phenyl, p-methylphenyl), an alkoxy group (having preferably from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methoxy, ethoxy), an aryloxy group (having preferably from 6 to 12 carbon atoms, more preferably from 6 to 10 carbon atoms, still more preferably from 6 to 8 carbon atoms, e.g., phenyloxy), an acyl group (having preferably from 1 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, still more preferably from 2 to 8 carbon atoms, e.g., acetyl), an alkoxycarbonyl group (having preferably from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, still more preferably from 2 to 8 carbon atoms, e.g., methoxy-carbonyl), an acyloxy group (having preferably from 1 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, still more preferably from 2 to 8 carbon atoms, e.g., acetoxy), an acylamino group (having preferably from 1 to 10 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., acetylamino), a sulfonylamino group (having preferably from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfonylamino), a sulfamoyl group (having from 0 to 10 carbon atoms, more preferably from 0 to 6 carbon atoms, still more preferably from 0 to 4 carbon atoms, e.g., sulfamoyl, methylsulfamoyl), a carbamoyl group (having preferably from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., carbamoyl, methylcarbamoyl), an alkylthio group (having preferably from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methylthio, ethylthio), a sulfonyl group (having preferably from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfonyl), a sulfinyl group (having preferably from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfinyl), a hydroxy group, a halogen atom (e.g., fluorine, chlorine, bromine, iodine), a cyano group, a sulfo group, a carboxyl group, a nitro group and a heterocyclic group (e.g., imidazolyl, pyridyl). These substituents each may be further substituted. When two or more substituents are present, they may be the same or different.

[0146] The substituent for the aliphatic hydrocarbon group represented by R_1 is preferably an alkoxy group, a carboxyl group, a hydroxy group or a sulfo group, more preferably a carboxy group or a hydroxy group.

[0147] The aliphatic hydrocarbon group represented by R_1 is preferably an alkyl group, more preferably a chained alkyl group, still more preferably methyl, ethyl, carboxymethyl, 1-carboxyethyl, 2-carboxyethyl, 1,2-dicarboxyethyl, 1-carboxy-2-hydroxyethyl, 2-carboxy-2-hydroxyethyl, 2-hydroxyethyl, 2-methoxyethyl, 2-sulfoethyl, 1-carboxypropyl, 1-carboxybutyl, 1,3-dicarboxypropyl, 1-carboxy-2-(4-imidazolyl)ethyl, 1-carboxy-2-phenylethyl, 1-carboxy-3-methylthiopropyl, 2-carbamoyl-1-carboxyethyl or 4-imidazolylmethyl, particularly preferably methyl, carboxymethyl, 1-carboxyethyl, 2-carboxyethyl, 1,2-dicarboxyethyl, 1-carboxy-2-hydroxyethyl, 2-carboxy-2-hydroxyethyl, 2-hydroxyethyl, 1-carboxypropyl, 1-carboxybutyl, 1,3-dicarboxypropyl, 1-carboxy-2-phenylethyl or 1-carboxy-3-methylthiopropyl.

[0148] The aryl group represented by R_1 is preferably a monocyclic or bicyclic aryl group having from 6 to 20 carbon atoms (e.g., phenyl, naphthyl), more preferably a phenyl group having from 6 to 15 carbon atoms, still more preferably a phenyl group having from 6 to 10 carbon atoms.

[0149] The aryl group represented by R_1 may have a substituent and examples of the substituent include those described above as the substituent for the aliphatic hydrocarbon group represented by R_1 and in addition, an alkyl group (having preferably from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methyl, ethyl), an alkenyl group (having preferably from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., vinyl, allyl) and an alkynyl group (having preferably from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., propargyl).

[0150] The substituent for the aryl group represented by R_1 is preferably an alkyl group, an alkoxy group, a hydroxy group or a sulfo group, more preferably an alkyl group, a carboxyl group or a hydroxy group.

[0151] Specific examples of the aryl group represented by R_1 include 2-carboxyphenyl and 2-carboxymethoxyphenyl.

[0152] The heterocyclic group represented by R_1 is a 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-membered saturated or unsaturated heterocyclic group containing at least one of N, O and S atoms, which may be monocyclic or may form a condensed ring with other ring.

[0153] The heterocyclic group is preferably 5- or 6-membered aromatic heterocyclic group, more preferably a 5- or 6-membered aromatic heterocyclic group containing a nitrogen atom, still more preferably a 5- or 6-membered aromatic heterocyclic group containing one or two nitrogen atoms.

[0154] Specific examples of the heterocyclic group include pyrrolidinyl, piperidyl, piperazinyl, imidazolyl, pyrazolyl, pyridyl and quinolyl, with imidazolyl and pyridyl being preferred.

[0155] The heterocyclic group represented by R_1 may have a substituent and examples of the substituent include those described above as the substituent for the aliphatic hydrocarbon group represented by R_1 and in addition, an alkyl group (having preferably from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methyl, ethyl), an alkenyl group (having preferably from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., vinyl, allyl) and an alkynyl group (having preferably from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., propargyl).

[0156] The substituent for the heterocyclic group represented by R_1 is preferably an alkyl group, an alkoxy group, a hydroxy group or a sulfo group, more preferably an alkyl group, a carboxy group or a hydroxy group.

[0157] R_1 is preferably a hydrogen atom or an alkyl group having from 1 to 8 carbon atoms, more preferably a hydrogen atom, methyl, ethyl, 1-carboxyethyl, 2-carboxyethyl, hydroxyethyl or 2-carboxy-2-hydroxyethyl, still more preferably a hydrogen atom.

[0158] The alkylene groups represented by L_1 and L_2 may be the same or different, may be linear, branched or cyclic, or may have a substituent. Examples of the substituent include those described above as the substituent for the aliphatic hydrocarbon group represented by R_1 and in addition, an alkenyl group (having preferably from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., vinyl, allyl) and an alkynyl group (having preferably from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., propargyl).

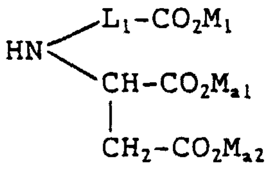
[0159] The substituent for the alkylene group represented by L_1 or L_2 is preferably an aryl group, an alkoxy group, a hydroxy group, a carboxy group or a sulfo group, more preferably an aryl group, a carboxy group or a hydroxy group.

[0160] The alkylene group represented by L_1 or L_2 is preferably an alkylene group with the alkylene group moiety having from 1 to 6 carbon atoms, more preferably an alkylene group with the alkylene group moiety having from 1 to 4 carbon atoms, still more preferably a substituted or unsubstituted methylene or ethylene.

[0161] Preferred examples of the alkylene group include methylene, ethylene, trimethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1,2-cyclohexylene, 1-carboxymethylene, carboxymethylmethylene, carboxyethylmethylene, hydroxymethylmethylene, 2-hydroxy-ethylmethylene, carbamoylmethylmethylene, phenylmethylene, benzylmethylene, 4-imidazolylmethylmethylene and 2-methylthioethyimethylene. Among these, more preferred are methylene, ethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1-carboxymethylene, carboxymethylmethylene, carboxyethylmethylene, hydroxymethylmethylene, benzylmethylene, 4-imidazolylmethylmethylene and 2-methylthioethylmethylene, and still more preferred are methylene, ethylene, methylmethylene, ethylmethylene, n-propylmethylene, n-butylmethylene, 1-carboxymethylene, carboxymethylmethylene, hydroxymethylmethylene and benzylmethylene.

[0162] The cation represented by M_1 or M_2 represents an organic or inorganic cation and examples thereof include an alkali metal (e.g., Li^+, Na^+, K^+, Cs^+), an alkaline earth metal (e.g., Mg^{2+}, Ca^{2+}), an ammonium (e.g., ammonium, trimethylammonium, triethylammonium, tetramethylammonium, tetraethylammonium, tetrabutylammonium, 1,2-ethanediammonium), a pyridinium, an imidazolium and a phosphonium (e.g., tetrabutylphosphonium). M_1 and M_2 each is preferably an alkali metal or an ammonium, more preferably Na^+, K^+ or NH_4^+.

[0163] The compound represented by formula (I) is preferably a compound represented by formula (I-a).



(I-a)

(wherein L_1 and M_1 have the same meaning and preferred range as those in formula (I), respectively, and M_{a1} and M_{a2} each has the same meaning as M_2 in formula (I)).

[0164] In formula (I-a), more preferably, L_1 is substituted or unsubstituted methylene or ethylene and M_1, M_{a1} and M_{a2} each is any one of a hydrogen atom, an alkali metal and an ammonium; still more preferably, L_1 is substituted or unsubstituted methylene and M_1, M_{a1} and M_{a2} each is any one of a hydrogen atom, an alkali metal and an ammonium; particularly preferably L_1 is a substituted or unsubstituted methylene having from 1 to 10 carbon atoms inclusive of substituents and M_1, M_{a1} and M_{a2} each is any one of a hydrogen atom, Na^+, K^+ and NH_4^+.

[0165] The compound represented by formula (II) is described in detail below.

[0166] The aliphatic hydrocarbon group, the aryl group and the heterocyclic group represented by R_{21}, R_{22}, R_{23}, or R_{24} have the same meaning and preferred range as the aliphatic hydrocarbon group, the aryl group and the heterocyclic group represented by R_1 in formula (I), respectively.

[0167] R_{21}, R_{22}, R_{23}, and R_{24} each is preferably a hydrogen atom or a hydroxy group, more preferably a hydrogen atom.

[0168] t and u each represents 0 or 1, preferably 1.

[0169] The divalent linking group represented by W is preferably represented by the following formula (W):

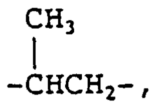
$$-(W^1\text{-}B)_v\text{-}(W^2)_w- \qquad \text{(W)}$$

wherein W^1 and W^2 may be the same or different and each represents a linear or branched alkylene group having from 2 to 8 carbon atoms (e.g., ethylene, propylene, trimethylene), a cycloalkylene group having from 5 to 10 carbon atoms (e.g., 1,2-cyclohexylene), an arylene group having from 6 to 10 carbon atoms (e.g., o-phenylene), an aralkylene group having from 7 to 10 carbon atoms (e.g., o-xylenylene), a divalent nitrogen-containing heterocyclic group or a carbonyl group. The divalent nitrogen-containing heterocyclic group is preferably a 5- or 6-membered heterocyclic group containing nitrogen as a hetero atom where W^1 and W^2 are linked through carbon atoms adjacent to each other as in the imidazolyl group. B represents -O-, -S- or $-N(R_W)-$, wherein R_w represents a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms (e.g., methyl) which may be substituted by a carboxyl group, a phosphono group, a hydroxy group or a sulfo group, or an aryl group having from 6 to 10 carbon atoms (e.g., phenyl) which may be substituted by a carboxyl group, a phosphono group, a hydroxy group or a sulfo group.

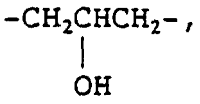
[0170] W^1 and W^2 each is preferably an alkylene group having from 2 to 4 carbon atoms.

[0171] v represents an integer of from 0 to 3, and when v is 2 or 3, the W^1-D groups may be the same or different. v is preferably from 0 to 2, more preferably 0 or 1, still more preferably 0. w represents an integer of from 1 to 3, and when w is 2 or 3, the W^2 groups may the same or different. w is preferably 1 or 2. Examples of W include the following:

$-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$,



$-CH(CH_3)CH_2-$,

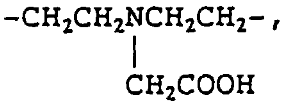


$-CH_2CH(OH)CH_2-$,

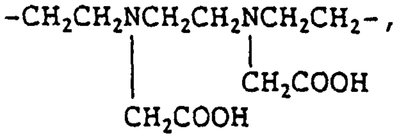
$-CH_2CH_2OCH_2CH_2-$,

$-CH_2CH_2OCH_2CH_2OCH_2CH_2-$, $-CH_2CH_2SCH_2CH_2-$,

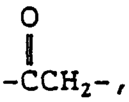
$-CH_2CH_2SCH_2CH_2SCH_2CH_2-$,



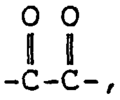
$-CH_2CH_2N(CH_2COOH)CH_2CH_2-$,



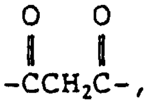
$-CH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)CH_2CH_2-$,



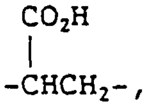
$-C(=O)CH_2-$,



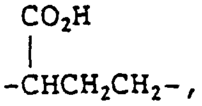
$-C(=O)-C(=O)-$,



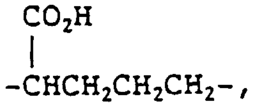
$-C(=O)CH_2C(=O)-$,



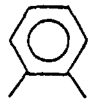
$-CH(CO_2H)CH_2-$,



$-CH(CO_2H)CH_2CH_2-$,



$-CH(CO_2H)CH_2CH_2CH_2-$,



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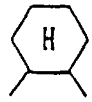

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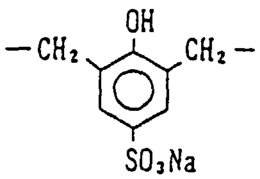

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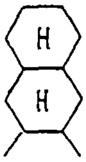

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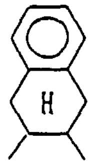

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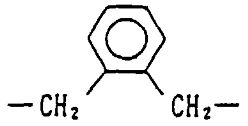

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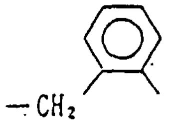

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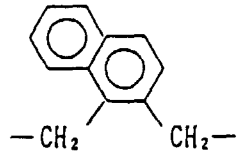

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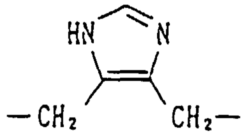

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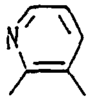

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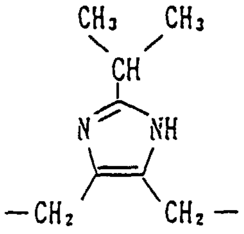

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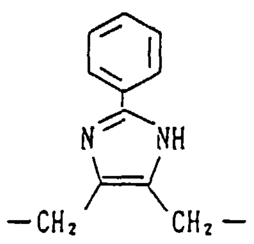

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$-CH_2-CH=CH-CH_2-$.

[0172] W is more preferably ethylene, propylene, trimethylene or 2,2-dimethyltrimethylene, still more preferably ethylene or trimethylene.

[0173] M_{21}, M_{22}, M_{23} and M_{24} each represents a hydrogen atom or a cation and they have the same meaning as M_1 and M_2 of formula (I).

[0174] Among the compounds represented by formula (II), preferred is a compound where R_{22} and R_{24} each is a hydrogen atom and t and u each is 1, more preferred is a compound where R_{21}, R_{22}, R_{23} and R_{24} each is a hydrogen atom, and t and u each is 1.

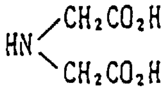
[0175] Among the compounds represented by formula (II), still more preferred are a compound where R_{21}, R_{22}, R_{23} and R_{24} each is a hydrogen atom, t and u each is 1, W is ethylene, and M_{21}, M_{22}, M_{23} and M_{24} each is selected from a hydrogen atom, Na^+, K^+ and NH_4^+, and a compound where R_{21}, R_{22}, R_{23} and R_{24} each is a hydrogen atom, t and u each is 1, W is trimethylene, and M_{21}, M_{22}, M_{23} and M_{24} each is selected from a hydrogen atom, Na^+, K^+ and NH_4^+.

[0176] When the compound represented by formula (I) or (II) has an asymmetric carbon in the molecule, at least one asymmetric carbon is preferably an L-form. Further, when two or more asymmetric carbons are present, the number of L-form structures is preferably larger in the asymmetric carbon moieties.

[0177] Specific examples of the compounds represented by formulae (I) and (II) are set forth below, but the present invention is by no means limited thereto.

[0178] The moiety marked L in the following compounds indicates that the asymmetric carbon moiety is an L-form. Otherwise, the moiety is a mixture of D-form and L-form.

I − 1



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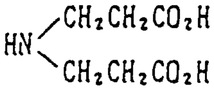

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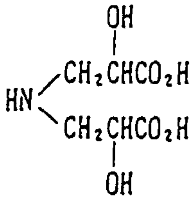

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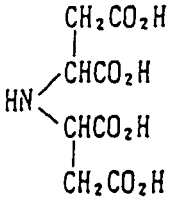

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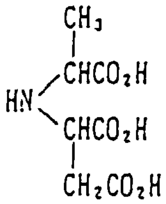

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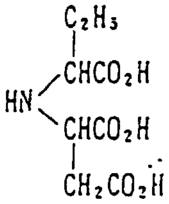

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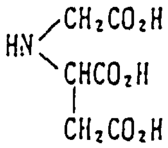

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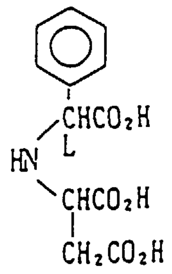

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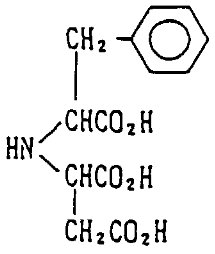

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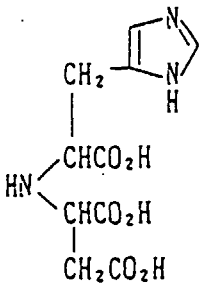

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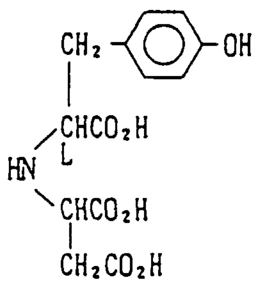

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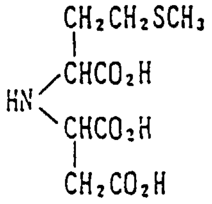

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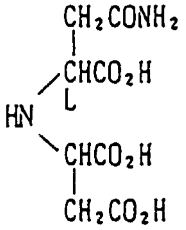

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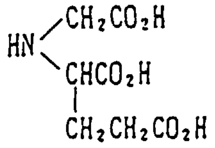

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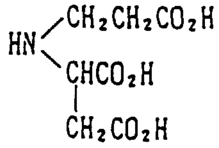

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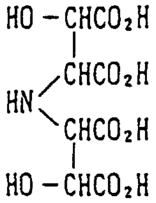

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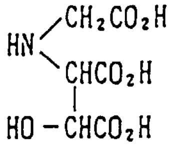

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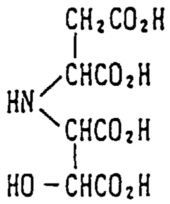

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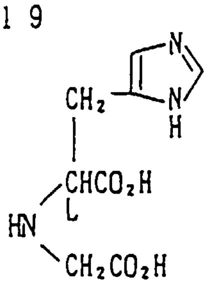

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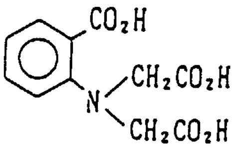

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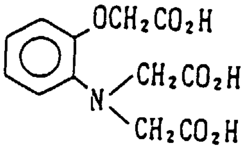

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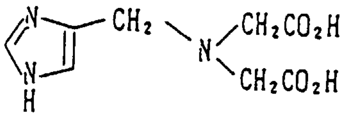

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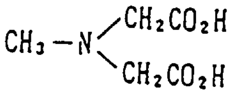

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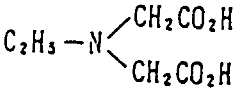

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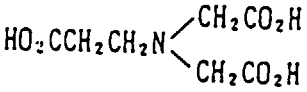

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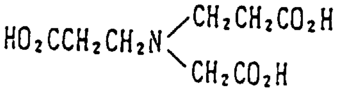

