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(54) A black-white image forming method

(57) A method for processing a silver halide photographic light-sensitive material with a processing solution, wherein said processing solution is supplied on a surface of said silver halide photographic light-sensitive material which is transferred in a gaseous phase to be processed and said silver halide photographic light-sensitive material possesses the following compositions; a support having thereon a first layer and a second layer opposite to said first layer, an emulsion layer containing a light-sensitive silver halide and an organic contrast accelerating agent which is coated on the same side as said first layer on said support.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to a processing method of a black-white silver halide photographic light-sensitive material.

BACKGROUND OF THE INVENTION

[0002] In recent years, because of abundance of information and easiness of expression color image prevails over black-white image. However, in a specified field such as medical field and graphic art field, the black-white image is still desirably used. In the graphic art, a light-sensitive material of a plate-making material for color image is used as black-white images separated according to each of printing inks and the black-white silver halide photographic light-sensitive material still in great demand for an industrial use.

[0003] Usually, the silver halide photographic light-sensitive material is processed by immersing it in processing solution which is accumulated in processing tank in a predetermined time. With respect to processing in processing tank, there have been problems such that the activity of a fresh processing solution is deferent from that of a running processing solution or change of composition of processing solution occurs by distillation and air-oxidation during accumulating processing solution in processing tank. To maintain the activity of the processing solution, it is widely employed to replenish a replenishing solution. The purpose of replenishing a replenishing solution is to dilute a compound which leach out of the light-sensitive material, adjust an amount of distillation and compensate a consumed component.

[0004] Especially in the graphic art field where high contrast image whose γ is not less than 10 is formed, the effect of the activity of the processing solution is remarkable. To maintain the activity of the processing solution, in stead of replenishing a replenishing solution, to decrease an open area of the processing tank and shorten renewal time of the processing solution in the processing tank, slit processing tank method described in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP-A) Nos. 9-211826, 9-230563, and shut up multi step processing tank method described in JP-A No. 9-133993 are known. However, since these methods substantially employ the processing tank method, it is insufficient to overcome the above mentioned problems with these methods.

[0005] Another method is so-called monobath process by which development and fix is performed in a processing solution.

[0006] The monobath processing has advantages to diminish a solution, compact an automatic processor and lessen preparing the processing solution, on the other hand, in forming black-white image with monobath processing, reproducibility of fine dot which is required in the light-sensitive for the graphic art is remarkably inferior and lowering of sensitivity is significant. Therefore, since there exist big problems in monobath processing as mentioned above to be solved.

[0007] In recent years, as a concern about environmental problem increases, decreasing the photographic processing effluent is strongly desired. Disposal of the photographic processing effluent is restricted and lowering replenishment rate is desired.

[0008] Accordingly, formerly an replenishment amount of the processing solution was not more than 350 ml per 1 m^2 of the light-sensitive material, however, recently it is necessary to process the light-sensitive material with the replenishment amount of the processing solution was not more than 250 ml per 1 m^2 of the light-sensitive material

[0009] However, in case where the processing with low replenishment rate is performed, reproducibility of fine dot is more remarkably inferior and lowering of sensitivity is more significant.

[0010] It is not preferable from the viewpoint of working environment that large amount of the processing solution accumulates in a processing tank at all time and improving the working environment is desired.

[0011] Spraying or coating the processing solution by ink-jet nozzle is disclosed in JP-A Nos. 2-64637, 9-80720. But these patents do not refer to high contrast black-white image forming method and with these technique described in these patents reproducibility of fine dot which is required in the light-sensitive for the graphic art is remarkably inferior and lowering of sensitivity is significant.

SUMMARY OF THE INVENTION

[0012] The first object of the invention is to provide the image forming method for the silver halide photographic light-sensitive material, wherein the problems such that the activity of a fresh processing solution is deferent from that of a running processing solution and change of composition of processing solution occurs by distillation and air-oxidation during accumulating processing solution in processing tank never occur. The second object of the invention is to provide the processing method for the silver halide photographic light-sensitive material, wherein in the light-sensitive photographic material having high contrast image whose γ is not less than 10, the problem of non-uniformity of processed

light-sensitive material never occurs. The third object of the invention is to provide the developer for the silver halide photographic light-sensitive material which is used in said image forming method. The fourth object of the invention is to provide the processing way in which the processed image has an excellent discrimination between high density and minimum density and an excellent image stability with desirable sharpness in a short time. The fifth object of the invention is to provide the processing method which is excellent from the viewpoint of working environment. The sixth object of the invention is to provide the image forming method by which the processed silver halide photographic material with high sensitivity, high γ and no black spot is obtained.

BRIEF DESCRIPTION OF DRAWINGS

[0013]

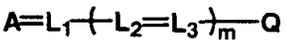
Fig. 1 to Fig. 8 illustrate outlines of the solution supplying apparatus and the light-sensitive material transferring apparatus according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

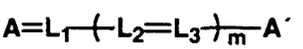
[0014] Above objects of the invention could be attained by the following methods.

1. A method for processing a silver halide photographic light-sensitive material with a processing solution, wherein said processing solution is supplied on a surface of said silver halide photographic light-sensitive material which is transferred in a gaseous phase to be processed and said silver halide photographic light-sensitive material comprises a support having a first surface and a second surface opposite to said first surface, component layers including a silver halide emulsion layer and hydrophilic colloidal layer which are coated on the same side as said first surface of said support, wherein said silver halide emulsion layer contains a light-sensitive silver halide and at least one of said component layers contains an organic contrast accelerating agent.
2. In a method for processing of item 1, said silver halide photographic light-sensitive material forms an image of which gamma is from 10 to 100 by said processing.
3. In a method for processing of item 1, said processing solution is supplied by spraying through a gaseous phase on said silver halide photographic light-sensitive material which is transferred in said gaseous phase.
4. In a method for processing of item 1, said silver halide emulsion layer of said silver halide photographic light-sensitive material contains transition metal of VI to X groups in a periodic table.
5. In a method for processing of item 1, said organic contrast accelerating agent is a hydrazine derivative or a 5,6-membered nitrogen containing heterocyclic derivative or a tetrazolium salt.
6. In a method for processing of item 1, at least one of said component layers contains the compound represented by the following formulae (1) - (6),

Formula (1)



Formula (2)



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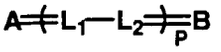
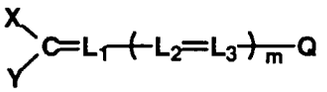
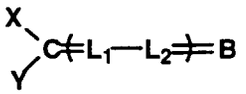


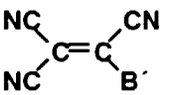
Formula (4)



Formula (5)



Formula (6)



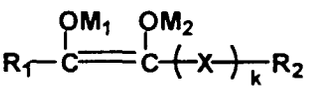
(In the formulae (1) - (6), A and A' may be either the same with or different from each other, and each of them represents an acidic nucleus, B represents a basic nucleus, Q represents an aryl group or a heterocyclic group, B' represents a heterocyclic group, X and Y may be either the same with or different from each other and each of them represents an electron withdrawing group, and each of L_1, L_2 and L_3 represents a methine group, m represents 0 or 1, n represents 0, 1 or 2, p represents 0 or 1.)

7. In a method for processing of item 1, said silver halide photographic light-sensitive material contains a developing agent of 0.3 to 5.0 g/m^2.

8. In a method for processing of item 1, said silver halide photographic light-sensitive material contains a developing agent of which amount can make not less than 15% of silver halide in said silver halide photographic light-sensitive material developable.

9. In a method for processing of item 1, said processing solution is a processing solution for development, wherein said developing solution contains the compound represented by the following formula (A),

Formula (A)



(In the formula (A), R_1 and R_2 each independently represents a substituted or an unsubstituted alkyl group, a substituted or an unsubstituted amino group, a substituted or an unsubstituted alkoxy group, and a substituted or an unsubstituted alkylthio group, and R_1 and R_2 may be linked with together to form ring, k is 0 or 1, and X is -CO- or -CS- when k is 1, and M_1 and M_2 are each a hydrogen atom or an alkali metal atom.)

10. In a method for processing of item 9, a processing solution containing the compound represented by the formula (A) and an alkaline aqueous solution of which pH is not less than 9 were supplied on the surface of said silver halide photographic light-sensitive material which is transferred in said gaseous phase.

11. In a method for processing of item 10, a processing solution containing the compound represented by the formula (A) is supplied on the surface of said silver halide photographic light-sensitive material which is transferred in said gaseous phase, thereafter said alkaline aqueous solution is supplied on the surface of said silver halide photographic light-sensitive material.

12. In a method for processing of item 1, ultra violet density of all layers coated on said second surface side of said support of said silver halide photographic light-sensitive material is not more than 0.3 and visual density of said all layers is not more than 0.3.

13. In a method for processing of item 12, said processing solution is a processing solution for development, wherein said processing solution for development contains at least one silver halide solvent of which amount is not less than a mol of developing agent.

14. In a method for processing of item 13, at least one of said silver halide solvent is an organic fixing agent.

15. In a method for processing of item 12, said processing solution is a processing solution for development, wherein said processing solution for development consists of only one kind of solution.

16. In a method for processing of item 12, said processing solution is a processing solution for development, wherein spraying said processing solution for development through a gaseous phase to supply said processing solution for development on the surface of said silver halide photographic light-sensitive material which is transferred in a gaseous phase, and supplied amount of said processing solution for development is 10 to 150 ml per 1 m^2 of said silver halide photographic light-sensitive material.

17. In a method for processing of item 12, an amount of silver contained in said silver halide photographic light-sensitive material is 0.3 to 3.4 g per 1 m^2 of said silver halide photographic light-sensitive material.

18. In a method for processing of item 12, an amount of absorbed water of all layers coated on said second surface side of said support of said silver halide photographic light-sensitive material is not more than 2 g/m^2.

19. In a method for processing of item 12, said processing solution is a processing solution for development, wherein water is supplied to said silver halide photographic light-sensitive material before said processing solution for development is supplied to said silver halide photographic light-sensitive material.

20. In a method for processing of item 12, said silver halide photographic light-sensitive material is carried with a carrier comprised of a gum containing layer before supplying said processing solution for development.

21. In a method for processing of item 1, the temperature of said silver halide photographic light-sensitive material is 25 to 50 °C when processing it with said processing solution.

22. In a method for processing of item 1, after beginning of the processing said silver halide photographic light-sensitive material, the temperature of said silver halide photographic light-sensitive material before 30% of total processing time is not more than 40 °C, and the temperature of said silver halide photographic light-sensitive material after 70% of total processing time is not less than 40 °C.

23. In a method for processing of item 1, said silver halide photographic light-sensitive material is exposed imagewise by laser beam.

24. In a method for processing of item 1, said silver halide photographic light-sensitive material is exposed imagewise by a light of which wave length is 600 to 850 nm..

25. In a method for processing of item 1, said processing solution is provided by dissolving a solid processing composition.

26. In a method for processing of item 1, said processing solution contains developing agent.

[0015] Next, the invention will be explained in detail.

[0016] The silver halide emulsion layer preferably contains at least one compound selected from transition metals of VI group to X group in a periodic table.

[0017] With respect to the transition metal complex used in the invention, sexidentate metal complex represented by the following formula is preferred.

$$[ML_6]^m$$

wherein, M represents a transition metal selected from the elements of VI group to X group in a periodic table, L represents a ligand, m is 0, -1, -2, or -3. Examples of the ligand represented by L are nitrosyl, thionitorosyl, halogen (fluoride, chloride, bromide and iodide), cyanide, cyanate, thicyanate, selenocyanate, tellurocyanate azido and aquo. The aquo preferably occupies one or two ligand(s). L may be the same or different.

[0018] Preferable examples of M are rhodium (Rh), ruthenium (Ru), rhenium (Re), osmium (Os) and iridium (Ir).

[0019] Examples of the transition metal complexes are shown below.

1: $[RhCl_6]^{3-}$
2: $[RuCl_6]^{3-}$
3: $[ReCl_6]^{3-}$
4: $[RuBr_6]^{3-}$
5: $[OsCl_6]^{3-}$
6: $[CrCl_6]^{3-}$

7: $[Ru(NO)Cl_5]^{2-}$
8: $[RuBr_4(H_2O)_2]^-$
9: $[Ru(NO)(H_2O)Cl_4]^-$
10: $[RHCl_5(H_2O)]^{2-}$
11: $[Re(NO)Cl_5]^{2-}$
12: $[Re(NO)(CN)_5]^{2-}$
13: $[Re(NO)Cl(CN)_4]^{2-}$
14: $[Rh(NO)_2Cl_4]^-$
15: $[Rh(NO)(H_2O)Cl_4]^-$
16: $[Ru(NO)(CN)_5]^{2-}$
17: $[Fe(CN)_6]^{3-}$
18: $[Rh(NS)Cl_5]^{2-}$
19: $[Os(NO)Cl_5]^{2-}$
20: $[Cr(NO)Cl_5]^{2-}$
21: $[Re(NO)Cl_5]^-$
22: $[Os(NS)Cl_4(TeCN)]^{2-}$
23: $[Ru(NS)Cl_5]^{2-}$
24: $[Re(NS)Cl_4(SeCN)]^{2-}$
25: $[Os(NS)Cl(SCN)_4]^{2-}$
26: $[Ir(NO)Cl_5]^{2-}$

The metal complex can be added in the silver halide during preparing the silver halide grain. The metal complex may be added uniformly throughout the silver halide, or in the interior of the silver halide grain. The preferable transition metals according to the invention are Ru, Rh and Ir. These transition metals are preferably added during preparing the silver halide grain, but there is no limitation thereto.

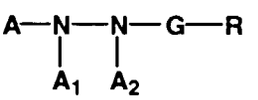
[0020] The added amount of these metal complexes is 10^{-8} to 10^{-3} mol per a mol of silver halide, preferably 10^{-8} to 10^{-6} mol.

[0021] As an organic contrast increasing agent, is cited a nucleating compound performing nucleation development described in The Journal of Japanese Society of Printing Science and Technology 24, p.299(1987), or a compound performing selective development described in The Journal of Japanese Society of Printing Science and Technology 24, p.307(1987).

[0022] The exemplified compounds are cited hydrazine derivatives, 5 or 6-membered nitrogen containing heterocyclic compounds, and tetrazolium compounds, and these compounds are preferably used in combination with nucleation accelerating compounds. The organic contrast accelerating agents are preferably contained in an adjacent layer to a silver halide emulsion layer.

[0023] An example of hydrazine derivative is represented by the following formula (H).

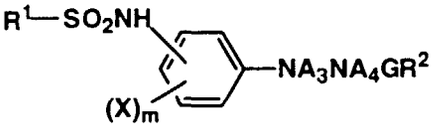
Formula (H)



wherein A represents an aryl group or a heterocycle containing therein a sulfur atom or oxygen atom; G represents a $-(CO)_n-$ group, a sulfonyl group, a sulfoxy group, a $-P(=O)R_2$ group or an iminomethylene group, in which n is 1 or 2; A_1 or A_2 both represent hydrogen atoms, or one of A_1 and A_2 represents a hydrogen atom and the other represents a substituted or unsubstituted alkylsulfonyl group, or a substituted or unsubstituted acyl group; R represents a hydrogen atom, or an alkyl group, alkenyl group, aryl group, alkoxy group, alkenyloxy group, aryloxy group, heterocyclic oxy group, amino group, carbamoyl group or oxycarbonyl group, each of which may be substituted; and R_2 represents an alkyl group, alkenyl group, alkynyl group, aryl group, alkoxy group, alkenyloxy group, alkynyloxy group, aryloxy group, or amino group, each of which may be substituted.

[0024] In the present invention, as a hydrazine derivative, the compound represented by the above-mentioned general formula (H) is preferable and the compound represented by the following general formula (Ha) is particularly preferable.

Formula (Ha)



[0025] In the formula, R^1 represents a substituted or unsubstituted aliphatic group, for example, octyl group, decyl group, etc.; a substituted or unsubstituted aromatic group, for example, phenyl group, 2-hydroxylphenyl group, chlorophenyl group, etc.; or a substituted or unsubstituted heterocyclic group, for example, a pyridyl group, a thienyl group, a furyl group, etc.; and these groups may be substituted by an appropriate substituent. Further, it is also preferable that R^1 contains at least one ballast group or a silver halide adsorption-accelerating group.

[0026] As a diffusion-proof group, ballast groups which are commonly used in the immobile photographic additives such as couplers are preferable, and for such ballast groups, for example, an alkyl group, an alkenyl group, an alkynyl group, an alkoxy group, a phenyl group, a phenoxy group, an alkylphenoxy group, etc., which are relatively photographically inert consisting of carbon atoms of not less than 8, are cited.

[0027] The silver halide adsorption-accelerating agent includes, for example, a thiourea group, a thiourethane group, a mercapto group, a thioether group, a thione group, a heterocyclic group, a thioamide heterocyclic group, mercapto heterocyclic group, or those adsorbing groups disclosed in Japanese Patent O.P.I. Publication No.64-90439(1989), etc.

[0028] In the general formula (Ha), X represents a group which is capable of being a substituent on a phenyl group, m represents an integer of zero through four, provided when m is two or more, X may be the same or different.

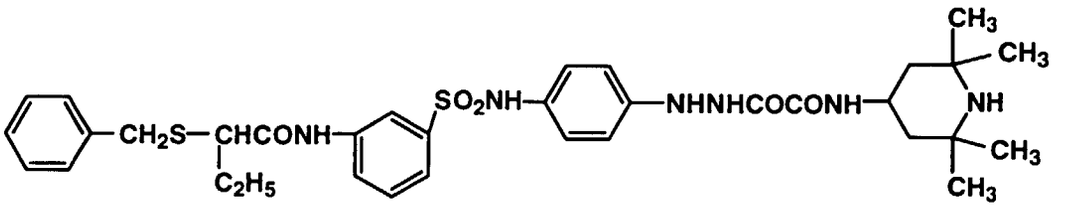
[0029] In the formula (Ha), A_3 and A_4 independently have the same definition as A_1 and A_2 in the formula (H) respectively, it is preferable that both A_3 and A_4 are hydrogen.

[0030] In the formula [Ha], G represents a carbonyl group, a sulfonyl group, a sulfoxy group, a phosphoryl group or an iminomethylene group, and carbonyl group is preferable as G.

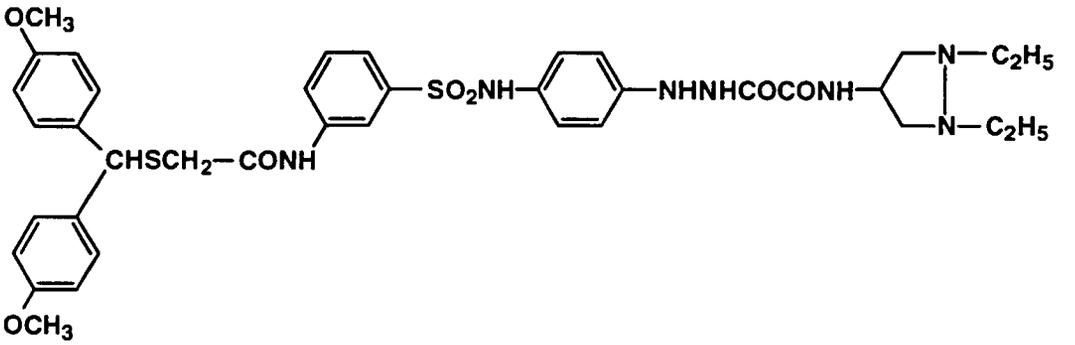
[0031] In the formula (Ha), R^2 represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted alkoxy group, a hydroxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted carbamoyl group and a substituted or unsubstituted oxy carbonyl group. The most preferable R^2s are -$COOR^1$ and - $CON(R^4)(R^5)$ group. R^3 represents an alkinyl group or a saturated heterocyclic group; R^4 represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group; and R^5 represents a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted saturated heterocyclic group, a hydroxy group or a substituted or unsubstituted alkoxy group.

[0032] Specific examples of the compound represented by the general formula (H) are given below, however, the scope of the present invention is limited by these.

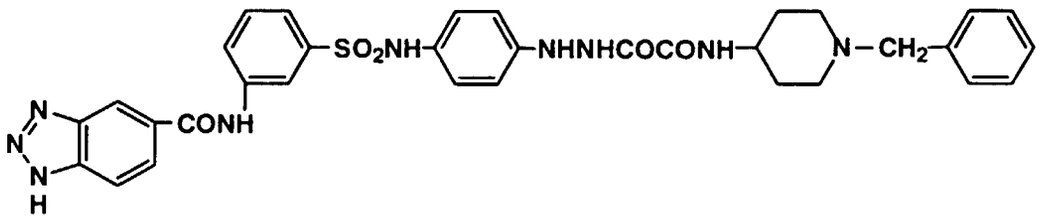
H—1


CH3
CH3
NH
CH3
CH3
CH2S
CHCONH
C2H5
SO2NH
NHNHCOCONH

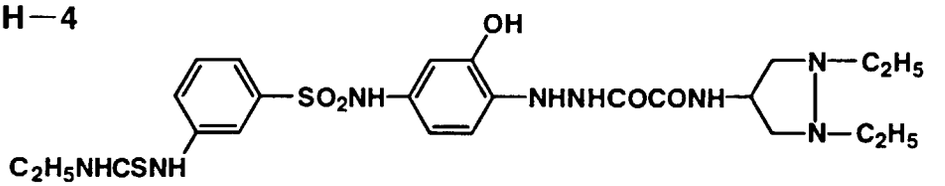
H—2


OCH3
OCH3
CHSCH2
CONH
SO2NH
NHNHCOCONH
N
C2H5
N
C2H5

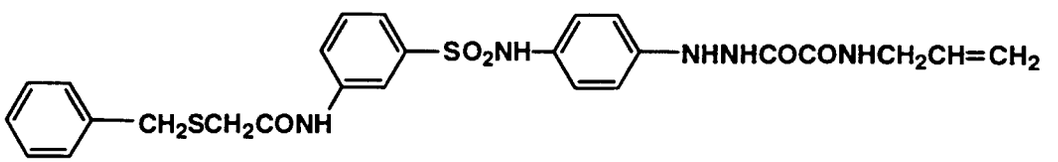
H—3


SO2NH
NHNHCOCONH
N
CH2
CONH
N
N
H

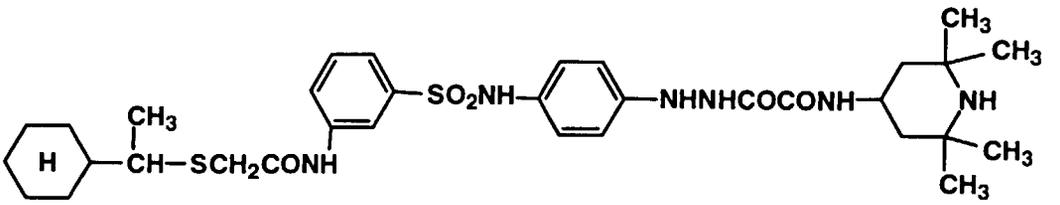
H—4


OH
SO2NH
NHNHCOCONH
N
C2H5
N
C2H5
C2H5NHCSNH

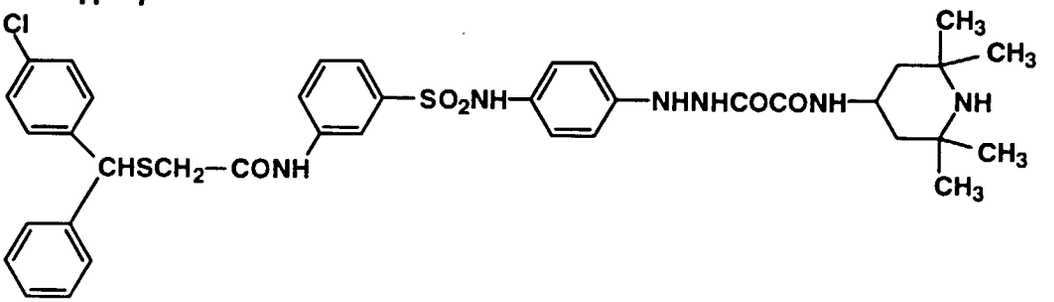
H—5


SO2NH
NHNHCOCONHCH2CH=CH2
CH2SCH2CONH

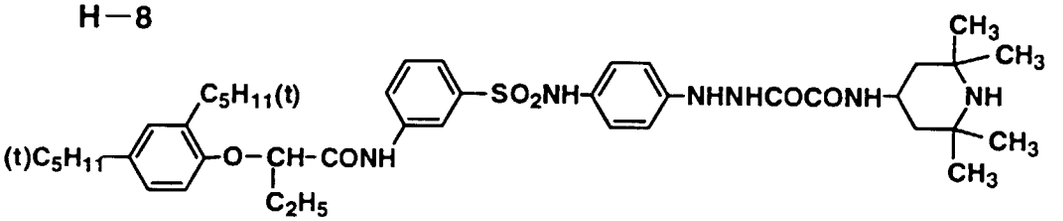
H−6



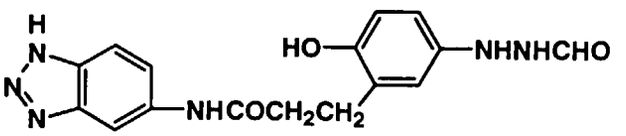
H−7



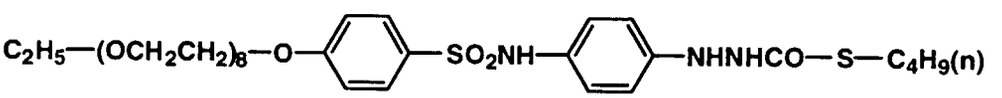
H−8



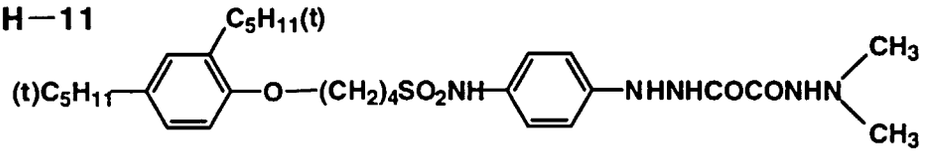
H−9



H−10



H—11



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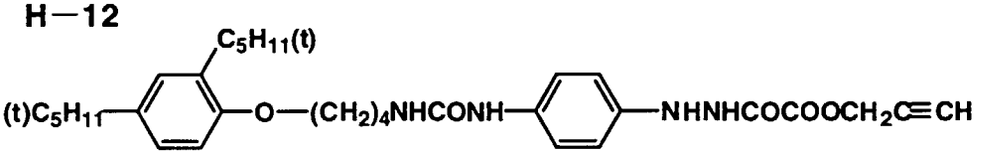