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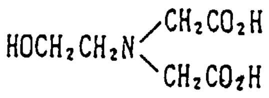

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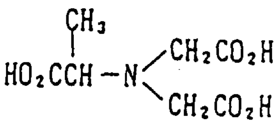

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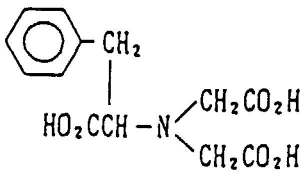

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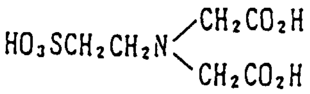

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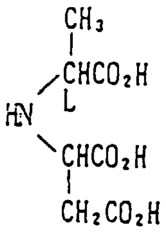

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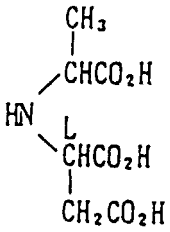

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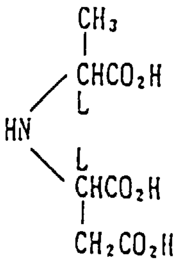

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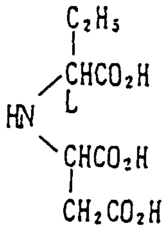

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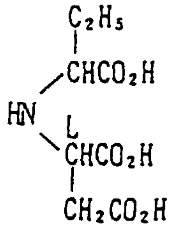

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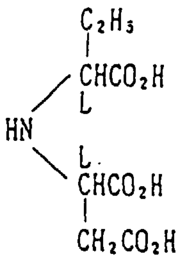

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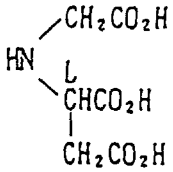

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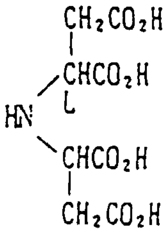

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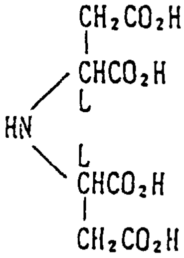

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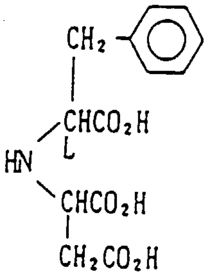

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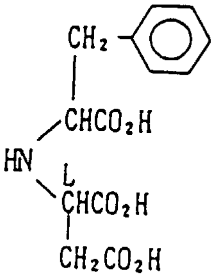

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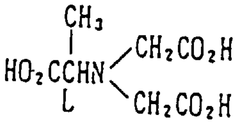

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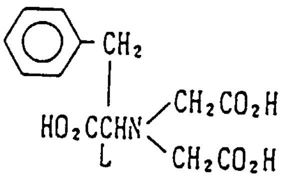

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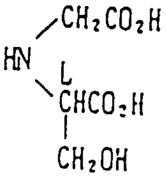

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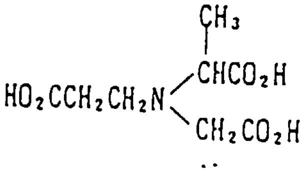

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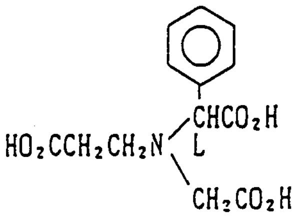

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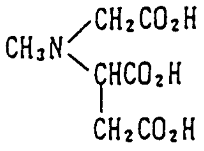

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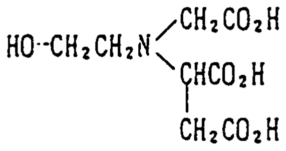

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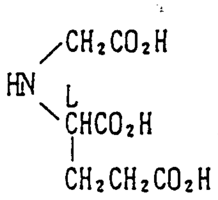

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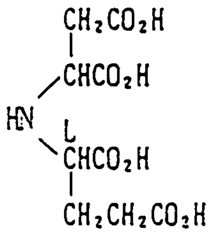

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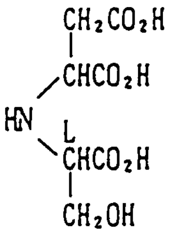

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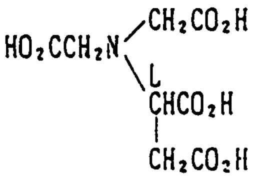

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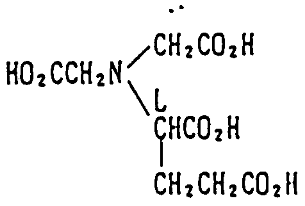

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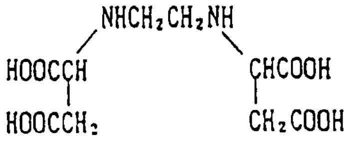

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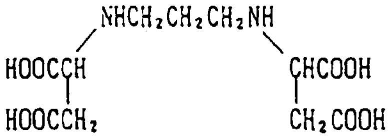

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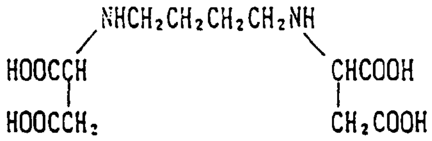

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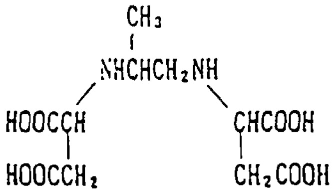

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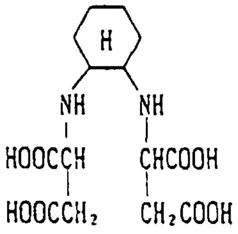

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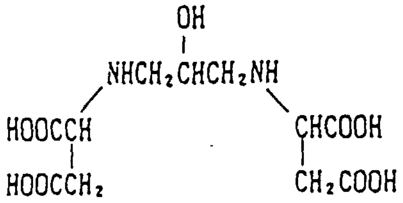

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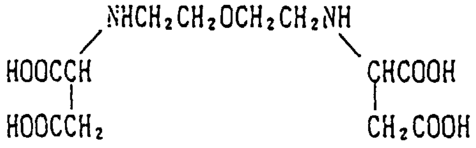

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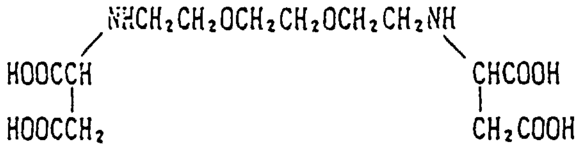

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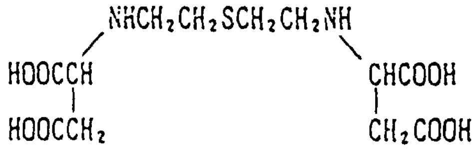

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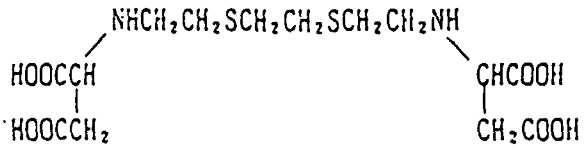

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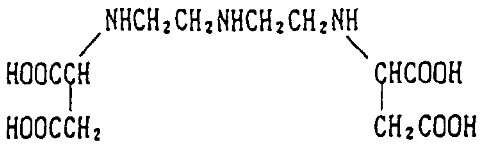

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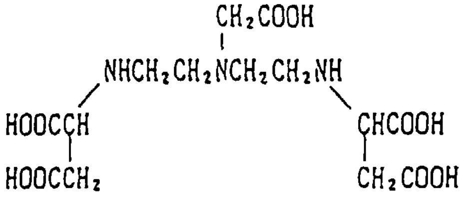

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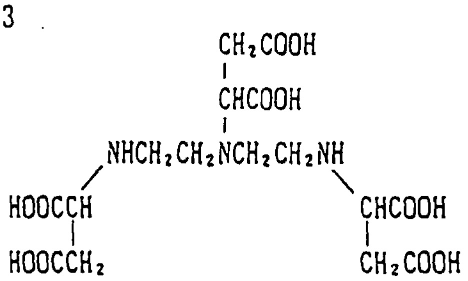

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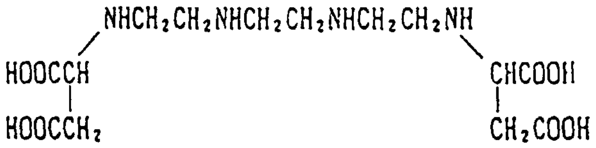

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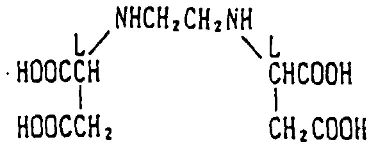

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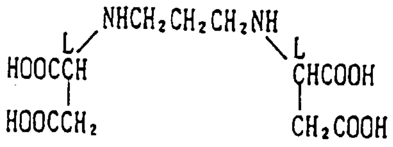

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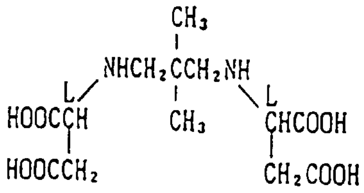

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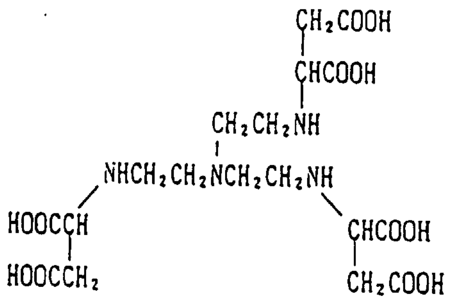

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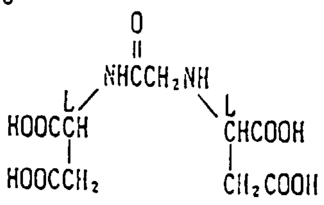

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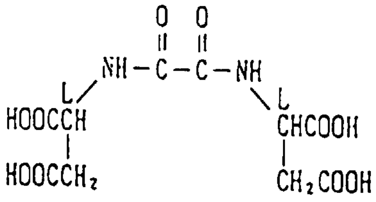

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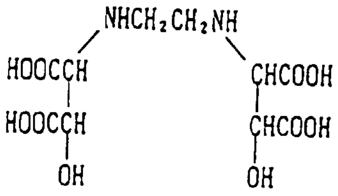

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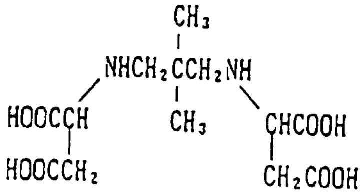

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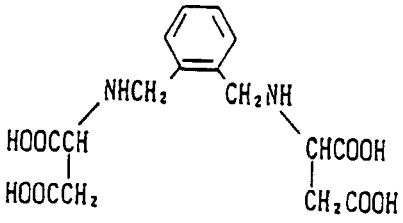

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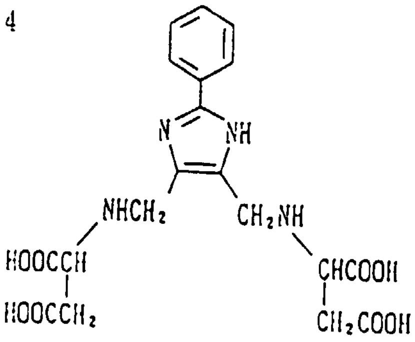

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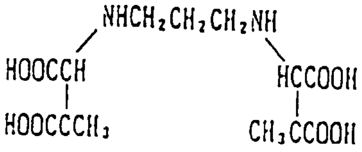
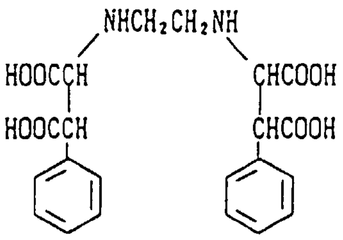


II－２６



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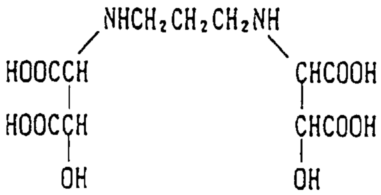
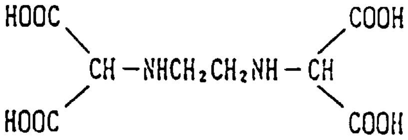
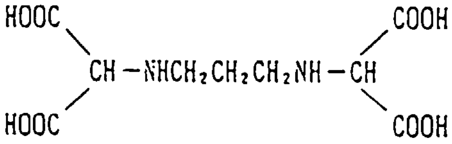


II－２８



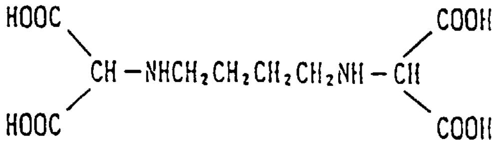
$$(HOOC)_2CH-NHCH_2CH_2NH-CH(COOH)_2$$

II－２９



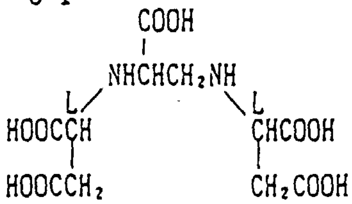
$$(HOOC)_2CH-NHCH_2CH_2CH_2NH-CH(COOH)_2$$

II－３０



$$(HOOC)_2CH-NHCH_2CH_2CH_2CH_2NH-CH(COOH)_2$$

II-31



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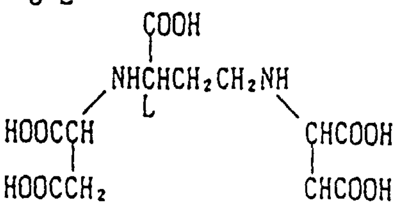

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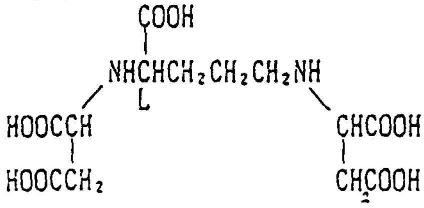

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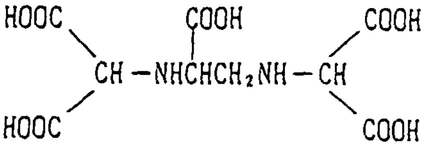

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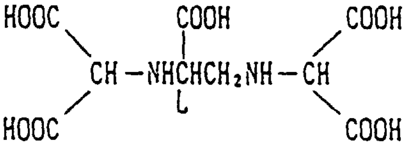


[0179] In the above-described compounds, the hydrogen atom of the carboxyl group may be replaced by a cation and the cation in this case has the same meaning as defined for the cation represented by M_1 or M_2 in formula (I).

[0180] The compound represented by formula (I) of the present invention may be synthesized according to the methods described, for example, in Journal of Inorganic and Nuclear Chemistry, vol. 35, p. 523 (1973), Swiss Patent 561,504, German Patents 3,912,551A1, 3,939,755A1 and 3,939,756A1, JP-A-5-265159, JP-A-6-59422 (Synthesis Examples 1, 2, 3, 4 and 6 are the synthesis methods of L-forms of Compounds I-42, I-43, I-46, I-52 and I-53, respectively), JP-A-6-95319 (Synthesis Examples 2 to 6 are the synthesis methods of L-forms of Compounds I-8, I-11, I-37, I-38 and I-40, respectively), JP-A-6-161054 and JP-A-6-161065.

[0181] Further, the compound represented by formula (II) may be synthesized according to the methods described, for example, in JP-A-63-199295, JP-A-3-173857, Bulletin of Chemical Society of Japan, vol. 46, p. 844 (1973), and Inorganic Chemistry, vol. 7, 2405 (1968) (the synthesis method of the L,L-form of Compound II-15 is described).

[0182] With respect to the iron(III) complex salt of the compound represented by formula (I) or (II) of the present invention, the compound previously taken out as an iron(III) complex salt may be added or the compound represented by formula (I) or (II) may be placed in a solution together with an iron(III) salt (e.g., iron(III) nitrate, ferric chloride) to form a complex in the processing solution.

[0183] The compounds represented by formula (I) or (II) of the present invention may be used individually or in combination of two or more thereof.

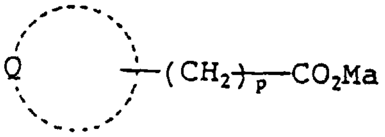
[0184] The compound represented by formula (I) or (II) of the present invention may be used in a slightly excessive amount more than the amount required for forming an iron(III) ion complex (for example, 0.5 equivalent by mol, equimolecule or 2 equivalents by mol to the iron(III) ions), and when the compound is used in excess, the excess is usually preferably from 0.01 to 15 mol%.

[0185] The organic acid iron(III) complex salt contained in the processing solution having bleaching ability may be used as an alkali metal salt or an ammonium salt. Examples of the alkali metal salt include a lithium salt, a sodium salt and a potassium salt, and examples of the ammonium salt include an ammonium salt and a tetraethylammonium salt, however, in the present invention, the ammonium ion concentration in the processing solution having bleaching ability is preferably from 0 to 0.4 mol/ℓ, more preferably from 0 to 0.2 mol/ℓ.

[0186] In the present invention, other than the iron(III) complex salt of the compound represented by formula (I) or (II), an inorganic oxidizing agent such as an iron(III) complex salt of known compounds (such as ethylene-diamine-N,N,N',N'-tetraacetic acid, diethylenetriaminepentaacetic acid, trans-1,2-cyclohexanediaminetetraacetic acid, glycol ether diaminetetraacetic acid and 1,3-propanediamine-N,N,N',N'-tetraacetic acid), a red prussiate of potash, a persulfate, or a hydrogen peroxide or a bromate may be used in combination as the bleaching agent. However, in view of the environmental conservation and the safety in handling, the compound represented by formula (I) or (II) of the present invention preferably occupies from 70 to 100 mol%, more preferably from 80 to 100 mol%, still more preferably 100 mol% of the entire bleaching agent.

[0187] The compound represented by formula (I) or (II) of the present invention is used in an amount of suitably from 0.003 to 3.00 mol/ℓ, preferably from 0.02 to 2.00 mol/ℓ, more preferably from 0.05 to 1.00 mol/ℓ, still more preferably from 0.08 to 0.5 mol/ℓ, however, in the case when the above-described inorganic oxidizing agent is used in combination, the total concentration of iron(III) complex salt is preferably from 0.005 to 0.030 mol/ℓ.

[0188] In the present invention, in order to improve the bleaching performance and reduce stains, the processing is preferably conducted in the presence of at least one compound represented by the following formula (A):



(A)

(wherein Q represents a nonmetallic atom group necessary for forming a heterocyclic ring, p represents 0 or 1 and Ma represents a hydrogen atom or a cation).

[0189] The compound represented by formula (A) of the present invention is described in detail below.

[0190] The heterocyclic residue formed by Q is a 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-membered, saturated or unsaturated heterocyclic residue containing at least one of N, O and S atoms and the ring may be monocyclic or may form a condensed ring with other ring.

[0191] The heterocyclic residue is preferably a 5- or 6-membered aromatic heterocyclic residue, more preferably a 5- or 6-membered aromatic heterocyclic residue containing a nitrogen atom, most preferably a 5- or 6-membered aromatic heterocyclic residue containing one or two nitrogen atoms.