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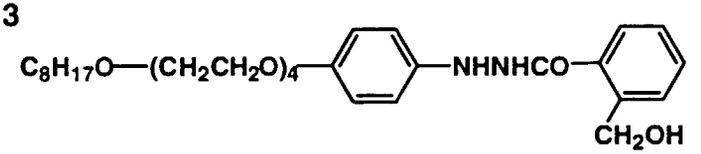

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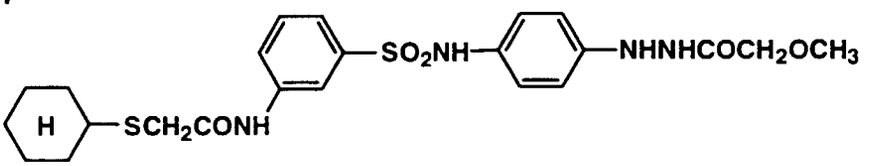

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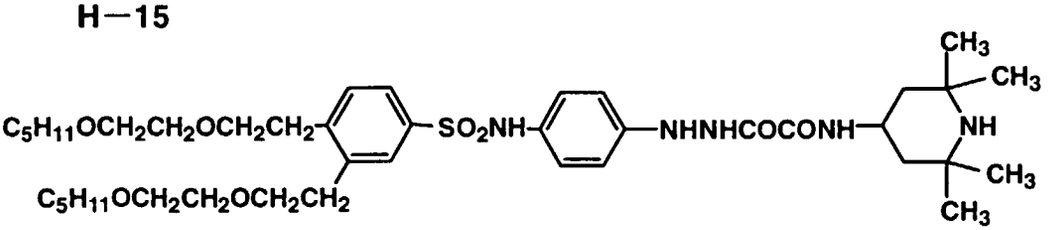

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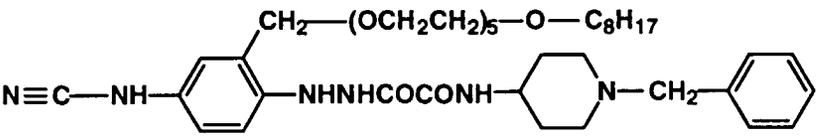

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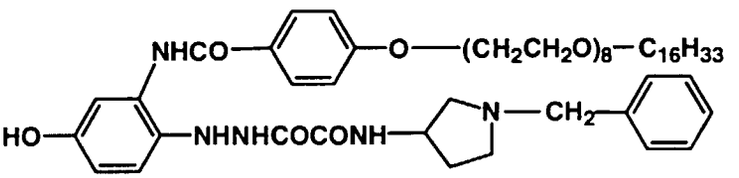

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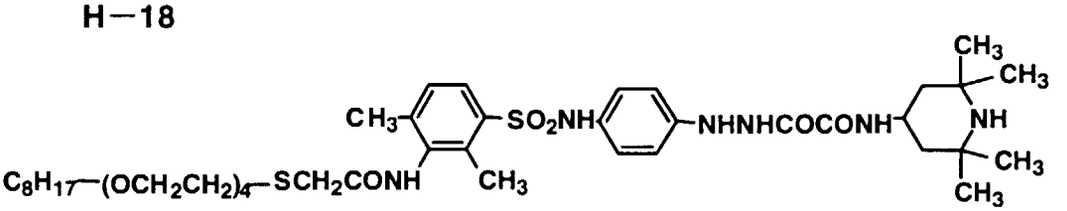

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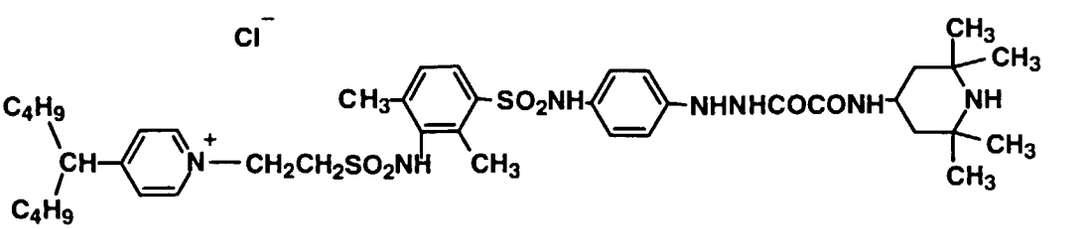

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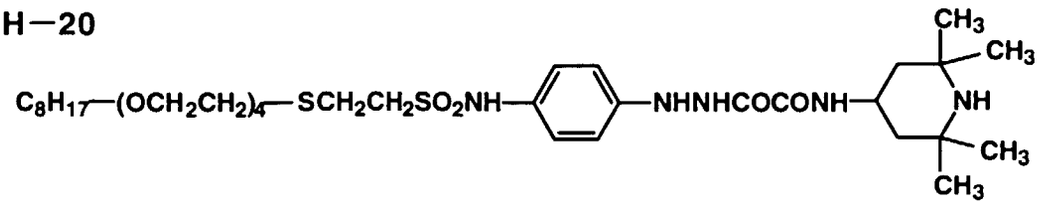

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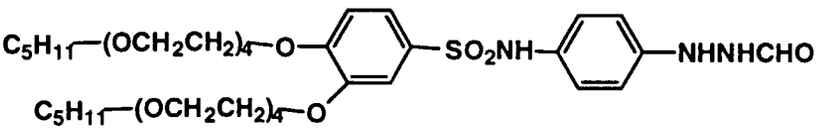

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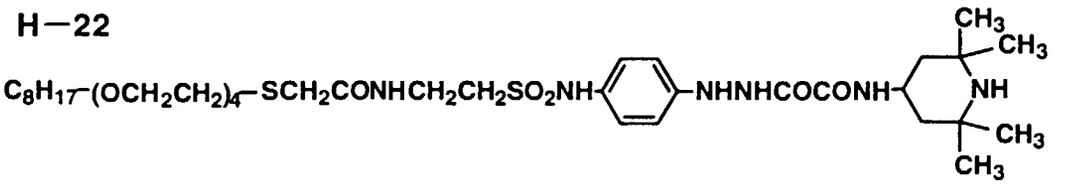

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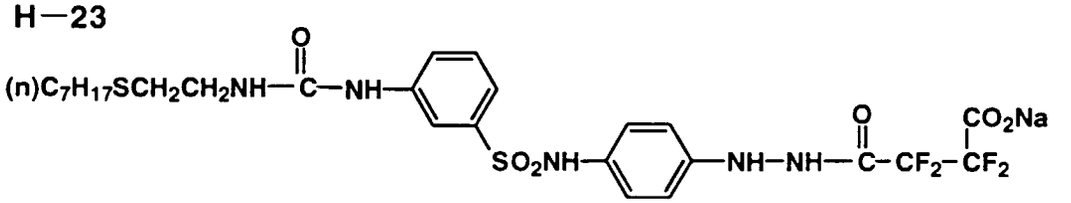

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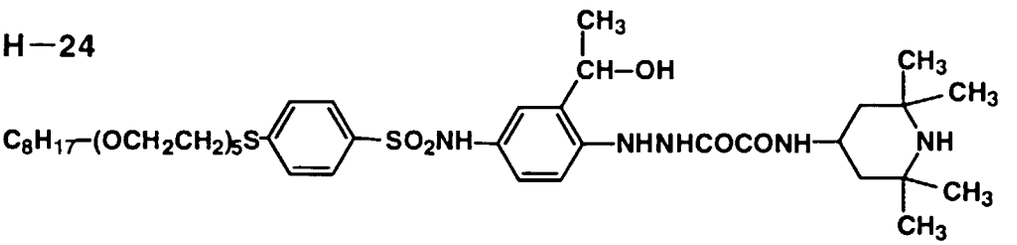

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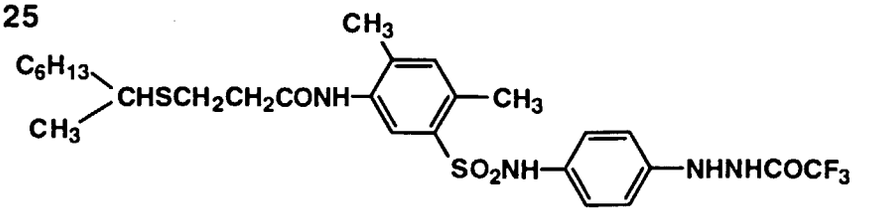

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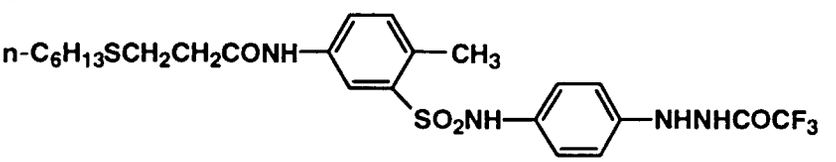


[0033] In addition, as examples of preferred hydrazine derivatives, for example, exemplified Compounds (1) through (252) disclosed on column 4 through 60 of United States Patent No.5,229,248 can be mentioned.

[0034] The hydrazine derivatives used in the present invention can be synthesized according to the conventionally known methods in the art. For example, they may be synthesized according to the method disclosed on column 59 through 80 in the United States Patent No.5,229,248.

[0035] The hydrazine derivatives used in the present invention can be added in any layer of photographic composition

layers of the silver halide emulsion layer side. Preferably, it is added in at least two layers of an emulsion layer and/or it's adjoining hydrophilic colloidal layer. The adding amount of the hydrazine derivative is usually within the range of 10^{-6} to 10^{-1} moles, preferably 10^{-5} to 10^{-2} moles, per mole of silver halide even though the optimum amount is varied depending on the diameter of the silver halide grain, halide composition, and the degree of chemical sensitization of silver halide grain, and the kind of stabilizing agent. According to the invention, a molar ratio of the total amount of the hydrazine compound contained in the first silver halide emulsion layer and/or hydrophilic colloidal layer(s) closer to the support than the first emulsion layer to that contained in the second silver halide emulsion layer and/or hydrophilic colloidal layer(s) farther from the support than the first emulsion layer is 0.2 - 0.8, preferably, 0.4 to 0.6. The hydrazine derivative can be used singly or in combination of two kinds or more.

[0036] The hydrazine derivatives according to the invention is preferably contained in the silver halide emulsion in the form of solid dispersion particle from the viewpoint of the stability of the light-sensitive material. With respect to the dispersion methods, the following two methods are recommended,

(i) a method that the hydrazine derivative is mixed with an aqueous solution which does not contain substantially an organic solvent such as ethylacetate, methyl alcohol and methylethylketone etc., but contains one or more kinds of stabilizer(s) or pulverizing agent(s), thereafter the organic solvent is removed by evaporation under a reduced pressure,

(ii) a method that solid hydrazine derivative is crashed with an inorganic pulverizing medium repeatedly in an aqueous solution containing one or more kinds of stabilizer(s) or pulverizing agent(s). As a hard inorganic pulverizing medium, is cited bead such as sand, silica ball, stainless steel, silicon carbide, glass, zirconium, zirconium oxide, alumina and titanium. The bead size of these mediums is in the range of 0.25 to 3.0 mm. Additionally as a method to decrease the particle size, is cited ball mill, media mill, attriter mill, jet mill and vibration mill etc.

[0037] The average particle diameter of the hydrazine derivative dispersion obtained by the above mentioned methods is generally 0.05 to 1.5 μm, preferably 0.1 to 1.0 μm.

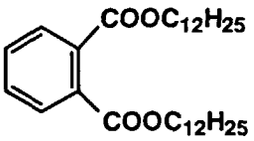
[0038] In the dispersion used in the invention, a stabilizer or an auxiliary dispersion agent is used. As the stabilizer or the auxiliary dispersion agent, is cited a surfactant or a hydrophilic colloid.

[0039] As surfactants, known anionic surfactant, cationic surfactant, nonionic surfactant, betainoic surfactant and fluoride containing surfactant can be used. The examples of anionic surfactants are cited alkyl carboxylate, alkyl sulfonate, alkylbenzene sulfonate, alkylnaphthalene sulfonate, alkyl sulfuric ester, alkyl phosphoric ester, N-acyl-N-alkyl taurine, sulfosuccinic acid ester, sulfoalkylpolyoxyethylene alkylphenyl ether and polyoxyethylenealkyl phosphoric ester. All these compounds mentioned above include acid groups such as carboxy group, sulfo group, phospho group, sulfuric ester group and phosphoric ester group. The examples of cation surfactants are cited alkylamine salt derivative, aliphatic or aromatic quaternary ammonium salt derivative, heterocyclic quaternary ammonium derivatives such as pyridinium and imidazolium and phosphonium or sulfonium salt containing aliphatic group or heterocyclic ring. The examples of non-ionic surfactants are cited steroid saponin, alkyleneoxide derivative, glycidol derivative, ester derived from polyhydric alcohol and fatty acid, and alkyl ester of sugar derivative.

[0040] As hydrophilic colloids, known water soluble polymer, for example, polyethylene glycohol, polyvinyl alcohol, polyvinyl pyrrolidone, polyacryl amide, polystyrene sulfonate, gelatin, gelatin derivatives (phthalated gelatin, phenylcarbamoylated gelatin), cellulose derivatives(cellulose ether, cellulose ester), starch, gum arabi, pluran, dextran, dextrin or natural high molecular compound etc. can be used.

[0041] An emulsified dispersion of the hydrazine derivative in a high boiling solvent is preferably used from the viewpoint of the stability of the light-sensitive material. To disperse the hydrazine derivative in the high boiling solvent, the similar method for dispersing an oil soluble coupler or an oil soluble ultra violet absorbing agent etc. can be employed. The hydrazine derivative is dissolved in the high boiling solvent optionally together with a low boiling solvent, thereafter thus obtained solution is mixed with a gelatin aqueous solution containing surfactant, then the mixture is dispersed by colloid mill etc. The examples of the high boiling solvents are carboxylic acid ester, phosphoric acid ester, carboxylic acid amide and hydrocarbon etc. The exemplified high boiling solvents are shown below.

O—1



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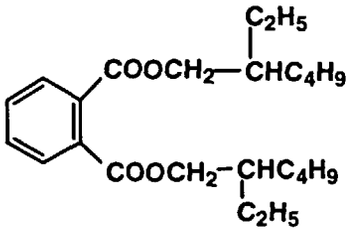

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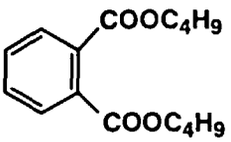

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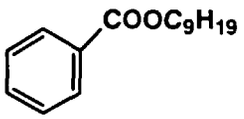

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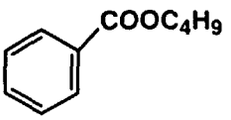

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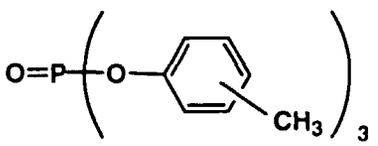

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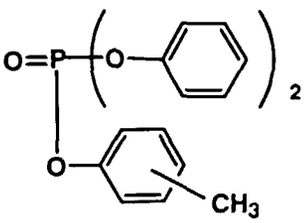

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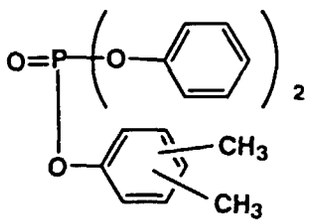


O—9

Paraffine

O—10

Paraffine Chloride

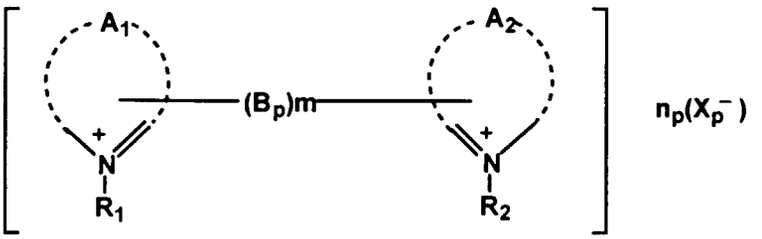
[0042] The surface pH of the silver halide light-sensitive material is preferably not more than 6. The surface pH is measured by dropping 0.5 ml of the aqueous solution whose concentration and composition are each the same as those of the comparative electrode interior solution (in the case of GS-5013F, KCl of 3.3 mol/l) onto 1 cm^2 of the surface of the light-sensitive material, then after leaving it for 5 min. under 80% RH, the pH is measured using silver chloride electrode(AgCl/KCl) as a standard electrode, and contacting a unit of plate-like glass electrode (plate-like complex electrode) with the surface to be measured after 5 min. An example of the plate-like complex electrode is GS-5013F produced Toadenpakogyo Co., Ltd.

[0043] To adjust the surface pH, a method by adding acid, a method by applying volatile alkali while drying the film, and a method by applying the compound which can release acid by reaction after drying the film, can be employed.

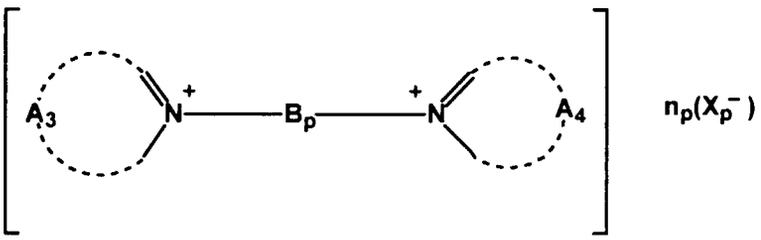
[0044] The hydrazine derivative according to the invention may be contained in an optional layer of the silver halide light-sensitive material, from the viewpoint of the stability of the light-sensitive material, it is preferable that it is contained in a layer other than a silver halide emulsion layer.

[0045] As 5 to 6 membered nitrogen containing heterocyclic derivatives according to the invention, the compounds represented by the following compounds represented by the following Formulae (Pa), (Pb) and (Pc).

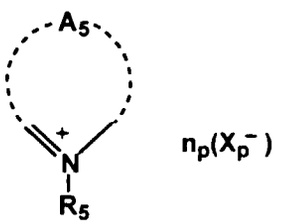
Formula (Pa)



Formula (Pb)



Formula (Pc)



[0046] In the above described formula (Pa), (Pb) or (Pc), A_1, A_2, A_3, A_4 or A_5 represent non-metal atoms to complete 5 to 6 membered nitrogen containing heterocyclic ring, and said heterocyclic ring may contain oxygen atom, nitrogen atom and sulfur atom, and said heterocyclic ring may be condensed with benzene ring. The 5 to 6 membered nitrogen containing heterocyclic ring composed of A_1, A_2, A_3, A_4 or A_5 may be substituted by substituents. The examples of substituents are an alkyl group, an aryl group, an aralkyl group. an alkenyl group, an alkynyl group, a halogen atom, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a slfo group, a carboxy group, a hydroxy group, an alkoxy group, an aryloxy group, an amide group, a sulfamoyl group, a carbamoyl group, an ureido group, an amino group, a sulfonamide group, a sulfonyl group, a cyano group, a nitro group, a mercapto group, an alkylthio group and an arylthio group.

[0047] As the 5 to 6 membered nitrogen containing heterocyclic ring composed of A_1, A_2, A_3, A_4 or A_5 is cited pyridine, imidazole, thiazole, oxazole, pyrazine and pyrimidine, and preferable one is pyridine.

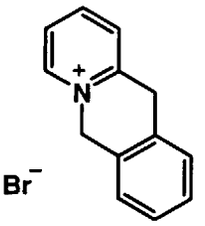
[0048] In the formula (Pa), (Pb), Bp represents divalent linking group. As the divalent linking group is cited alkylene, arylene, alkenylene, $-SO_2-$, -SO-, -O-, -S-, -CO-, and $-N(R_6)-$(R_6 represent an alkyl group, an aryl group and a hydrogen atom), and these divalent linking group can be used singly or in combination of these groups arbitrarily selected. Preferable Bp are alkylene, alkenylene and alkyleneoxy. m is 0 or 1.

[0049] In the formula (Pa), (Pc), R_1, R_2 and R_5 each represents a saturated or an unsaturated alkyl group or aryl group having 1 to 20 carbon atoms, and these groups may be substituted by the same substituents as cited for A_1, A_2, A_3, A_4 or A_5.

[0050] Preferable examples for R_1, R_2 and R_5 are the alkyl group having 4 to 10 carbon atoms or the substituted or unsubstituted aryl group, and more preferable ones are the substituted or unsubstituted phenyl group, the unsaturated alkyl group or the alkyl group substituted by phenyl group.

[0051] In the formula [Pa], [Pb] or [Pc], X_p^- represents a counter ion necessary to neutralize whole electric charge of the molecules, for example, chloride ion, bromide ion, iodide ion, nitric ion, sulfuric ion, p-toluenesulfonate and oxalate, n_p represents number of counter ion necessary to neutralize whole electric charge of the molecules. In the case of internal salt, n_p is 0. The exemplified compounds are shown below.

P—1



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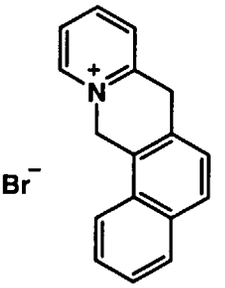

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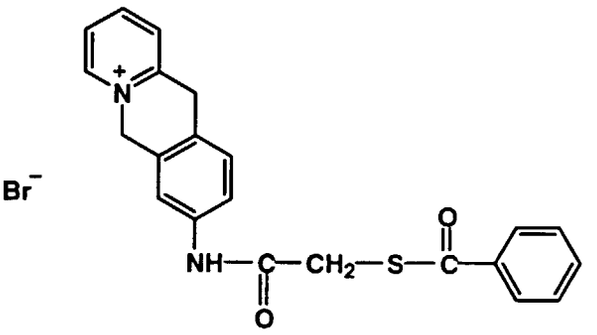

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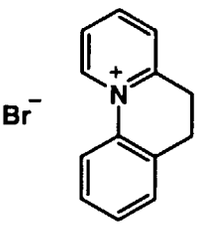

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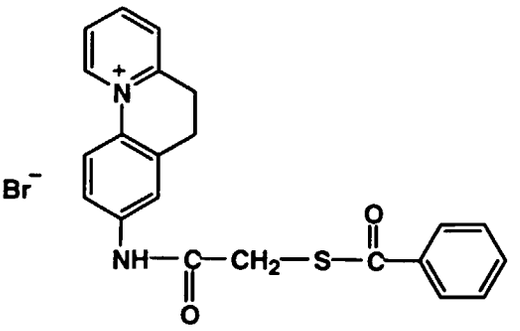

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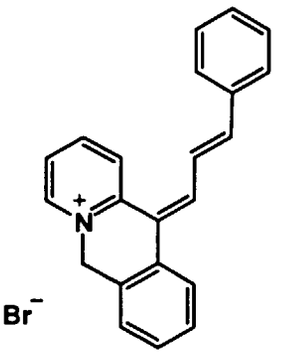

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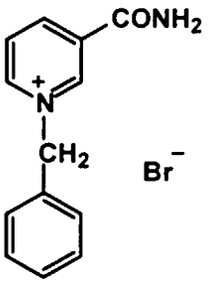

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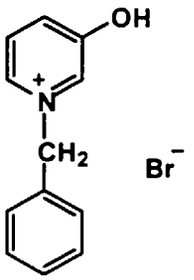

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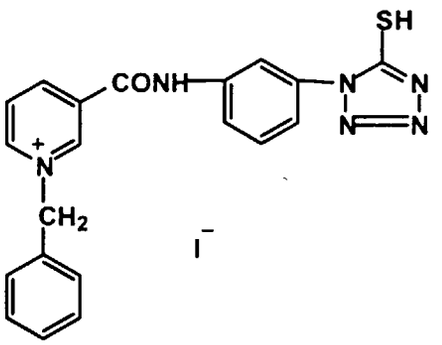

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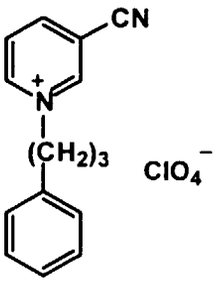

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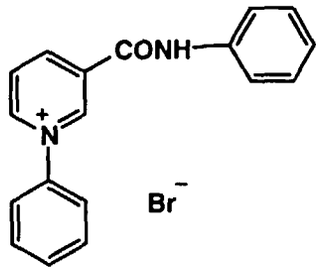

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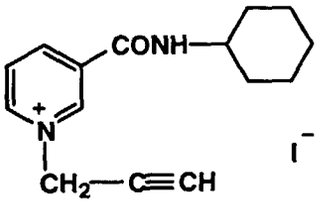

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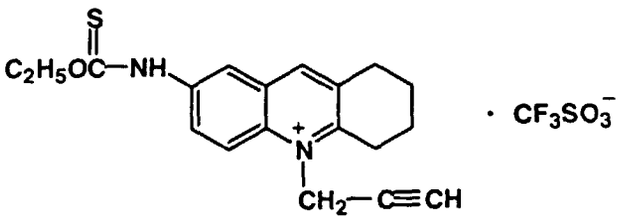

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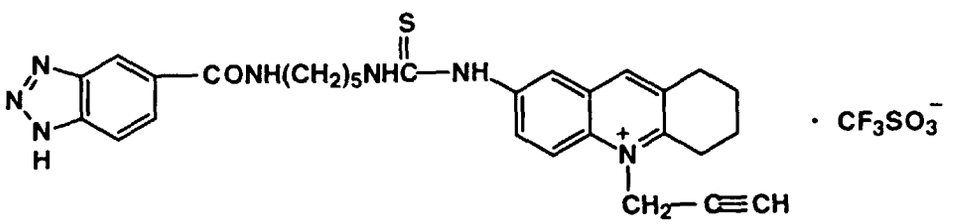