[0192] Specific examples of the heterocyclic residue include 2-pyrrolidinyl, 3-pyrrolidinyl, 2-piperidinyl, 3-piperidyl, 4-piperidyl, 2-piparazinyl, 2-morpholinyl, 3-morpholinyl, 2-thienyl, 2-furyl, 3-furyl, 2-pyrrolyl, 3-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 4-pyrazolyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-pyrazinyl, 3-pyridazinyl, 4-pyridazinyl, 3-(1,2,4-triazolyl), 4-(1,2,3-triazolyl), 2-(1,3,5-triazinyl),3-(1,2,4-triazinyl),5-(1,2,4-triazinyl),6- (1,2,4-triazinyl), 2-indolyl, 3-indolyl, 4-indolyl, 5-indolyl, 6-indolyl, 7-indolyl, 3-indazolyl, 4-indazolyl, 5-indazolyl, 6-indazolyl, 7-indazolyl, 2-purinyl, 6-purinyl, 8-purinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 3-quinolyl, 4-quinolyl, 5-quinolyl, 6-quinolyl, 7-quinolyl, 8-quinolyl, 1-phthalizinyl, 5-phthalazinyl, 6-phthalazinyl, 2-naphthyridinyl, 3-naphthyridinyl, 4-naphthyridinyl, 2-quinoxalinyl, 5-quinoxalinyl, 6-quinoxalinyl, 2-quinazolinyl, 4-quinazolinyl, 5-quinazolinyl, 6-quinazolinyl, 7-quinazolinyl, 8-quinazolinyl, 3-cinnolinyl, 4-cinnolinyl, 5-cinnolinyl, 6-cinnolinyl, 7-cinnolinyl, 8-cinnolinyl, 2-pteridinyl, 4-pteridinyl, 6-pteridinyl, 7-pteridinyl, 1-acridinyl, 2-acridinyl, 3-acridinyl, 4-acridinyl, 9-acridinyl, 2-(1,10-phenanthrolinyl), 3-(1,10-phenanthrolinyl), 4-(1,10-phenanthrolinyl), 5-(1,10-phenanthrolinyl), 1-phenazinyl, 2-phenazinyl, 5-tetrazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolidyl, 4-thiazolidyl and 5-thiazolidyl.

[0193] The heterocyclic residue is preferably 2-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 2-pyridyl, 2-pyrazinyl, 3-pyridazinyl, 3-(1,2,4-triazolyl), 4-(1,2,3-triazolyl), 2-(1,3,5-triazinyl),3-(1,2,4-triazinyl),5-(1,2,4-triazinyl),6-(1,2,4-triazinyl), 2-indolyl, 3-indazolyl, 7-indazolyl, 2-purinyl, 6-purinyl, 8-purinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 8-quinolyl, 1-phthalazinyl, 2-quinoxalinyl, 5-quinoxalinyl, 2-quinazolinyl, 4-quinazolinyl, 8-quinazolinyl, 3-cinnolinyl, 8-cinnolinyl, 2-(1,10-phenanthrolinyl), 5-tetrazolyl, 2-thiazolyl, 4-thiazolyl, 2-oxazolyl or 4-oxazolyl, more preferably 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 2-pyridyl, 2-pyrazinyl, 2-indolyl, 3-indazolyl, 7-indazolyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 8-quinolyl, 2-thiazolyl, 4-thiazolyl, 2-oxazolyl or 4-oxazolyl, still more preferably 2-imidazolyl, 4-imidazolyl, 2-pyridyl, 2-quinolyl or 8-quinolyl, particularly preferably 2-imidazolyl, 4-imidazolyl, 2-pyridyl or 2-quinolyl, and most preferably 2-pyridyl.

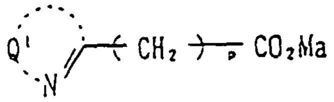
[0194] The heterocyclic residue may have a substituent other than $(CH_2)_pCO_2Ma$ and examples of the substituent include an alkyl group (having preferably from 1 to 12 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 3 carbon atoms, e.g., methyl, ethyl), an aralkyl group (having preferably from 7 to 20 carbon atoms, more preferably from 7 to 15 carbon atoms, still more preferably from 7 to 11 carbon atoms, e.g., phenylmethyl, phenylethyl), an alkenyl group (having preferably from 2 to 12 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., allyl), an alkynyl group (having preferably from 2 to 12 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., propargyl), an aryl group (having preferably from 6 to 20 carbon atoms, more preferably from 6 to 15 carbon atoms, still more preferably from 6 to 10 carbon atoms, e.g., phenyl, p-methylphenyl), an amino group (having preferably from 0 to 20 carbon atoms, more preferably from 0 to 10 carbon atoms, still more preferably from 0 to 6 carbon atoms, e.g., amino, methylamino, dimethylamino, diethylamino), an alkoxy group (having preferably from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methoxy, ethoxy), an aryloxy group (having preferably from 6 to 12 carbon atoms, more preferably from 6 to 10 carbon atoms, still more preferably from 6 to 8 carbon atoms, e.g., phenyloxy), an acyl group (having preferably from 1 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, still more preferably from 2 to 8 carbon atoms, e.g., acetyl), an alkoxycarbonyl group (having preferably from 2 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, still more preferably from 2 to 8 carbon atoms, e.g., methoxycarbonyl), an acyloxy group (having preferably from 1 to 12 carbon atoms, more preferably from 2 to 10 carbon atoms, still more preferably from 2 to 8 carbon atoms, e.g., acetoxy), an acylamino group (having preferably from 1 to 10 carbon atoms, more preferably from 2 to 6 carbon atoms, still more preferably from 2 to 4 carbon atoms, e.g., acetylamino group), a sulfonylamino group (having preferably from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfonylamino), a sulfamoyl group (having from 0 to 10 carbon atoms, more preferably from 0 to 6 carbon atoms, still more preferably from 0 to 4 carbon atoms, e.g., sulfamoyl, methylsulfamoyl), a carbamoyl group (having preferably from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., carbamoyl, methylcarbamoyl), an alkylthio group (having preferably from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methylthio, ethylthio), an arylthio group (having preferably from 6 to 20 carbon atoms, more preferably from 6 to 10 carbon atoms, still more preferably from 6 to 8 carbon atoms, e.g., phenylthio), a sulfonyl group (having preferably from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfonyl), a sulfinyl group (having preferably from 1 to 8 carbon atoms, more preferably from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms, e.g., methanesulfinyl), a ureido group, a hydroxy group, a halogen atom (e.g., fluorine, chlorine, bromine, iodine), a cyano group, a sulfo group, a carboxyl group, a nitro group, a hydroxamic acid group, a mercapto group and a heterocyclic group (e.g., imidazolyl, pyridyl).

[0195] These substituents each may be further substituted. When two or more substituents are present, they may be the same or different. The substituent is preferably an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxy group, a halogen atom, a cyano group, a nitro group or a mercapto group, more preferably an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxy group or a halogen atom, still more preferably an amino group, a carboxyl group or a hydroxy group, particularly preferably a carboxyl group.

[0196] p represents 0 or 1, preferably 0.

[0197] The cation represented by Ma is an organic or inorganic cation and examples thereof include an alkali metal ion (e.g., Li^+, Na^+, K^+, Cs^+), an alkaline earth metal ion (e.g., Ca^{2+}, Mg^{2+}), an ammonium (e.g., ammonium, tetraethylammonium), a pyridinium and a phosphonium (e.g., tetrabutylphosphonium, tetraphenylphosphonium)

[0198] Among the compounds represented by (A), preferred is a compound represented by the following formula (A-a):



(A-a)

(wherein p and Ma have the same meaning as those in formula (A), respectively, and Q^1 represents a nonmetallic atom group necessary for forming a nitrogen-containing heterocyclic ring).

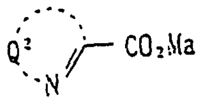
[0199] The nitrogen-containing heterocyclic residue represented by Q^1 is a 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-membered, saturated or unsaturated heterocyclic residue containing at least one nitrogen atom and the ring may be monocyclic or may form a condensed ring with other ring.

[0200] The nitrogen-containing heterocyclic residue is preferably a 5- or 6-membered nitrogen-containing aromatic heterocyclic residue, more preferably a 5- or 6-membered nitrogen-containing aromatic heterocyclic residue containing one or two nitrogen atoms.

[0201] Specific examples of the nitrogen-containing heterocyclic residue include 2-pyrrolidinyl, 3-pyrrolidinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 2-piparazinyl, 2-morpholinyl, 3-morpholinyl, 2-pyrrolyl, 3-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 4-pyrazolyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-pyrazinyl, 3-pyridazinyl, 4-pyridazinyl, 3-(1,2,4-triazolyl), 4-(1,2,3-triazolyl), 2-(1,3,5-triazinyl),3-(1,2,4-triazinyl),5-(1,2,4-triazinyl),6-(1,2,4-triazinyl), 2-indolyl, 3-indolyl, 4-indolyl, 5-indolyl, 6-indolyl, 7-indolyl, 3-indazolyl, 4-indazolyl, 5-indazolyl, 6-indazolyl, 7-indazolyl, 2-purinyl, 6-purinyl, 8-purinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 3-quinolyl, 4-quinolyl, 5-quinolyl, 6-quinolyl, 7-quinolyl, 8-quinolyl, 1-phthalizinyl, 5-phthalazinyl, 6-phthalazinyl, 2-naphthyridinyl, 3-naphthyridinyl, 4-naphthyridinyl, 2-quinoxalinyl, 5-quinoxalinyl, 6-quinoxalinyl, 2-quinazolinyl, 4-quinazolinyl, 5-quinazolinyl, 6-quinazolinyl, 7-quinazolinyl, 8-quinazolinyl, 3-cinnolinyl, 4-cinnolinyl, 5-cinnolinyl, 6-cinnolinyl, 7-cinnolinyl, 8-cinnolinyl, 2-pteridinyl, 4-pteridinyl, 6-pteridinyl, 7-pteridinyl, 1-acridinyl, 2-acridinyl, 3-acridinyl, 4-acridinyl, 9-acridinyl, 2-(1,10-phenanthrolinyl), 3-(1,10-phenanthrolinyl), 4-(1,10-phenanthrolinyl), 5-(1,10-phenanthrolinyl), 1-phenazinyl, 2-phenazinyl, 5-tetrazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolidyl, 4-thiazolidyl and 5-thiazolidyl. Among these, preferred are 2-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 2-pyridyl, 2-pyrazinyl, 3-pyridazinyl, 3-(1,2,4-triazolyl), 4-(1,2,3-triazolyl), 2-(1,3,5-triazinyl), 3-(1,2,4-triazinyl), 5-(1,2,4-triazinyl), 6-(1,2,4-triazinyl), 2-indolyl, 3-indazolyl, 7-indazolyl, 2-purinyl, 6-purinyl, 8-purinyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 8-quinolyl, 1-phthalazinyl, 2-quinoxalinyl, 5-quinoxalinyl, 2-quinazolinyl, 4-quinazolinyl, 8-quinazolinyl, 3-cinnolinyl, 8-cinnolinyl, 2-(1,10-phenanthrolinyl), 5-tetrazolyl, 2-thiazolyl, 4-thiazolyl, 2-oxazolyl and 4-oxazolyl, more preferred are 2-imidazolyl, 4-imidazolyl, 3-pyrazolyl, 2-pyridyl, 2-pyrazinyl, 2-indolyl, 3-indazolyl, 7-indazolyl, 2-(1,3,4-thiadiazolyl), 2-(1,3,4-oxadiazolyl), 2-quinolyl, 8-quinolyl, 2-thiazolyl, 4-thiazolyl, 2-oxazolyl and 4-oxazolyl, still more preferred are 2-imidazolyl, 4-imidazolyl, 2-pyridyl, 2-quinolyl or 8-quinolyl, particularly preferably 2-imidazolyl, 4-imidazolyl, 2-pyridyl and 2-quinolyl, and most preferred is 2-pyridyl.

[0202] The nitrogen-containing heterocyclic residue may have a substituent other than $(CH_2)_pCO_2Ma$, and examples of the substituent and preferred substituents are the same as described above for the substituent of the heterocyclic group formed by Q in formula (A).

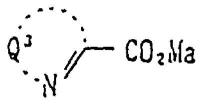
[0203] p and Ma have the same meaning and preferred range as those in formula (A), respectively. Among the compounds represented by formula (A-a), preferred is a compound represented by the following formula (A-b):



(A-b)

(wherein Ma has the same meaning as that in formula (A) and Q^2 represents a 5- or 6-membered nitrogen-containing heterocyclic group which may be substituted by an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxy group, a halogen atom, a cyano group, a nitro group or a mercapto group).

[0204] Among the compounds represented by formula (A-b), preferred is a compound represented by the following formula (A-c):

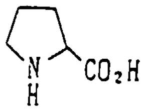


(A-c)

(wherein Ma has the same meaning as that in formula (A) and Q^3 represents an atomic group necessary for forming a pyridine or imidazole ring which may be substituted by an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxy group, a halogen atom, a cyano group, a nitro group or a mercapto group).

[0205] Specific examples of the compound represented by formula (A) are set forth below, but the present invention is by no means limited thereto.

A-1



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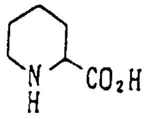

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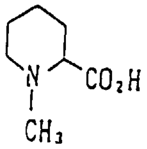

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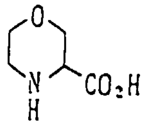

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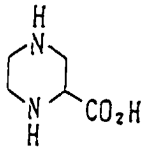

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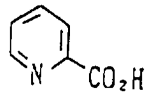

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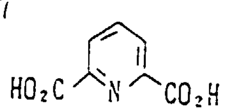

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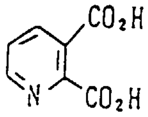

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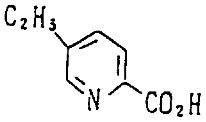

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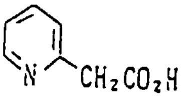

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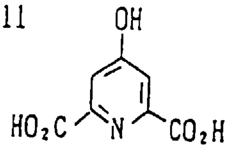

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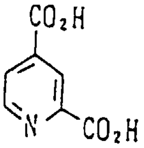

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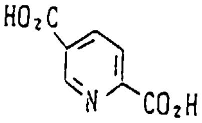

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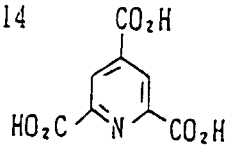

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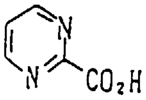

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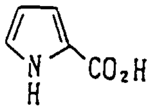

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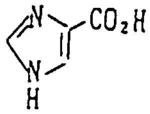

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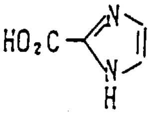

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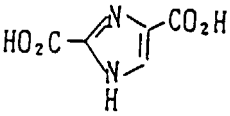

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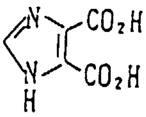

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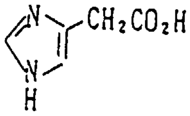

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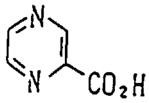

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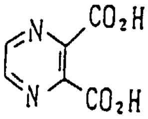

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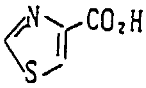

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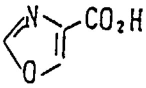

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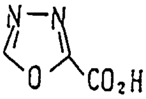

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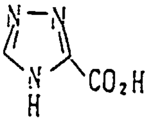

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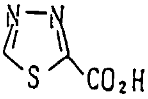

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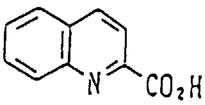

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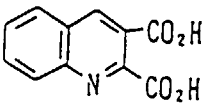

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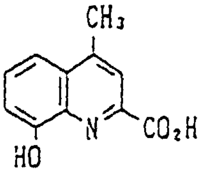

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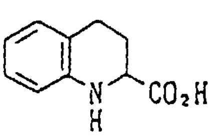

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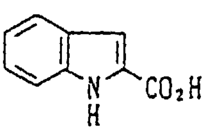

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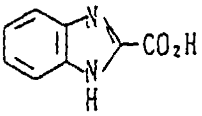

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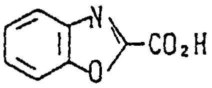

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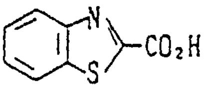

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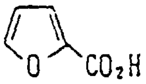

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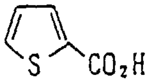

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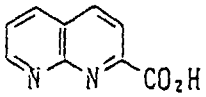

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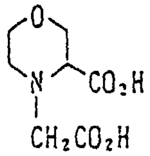

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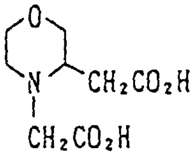

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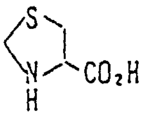

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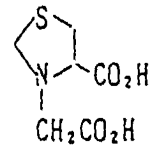

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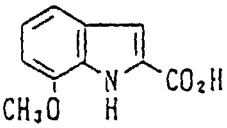

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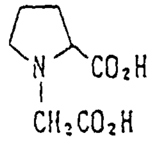

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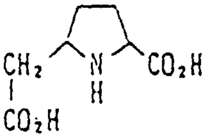

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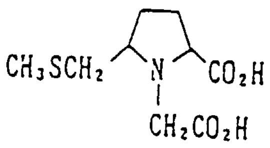

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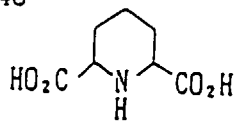

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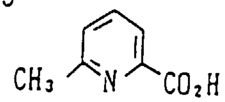

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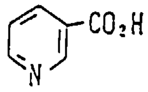

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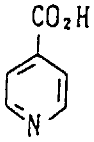

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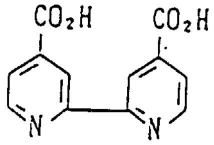

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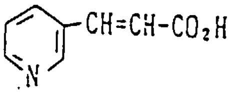

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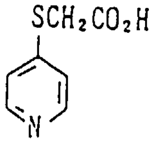

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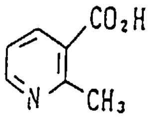

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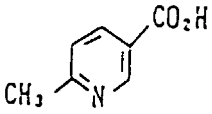

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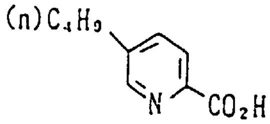

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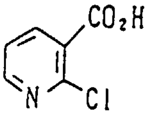

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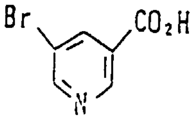

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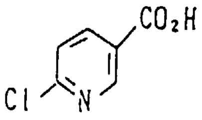

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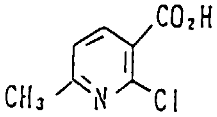

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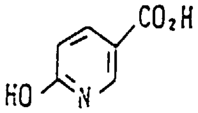

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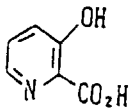

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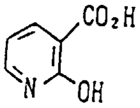

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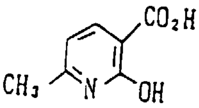

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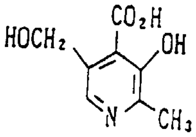

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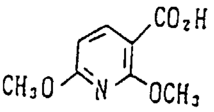

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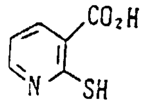

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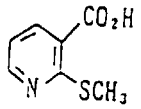

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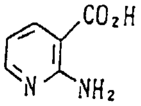

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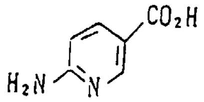

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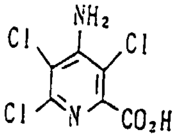

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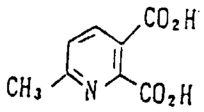

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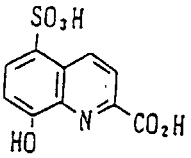

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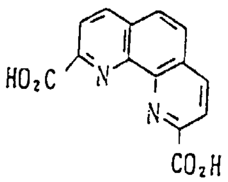

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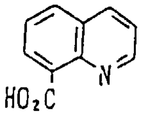

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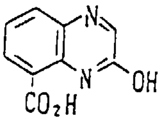

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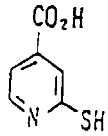

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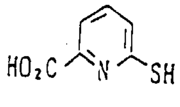

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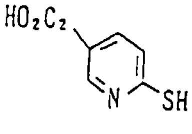

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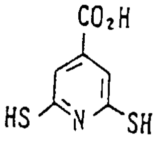


[0206] The above-described compounds may be used in the form of an ammonium salt or an alkali metal salt.

[0207] The compound represented by formula (A) can be synthesized according to the method described in

Organic Syntheses Collective, vol. 3, p. 740, or a commercially available product may be used.

[0208] Among the above-described compounds, (A-6), (A-7), (A-8), (A-13), (A-14), (A-20), (A-22), (A-29) and (A-49) are preferred, and (A-7) is more preferred.

[0209] The compound represented by formula (A) of the present invention may be added to the photographic material or to the processing solution. In the case of adding the compound to the photographic material, the addition amount is preferably from 1.0×10^{-5} to 1.0×10^{-2} mol, more preferably from 1.0×10^{-4} to 1.0×10^{-3} mol, per m^2 of the photographic material. In the case of incorporating the compound into the processing solution, it is contained preferably in an amount of from 0.001 to 0.3 mol, more preferably from 0.005 to 0.2 mol, still more preferably from 0.01 to 0.10 mol, per ℓ of the processing solution.

[0210] When the compound represented by formula (A) of the present invention is added to the processing solution, the compound may be added to the processing solution at any processing step of color development, desilvering and stabilization, however, the compound is preferably added at desilvering step and particularly preferably added to the bleaching solution. In this case, the compound may be incorporated thereinto by the solution carried over from the previous bath. The compounds may be used individually or in combination of two or more thereof.

[0211] The bleaching solution preferably contains a pH buffer agent, preferably a less odorous organic acid such as glycolic acid, succinic acid, maleic acid, malonic acid and glutaric acid, more preferably a glycolic acid, a malonic acid or a succinic acid. The concentration of the buffer agent is preferably from 0 to 3 mol/ℓ, more preferably from 0.2 to 1.5 mol/ℓ.

[0212] In the present invention, the replenishing agent for the processing solution having bleaching ability may be a liquid or a solid (e.g., powder, granule, tablet), and in the case of a granule or a tablet, a polyethylene glycol-base surface active agent is preferably used, which also serves as a binder.

[0213] The photographic processing agent may be formed into a solid by any technique and, for example, a condensed solution or powder or granule photographic processing agent and a water-soluble binder are mixed, kneaded and shaped, or a water-soluble binder is sprayed onto the surface of a temporarily formed photographic processing agent to form a coated layer, as described in JP-A-4-29136, JP-A-4-85535, JP-A-4-85536, JP-A-4-88533, JP-A-4-85534 and JP-A-4-172341.

[0214] The tablet processing agent may be produced by a general production method described, for example, in JP-A-51-61837, JP-A-54-155038, JP-A-52-88025 and British patent 1,213,808. The granule processing agent may be produced by a general production method described, for example, in JP-A-2-109042, JP-A-2-109043, JP-A-3-39735 and JP-A-3-39739. The powder processing agent may be produced by a general production method described, for example, in JP-A-54-133332, British Patents 725,892 and 729,862, and German Patent 3,733,861.

[0215] When the replenishing agent for the processing solution having bleaching ability is a liquid, one part solution or plural part solution comprising different components may be used, however, in view of the storage space for or the operationability at the preparation of, the replenishing agent, one part solution and two part solution are preferred, and one part solution is more preferred. In this case, the specific gravity of the replenishing agent is preferably from 1.0 to 5 times, more preferably from 1.5 to 3 times, the specific gravity of the replenisher.

[0216] The pH of the processing solution having bleaching ability of the present invention is suitably from 3.0 to 7.0, and in the case of a bleaching solution, the pH is particularly preferably from 3.5 to 5.0, whereas in the case of a bleach-fixing solution, the pH is particularly preferably from 4.0 to 6.5. In the present invention, to adjust the pH to fall in the above-described range, an organic acid described above is preferably added as a buffer agent. As the alkali agent used for adjusting the pH, aqueous ammonia, potassium hydroxide, sodium hydroxide, potassium carbonate and sodium carbonate are preferably used.

[0217] In order to adjust the processing solution having bleaching ability of the present invention to have a pH in the above-described range, the above-described alkali agent and a known acid (inorganic acid or organic acid) may be used.

[0218] The processing with the solution having bleaching ability of the present invention is preferably conducted immediately after the color development, however, in the case of reversal processing, it is commonly conducted through a regulating bath (a bleaching accelerating bath may be used). The regulating bath may contain an image stabilizer which will be described later.

[0219] In the present invention, the solution having bleaching ability may contain, in addition to the bleaching agent, a rehalogenating agent described in JP-A-3-144446, page (12), a pH buffer agent and known additives, aminopolycarboxylic acids, and organic phosphonic acids. The rehalogenating agent is preferably sodium bromide, potassium bromide, ammonium bromide or potassium chloride and the content thereof is preferably from 0.1 to 1.5 mol, more preferably from 0.1 to 1.0 mol, still more preferably from 0.1 to 0.8, per ℓ of the solution having bleaching ability.

[0220] In the present invention, the solution having bleaching ability preferably uses a nitric acid compound such as ammonium nitrate and sodium nitrate. In the present invention, the concentration of the nitric acid compound in the solution having bleaching ability is preferably from 0 to 0.3 mol/ℓ, more preferably from 0 to 0.2 mol/ℓ.

[0221] In order to prevent corrosion of the stainless steel, a nitric acid compound such as ammonium nitrate and sodium nitrate is usually added, however, in the present invention, corrosion is hardly generated and good desilvering is achieved even when the nitric acid compound is used in a small amount.

[0222] The replenishing amount of the solution having bleaching ability is preferably from 30 to 600 ml, more preferably from 50 to 400 ml, per m^2 of the photographic material.

[0223] The processing time in the processing with a bleaching solution is preferably 7 minutes or less, more preferably from 10 seconds to 5 minutes, most preferably from 15 seconds to 3 minutes.

[0224] It is preferred that the total processing time in the desilvering step is as short as possible as long as desilverization failure is not caused, and it is preferably from 1 to 12 minutes, more preferably from 1 to 8 minutes. The processing temperature is from 25 to 50°C, preferably from 35 to 45°C. Within the preferred temperature range, the desilvering rate is improved and generation of stains after the processing is effectively prevented.

[0225] The processing solution having bleaching ability of the present invention is particularly preferably aerated at the time of processing because the photographic performance can be maintained very stably. The aeration can be conducted using a technique known in the art and, for example, the blowing of air into or the absorption of air using an ejector in the processing solution may be used.

[0226] In blowing air, the air is preferably released into the solution through a diffusion tube having micropores. The tube diffuser is widely used, for example, in the aeration tank for processing activated sludge. With respect to the aeration, the matters described in Z-121, Using Process • C-41, 3rd ed., pages BL-1 to BL-2, issued by Eastman Kodak Co. (1982) may be used. In the processing using the processing solution having bleaching ability of the present invention, stirring is preferably intensified and for intensifying the stirring, the description of JP-A-3-33847, page 8, from right upper column, line 6 to left lower column, line 2, may be wholly used.

[0227] In the present invention, various bleaching accelerators may be added to the previous bath of the processing solution having bleaching ability. Examples of the bleaching accelerator include compounds having a mercapto group or a disulfide group described in U.S. Patent 3,893,858, German Patent 1,290,821, British Patent 1,138,842, JP-A-53-95630 and Research Disclosure, No. 17129 (July, 1978); thiazolidine derivatives described in JP-A-50-140129; thiourea derivatives described in U.S. Patent 3,706,561; iodides described in JP-A-58-16235; polyoxyethylene oxides described in German Patent 2,748,430; and polyamine compounds described in JP-B-45-8836. Further, compounds described in U.S. Patent 4,552,834 are also preferred. The bleaching accelerator may be incorporated into the photographic material.

[0228] The processing solution having fixing ability may contain, as a preservative, a sulfite (e.g., sodium sulfite, potassium sulfite, ammonium sulfite), a hydroxylamine, hydrazines, a bisulfite adduct of aldehyde compounds (e.g., sodium acetaldehyde bisulfite, particularly preferably compounds described in JP-A-3-158848) or a sulfinic acid compound described in JP-A-1-231051. Further, various fluorescent brightening agents, defoaming agents, surface active agents and organic solvents such as polyvinyl pyrrolidone or methanol may be added.

[0229] Further, in order to stabilize the processing solution, a chelating agent such as various aminopolycarboxylic acid and organic phosphonic acids is preferably added to the processing solution having fixing ability. Preferred examples of the chelating agent include 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediamine-N,N,N',N'-tetrakis(methylenephosphonic acid), nitrilotrimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetraacetic acid, diethylenetriaminepentaacetic acid, trans-1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid and 1,2-propylenediaminetetraacetic acid.

[0230] The bleach-fixing solution or the fixing solution preferably contains a buffer agent so as to maintain the pH of the solution constant. Examples of the buffer agent include phosphate, imidazoles such as imidazole, 1-methylimidazole, 2-methylimidazole and 1-ethylimidazole, triethanolamine, N-allylmorpholine and N-benzoylpiperazine.

[0231] In the desilverization, the stirring is preferably intensified as highly as possible. Specific examples of the method for intensifying stirring include a method of colliding a jet stream of a processing solution against the emulsion surface of the photographic material described in JP-A-62-183460 and JP-A-3-33847, page 8, from right upper column, line 6 to left lower column, line 2, a method of increasing the stirring effect using a rotary means described in JP-A-62-183461, a method of increasing the stirring effect by moving the photographic material while bringing the emulsion surface into contact with a wire blade provided in the solution to cause turbulence on the emulsion surface, and a method of increasing the circulative flow rate of the entire processing solutions. Such techniques for intensifying the stirring are effective in any of the bleaching solution, the bleach-fixing solution and the fixing solution. The intensification of stirring is considered to increase the supply rate of the bleaching agent or the fixing agent into the emulsion layer and as a result, to elevate the desilverization rate. The above-described techniques for intensifying stirring is more effective when a bleaching accelerator is used and in this case, the acceleration effect can be outstandingly increased or the fixing inhibitory action of the bleaching accelerator can be eliminated.

[0232] The automatic processor used for the photographic material of the present invention preferably has a transportation means of a photographic material described in JP-A-60-191257, JP-A-60-191258 and JP-A-60-191259. As described in JP-A-60-191257, by using the transportation means, the amount of a processing solution carried over from a previous bath to a post bath can be remarkably reduced and a great effect can be achieved on the prevention of deterioration in the performance of the processing solution. This effect is particularly useful for the reduction in the processing time or for the decrease in the replenishing amount of the processing solution in each processing step.

[0233] The solution having bleaching ability of the present invention can be re-used by recovering the overflow solution after use in the processing and adding thereto components to correct the composition. This use method is usually called regeneration and the regeneration is preferred also in the present invention. With respect to the details of the regeneration, matters described in Fuji Film Processing Manual, Fuji Color Negative Film, CN-16 Processing, issued by Fuji Photo Film Co., Ltd., pp. 39-40 (revised in August, 1990) may be applied.

[0234] For regenerating the solution having bleaching ability, in addition to the above-described aeration, the methods described in Shashin Kogaku no Kiso -Gin'en Shashin Hen- (Basis of Photographic Engineering - Silver Salt Photography Version), Nippon Shashin Gakkai (compiler), Corona Sha (1979) may be used. More specifically, electrolytic regeneration and other regeneration methods of the bleaching solution by hydrogen peroxide, bromous acid and ozone, using bromic acid, chlorous acid, bromine, bromine precursor, persulfate, hydrogen peroxide or a catalyst, may be used.

[0235] In the regeneration by electrolysis, a cathode and an anode are placed in the same bleaching bath or an anode tank and a cathode tank are provided as separate baths using a diaphragm to regenerate the solution, or the bleaching solution and the developer and/or the fixing solution may be simultaneously regenerated also using a diaphragm.

[0236] The fixing solution and the bleach-fixing solution each is regenerated by electrolytic reduction of silver ions accumulated. Also, it is preferred in order to maintain the fixing performance to remove halogen ions accumulated using an anion exchange resin.

[0237] The solution having bleaching ability of the present invention is preferably stored by housing it in a closed container having an oxygen permeation rate of 1 cc/m^1 • day • atm or more.

[0238] The bleaching solution of the present invention preferably contains at least one of 1,2-benzoisothiazolin-3-one and derivatives thereof. Specific examples of the compound are described below, but are by no means limited thereto.

[0239] 1,2-Benzoisothiazolin-3-one, 2-methyl-1,2-benzoisothiazolin-3-one, 2-ethyl-1,2-benzoisothiazolin-3-one, 2-(n-propyl)-1,2-benzoisothiazolin-3-one, 2-(n-butyl)-1,2-benzoisothiazolin-3-one, 2-(sec-butyl)-1,2-benzoisothiazolin-3-one, 2-(t-butyl)-1,2-benzoisothiazolin-3-one, 2-methoxy-1,2-benzoisothiazolin-3-one, 2-ethoxy-1,2-benzoisothiazolin-3-one, 2-(n-propyloxy)-1,2-benzoisothiazolin-3-one, 2-(n-butyloxy)-1,2-benzoisothiazolin-3-one,5-chloro-1,2-benzoisothiazolin-3-one, 5-methyl-1,2-benzoisothiazolin-3-one, 6-ethoxy-1,2-benzoisothiazolin-3-one, 6-cyano-1,2-benzoisothiazolin-3-one and 5-nitro-1,2-benzoisothiazolin-3-one.

[0240] The addition amount of the compound is preferably from 0.001 to 1 g, more preferably from 0.01 to 0.5 g, still more preferably from 0.02 to 0.2 g, per ℓ of the bleaching solution. The compound may be added in the form of a salt, or two or more compounds may be used in combination.

[0241] The replenisher of the solution having bleaching ability fundamentally contains respective components in a concentration calculated according to the following formula, whereby the concentration of the mother solution can be kept constant:

$$C_R = C_T \times (V_1+V_2)/V_1+C_P$$

wherein

C_R: concentration of the component in the replenisher
C_T: concentration of the component in the mother solution (processing tank solution)
C_P: concentration of the component consumed during the processing
V_1: replenishing amount (ml) of the replenisher having bleaching ability per m^2 of the photographic material
V_2: amount (ml) of the solution carried over from the previous bath by 1 m^2 of the photographic material The color developer is described below.

[0242] The color developer may use the compounds described in JP-A-4-121739, from page 9, right upper column, line 1 to page 11, left lower column, line 4. Particularly, in conducting rapid processing, preferred as the color developing agent are 2-methyl-4-[N-ethyl-N-(2-hydroxyethyl)amino]aniline,2-methyl-4-[N-ethyl-N-(3-hydroxypropyl)amino]aniline and 2-methyl-4-[N-ethyl-N-(4-hydroxybutyl)amino]aniline.

[0243] The color developer contains the color developing agent in an amount of preferably from 0.01 to 0.08 mol/ℓ, more preferably from 0.015 to 0.06 mol/ℓ, still more preferably from 0.02 to 0.05 mol/ℓ. The replenisher of the color developer preferably contains the color developing agent in an amount of from 1.1 to 3 times the above-described range.

[0244] The color developer usually contains a pH buffer agent such as a carbonate, a borate and a phosphate of an alkali metal, and a development inhibitor or antifoggant such as a chloride, a bromide, an iodide, a benzimidazole, a benzothiazole and a mercapto compound. Further, the color developer may contain a preservative such as hydroxylamines (e.g., hydroxylamine, diethylhydroxylamine, those represented by formula (I) of JP-A-3-144446 including N,N-bis(2-sulfonatoethyl)hydroxylamine), sulfites, hydrazines (e.g., N,N-bis-carboxymethylhydrazine), phenylsemicarbazides, triethanolamine and catecholsulfonic acids; an organic solvent such as ethylene glycol and diethylene glycol; a development accelerator such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts and amines; a dye forming coupler; a competitive coupler; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a tackifying agent; and a chelating agent represented by aminopolycarboxylic acid, aminopolyphosphonic acid, alkylphosphonic acid and phosphonocarboxylic acid, representative examples thereof including ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N,N-tetramethylenephosphonic acid, ethylenediamine-di(o-hydroxyphenylacetic acid) and salts thereof.

[0245] The processing temperature in the processing with the color developer of the present invention is generally from 20 to 55°C, preferably from 30 to 55°C. The processing time is, in the case of a photographic material for photographing, from 20 seconds to 10 minutes, preferably from 30 seconds to 8 minutes, more preferably from 1 to 6 minutes, still more preferably from 1 minute and 10 seconds to 3 minutes and 30 seconds, and in the case of a material for printing, it is from 10 seconds to 1 minute and 20 seconds, preferably from 10 to 60 seconds, more preferably from 10 to 40 seconds.

[0246] In carrying out reversal processing, the color development usually follows black-and-white development. The black-and-white developer may use a known black-and-white developing agent such as dihydroxybenzenes (e.g., hydroquinone, hydroquinone monosulfonate), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone) and aminophenols (e.g., N-methyl-p-aminophenol), which may be used individually or in combination. Also, in the processing of a black-and-white photographic material, the above-described black-and-white developer is used.

[0247] The color developer and the black-and-white developer each usually has a pH of from 9 to 12. The replenishing amount of these developers is, although it depends on the color photographic material processed, usually 3 ℓ or less per m^2 of the photographic material and may be reduced to 500 ml or less by reducing the bromine ion concentration in the replenisher. When the replenishing amount is reduced, the contact area of the processing tank with air is preferably made small so that evaporation or air oxidation of the solution can be prevented.

[0248] The contact area between a photographic processing solution and air in a processing tank can be expressed by an opening ratio defined below. Namely,

$$\text{Opening ratio} = (\text{contact area of the processing solution with air } (\text{cm}^2)) \div (\text{volume of the processing solution } (\text{cm}^3))$$

[0249] The opening ratio as defined above is preferably 0.1 or less, more preferably from 0.001 to 0.05. The opening ratio can be reduced by providing a shielding material such as a floating lid on the surface of the photographic processing solution in the processing tank, by a method of using a movable lid described in JP-A-1-82033 or by a slit development method described in JP-A-63-216050. Also, a method of bringing into contact with the processing solution surface a liquid capable of covering the processing solution surface such as liquid paraffin or a low oxidative and/or non-oxidative gas may also be used. The reduction in the opening ratio is preferably applied not only to the color development and the black-and-white development but also to all of subsequent steps such as bleaching, bleach-fixing, fixing, water washing and stabilization. Furthermore, means of preventing accumulation of bromide ion in the developer enables reduction of the replenishing amount.

[0250] When the replenishing amount is reduced or when the bromide ion concentration is set high, in order to increase the sensitivity, a pyrazolidone represented by 1-phenyl-3-pyrazolidone and 1-phenyl-2-methyl-2-hydroxymethyl-3-pyrazolidone, a thioether compound represented by 3,6-dithia-1,8-octanediol, a sodium thiosulfate or a potassium thiosulfate is preferably used as a development accelerator.

[0251] The above-described development accelerator is also preferably used in the color developer.

[0252] The shape and the structure of the container for housing a color developer constituting the color developer solution may be freely designed, but preferred are a container having a freely shrinkable structure as described in JP-A-58-97046, JP-A-63-50839, JP-A-1-235950 and JP-U-A-63-45555 (the term "JP-U-A" as used herein means an "unexamined published Japanese utility model application"), a container capable of housing a waste having a flexible partition described in JP-A-58-52065, JP-A-62-246061 and JP-A-62-134646, and a structure where a plurality of containers variable in the content volume are connected described in JP-A-2-264950.