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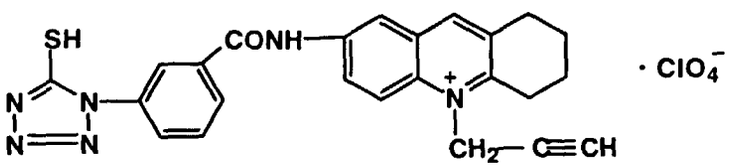

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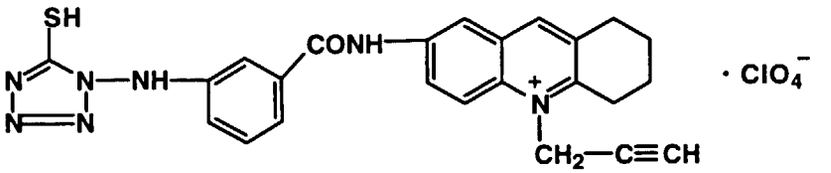

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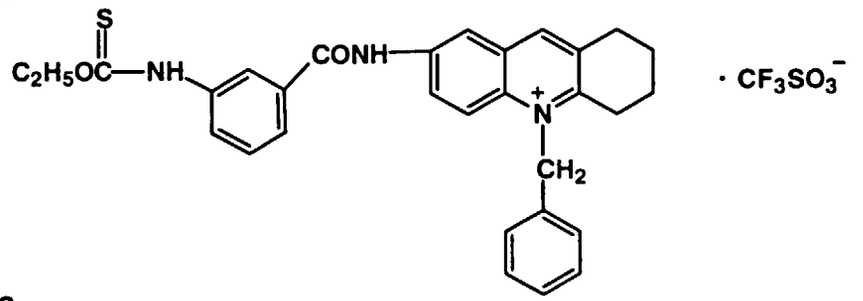

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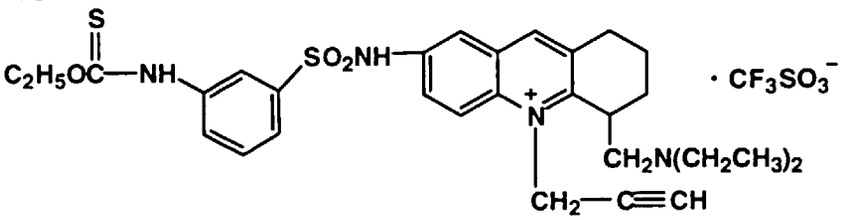

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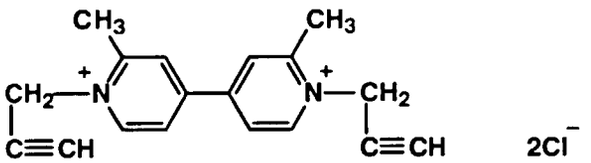

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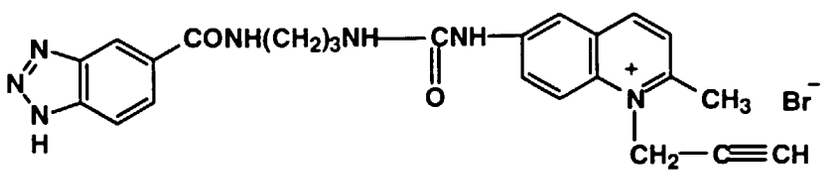

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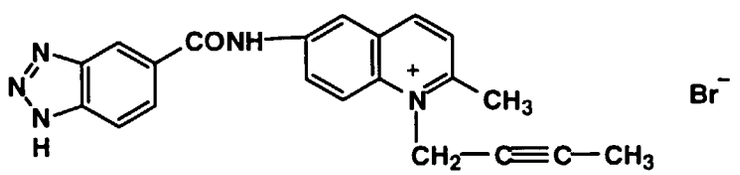

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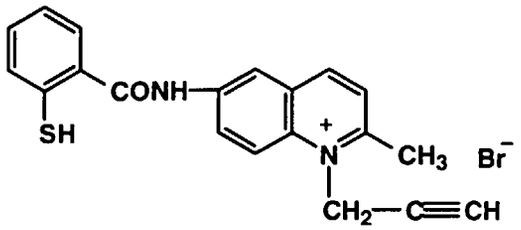

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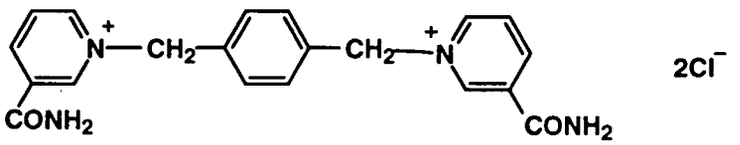

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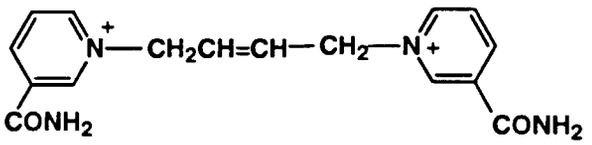

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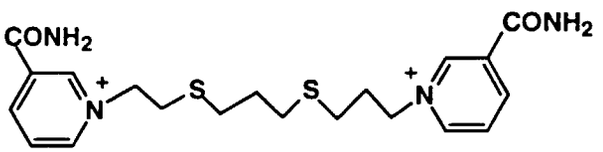

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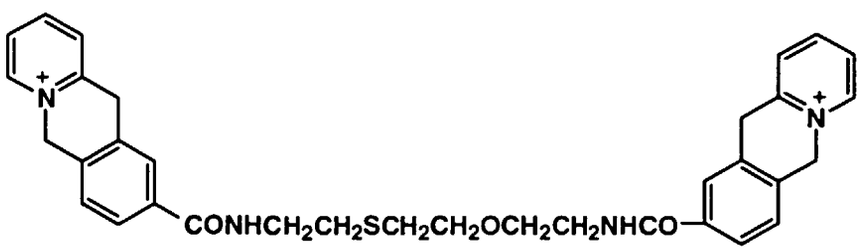

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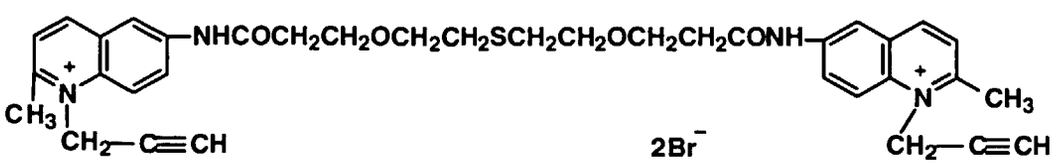

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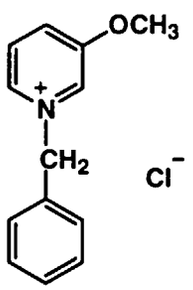

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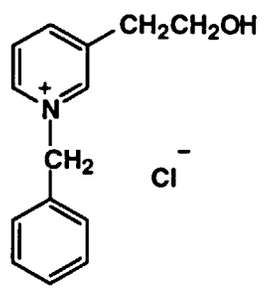

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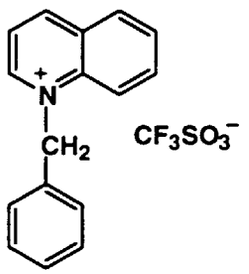

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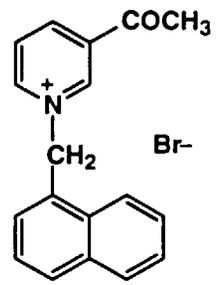

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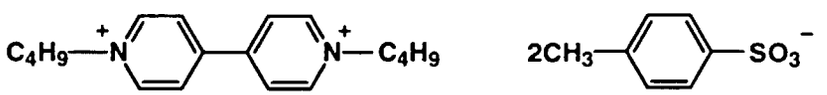

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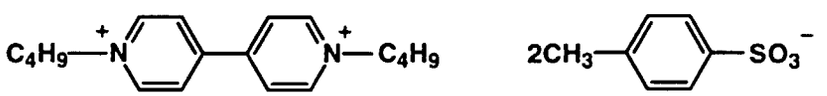

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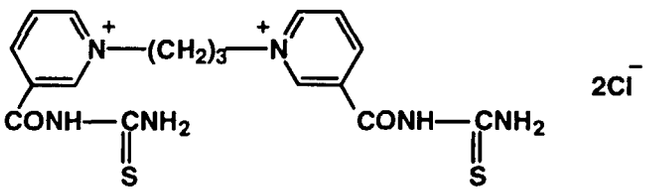

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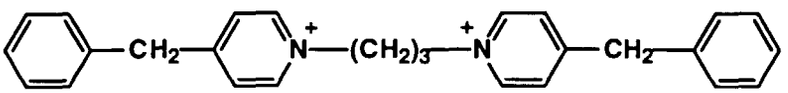

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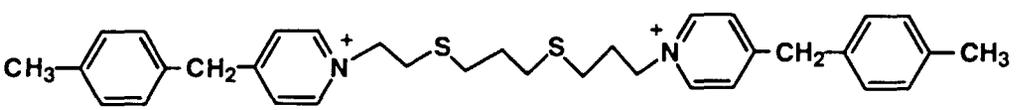

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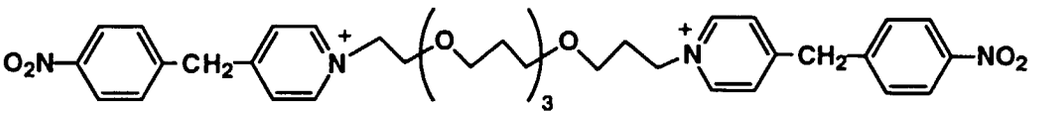

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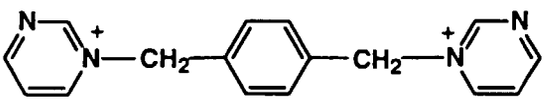

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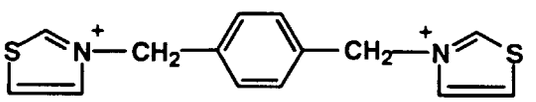

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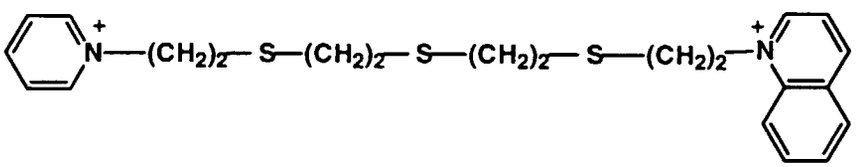


[0052] With respect to more preferable embodiment of the invention, a quaternary compound represented by the formula [I] described in U.S. Patent No. 3,719,494, the compound represented by the formula [I] described in U.S. Patent No. 4,115,122, a quaternary compound described in U.S. Patent No. 4,877,723, the compound represented by the formula [I] described in JP-A No. 4-437, the compound represented by the formula [I], [II] and [III] described in JP-A No. 8-220706, and nicotinamide derivative described in JP-A No. 7-92598, are preferably used.

[0053] Added amount of the compound represented by the formula (Pa), (Pb) or (Pc) is 1×10^{-6} mol to 1×10^{-1} mol per a mol silver, preferably 1×10^{-5} mol to 5×10^{-2} mol.

[0054] The compound represented by the formulae (Pa), (Pb) or (Pc) according to the invention can be used by dissolving them in an appropriate solvent, for example, alcohol (methyl alcohol, ethyl alcohol, propyl alcohol, alcohol containing fluorine atom in it's molecule), ketone (acetone, methylethylketone), dimethylformamide, dimethyl sulfoxide and methyl cellosolve. The compound represented by the formulae (Pa), (Pb) or (Pc) can be used by known emulsification dispersion method, in which these compounds are dissolved in oil such as dibutylphthalate, tricresylphosphate, glyceryltriacetate or diethylphthalate together with auxiliary solvent such as ethylacetate and cyclohexanone, thereafter the

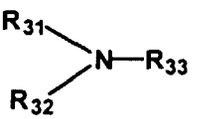
mixture is mechanically dispersed to obtain the emulsified dispersion. The compound represented by the formulae (Pa), (Pb) or (Pc) can be also used by known solid dispersion method, in which powder of these compounds are dispersed by ball mill, colloid mill or ultrasonic homogenizer.

[0055] To the light-sensitive material according to the invention is preferably added nucleation accelerating agent such as hydrazine derivative, amine derivative, onium derivative, disulfido derivative and hydroxyl amine derivative in combination with the compound represented by the formula (Pa), (Pb) or (Pc). As examples of nucleation accelerating agents, the exemplified compounds (2-1) - (2-20) and (3-1) - (3-6) described in JP-A No. 8-314066 and JP-A No. 6-258751, the compound represented by the formula I described in JP-A No. 7-104420, the compound described in JP-A No. 2-103536, page 17 - 18, and thiosulfonic acid described in JP-A No. 1-237538, are preferably used. More preferable one is the compound described in JP-A No. 8-314066.

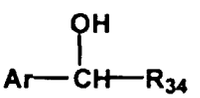
[0056] For the purpose of accelerating the high contrast by means of hydrazine compound or 5,6 membered nitrogen containing heterocyclic derivative effectively, it is preferable to use a nucleation accelerating agent.

[0057] The nucleation accelerating agent represented by the following formula (Na) or (Nb) is preferably used.