[0253] In feeding the color developer from the above-described container to the processing solution tank in a processor, the developer may be once placed in a supply tank and automatically or manually mixed and diluted with water there, or the liquid color developer and water may be separately transferred directly to the processing solution tank.

[0254] In the working as described above, it is preferred that the cover of the container has a touch-and-open structure and examples thereof are described in JP-U-A-61-128646, JP-A-3-265849 and JP-A-4-240850.

[0255] The above-described color developer is preferably packed in a container made of a material having a carbon dioxide permeation rate of 25 $ml/m^2 \cdot 24$ hrs • atm or less to give a void ratio of from 0.15 to 0.05.

[0256] Preferred examples of the material having the above-described carbon dioxide permeation rate include polyethylene terephthalate, polyvinyl chloride, polyvinylidene chloride, a laminate material of polyethylene or polypropylene and nylon, a laminate material of polyethylene or polypropylene and aluminum, and a glass, each having a thickness of from 300 to 2,000 μm. In particular, a polyethylene terephthalate and a laminate material of polyethylene and nylon, having a thickness of from 500 to 1,000 μm are most preferred because the carbon dioxide permeation rate, the mechanical strength and the weight are balanced. Further, the material for the container used in the present invention preferably has an oxygen permeation rate of 20 $ml/m^2 \cdot 24$ hrs • atm or less.

[0257] The void ratio used herein means a value obtained by subtracting the packed amount (ml) of the color developer from the volume (ml) of the container housing the color developer and dividing the value obtained by the volume (ml) of the container. The liquid color developer of the present invention is preferably packed in the above-described container to give a void ratio of from 0.15 to 0.05.

[0258] The above-described color developer may be used directly as a color developer solution or a replenisher solution, however, it is preferably mixed and diluted with water before using it as a color developer solution or a replenisher solution. When the color developer is used as a color developer solution, a starter containing water, a pH adjusting agent and a bromide is preferably added thereto.

[0259] When the color developer is used as a replenisher solution, it may be previously mixed and diluted with water, stocked in a replenisher tank and supplied therefrom to the processing solution tank in a constant amount, or it may be supplied directly to the processing solution tank in a constant amount separately from water and mixed and diluted in the processing solution tank. Also, as a middle method, the color developer may be transferred to the processing solution tank while continuously mixing and diluting it with water. In this case, known methods such as disposition of a mixing tank in the middle may be used.

[0260] In the present invention, when the color developing agent is incorporated into the photographic material, an activator described below is used in place of the above-described color developer solution.

[0261] The activator solution must contain an alkali agent for starting the development. It is preferred that the activator is a solution having buffering ability to give a pH of preferably from 8 to 13, more preferably from 9 to 12.

[0262] Preferred examples of the buffer which can be used to keep the pH in the above-described range include carbonate, phosphate, borate, tetraborate, hydroxybenzoate, glycyl salt, N,N-dimethylglycine salt, leucine salt, norleucine salt, guanine salt, 3,4-dihydroxyphenylalanine salt, alanine salt, aminobutyrate, 2-amino-2-methyl-1,3-propanediol salt, valine salt, proline salt, trishydroxyaminomethane salt and lysine salt. Among these, carbonate and phosphate are preferred.

[0263] The amount of the buffer to the activator is preferably 0.1 mol/ℓ or more, more preferably from 0.1 to 0.4 mol/ℓ.

[0264] The activator for use in the present invention may contain a hydroxylamine or a sulfite ion as an antioxidant for the developing agent dissolved out and in addition, the activator preferably contains an organic preservative.

[0265] The organic preservative as used herein means the organic compound at large which is added to the processing solution of a color photographic material and reduces the deterioration rate of the aromatic primary amine color developing agent, more specifically, an organic compound having a function to prevent oxidation of the color developing agent due to air. Particularly preferred examples of the organic preservative include hydroxylamine derivatives, hydroxamic acid, hydrazines, hydrazides, phenols, α-hydroxyketones, α-aminoketones, saccharides, monoamines, diamines, polyamines, quaternary ammonium salts, nitroxy radicals, alcohols, oximes, diamide compounds and condensed ring amines. In particular, an alkanolamine such as triethanolamine, a dialkylhyroxylamine such as N,N-diethylhydroxylamine and N,N-di(sulfoethyl)-hydroxylamine, a hydrazine derivative (excluding hydrazine) such as N,N-bis(carboxymethyl)hydrazine or an aromatic polyhydroxy compound such as sodium catechol-3,5-disulfonate is preferably added.

[0266] In a preferred embodiment, the above-described preservative acts as a nucleophilic agent in the activator processing solution and accelerates the release of a color developing agent from the photographic material.

[0267] The activator for use in the present invention may contain an antifoggant, if desired. Examples of the antifoggant include alkali metal halides such as sodium chloride, potassium bromide and potassium iodide, and organic antifoggants. Representative examples of the organic antifoggant include nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 2-thiazolylbenzimidazole, 2-thiazolylmethylbenzimidazole, indazole, hydroxyazaindolizine and adenine. In particular, chloride and bromide are preferred. In the former case, the addition amount is preferably from 0.01

to 0.5 mol/ℓ and in the latter case, the addition amount is preferably from 0.0001 to 0.01 mol/ℓ. They may be designed to dissolve out from the photographic material to keep the concentration in the above-described range.

[0268] In addition, the activator solution may use various chelating agents as a precipitation preventing agent for calcium or magnesium or to improve stability of the activator. Examples thereof include nitrilotriacetic acid, diethylenetriaminepentaacetic acid, ethylenediaminetetraacetic acid, N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, transcyclohexanediaminetetraacetic acid, 1,2-diaminopropanetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediamineorthohydroxyphenylacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid and hydroxyethyliminodiacetic acid. The chelating agent may be used in combination of two or more thereof, if desired.

[0269] The chelating agent can be used in an amount sufficiently large to sequester metal ions in the developer, and it is, for example, approximately from 0.1 to 10 g/ℓ.

[0270] The activator may contain a development accelerator, if desired. Examples of the development accelerator include thioether-base compounds described in JP-B-37-16088, JP-B-37-5987, JP-B-38-7826, JP-B-44-12380, JP-B-45-9019 and U.S. Patent 3,813,247, p-phenylenediamine-base compounds described in JP-A-52-49829 and JP-A-50-15554, quaternary ammonium salts described in JP-A-50-137726, JP-B-44-30074, JP-A-56-156826 and JP-A-52-43429, amine-base compounds described in U.S. Patent 2,494,903, 3,128,182, 4,230,796 and 3,253,919, JP-B-41-11431, U.S. Patents 2,482,546, 2,596,926 and 3,582,346, polyalkylene oxides described in JP-B-37-16088, JP-B-42-25201, U.S. Patent 3,128,183, JP-B-41-11431, JP-B-42-23883 and U.S. Patent 3,532,501, 1-phenyl-3-pyrazolidones and imidazoles.

[0271] The activator solution which can be used in the present invention may contain a fluorescent brightening agent. The fluorescent brightening agent is preferably a 4,4'-diamino-2,2'-disulfostilbene-base compound. The amount thereof is generally from 0 to 5 g/ℓ, preferably from 0.1 to 4 g/ℓ.

[0272] It is not an essential for the activator solution of the present invention to contain a developing agent, however, the developing agent may be added, if desired, to control the photographic properties. The preferred developing agent is an aromatic primary amine color developing agent and a preferred example thereof is a p-phenylenediamine derivative. Representative examples thereof include N,N-diethyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene, 2-amino-5-(N-ethyl-N-laurylamino)toluene, 3-methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline, 3-methyl-4-[N-ethyl-N-(δ-hydroxybutyl)amino]aniline, 2-methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline, 4-amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]aniline, N-(2-amino-5-diethylaminophenylethyl)methanesulfonamido, N,N-dimethyl-p-phenylenediamine, 4-amino-3-methyl-N-ethyl-N-methoxyethylaniline, 4-amino-3-methyl-N-ethyl-N-β-ethoxyethylaniline and 4-amino-3-methyl-N-ethyl-N-β-butoxyethylaniline. Among these, preferred are 4-amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]aniline, 2-methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline and 2-methyl-4-[N-methyl-N-(δ-hydroxybutyl)amino]aniline.

[0273] More preferred are 4-amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]aniline and 3-methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline.

[0274] These p-phenylenediamine derivatives may be used in the form of a salt such as sulfate, chloride, sulfite or p-toluenesulfonate.

[0275] The replenishing amount of the activator of the present invention is preferably small as much as possible and it is approximately from 20 to 600 ml/m^2, preferably from 60 to 300 ml/m^2.

[0276] The processing temperature in the processing with the activator is from 25 to 50°C, preferably from 30 to 45°C, most preferably from 35 to 45°C.

[0277] The processing time is not particularly limited, however, it is preferably from 5 seconds to 2 minutes, more preferably approximately from 10 seconds to 1 minute.

[0278] With respect to the processing solution having fixing ability, the compounds and the processing conditions described in JP-A-4-125558, from page 7, left lower column, line 10 to page 8, right lower column, line 19 may be applied.

[0279] In order to improve the fixing rate and the preservability, the compounds represented by formulae (I) and (II) of JP-A-6-301169 are preferably added to the processing solution having fixing ability, singly or in combination. Further, sulfinic acids such as p-toluenesulfinate described in JP-A-1-224762 are preferably used in order to improve preservability. The solution having bleaching ability or the solution having fixing ability preferably uses ammonium as a cation in view of improvement in the desilvering property, but, for the purpose of reducing the environmental pollution, the ammonium is preferably reduced or not used at all.

[0280] In the bleaching, bleach-fixing and fixing steps, it is particularly preferred to carry out jet stirring described in JP-A-1-309059.

[0281] The replenishing amount of the replenisher in the bleach-fixing or fixing step is from 100 to 1,000 ml, preferably from 150 to 700 ml, more preferably from 200 to 600 ml, per m^2 of the photographic material.

[0282] In the bleach-fixing or fixing step, a silver recovery apparatus is preferably installed in line or off line. By installing the apparatus in line, the processing can be carried out at a low silver concentration of the processing solution and thereby the replenishing amount can be reduced. Or, the silver is recovered off line and the remaining solution can be re-used as a replenisher.

[0283] The bleach-fixing or the fixing may be constituted by a plurality of processing tanks, and a multi-stage counter-current system is preferably used by piping respective tanks in cascade. Taking account of the balance with the size of processor, two tank cascade constitution is usually efficient and the ratio of the processing time in the pre-stage tank to the processing time in the post-stage tank is preferably from 0.5:1 to 1:0.5, more preferably from 0.8:1 to 1:0.8.

[0284] It is preferred in view of improvement of preservability that a free chelating agent not converted into a metal complex is present in the bleach-fixing solution or the fixing solution, and at least one compound represented by formula (I), (II) or (A) of the present invention is preferably used as the chelating agent.

[0285] With respect to the water washing and the stabilization, the description in JP-A-4-125558, from page 12, right lower column, line 6 to page 13, right lower column, line 16, may be suitably applied. In particular, preferred in view of conservation of the working environment are the use of azolylmethylamines described in European Unexamined Patent Publication Nos. 504609 and 519190 or N-methylolazoles described in JP-A-4-362943, in place of formaldehyde in the stabilizing solution, and the formation of a surface active agent solution containing no image stabilizer such as formaldehyde by converting the magenta coupler into a two-equivalent coupler.

[0286] In the present invention, it is particularly preferred for improving the reading performance of magnetic recording information that the bath at the final step contains no image stabilizer.

[0287] In the processing solution, various ion components are present such as calcium ion, magnesium ion, sodium ion and potassium ion, which components are dissolved out from the preparation-use solution used for preparing a solution of the replenishing agent or from the photographic material. However, in the present invention, the sodium ion concentration in the final bath at the water washing and stabilization step is preferably from 0 to 50 mg/ℓ, more preferably from 0 to 20 mg/ℓ.

[0288] In order to ensure the water washing or stabilization function and at the same time, to reduce the waste in view of the environmental conservation, the washing water or the stabilizing solution is replenished in an amount of preferably from 80 to 1,000 ml, more preferably from 100 to 500 ml, still more preferably from 150 to 300 ml, per m^2 of the photographic material. In the processing conducted at the above-described replenishing rate, in order to prevent proliferation of bacteria and mold, a known antimold such as thiabendazole, 1,2-benzoisothiazolin-3-one and 5-chloro-2-methylisothiazolin-3-one, an antibiotic such as gentamicin, or water subjected to deionization treatment with an ion exchange resin is preferably used. The deionized water and the bactericide or antibiotic are more effective when they are used in combination.

[0289] Also, the solution in the washing water or stabilizing solution tank is preferably treated with a reverse osmosis membrane described in JP-A-3-46652, JP-A-3-53246, JP-A-3-121448 and JP-A-3-126030 to reduce the replenishing amount and in this case, the reverse osmosis membrane is preferably a low pressure reverse osmosis membrane.

[0290] In the processing of the present invention, the processing solution is preferably subjected to evaporation correction disclosed in JIII Journal of Technical Disclosure, No. 94-4992. In particular, a method of correcting evaporation using the temperature and humidity information of the environment where the processor is installed, according to (formula-1) at page 2 of the above-described publication, is preferred. The water used in the evaporation correction is preferably sampled from the replenishing tank of washing water and in this case, deionized water is preferably used as the washing water replenisher.

[0291] The automatic processor for use in the present invention is preferably a film processor described in JIII Journal of Technical Disclosure, supra, at page 3, right column, lines 22 to 28.

[0292] Examples of the processing agent, the automatic processor and the evaporation correction method preferred in the practice of the present invention are described in JIII Journal of Technical Disclosure, supra, from page 5, right column, line 11 to page 7, right column, the last line.

[0293] The photographic material of the present invention may carry magnetic recording.

[0294] The silver halide photographic material carrying magnetic recording may be prepared in such a manner that a polyester thin layer support previously subjected to heat treatment, described in detail in JP-A-6-35118, JP-A-6-17528 and JIII Journal of Technical Disclosure, No. 94-6023, such as a polyethylene aromatic dicarboxylate-base polyester support, having a thickness of from 50 to 300 μm, preferably from 50 to 200 μm, more preferably from 80 to 115 μm, still more preferably from 85 to 105 μm, is subjected to heat treatment (annealing) at a temperature of from 40°C to a glass transition temperature for from 1 to 1,500 hours, the support is then subjected to surface treatment such as ultraviolet irradiation described in JP-B-43-2603, JP-B-43-2604 and JP-B-45-3828, corona discharge described in JP-B-48-5043 and JP-A-51-131576 or glow discharge described in JP-B-35-7578 and JP-B-46-43480, undercoating described in U.S. Patent 5,326,689 is applied thereon, a subbing layer described in U.S. Patent 2,761,791 is provided, if desired, and ferromagnetic particles described in JP-A-59-23505, JP-A-4-195726 and JP-A-6-59357 are coated thereon.

[0295] The above-described magnetic layer may be in the form of a stripe described in JP-A-4-124642 and JP-A-

4-124645.

[0296] The support is further subjected to antistatic treatment described in JP-A-4-62543, if desired, and a silver halide emulsion is finally coated thereon.

[0297] The silver halide emulsion used here includes those described in JP-A-4-166932, JP-A-3-41436 and JP-A-3-41437.

[0298] The photographic material prepared as above is produced according to a production control method described in JP-B-4-86817 and the production data are preferably recorded thereon according to the method described in JP-B-6-87146. After or before the recording, the photographic material is cut into a film smaller in the width than the conventional 135 size film and two perforations are formed on one side per one small-format picture so as to match the small format picture reduced in the size than the conventional one according to the method described in JP-A-4-125560.

[0299] The thus-prepared film is loaded before use in a cartridge package described in JP-A-4-157459, a cartridge described in JP-A-5-210202, Fig. 9, a film patrone described in U.S. Patent 4,221,479 or a cartridge described in U.S. Patents 4,834,306, 4,834,366, 5,226,613 and 4,846,418.

[0300] A film cartridge or film patrone of type such that the tongue can be housed as described in U.S. Patents 4,848,693 and 5,317,355 is preferred here in view of the light-shielding property.

[0301] Further, a cartridge having a lock mechanism described in U.S. Patent 5,296,886, a cartridge capable of displaying the use state described in U.S. Patent 5,347,334 or a cartridge having a double exposure preventing function is preferred.

[0302] Furthermore, a cartridge where the film can be easily loaded by merely inserting the film into the cartridge described in JP-A-6-85128 may also be used.

[0303] The thus produced film cartridge may be photographed, developed and variously enjoyed to satisfy the object using a camera, a processor or a lab. machine which will be described below.

[0304] The film cartridge (patrone) can exert its function sufficiently when it is used, for example, in a camera having a simple loading system described in JP-A-6-8886 and JP-A-6-99908, a camera having an automatic winding-up system described in JP-A-6-57398 and JP-A-6-101135, a camera capable of taking out the film and exchanging the kind of film on the way of photographing described in JP-A-6-205690, a camera capable of magnetic recording photographing information such as panorama photographing, high-vision photographing or normal photographing (capable of magnetic recording by selecting the print aspect ratio) on the film described in JP-A-5-293138 and JP-A-5-283382, a camera having a double exposure preventing function described in JP-A-6-101194, or a camera with a function to indicate the use state, for example, of the film described JP-A-5-150577.

[0305] The thus photographed film may be processed in an automatic processor described in JP-A-6-222514 and JP-A-6-222545 and the method for using the magnetic recording on the film described in JP-A-6-95265 and JP-A-4-123054 may be used before, during or after the processing, or the aspect ratio selection function described in JP-A-5-19364 may be used.

[0306] In the case of a cine-type development, the film is spliced according to the method described in JP-A-5-119461 before the processing.

[0307] During or after the development, the film may be subjected to attaching/detaching treatment described in JP-A-6-148805.

[0308] After the processing as described above, the film information may be converted into a print through back printing or front printing on a color paper according to the method described in JP-A-2-184835, JP-A-4-186335 and JP-A-6-79968.

[0309] Then, the film may be returned to the user together with the index print described in JP-A-5-11353 and JP-A-5-232594 and the cartridge for return.

EXAMPLES

EXAMPLE 1

Preparation of Emulsion A-1 (Silver Iodobromide Tabular Emulsion) (Comparative Example)

[0310] A silver bromide tabular grain having a thickness of 0.08 μm and a circle-corresponding diameter of 0.5 μm was prepared as a seed crystal. Seed crystals containing 8 g of Ag were dissolved in 1.0 ℓ of distilled water, the pAg and the pH were adjusted to 8.2 and 5, respectively, the temperature was kept at 70°C and the solution was vigorously stirred. Thereafter, grains were formed through the following procedure.

(i) An aqueous solution of $AgNO_3$ (141 g) and an aqueous KBr solution were added while keeping the pAg at 8.4.
(ii) The temperature was lowered to 55°C and an aqueous solution of KI (4 g) was added at a constant flow rate.

(iii) An aqueous solution of $AgNO_3$ (63 g) and an aqueous KBr solution were added while keeping the pAg at 8.9.

[0311] The solution was cooled to 35°C and washed with water according to a normal flocculation method, 50 g of gelatin was added thereto, and the pH and the pAg were adjusted to 6.0 and 8.2, respectively.

[0312] In the emulsion, tabular grains having an average sphere-corresponding diameter of 0.7 µm and an aspect ratio of 3.0 or more occupied 70% of the total projected area.

[0313] The emulsion was subjected to gold-sulfur-selenium sensitization as follows.

[0314] The emulsion was heated up to 64°C, Sensitizing Dyes ExS-1, ExS-2 and ExS-3 shown below were added thereto in an amount and at a ratio such that the emulsion could have a desired spectral sensitivity, and then the emulsion was subjected to optimal chemical sensitization by adding thereto 7.4×10^{-6} mol/mol-Ag of sodium thiosulfate, 1.9×10^{-6} mol/mol-Ag of chloroauric acid, 1.9×10^{-3} mol/mol-Ag of potassium thiocyanate and 1.5×10^{-6} mol/mol-Ag of N,N-dimethylselenourea.