Formula (Na)



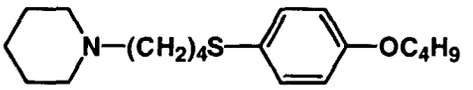
Formula (Nb)



[0058] In the formula (Na), R_{31}, R_{32} and R_{33} represent a hydrogen atom, an alkyl group, a substituted alkyl group, an alkenyl group, a substituted alkenyl group, an alkinyl group, an aryl group and a substituted aryl group, R_{31}, R_{32} and R_{33} may form a ring. Especially preferable one is an aliphatic tertiary amine compound. The compound having a nondiffusing group or an adsorption group onto silver halide in a molecule are preferable. In order to have a nondiffusing property, a compound having molecular weight of not less than 100 is preferable, and one having molecular weight of not less than 300 is more preferable. As a preferable adsorption-promoting group, there are given a heterocyclic ring, a mercapto group, a thioether group, a thion group and a thiourea group. An especially preferable one as the formula (Na) is a compound having at least one thioether group in a molecule as a adsorption-promoting group onto silver halide.

[0059] Exemplary examples of these nucleation accelerating agent (Na) will be given as follows.

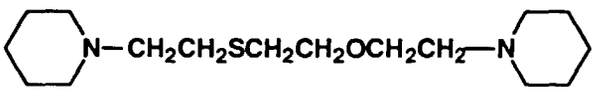
Na—1



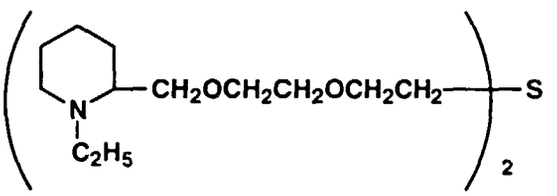
Na—2

$$[\,(C_3H_7)_2N(CH_2)_3OCH_2CH_2\,]_2S$$

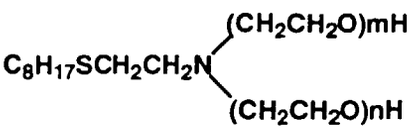
Na—3



Na—4

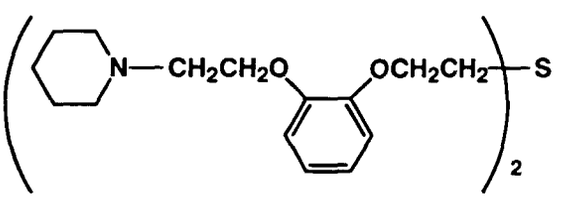


Na—5

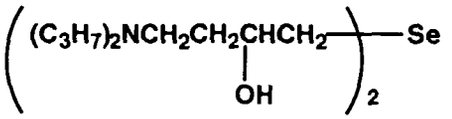


m+n=20

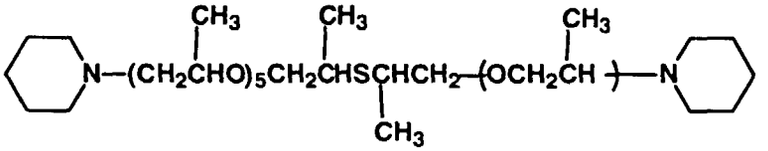
Na—6



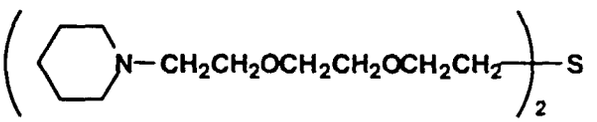
Na—7



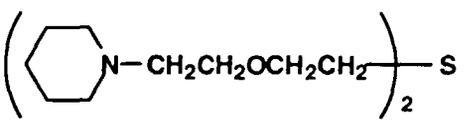
Na—8



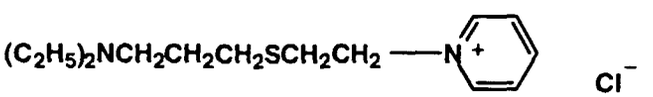
Na—9



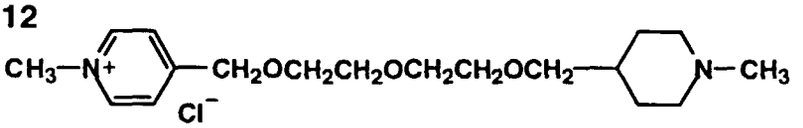
Na—10



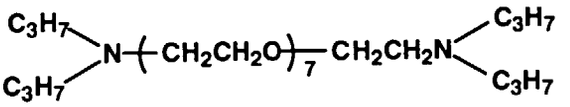
Na—11



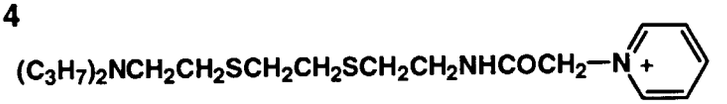
Na—12



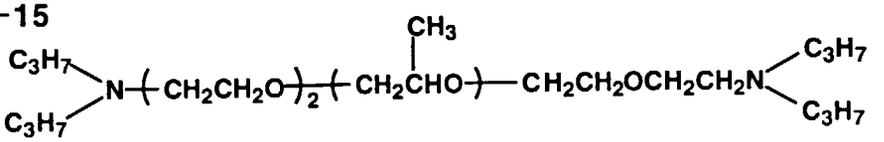
Na—13



Na—14

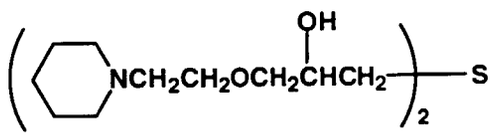


Na—15

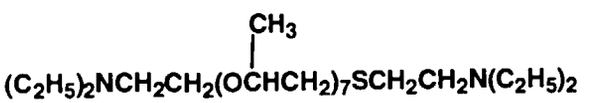


Na—16

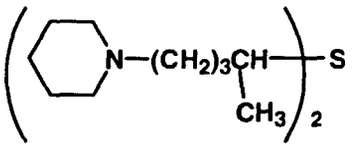
Na—17



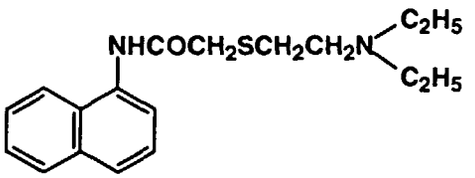
Na—18



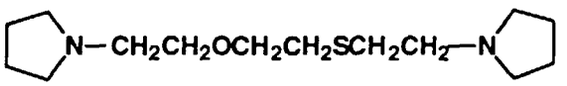
Na—19



Na—20



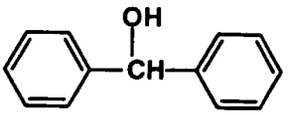
Na—21



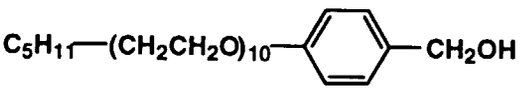
[0060] In the formula (Nb), Ar represents a substituted or unsubstituted aromatic group or heterocyclic group. R_{34} represents a hydrogen atom, an alkyl group, an alkinyl group or an aryl group, and Ar and R_{34} may be coupled with a coupling group to form a ring. These compounds are preferable when they contain a nondiffusing group or a silver halide adsorption group in a molecule. A preferable molecular weight to cause a preferable nondiffusing property to be contained is 120 or more, and 300 or more is especially preferable. As a silver halide adsorption group is cited similar silver halide adsorption group cited for the compound represented by the formula (H).

[0061] Exemplary compounds represented by Formula [Nb] are shown below.

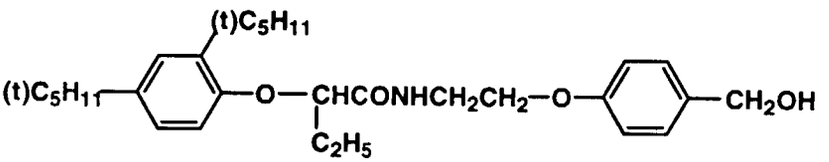
Nb—1



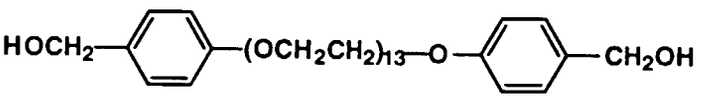
Nb—2



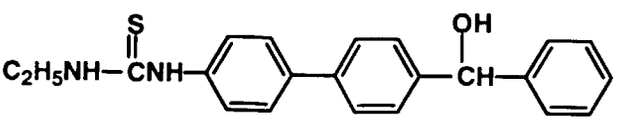
Nb—3



Nb—4



Nb—5



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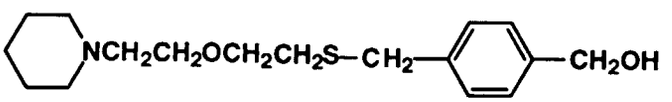

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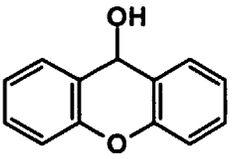

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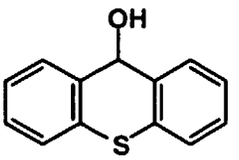

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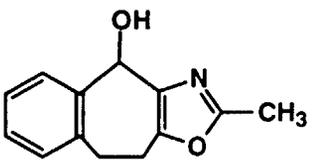

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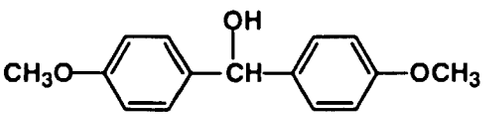

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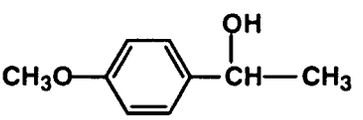

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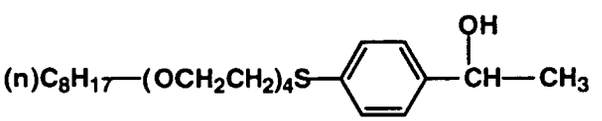


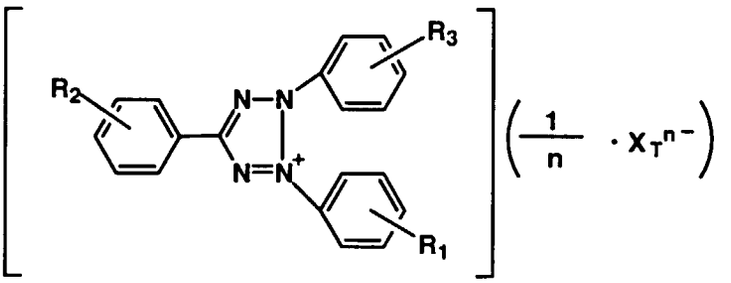
[0062] Exemplary examples of other preferable nucleation accelerating compound are those of (2-1) - (2-20) described in JP-A No. 6-258751, and those of (3-1) - (3-6) described in JP-A No. 6-258751, the onium salt compound described in JP-A No. 7-270957, the compound represented by the formula I described in 7-104420, the compound described in JP-A No. 2-103536, page 17 - 18, and thiosulfonic acid described in JP-A No. 1-237538, are preferably used.

[0063] A nucleation accelerating agent used in the invention can be used for any layer provided that the layer is a photographic component layer provided on the silver halide emulsion layer side, and it is preferable to use it for a silver halide emulsion layer or for a layer adjoining the silver halide emulsion layer. With regard to an added amount, though an optimum amount varies depending on a grain size of a silver halide grain, halogen composition, a degree of chemical

sensitization and a kind of an inhibiting agent, an amount ranging from 10^{-6} to 10^{-1} mol per mol of silver halide is generally preferable, and a range of 10^{-5} to 10^{-2} mol is especially preferable.

[0064] It is preferable to use a tetrazolium compound as an organic high contrast accelerating agent, as a tetrazolium compound the compound represented by the following general formula (T) is preferable.

Formula (T)



[0065] Each of R_1, R_2 and R_3 substituted on the phenyl groups of the compound represented by the general formula (T) preferably represents a hydrogen atom or a group, of which Hammett's σ-value showing degree of electron withdrawal is in the negative.

[0066] The σ values of the phenyl substituents are disclosed in lots of reference books. For example, a report by C.Hansch in "The Journal of Medical Chemistry", vol.20, on page 304(1977), etc. can be mentioned. Groups showing particularly preferable negative σ-values include, for example, methyl group (σ_p=-0.17, and in the following, values in the parentheses are in terms of σ_p value), ethyl group (-0.15), cyclopropyl group (-0.21), n-propyl group (-0.13), iso-propyl group (-0.15), cyclobutyl group (-0.15), n-butyl group (-0.16), iso-butyl group (-0.20), n-pentyl group (-0.15), cyclohexyl group (-0.22), amino group (-0.66), acetylamino group (-0.15), hydroxyl group (-0.37), methoxy group (-0.27), ethoxy group (-0.24), propoxy group (-0.25), butoxy group (-0.32), pentoxy group (-0.34), etc. can be mentioned. All of these groups are useful as the substituent for the compound represented by the general formula (T) according to the present invention.