Preparation of Emulsions A-2 and A-3

[0315] Emulsion A-2 was prepared in the same manner as Emulsion A-1 except for using Sensitizing Dyes ExS-4, ExS-5 and ExS-6 in place of Sensitizing Dyes ExS-1, ExS-2 and ExS-3, and Emulsion A-3 was prepared in the same manner except for using Sensitizing Dye ExS-7 instead.

Preparation of Emulsion B-1 (Silver Chloride (100) Tabular Emulsion) (Invention)

[0316] Into a reaction vessel, 1,200 ml of an aqueous gelatin solution (containing 12 g of deionized alkali-treated ossein gelatin having a methionine content of about 40 µmol/g and having a pH of 4.8) was placed, and thereto Solution Ag-1 (containing 14 g of $AgNO_3$, 0.8 g of gelatin and 0.2 ml of 1N solution of HNO_3 in 100 ml) and Solution X-1 (containing 6.9 g of NaCl, 0.8 g of gelatin and 0.3 ml of 1N solution of NaOH in 100 ml) were added each in an amount of 12 ml by a double jet method while keeping the temperature at 40°C at an addition rate of 24 ml/min. After stirring the mixture for 2 minutes, Solution Ag-2 (containing 2 g of $AgNO_3$, 0.8 g of gelatin and 0.2 ml of 1N solution of HNO_3 in 100 ml) and Solution X-2 (containing 1.4 g of KBr, 0.8 g of gelatin and 0.2 ml of 1N solution of NaOH in 100 ml) were added each in an amount of 19 ml by a double jet method at an addition rate of 31 ml/min. After stirring the mixture for one minute, Solution Ag-1 and Solution X-1 were added each in an amount of 36 ml at a rate of 48 ml/min. Thereto, 20 ml of an NaCl solution (containing 10 g of NaCl in 100 ml) was added, the pH was adjusted to 4.8 and the temperature was raised to 75°C. After ripening for 20 minutes, the temperature was lowered to 60°C, the pH was adjusted to 5.0 and then Solution Ag-3 (containing 10 g of $AgNO_3$ in 100 ml) and Solution X-3 (containing 3.6 g of NaCl in 100 ml) were added at a silver potential of 130 mV by a C.D.J. (controlled double jet) method. The flow rate was 7 ml/min at the initiation of addition and accelerated by 0.1 ml/min, and as a result, 400 ml of Solution Ag-3 was added.

[0317] Thereafter, AgBr fine grains having an average sphere-corresponding diameter of 0.03 µm were added in an amount corresponding to 0.2 mol% per mol of silver halide and ripened for about 5 minutes to accomplish halogen conversion.

[0318] Then, a precipitating agent was added, the temperature was lowered to 30°C, the emulsion was precipitated and washed with water, an aqueous gelatin solution was added and the pH and the pCl were adjusted at 38°C to 6.2 and 3.0, respectively.

[0319] The thus-prepared silver halide emulsion contained tabular grains having an average sphere-corresponding diameter of 0.7 µm, an average silver chloride content of 95.6 mol%, an aspect ratio of 4.0 or more, and a main plane adjacent edges ratio of 2 or less, in a proportion of 70% of the total projected area.

[0320] The emulsion obtained was subjected to gold-sulfurselenium sensitization as follows.

[0321] The emulsion was heated up to 64°C, Sensitizing Dyes ExS-1, ExS-2 and ExS-3 shown below were added in an amount and at a ratio such that the emulsion could have a desired spectral sensitivity, and then the emulsion was subjected to optimal chemical sensitization by adding thereto 9.4×10^{-6} mol/mol-Ag sodium thiosulfate, 3.3×10^{-6} mol/mol-Ag of chloroauric acid, 2.9×10^{-3} mol/mol-Ag of potassium thiocyanate and 2.5×10^{-6} mol/mol-Ag of N,N-dimethylselenourea.

Preparation of Emulsions B-2 and B-3

[0322] Emulsion B-2 was prepared in the same manner as Emulsion B-1 except for using Sensitizing Dyes ExS-4, ExS-5 and ExS-6 in place of Sensitizing Dyes ExS-1, ExS-2 and ExS-3, and Emulsion B-3 was prepared in the same manner except for using Sensitizing Dye ExS-7 instead.

Preparation of Emulsion C-1 (Silver Chloride (111) Tabular Emulsion) (Invention)

[0323] To a reaction vessel, 1,000 ml of an aqueous gelatin solution (containing 25 g of a deionized alkali-treated gelatin having a methionine content of about 40 μmol/g and 1.0 g of NaCl, and having a pH of 4.8) and 0.50 g of Compound (11) exemplified in JP-A-2-32 were added and the temperature was set at 60°C. To the solution, 500 ml of an aqueous $AgNO_3$ solution (containing 136 g of $AgNO_3$) and 400 ml of an aqueous NaCl solution (containing 52 g of NaCl) were added over 50 minutes while keeping the temperature at 60°C by a double jet method. At this time, a thiosulfonic acid compound ($C_2H_5SO_2SNa$) was added.

[0324] Then, AgBr fine grains having an average sphere-corresponding diameter of 0.03 μm were added in an amount corresponding to 0.2 mol% per mol of silver halide and ripened for about 5 minutes to accomplish halogen conversion.

[0325] Thereafter, a precipitating agent was added, the temperature was lowered to 30°C, the emulsion was precipitated and washed with water, an aqueous gelatin solution was added and the pH and the pCl were adjusted to 6.2 and 3.0, respectively, at 38°C.

[0326] The thus-prepared silver halide emulsion contained tabular grains having an average grain size of 0.7 μm, an average silver chloride content of 99.8 mol%, an aspect ratio of 4.0 or more and a main plane adjacent sides ratio of 1.5 or less, in a proportion of 70% of the total projected area.

[0327] After adding Sensitizing Dyes ExS-1, ExS-2 and ExS-3 shown below in an amount and at a ratio such that the emulsion could have a desired spectral sensitivity, the emulsion was heated up to 64°C and subjected to optimal chemical sensitization by adding thereto 9.4×10^{-6} mol/mol-Ag of sodium thiosulfate, 3.3×10^{-6} mol/mol-Ag of chloroauric acid, 2.9×10^{-3} mol/mol-Ag of potassium thiocyanate and 2.5×10^{-6} mol/mol-Ag of N,N-dimethylselenourea.

Preparation of Emulsions C-2 and C-3

[0328] Emulsion C-2 was prepared in the same manner as Emulsion C-1 except for using Sensitizing Dyes ExS-4, ExS-5 and ExS-6 in place of Sensitizing Dyes ExS-1, ExS-2 and ExS-3, and Emulsion C-3 was prepared in the same manner except for using Sensitizing Dye ExS-7 instead.

Preparation of Photographic Materials

[0329] Sample 101 as a multi-layer color photographic material was prepared by coating layers each having the following composition on an undercoated cellulose triacetate film support.

(Composition of Light-Sensitive Layer)

[0330] The main materials used in each layer are classified as follows.

ExC: cyan coupler
ExM: magenta coupler
ExY: yellow coupler
ExS: sensitizing dye
UV: ultraviolet absorbent
HBS: high-boiling point organic solvent
H: gelatin hardening agent

[0331] Numerals corresponding to respective ingredients show coating amounts expressed by the unit g/m^2 and in the case of silver halide, they show coating amounts calculated in terms of silver. With respect to sensitizing dyes, the coating amount is shown by the unit mol per mol of silver halide in the same layer.

(Sample 101)

[0332]

First Layer (antihalation layer)	
Black colloidal silver	0.09 as silver

(continued)

First Layer (antihalation layer)	
Gelatin	1.30
ExF-1	2.0×10^{-3}
Solid Disperse Dye ExF-2	0.030
Solid Disperse Dye ExF-3	0.040
HBS-1	0.15
HBS-2	0.02

Second Layer (interlayer)	
Polyethyl acrylate latex	0.20
Gelatin	1.04

Third Layer (red-sensitive emulsion layer)	
Emulsion A-1	1.3 as silver
ExS-1	6.0×10^{-4}
ExS-2	3.2×10^{-5}
ExS-3	9.0×10^{-4}
ExC-1	0.43
ExC-2	0.20
Cpd-2	0.023
HBS-1	0.20
Gelatin	1.50

Fourth Layer (interlayer)	
Cpd-1	0.090
Solid Dispersion Dye ExF-4	0.030
HBS-1	0.050
Polyethyl acrylate latex	0.15
Gelatin	1.10

Fifth Layer (green-sensitive emulsion layer)	
Emulsion A-2	1.1 as silver
ExS-4	3.8×10^{-5}
ExS-5	2.9×10^{-4}
ExS-6	9.8×10^{-4}
ExM-1	0.28
HBS-1	0.18
HBS-3	4.0×10^{-3}
Gelatin	1.0

Sixth Layer (yellow filter layer)	
Yellow colloidal silver	0.005 as silver
Cpd-1	0.16
Solid Disperse Dye ExF-5	0.060
Solid Disperse Dye ExF-6	0.060
Oil-Soluble Dye ExF-7	0.010
HBS-1	0.60
Gelatin	0.70

Seventh Layer (blue-sensitive emulsion layer)	
Emulsion A-3	1.00 as silver
ExS-7	4.0×10^{-4}
ExY-1	0.35
Cpd-2	0.10
Cpd-3	1.0×10^{-3}
HBS-1	0.070
Gelatin	0.70

Eighth Layer (first protective layer)	
UV-1	0.19
UV-2	0.075
UV-3	0.065
HBS-1	5.0×10^{-2}
HBS-4	5.0×10^{-2}
Gelatin	1.2

Ninth Layer (second protective layer)	
Silver Chloride Emulsion M	0.10 as silver
H-1	0.40
B-1 (diameter: 1.7 μm)	5.0×10^{-2}
B-2 (diameter: 1.7 μm)	0.15
B-3	0.05
S-1	0.20
Gelatin	0.70

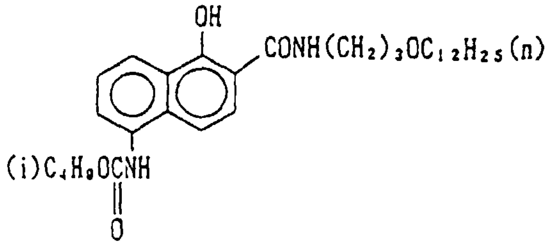
[0333] In addition, to each layer, W-1 to W-3, B-4 to B-6, F-1 to F-17, an iron salt, a lead salt, a gold salt, a platinum salt, a palladium salt, an iridium salt and a rhodium salt were appropriately added to improve preservability, processability, pressure durability, antimold and bactericidal property, antistatic property and coatability.

Preparation of Dispersion of Organic Solid Disperse Dye

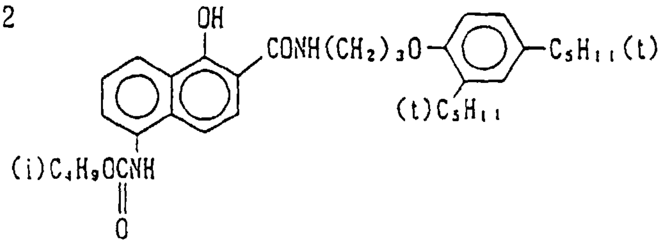
[0334] ExF-2 shown below was dispersed in the following manner. Namely, 21.7 ml of water, 3 ml of a 5% aqueous solution of sodium p-octylphenoxyethoxyethoxyethanesulfonate and 0.5 g of a 5% aqueous solution of p-octylphenoxypolyoxyethylene ether (polymerization degree: 10) were poured in a 700 ml-volume pot mill, then thereto 5.0 g of Dye ExF-2 and 500 ml of zirconium oxide beads (diameter: 1 mm) were added and the content was dispersed for 2 hours. The dispersion was conducted using a BO-type vibrating ball mill manufactured by Chuo Koki K.K. After the dispersion, the content was taken out and added to 8 g of a 12.5% aqueous gelatin solution and beads were removed by filtration to obtain a gelatin dispersion of the dye. The fine dye particles had an average particle diameter of 0.44 μm.

[0335] In the same manner, solid dispersions of ExF-3, ExF-4 and ExF-6 were obtained. The fine dye particles had an average particle diameter of 0.24 μm, 0.45 μm and 0.52 μm, respectively. ExF-5 was dispersed by a microprecipitation dispersion method described in Example 1 of European Unexamined Patent Publication (EP) 549489A. The average particle diameter thereof was 0.06 μm.

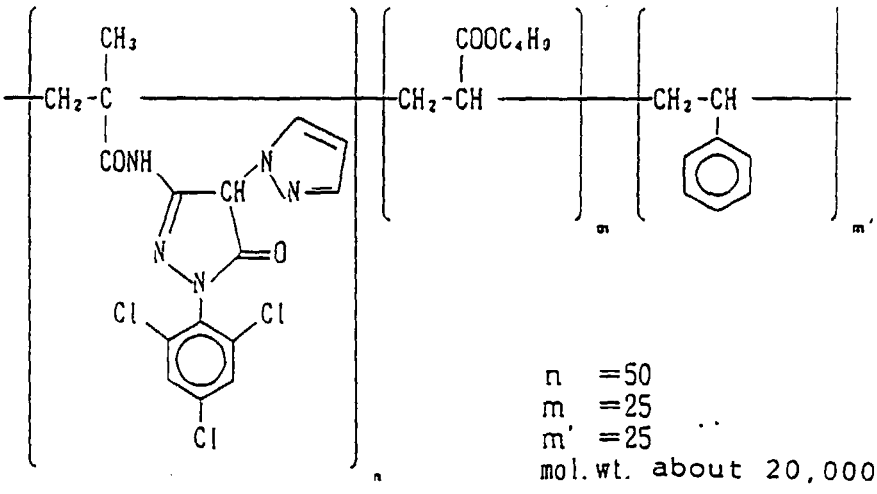
ExC-1



ExC-2

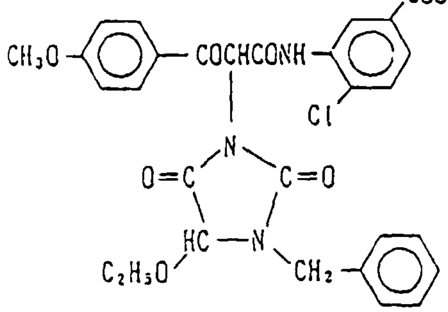


ExM-1

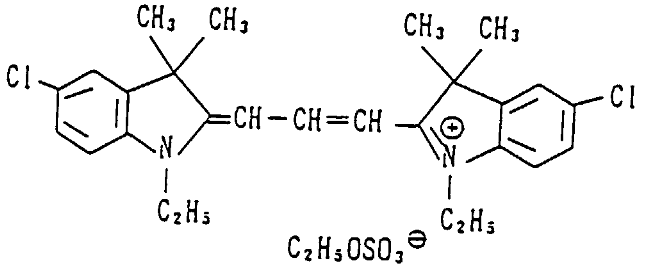


n =50
m =25
m' =25
mol.wt. about 20,000

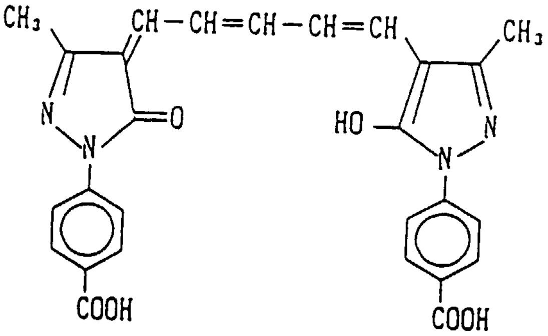
ExY-1



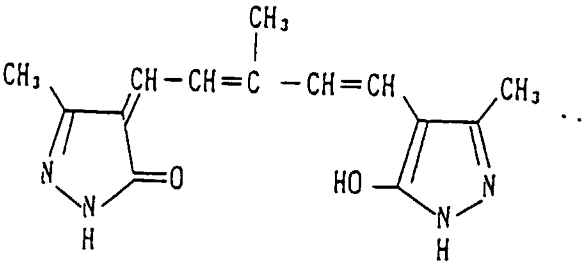
ExF-1



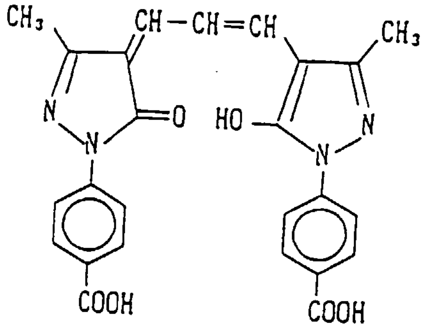
ExF-2



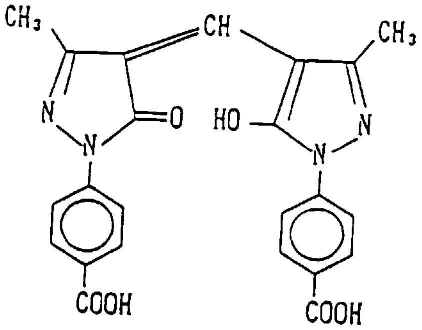
ExF-3



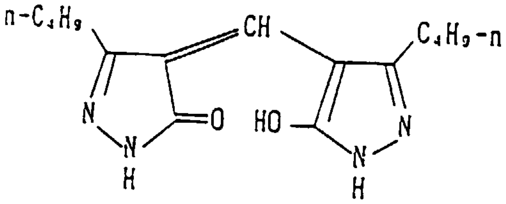
ExF-4



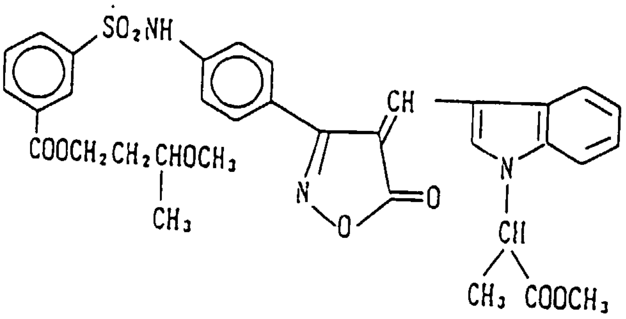
ExF-5



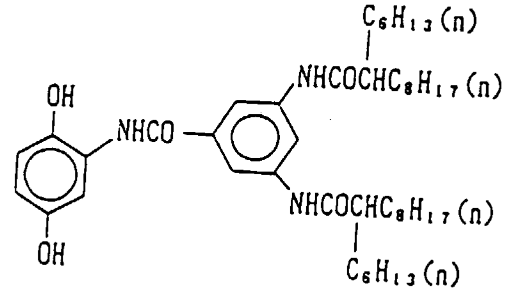
ExF-6



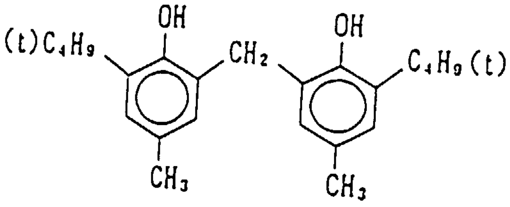
ExF-7



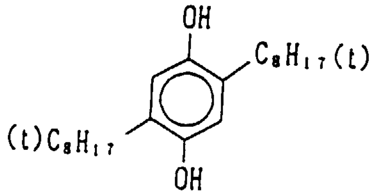
Cpd-1



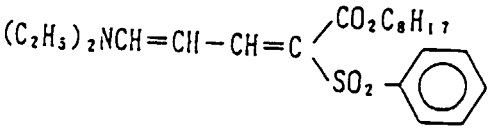
Cpd-2



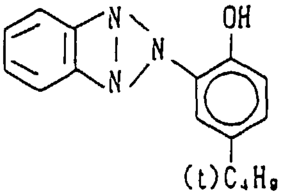
Cpd-3



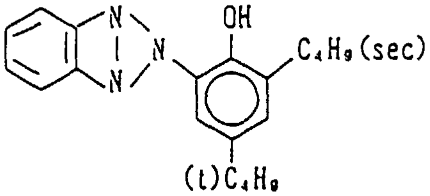
UV-1



UV-2



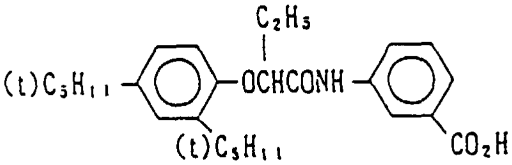
UV-3



HBS-1 Tricresyl phosphate

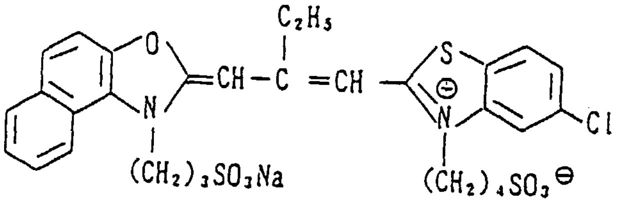
HBS-2 Di-n-butyl phthalate

HBS-3

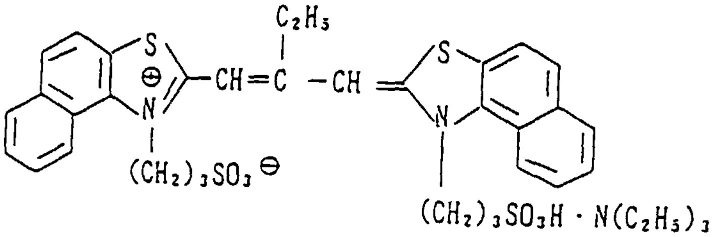


HBS-4 Tri(2-ethylhexyl) phosphate

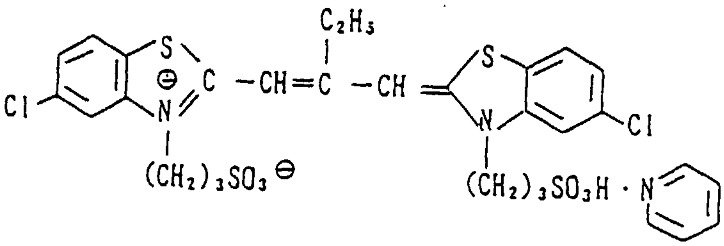
ExS-1



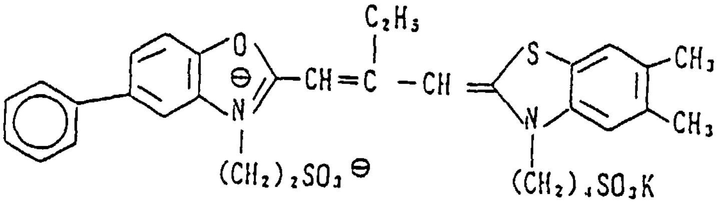
ExS-2



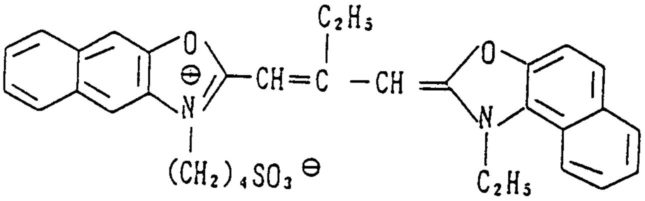
ExS-3



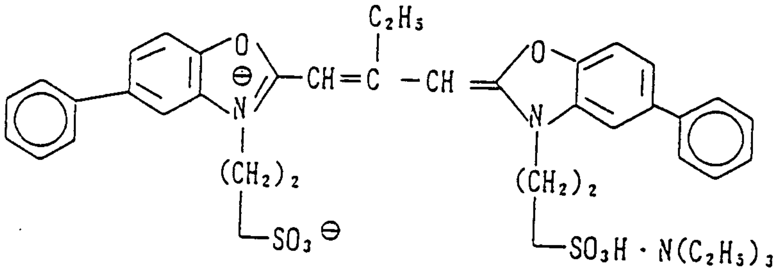
ExS-4



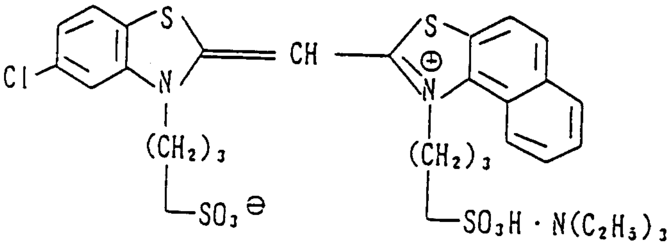
ExS－5



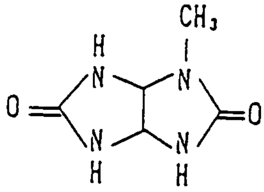
ExS－6



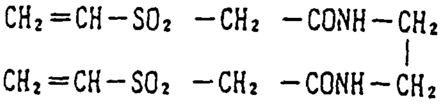
ExS－7



S－1

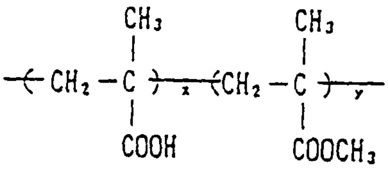


H－1



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

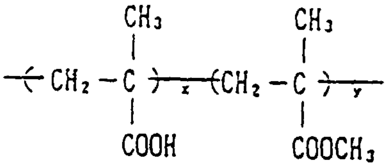
B－1



$$-\!\left(CH_2-\underset{COOH}{\overset{CH_3}{C}}\right)_x\!\!-\!\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\right)_y\!\!-$$

x/y＝10／90

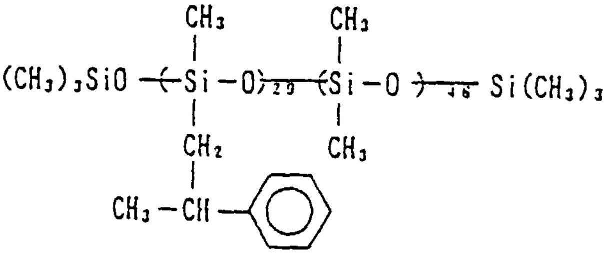
B－2



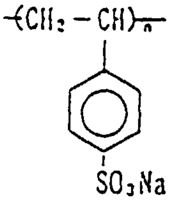
$$-\!\left(CH_2-\underset{COOH}{\overset{CH_3}{C}}\right)_x\!\!-\!\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\right)_y\!\!-$$

x/y＝40／60

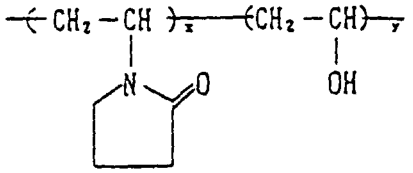
B－3



B－4

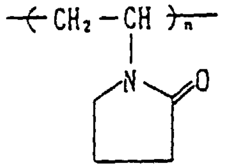


B-5



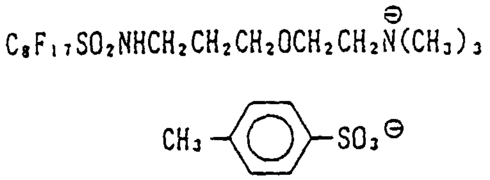
x/y=70/30

B-6



(mol. wt. about 10,000)

W-1



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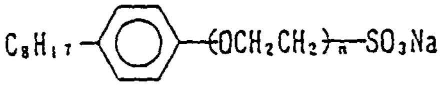
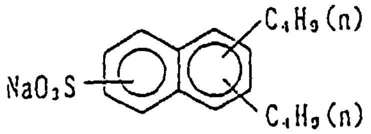
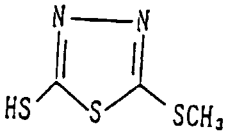


$n = 2 \sim 4$

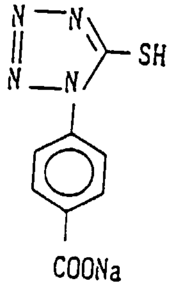
W-3



F－1



F－2



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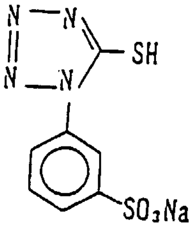

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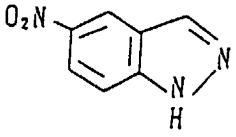

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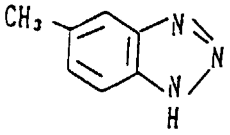

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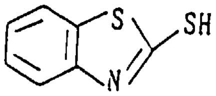

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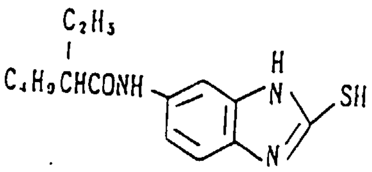

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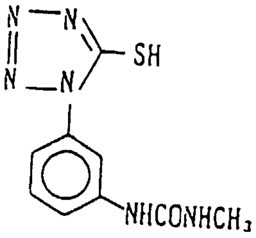

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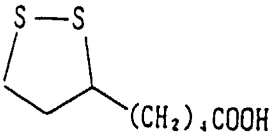

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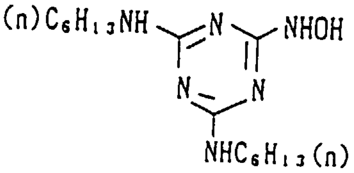

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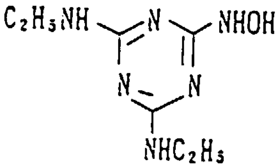

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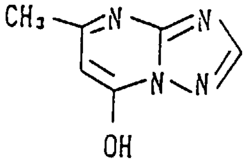

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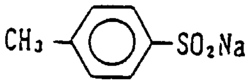
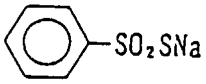
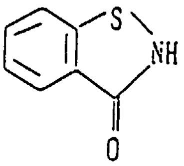


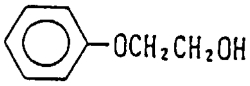
F-14



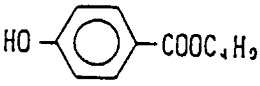
F-15



F-16



F-17



[0336] Samples 102 and 103 were prepared in the same manner as Sample 101 except for changing the emulsions in the layers as follows.

Sample	3rd Layer	5th Layer	7th Layer
101	A-1	A-2	A-3
102	B-1	B-2	B-3
103	C-1	C-2	C-3

[0337] Samples 201 to 203 were prepared in the same manner as Samples 101 to 103 except for incorporating Compound D-(6) of the present invention to the 3rd, 5th and 7th layers in an amount of 10% (3rd layer), 3.3% (5th layer) and 5% (7th layer) in terms of the molar ratio to the silver halide of each layer.

[0338] The total layer thickness of all hydrophilic colloid layers on the side having emulsion layers was 13.5 μm in Samples 101 to 103 and 14.5 μm in Samples 201 to 203.

[0339] Samples 302 and 303 were prepared in the same manner as Samples 102 and 103 except for incorporating Compound D-(6) of the present invention in an amount of 50% (3rd, 5th and 7th layers) in terms of the molar ratio to the silver halide of each layer.

Processing A: Processing for Silver Iodobromide

[0340] Sample 101 was subjected to the following development processing.

[0341] The development was conducted here at 38°C under the following conditions.

1. Color Development	2 min. 45 sec.
2. Bleaching	6 min. 30 sec.
3. Water Washing	3 min. 15 sec.
4. Fixing	6 min. 30 sec.
5. Water Washing	3 min. 15 sec.
6. Stabilization	3 min. 15 sec.

[0342] The processing composition used in each step is shown below.

Color Developer:	
Diethylenetriaminepentaacetic acid	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Sodium sulfite	4.0 g
Sodium carbonate	30.0 g
Potassium bromide	1.4 g
Hydroxylamine sulfate	2.4 g
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5 g
Water to make	1 ℓ
pH (adjusted with potassium hydroxide and sulfuric acid)	10.00

Bleaching Solution:	
Ammonium bromide	160.0 g
Aqueous ammonia (28%)	25.0 ml
Iron(III) nitrate nonahydrate	80.0 g
Chelating agent (shown in Tables 1 and 2)	0.23 mol
Compound of the Invention (shown in Tables 1 and 2)	0.04 mol
Glacial acetic acid	14 ml
Water to make	1 ℓ
pH (adjusted with aqueous ammonia and nitric acid)	4.3

Fixing Solution:	
Sodium tetrapolyphosphate	2.0 g
Sodium sulfite	4.0 g
Ammonium thiosulfate (700 g/ℓ)	175.0 ml
Sodium bisulfite	4.6 g
Water to make	1 ℓ
pH (adjusted with aqueous ammonia and acetic acid)	7.4

Stabilizing Solution	
Formalin	8.0 ml
Water to make	1 ℓ

Processing B: Processing for Silver Chloride

[0343] Samples 102 and 103 were subjected the following development processing.

(Processing Step)		
Step	Processing Time (sec)	Processing Temperature (°C)
Color development	45	38
Bleaching	30	38

(continued)

(Processing Step)		
Step	Processing Time (sec)	Processing Temperature (°C)
Fixing	45	38
Stabilization (1)	20	38
Stabilization (2)	20	38
Stabilization (3)	20	38
Drying	30	60
* Stabilization was conducted in a countercurrent system from (3) to (1).		

[0344] The composition of each processing solution is shown below.

(Color Developer)	
Ethylenediaminepentaacetic acid	3.0 g
Disodium 4,5-dihydroxybenzene-1,3-disulfonate	0.3 g
Potassium carbonate	30.0 g
Sodium chloride	5.0 g
Disodium N,N-bis(sulfonatoethyl)hydroxylamine	6.0 g
4-[N-Ethyl-N-(β-hydroxylethyl)amino]-2-methylaniline sulfate	5.0 g
Water to make	1.0 ℓ
pH (adjusted with potassium hydroxide and sulfuric acid)	10.00

(Bleaching Solution)	
Iron(III) nitrate nonahydrate	80.0 g
Chelating agent (shown in Tables 1 and 2)	0.23 mol
Compound of the Invention (shown in Tables 1 and 2)	0.04 mol
Ammonium bromide	80 g
Ammonium nitrate	15 g
Hydroxyacetic acid	25 g
Acetic acid (98%)	40 g
Water to make	1.0 ℓ
pH (adjusted with aqueous ammonia and acetic acid)	4.3

(Fixing Solution)	
Disodium ethylenediaminetetraacetate	15 g
Ammonium sulfite	19 g
Imidazole	15 g
Ammonium thiosulfate (700 g/ℓ)	280 ml
Water to make	1.0 ℓ
pH (adjusted with aqueous ammonia and acetic acid)	7.4

(Stabilizing Solution)	
Sodium p-toluenesulfinate	0.03 g
Polyoxyethylene-p-monononylphenyl ether (average polymerization degree: 10)	0.2 g
Disodium ethylenediaminetetraacetate	0.05 g
1,2,4-Triazole	1.3 g
1,4-Bis(1,2,4-triazol-1-ylmethyl)-piperazine	0.75 g
Water to make	1.0 ℓ
pH (adjusted with aqueous ammonia and acetic acid)	8.5

Processing C: Processing for Developing Agent-Containing Material

[0345] Samples 201 to 203 were subjected to the following development.

Processing Step		
Step	Processing Time (sec)	Processing Temperature (°C)
Color development (Processing with Activator)	20	38
Bleaching	10	38
Fixing	15	38
Stabilization (1)	10	38
Stabilization (2)	10	38
Stabilization (3)	10	38
Drying	30	60
* Stabilization was conducted in a countercurrent system from (3) to (1).		

[0346] The composition of each processing solution is shown below.

Color Developer (Activator Solution)	
Diethylenetriaminepentaacetic acid	3.0 g
Potassium carbonate	30.0 g
Sodium chloride	5.0 g
Water to make	1.0 ℓ
pH (adjusted with potassium hydroxide and sulfuric acid)	10.00

Bleaching Solution	
Iron(III) nitrate nonahydrate	80.0 g
Chelating agent (shown in Tables 1 and 2)	0.23 mol
Compound of the Invention (shown in Tables 1 and 2)	0.04 mol
Ammonium bromide	85 g
Ammonium nitrate	18 g
Aqueous ammonia (27%)	10 g
Acetic acid (98%)	50 g
Potassium carbonate	10 g
Water to make	1.0 ℓ
pH (adjusted with aqueous ammonia and acetic acid)	4.3

Fixing Solution	
Disodium ethylenediaminetetraacetate	2 g
Sodium sulfite	14 g
Sodium bisulfite	10 g
Ammonium thiosulfate (700 g/ℓ)	210 ml
Ammonium thiocyanate	160 g
Thiourea	2 g
Water to make	1.0 ℓ
pH (adjusted with aqueous ammonia and acetic acid)	6.5

Stabilizing Solution	
Surface active agent [$C_{10}H_{21}$-O-(CH_2CH_2O)-H]	0.2 g
Polymaleic acid (average molecular weight: 2,000)	0.1 g
1,2-Benzisothiazolin-3-one	0.05 g
Hexamethylenetetramine	5.5 g
Water to make	1.0 ℓ
pH (adjusted with aqueous ammonia and acetic acid)	8.5

[0347] Sample Nos. 101 to 103 and 201 to 203 each was subjected to wedgewise exposure for sensitometry (3,200K, 1/10", 0.1 CMS). Then, Sample 101 was subjected to Processings A and B, Samples 102 and 103 each was subjected to Processing B, and Samples 201 to 203, 302 and 303 each was subjected to Processing C. Each color image obtained was measured on the cyan density.

[0348] Further, each color image was observed through a red filter by means of a 10-magnification loupe to sensorially evaluate the graininess. The evaluation was relative evaluation taking the graininess of the color image of Sample 101 subjected to Processing A as 100 and the graininess of Sample 103 subjected to Processing B as 30. The larger the number is, the better the graininess is.

[0349] Further, the residual silver amount on the maximum color density portion was measured by the fluorescent X-ray analysis.

[0350] Furthermore, the photographic material samples obtained after the processing each was measured for the Dmin value measured with green light (G light).

[0351] Then, a multi-layer color photographic material Sample No. 101 was stored under the following conditions and determined on change in the density Dmin on the uncolored portion to examine the increase of stains during storage of the processed photographic material.

Dark/wet heat condition:

[0352]

$$\text{Increase of stains during storage at } 60^\circ\text{C and } 70\%\text{RH for 4 weeks } (\Delta D) \\ = (\text{Dmin after storage}) - (\text{Dmin before storage})$$

[0353] The results obtained are shown in Tables 1 and 2.