[0067] n represents 1 or 2, and as anions represented by X^{n-}_T for example, halide ions such as chloride ion, bromide ion, iodide ion, etc.; acid radicals of inorganic acids such as nitric acid, sulfric acid, perchloric acid, etc.; acid radicals of organic acids such as sulfonic acid, carboxylic acid, etc.; anionic surface active agents, specifically including lower alkyl benzenesulfonic acid anions such as p-toluenesulfonic anion, etc.; higher alkylbenzene sulfonic acid anions such as p-dodecyl benzenesulfonic acid anion, etc.; higher alkyl sulfate anions such as lauryl sulfate anion, etc.; boric acid-type anions such as tetraphenyl borone, etc.; dialkylsulfo succinate anions such as di-2-ethylhexylsulfo succinate anion, etc.; polyetheralcoholsurfuric acid ester anion such as cetyl polyethenoxy sulfate anion, etc.; higher aliphatic acid anions such as stearic acid anion, etc.; and those in which an anionic radical is attached to a polymer, such as polyacrylic acid anion, etc. can be mentioned.

[0068] specific exemplified compounds represented by the general formula T are given. However, the scope of the present invention is not limited by these tetrazolium compounds.

Compound No.	R_1	R_2	R_3	X^{n-}_T
T-1	H	H	p-CH_3	Cl^-
T-2	p-CH_3	H	p-CH_3	Cl^-
T-3	p-CH_3	p-CH_3	p-CH_3	Cl^-
T-4	H	p-CH_3	p-CH_3	Cl^-
T-5	p-OCH_3	p-CH_3	p-CH_3	Cl^-
T-6	p-OCH_3	H	p-CH_3	Cl^-

(continued)

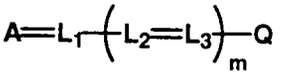
Compound No.	R_1	R_2	R_3	X_T^{n-}
T-7	p-OCH_3	H	p-OCH_3	Cl^-
T-8	m-C_2H_5	H	m-C_2H_5	Cl^-
T-9	p-C_2H_5	p-C_2H_5	p-C_2H_5	Cl^-
T-10	p-C_3H_7	H	p-C_3H_7	Cl^-
T-11	p-isoC_3H_7	H	p-isoC_3H_7	Cl^-
T-12	p-OC_2H_5	H	p-OC_2H_5	Cl^-
T-13	p-OCH_3	H	p-isoC_5H_7	Cl^-
T-14	H	H	p-n$C_{12}H_{25}$	Cl^-
T-15	p-n$C_{12}H_{25}$	H	p-n$C_{12}H_{25}$	Cl^-
T-16	H	p-NH_2	H	Cl^-
T-17	p-NH_2	H	H	Cl^-
T-18	p-CH_3	H	p-CH_3	ClO_4^-

[0069] The above-mentioned tetrazolium compounds can be synthesized according to the method described on pages 335 through 483, vol. 55 of The Chemical Review.

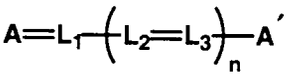
[0070] The tetrazolium compound represented by the formula (T) may be used singly or in combination of not less than two kinds of them in any ratio.

[0071] Next, dye stuffs in the form of a solid dispersion represented by the following general formulae (1) -(6) will be explained.

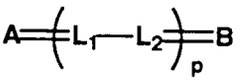
Formula (1)



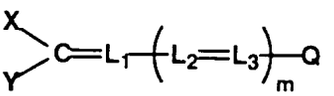
Formula (2)



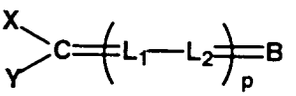
Formula (3)



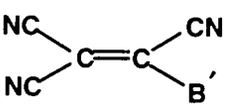
Formula (4)



Formula (5)



Formula (6)



[0072] In the formulae (1) - (6), A and A' may be either the same with or different from each other, and each of them represents an acidic nucleus, B represents a basic nucleus, Q represents a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, B' represents a substituted or unsubstituted heterocyclic group, X and Y may be either the same with or different from each other and each of them represents an electron withdrawing group, and each of L_1, L_2 and L_3 represents a substituted or unsubstituted methine group. The symbol m represents 0 or 1, n represents 0, 1 or 2, p represents 0 or 1. However, each of dyes represented by the formulae (1) - (6) preferably contains in a molecule at least one group selected from the group of a carboxy group, a sulfonamide group and a sulfamoyl group.

[0073] Acidic nuclei represented by A and A' in the formulae (1), (2) and (3) preferably include 5-pyrazolone, barbituric acid, thiobarbituric acid, rhodanine, hydantoin, thiohydantoin, oxazolone, isooxazolone, indanedione, pyrazolidinedione, oxazolidinedione, hydroxypyridone and pyrazolopyridone.

[0074] Basic nucleuses represented by B in Formulas (3) and (5) preferably include pyridine, quinolin, oxazole, ben-

zoxazole, naphthoxazole, thiazole, benzthiazole, naphthothiazole, indolenin, pyrole and indole.

[0075] As an aryl group represented by Q in the above-mentioned formulae (1) - (4), there may be given a phenyl group and a naphthyl group or the like, for example. As a heterocyclic group represented by Q, there may be given pyridine, quinoline, isoquinoline, pyrole, pyrazole, imidazole, indole, furyl and thienyl residues. Aforesaid aryl group and heterocyclic group include those having substituents which are represented by, for example, an alkyl group, a cycloalkyl group, an aryl group, a halogen atom, an alkoxycarbonyl group, an aryloxycarbonyl group, a carboxy group, a cyano group, a hydroxy group, a mercapto group, an amino group, an alkoxy group, an aryloxy group, an acyl group, a carbamoyl group, an acylamino group, an ureido group, a sulfamoyl group and a sulfonamide group, and two or more kinds of these substituents may be combined. Preferable one include an alkyl group having 1-6 carbon atoms (e.g., a methyl group, an ethyl group, a butyl group, a 2-hydroxyethyl group, etc.), a hydroxyl group, a halogen atom (e.g., a fluorine atom, a chlorine atom, etc.), an alkoxy group (e.g., a methoxy group, an ethoxy group, a methylenedioxy group, a 2-hydroxyethoxy group, an n-buthoxy group, etc.), a substituted amino group (e.g., a dimethylamino group, a diethylamino group, a di(n-butyl)amino group, an N-ethyl-N-hydroxyethylamino group, an N-ethyl-N-methanesulfonamido-ethylamino group, a morpholino group, a piperidino group, pyrolidino group, etc.), a carboxy group, a sulfonamido group (e.g., a methanesulfonamido group, a benzenesulfonamido group, etc.), a sulfamoyl group (e.g., a sulfamoyl group, a methylsulfamoyl group, a phenylsulfamoyl group, etc.), and these substituents may be combined.

[0076] Electron withdrawing groups represented by X and Y in the formulae (4) and (5) may be either the same with or different from each other. For example, the preferable groups include a cyano group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, a carboxy group, an acyl group, an alkylsulfonyl group, an arylsulfonyl group, and a sulfamoyl group.

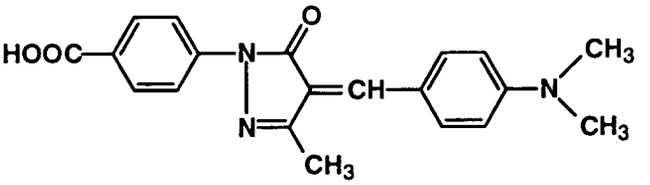
[0077] Heterocyclic rings represented by B' in the formula (6) include, for example, pyridine, pyridazine, quinolin, pyrole, pyrazole, imidazole and indole.

[0078] Methine groups represented by L_1, L_2 and L_3 in Formulas (1) - (5) include those having a substituent, and the substituent includes, for example, an alkyl group having 1-6 carbon atoms (e.g., methyl, ethyl, propyl, isobutyl, etc.), an aryl group (e.g., phenyl, p-tolyl, p-chlorophenyl, etc.), an alkoxy group having 1-4 carbon atoms (e.g., a methoxy group, an ethoxy group, etc.), an aryloxy group (e.g., a phenyl group, etc.), an aralkyl group (e.g., a benzyl group, a phenethyl group, etc.), a heterocyclic group (e.g., pyridyl, furyl, thienyl, etc.), a substituted amino group (e.g., dimethylamino, tetramethylene-amino, anilino, etc.), and an alkylthio group (e.g., a metylthio group, etc.).

[0079] In the invention, among the dyes represented by the formulas (1) - (6), those having at least one carboxyl group in a molecule are preferably used, and dyes represented by the formula (1) are more preferable, in which the dyes represented by the formula (1) wherein Q is a furyl group are especially preferable.

[0080] Exemplary examples of dyes used in the invention will be shown below, but is not limited thereto.

1-1



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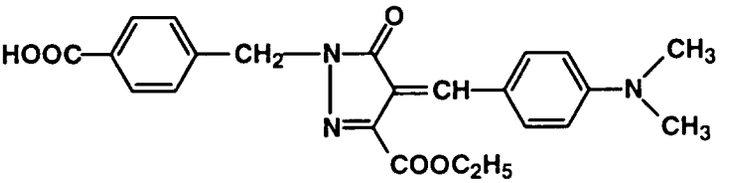

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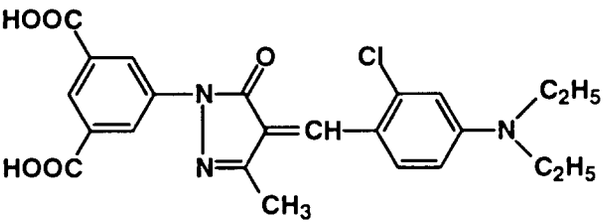

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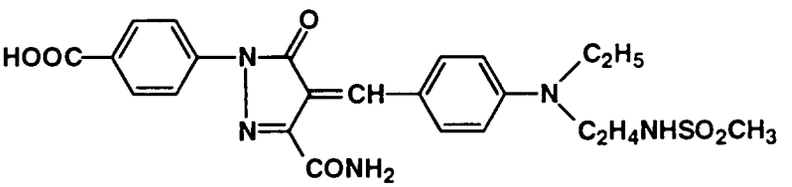

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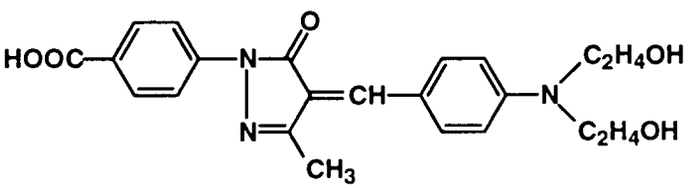

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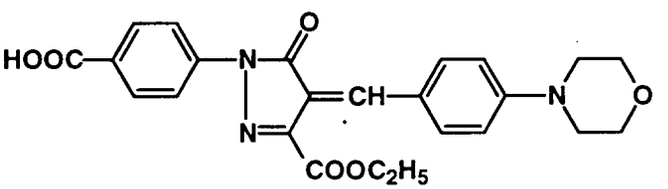

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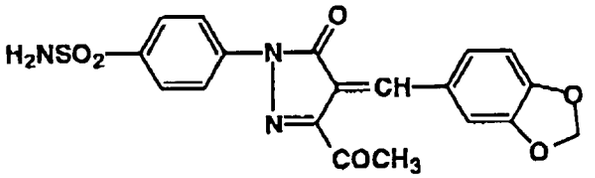

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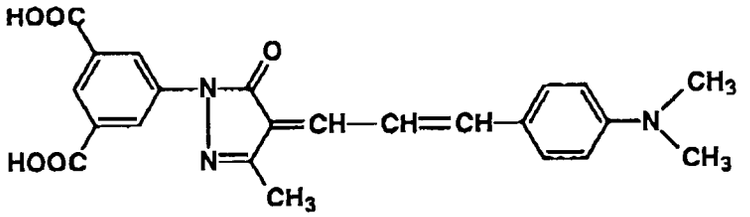

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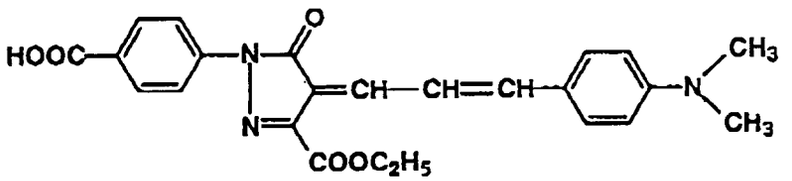

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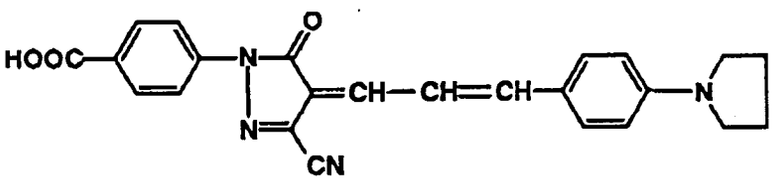

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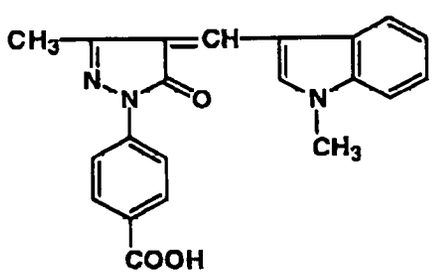

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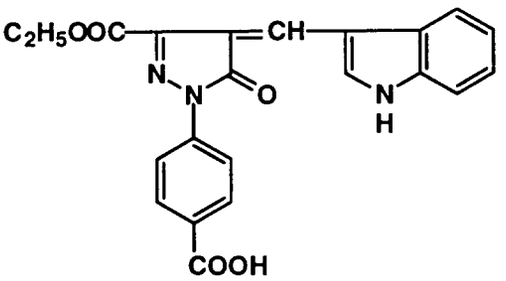