TABLE 1

Run	Photographic Material	Processing	Chelating Agent	Compound of the Invention	Cyan (Dmax)	Graininess	Residual Silver Amount (g/m^2)	Increase of Stain ΔD (G)	Remarks
1	101	A	ethylenediamine-tetraacetic acid	-	1.3	90	0.29	0.07	Comparison
2	"	A	1,3-propanediamine-tetraacetic acid	-	1.6	100	0.06	0.18	"
3	"	B	1,3-propanediamine-tetraacetic acid	-	0.4	30	0.13	0.15	"
4	201	C	1,3-propanediamine-tetraacetic acid	-	0.2	50	0.10	0.13	"
5	102	B	ethylenediamine-tetraacetic acid	-	0.3	40	0.42	0.08	"
6	103	"	ethylenediamine-tetraacetic acid	-	0.4	35	0.38	0.07	"
7	102	"	1,3-propanediamine-tetraacetic acid	-	1.9	30	0.13	0.13	"
8	103	"	1,3-propanediamine-tetraacetic acid	-	1.9	30	0.13	0.15	"
9	102	B	Compound I-5	-	2.0	110	0.07	0.08	Invention
10	"	"	" I-5	A-6	2.0	110	0.05	0.07	"
11	"	"	" I-5	A-7	2.0	110	0.03	0.05	"
12	"	"	" I-7	-	1.9	120	0.08	0.07	"
13	"	"	" I-7	A-1	2.0	120	0.06	0.06	"
14	"	"	" I-7	A-7	2.0	120	0.05	0.04	"
15	"	"	" I-40	-	2.0	115	0.07	0.07	"
16	"	"	" I-40	A-7	2.0	115	0.02	0.05	"
17	"	"	" I-42	-	1.9	110	0.08	0.07	"
18	"	"	" I-42	A-23	2.0	110	0.07	0.05	"
19	"	"	" II-15	-	1.9	110	0.08	0.05	"
20	"	"	" II-15	A-7	1.9	110	0.07	0.04	"

TABLE 2

Run	Photographic Material	Processing	Chelating Agent	Compound of the Invention	Cyan (Dmax)	Graininess	Residual Silver Amount (g/m^2)	Increase of Stain AD (G)	Remarks
21	103	B	Compound I-5	A-7	1.9	110	0.03	0.05	Invention
22	"	"	" I-7	"	2.0	120	0.04	0.05	"
23	"	"	" I-40	"	2.0	110	0.03	0.05	"
24	"	"	" II-15	"	2.0	110	0.05	0.04	"
25	202	C	" I-5	-	2.1	120	0.07	0.08	"
26	"	"	" I-5	A-7	2.1	125	0.03	0.04	"
27	"	"	" I-7	-	2.0	125	0.08	0.07	"
28	"	"	" I-7	A-7	2.1	125	0.04	0.04	"
29	"	"	" I-40	-	2.1	120	0.07	0.07	"
30	"	"	" I-40	A-7	2.1	125	0.03	0.05	"
31	"	"	" I-42	-	2.0	115	0.08	0.06	"
32	"	"	" I-42	A-7	2.0	110	0.04	0.05	"
33	"	"	" II-15	-	2.0	110	0.08	0.05	"
34	"	"	" II-15	A-7	2.0	110	0.05	0.04	"
35	203	"	" I-5	"	2.1	120	0.03	0.04	"
36	"	"	" I-7	"	2.1	125	0.04	0.04	"
37	"	"	" I-40	"	2.1	120	0.03	0.05	"
38	302	"	" I-5	"	2.1	120	0.04	0.05	"
39	"	"	" I-7	"	2.1	125	0.05	0.05	"
40	"	"	" I-40	"	2.1	120	0.04	0.06	"
41	303	"	" I-5	"	2.1	120	0.04	0.05	"
42	"	"	" I-7	"	2.1	120	0.05	0.05	

[0354] Sample No. 101 using silver iodobromide tabular grains conventionally used in a color photographic material was low in Dmax and large in the residual silver amount when subjected to Rapid Processing B. Sample No. 201 as a developing agent-containing material using the same emulsion was low in the cyan Dmax when subjected to Processing C. Further, when Sample Nos. 102 and 103 using silver chloride tabular grains were processed with a bleaching solution using ethylenediaminetetraacetic acid which had been conventionally used, the residual silver amount was large, and when processed with the bleaching solution using 1,3-propanediaminetetraacetic acid, the graininess was inferior and stains increased, thus, samples failed in satisfying all capabilities.

[0355] On the other hand, when Sample Nos. 102 and 103 were processed using the compound represented by formula (I) or (II) of the present invention, good results could be obtained in all capabiliyties. Further, when Sample Nos. 202, 203, 302 and 303 as a developing agent self-containing material were processed using the chelating agent (compound represented by formula (I) or (II)) of the present invention, the cyan Dmax and the graininess were further improved. Furthermore, when the bleaching solution contained the compound represented by formula (A) of the present invention, the residual silver amount and the stain were further improved.

EXAMPLE 2

〈Preparation of Emulsion E-1 (silver chloride (100) tabular emulsion)〉 (Invention)

[0356] Into a reaction vessel, 1,200 ml of an aqueous gelatin solution (containing 12 g of deionized alkali-treated ossein gelatin having a methionine content of about 40 μmol/g and having a pH of 3.8) was placed, and thereto Solution Ag-1 (containing 11.2 g of $AgNO_3$, 0.8 g of gelatin and 0.2 ml of 1N solution of HNO_3 in 100 ml) and Solution X-1 (containing 5.5 g of NaCl, 0.8 g of gelatin and 0.3 ml of 1N solution of NaOH in 100 ml) were added each in an amount of 12 ml and at an addition rate of 24 ml/min by a double jet method while keeping the temperature at 50°C. After stirring the mixture for 2 minutes, Solution Ag-2 (containing 2 g of $AgNO_3$, 0.8 g of gelatin and 0.2 ml of 1N solution of HNO_3 in 100 ml) and Solution X-2 (containing 1.4 g of KBr, 0.8 g of gelatin and 0.2 ml of 1N solution of NaOH in 100 ml) were added each in an amount of 19 ml by a double jet method at an addition rate of 31 ml/min. After stirring the mixture for 2 minutes, Solution Ag-1 and Solution X-1 were added each in an amount of 36 ml at a rate of 48 ml/min. Thereto, 20 ml of an NaCl solution (containing 10 g of NaCl in 100 ml) was added, the pH was adjusted to 6.0 and the temperature was raised to 75°C. After ripening for 30 minutes, Solution Ag-3 (containing 10 g of $AgNO_3$ in 100 ml) and Solution X-3 (containing 3.6 g of NaCl in 100 ml) were added at a silver potential of 130 mV by a C.D.J. (controlled double jet) method. The flow rate was 7 ml/min at the initiation of addition and accelerated by 0.1 ml/min, and as a result, 400 ml of Solution Ag-3 was added.

[0357] Thereafter, AgBr fine grains having an average sphere-corresponding diameter of 0.03 μm were added in an amount corresponding to 0.2 mol% per mol of silver halide and ripened for about 5 minutes to accomplish halogen conversion.

[0358] Then, a precipitating agent was added, the temperature was lowered to 30°C, the emulsion was precipitated and washed with water, an aqueous gelatin solution was added and the pH and the pCl were adjusted at 38°C to 6.2 and 3.0, respectively.

[0359] The thus-prepared silver halide emulsion contained tabular grains having an average sphere-corresponding diameter of 1.1 μm, an average silver chloride content of 95.6 mol%, an aspect ratio of from 4.0 to 10, and a main plane adjacent edges ratio of 2 or less, in a proportion of 70% of the total projected area.

[0360] The emulsion obtained was subjected to gold-sulfur-selenium sensitization as follows.

[0361] The emulsion was heated up to 64°C, Sensitizing Dyes ExS-1, ExS-2 and ExS-3 shown above were added in an amount and at a ratio such that the emulsion could have a desired spectral sensitivity, and then the emulsion was subjected to optimal chemical sensitization by adding thereto 9.4×10^{-6} mol/mol-Ag sodium thiosulfate, 3.3×10^{-6} mol/mol-Ag of chloroauric acid, 2.9×10^{-3} mol/mol-Ag of potassium thiocyanate and 2.5×10^{-6} mol/mol-Ag of N,N-dimethylselenourea.

[0362] Emulsion E-2 was prepared in the same manner as Emulsion E-1 except for using Sensitizing Dyes ExS-4, ExS-5 and ExS-6 in place of Sensitizing Dyes ExS-1, ExS-2 and ExS-3, and Emulsion E-3 was prepared in the same manner except for using Sensitizing Dye ExS-7 instead.

〈Preparation of Emulsion F-1 (silver chloride (111) tabular emulsion)〉 (Invention)

[0363] To a reaction vessel, 1,000 ml of an aqueous gelatin solution (containing 25 g of a deionized alkali-treated gelatin having a methionine content of about 40 μmol/g and 1.6 g of NaCl, and having a pH of 4.8) and 0.50 g of Compound (11) described in JP-A-2-32 were added and the temperature was set at 75°C. To the solution, 500 ml of an aqueous $AgNO_3$ solution (containing 136 g of $AgNO_3$) and 400 ml of an aqueous NaCl solution (containing 52 g of NaCl) were added while keeping the temperature at 75°C by a double jet method over 80 minutes. At this time, a thiosulfonic acid compound ($C_2H_5SO_2SNa$) was added.

[0364] Then, AgBr fine grains having an average sphere-corresponding diameter of 0.03 μm were added in an amount corresponding to 0.2 mol% per mol of silver halide and ripened for about 5 minutes to accomplish halogen conversion.

[0365] Thereafter, a precipitating agent was added, the temperature was lowered to 30°C, the emulsion was precipitated and washed with water, an aqueous gelatin solution was added and the pH and the pCl were adjusted at 38°C to 6.2 and 3.0, respectively.

[0366] The thus-prepared silver halide emulsion contained tabular grains having an average grain size of 1.1 µm, an average silver chloride content of 99.8 mol%, an aspect ratio of from 4.0 to 10 and a main plane adjacent sides ratio of 1.5 or less, in a proportion of 70% of the total projected area.

[0367] After adding Sensitizing Dyes ExS-1, ExS-2 and ExS-3 shown above in an amount and at a ratio such that the emulsion could have a desired spectral sensitivity, the emulsion was heated up to 64°C and subjected to optimal chemical sensitization by adding thereto 9.4×10^{-6} mol/mol-Ag of sodium thiosulfate, 3.3×10^{-6} mol/mol-Ag of chloroauric acid, 2.9×10^{-3} mol/mol-Ag of potassium thiocyanate and 2.5×10^{-6} mol/mol-Ag of N,N-dimethylselenourea.

[0368] Emulsion F-2 was prepared in the same manner as Emulsion F-1 except for using Sensitizing Dyes ExS-4, ExS-5 and ExS-6 in place of Sensitizing Dyes ExS-1, ExS-2 and ExS-3, and Emulsion F-3 was prepared in the same manner except for using Sensitizing Dye ExS-7 instead.

[0369] Sample 304 was prepared in the same manner as Sample No. 302 except for providing 3-A layer and 3-B layer in place of the 3rd layer, 5-A layer and 5-B layer in place of the 5th layer, and 7-A layer and 7-B layer in place of the 7th layer of Sample No. 302 in Example 1.

3-A Layer (high-sensitivity red-sensitive emulsion layer)	
Emulsion E-1	0.65 as silver
ExS-1	3.0×10^{-4}
ExS-2	1.6×10^{-5}
ExS-3	4.5×10^{-4}
ExC-1	0.22
ExC-2	0.10
Cpd-2	0.012
HBS-1	0.10
Gelatin	0.75
Compound D-(7)	10 mol% to silver

3-B Layer (low-sensitivity red-sensitive emulsion layer)	
Emulsion C-1	as silver 0.65
The others: the same as 3-A Layer	

5-A Layer (high-sensitivity green-sensitive emulsion layer)	
Emulsion E-2	0.60 as silver

(continued)

5-A Layer (high-sensitivity green-sensitive emulsion layer)	
ExS-4	7.9×10^{-5}
ExS-5	1.4×10^{-4}
ExS-6	0.4×10^{-4}
ExM-1	0.14
HBS-1	0.09
HBS-3	2.0×10^{-3}
Gelatin	0.5
Compound D-(7)	3.3 mol% to silver

5-B Layer (low-sensitivity green-sensitive emulsion layer)	
Emulsion C-2	0.60 as silver
The others: the same as 5-A Layer	

7-A Layer (high-sensitivity blue-sensitive emulsion layer)	
Emulsion E-3	0.50 as silver
ExS-7	2.0×10^{-4}
ExY-1	0.17
Cpd-2	0.05
Cpd-3	5×10^{-4}
HBS-1	0.035
Gelatin	0.35
Compound D-(8)	5 mol% to silver

7-B Layer (low-sensitivity blue-sensitive emulsion layer)	
Emulsion C-3	0.50 g as silver
The others: the same as 7-A Layer	

[0370] Sample 305 was prepared in the same manner as Sample 304 except for changing the use amount of Compound 7, in terms of the molar ratio to silver, to 5% (3-A layer), 15% (3-B layer), 1.2% (5-A layer) or 5.4% (5-B layer) and the use amount of Compound D-(8), in terms of the molar ratio to silver, to 0.8% (7-A layer) or 9.2% (7-B layer).

[0371] Further, Samples 306 and 307 were prepared in the same manner as Samples 304 and 305, respectively, except for changing Emulsion E-1 to Emulsion F-1, Emulsion E-2 to Emulsion F-2, Emulsion E-3 to Emulsion F-3, Emulsion C-1 to D-1, Emulsion C-2 to Emulsion D-2, and Emulsion C-3 to Emulsion D-3.

[0372] Each sample was exposed in the same manner as in Example 1 and then subjected to Processing C to obtain a color image. The color images were evaluated in the same manner as in Example 1 and the results are shown in Table 3 below.

TABLE 3

Run	Photographic Material	Chelating Agent	Compound of the Invention	Magenta Image Relative Value of Graininess
1	304	Compound I-7	A-7	75
2	305	"	"	65
3	306	"	"	100
4	307	"	"	90

[0373] Samples 306 and 307 where the ratio of the developing agent per silver halide of the low-sensitive layer was set larger than that of the high-sensitive layer, were better in the graininess and more preferred than Samples 304 and 305 where the ratio of the low-sensitive layer was the same as that of the high-sensitive layer.

EXAMPLE 3

[0374] Compounds I-5, I-7, I-40, II-15, A-6 and A-7 of the present invention were subjected to the biodegradability test according to the 302B-modified Zahn-Wellen method defined in the OECD Chemical Products Test Guide Line and as a result, all exhibited good biodegradability (degradation of 70% or more within 28 days). Accordingly, the compounds used in the present invention were verified to be advantageous in view of environmental protection of the globe.

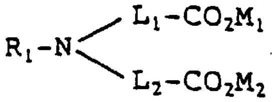
[0375] While the invention has been described in detail with reference to specific embodiments, it will be apparent to one skilled in the art that various changes and modifications can be made to the invention without departing from its spirit and scope.

Claims

1. A method for processing a silver halide color photographic material comprising color developing

a silver halide color photographic material comprising a support having thereon at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer, at least one blue-sensitive silver halide emulsion layer and at least one light-insensitive layer, wherein at least one of said light-sensitive silver halide emulsion layers comprises a silver halide emulsion comprising silver halide grains having a silver chloride content of 50 mol% or more, and

then processing the silver halide color photographic material with a processing solution having bleaching ability which contains at least one ferric complex salt of the compound represented by the following formula (I):

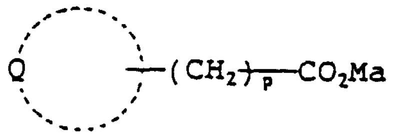


$$R_1-N\begin{cases} L_1-CO_2M_1 \\ L_2-CO_2M_2 \end{cases}$$

(I)

wherein R_1 represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group, L_1 and L_2 each represents an alkylene group, and M_1 and M_2 each represents a hydrogen atom or a cation.

2. The method for processing a silver halide color photographic material of claim 1, wherein the processing is conducted in the presence of at least one compound represented by the following formula (A):



(A)

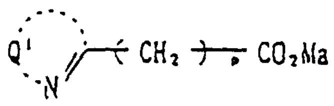
wherein Q represents a nonmetallic atom group necessary for forming a heterocyclic ring, p represents 0 or 1 and Ma represents a hydrogen atom or a cation.

3. The method for processing a silver halide color photographic material of claim 1, wherein the at least one of the light-sensitive layers or the at least one light-insensitive layer contains a color developing agent.

4. The method for processing a silver halide color photographic material of claim 3, wherein said color developing agent is incorporated into the at least one light-sensitive layer in an amount of from 0.5 to 40 mol% based on the silver halide in the same layer.

5. The method for processing a silver halide color photographic material of claim 3 or 4, wherein said at least one of the light-sensitive layers comprises a high-sensitive layer and a low-sensitive layer each containing a color developing agent and the ratio of the color developing agent to the silver halide of the high-sensitive layer is smaller than the ratio of the low-sensitive layer.

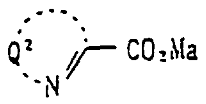
6. The method for processing a silver halide color photographic material of claim 2, wherein the compound represented by formula (A) is one represented by formula (A-a):



(A-a)

wherein Q^1 represents a nonmetallic atom group necessary for forming a nitrogen-containing heterocyclic ring, p represents 0 or 1, and Ma represents a hydrogen atom or a cation.

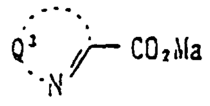
7. The method for processing a silver halide color photographic material of claim 2, wherein the compound represented by formula (A) is one represented by formula (A-b):



(A-b)

wherein Q^2 represents a 5- or 6-membered nitrogen-containing heterocyclic group which may be substituted by an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxy group, a halogen atom, a cyano group, a nitro group or a mercapto group and Ma represents a hydrogen atom or a cation.

8. The method for processing a silver halide color photographic material of claim 2, wherein the compound represented by formula (A) is one represented by formula (A-c):



(A-c)

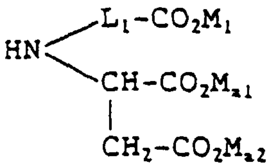
wherein Q^3 represents an atomic group necessary for forming a pyridine or imidazole ring which may be substituted by an alkyl group, an amino group, an alkoxy group, a carboxyl group, a hydroxy group, a halogen atom, a cyano group, a nitro group or a mercapto group, and Ma represents a hydrogen atom or a cation.

9. The method for processing a silver halide color photographic material of claim 2, wherein the compound represented by formula (A) is contained in a processing solution at desilvering step.

10. The method for processing a silver halide color photographic material of claim 2, wherein the compound represented by formula (A) is contained in a bleaching solution.

11. The method for processing a silver halide color photographic material of claim 2, wherein the compound represented by formula (A) is contained in a processing solution in an amount of from 0.01 to 0.10 mol per liter.

12. The method for processing a silver halide color photographic material of claim 1, wherein the compound represented by formula (I) is one represented by formula (I-a):



(I-a)

wherein L_1 represents an alkylene group and M_1, M_{a1}, and M_{a2} each represents a hydrogen atom or a cation.

13. The method for processing a silver halide color photographic material of claim 1, wherein the silver halide grains are tabular silver halide grains.

14. The method for processing a silver halide color photographic material of claim 1, wherein the silver halide emulsion is subjected to selenium sensitization.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 00 10 1973

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.7)
Y	EP 0 588 289 A (FUJI PHOTO FILM) 23 March 1994 (1994-03-23) * page 3, line 3 - line 8 * * page 7, line 24 - line 45 * * page 28, line 37 - page 29, line 19 * * page 36, line 57 - page 37, line 5; example 1 * ---	1,12-14	G03C7/42 G03C7/407 G03C7/30
Y	EP 0 532 003 A (KONICA) 17 March 1993 (1993-03-17) * page 14, line 54 - page 16, line 22; example 1 * ---	1-14	
Y	DATABASE WPI Section Ch, Week 9529 Derwent Publications Ltd., London, GB; Class E13, AN 95-218107 XP002012980 & JP 07 128768 A (FUJI PHOTO FILM CO LTD), 19 May 1995 (1995-05-19) * abstract * ---	1-14	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 March 2000	Philosoph, L

CATEGORY OF CITED DOCUMENTS

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

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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