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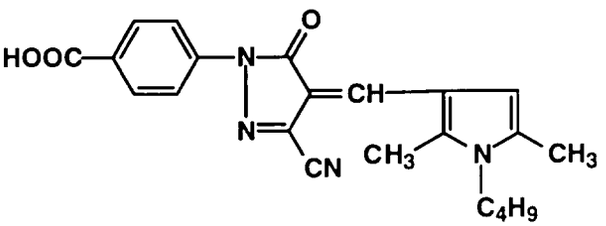

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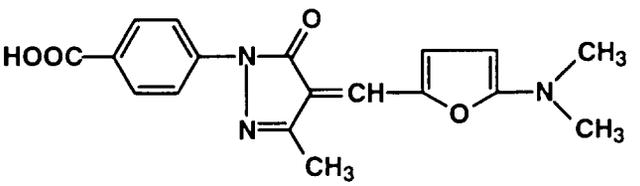

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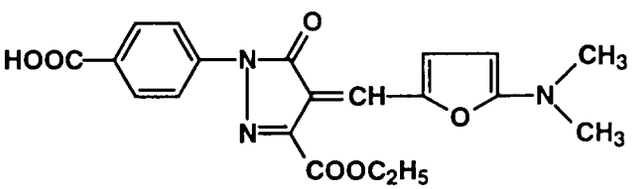

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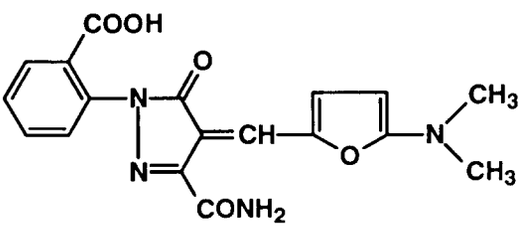

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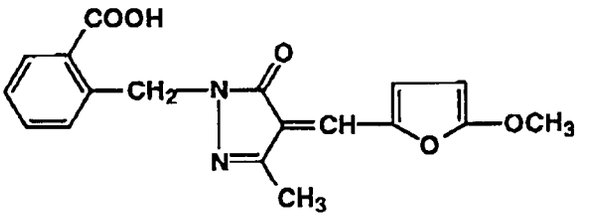

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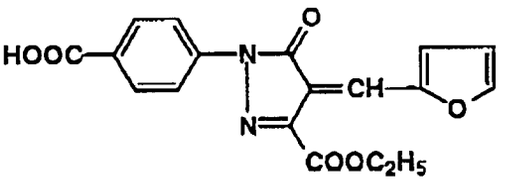

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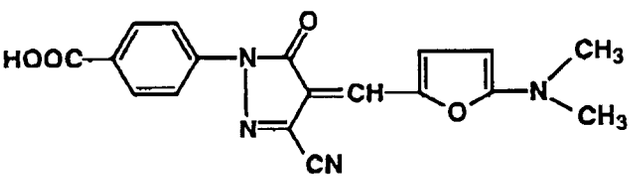

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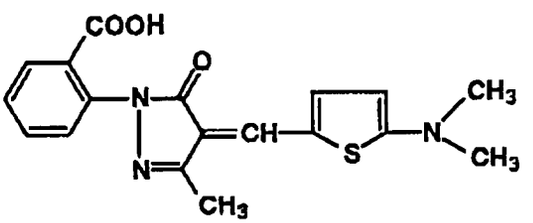

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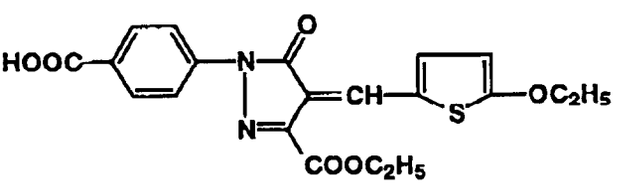

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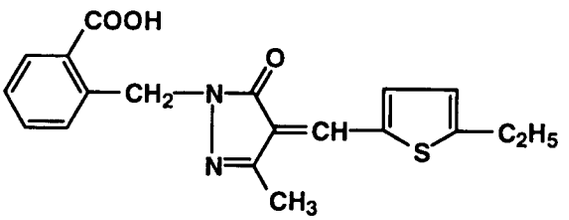

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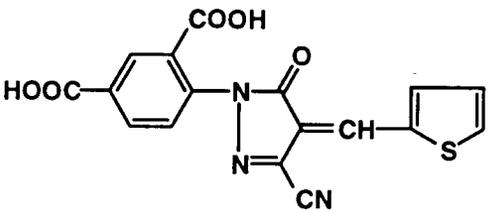

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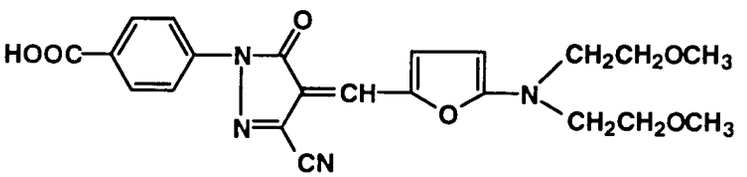

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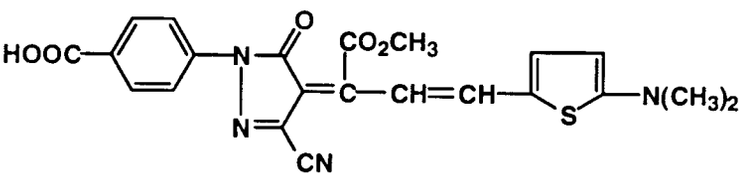

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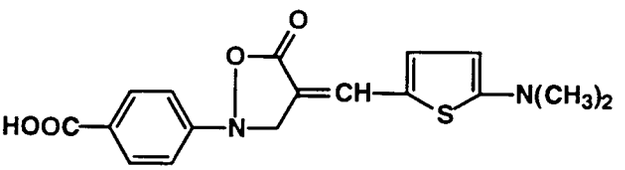

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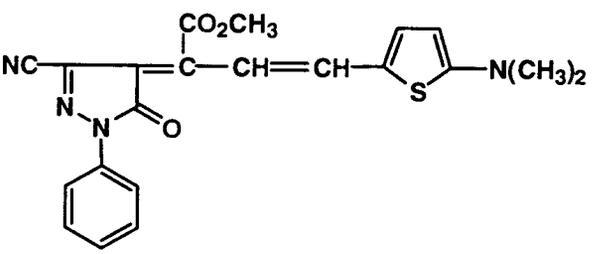

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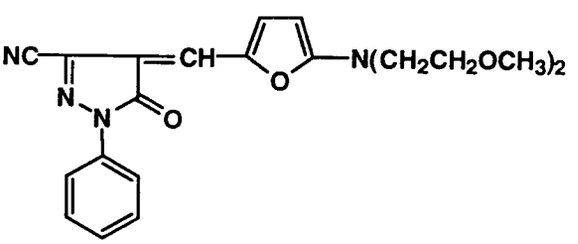

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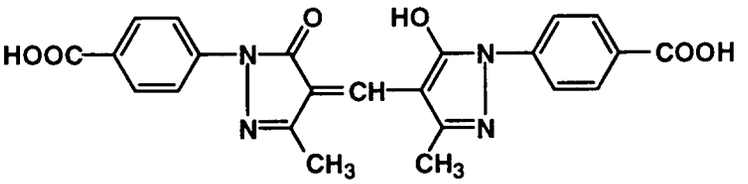

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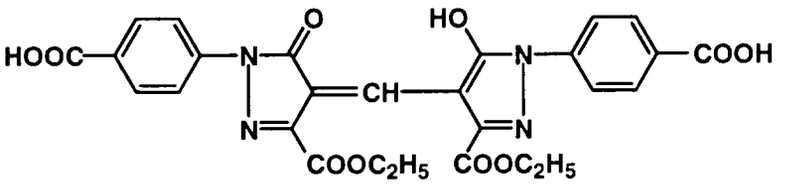

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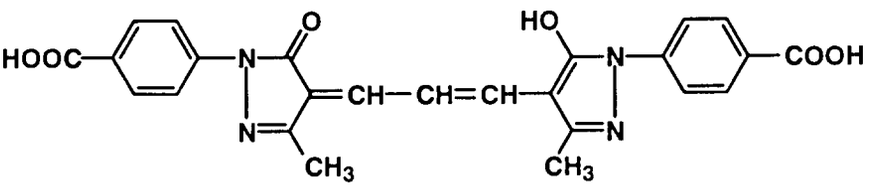

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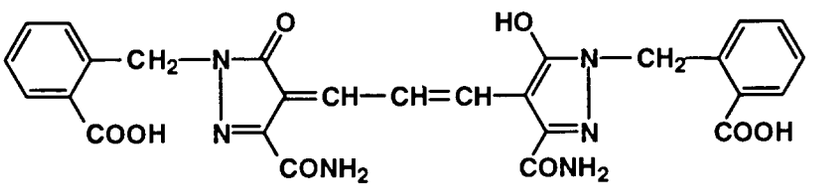

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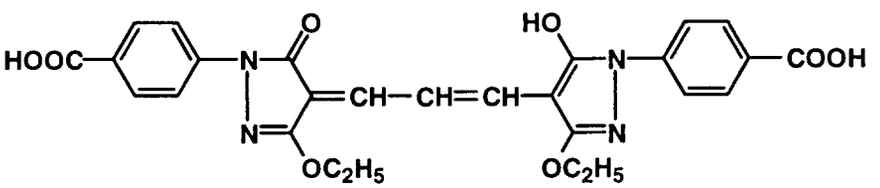

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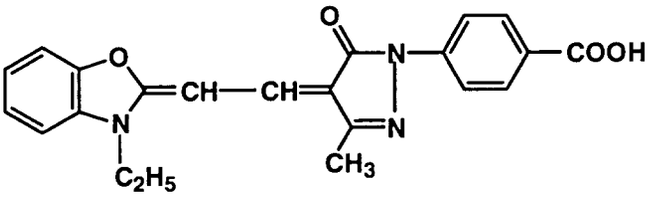

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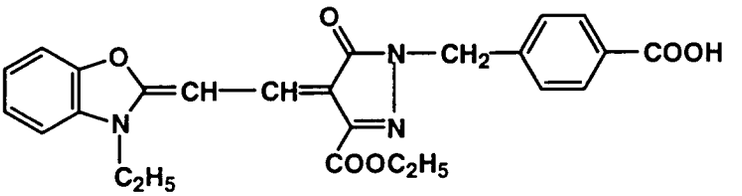

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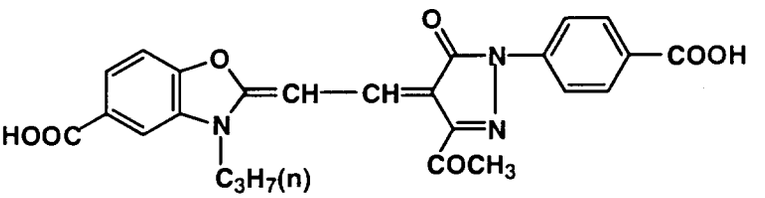

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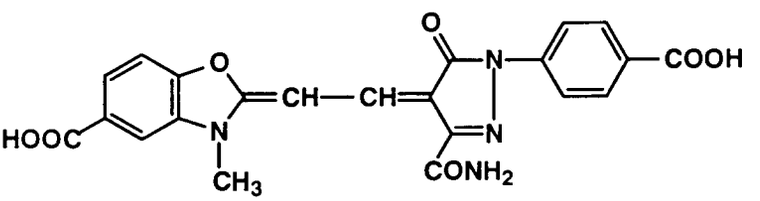

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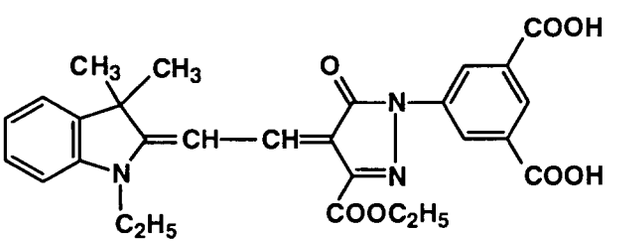

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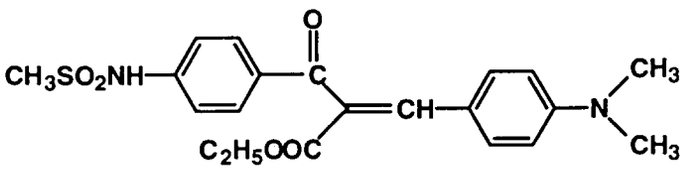

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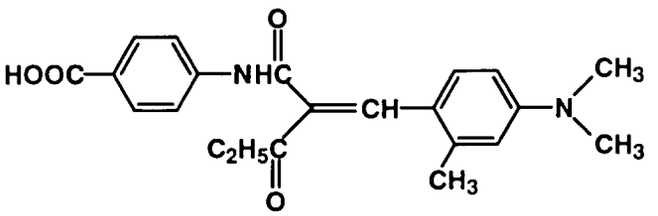

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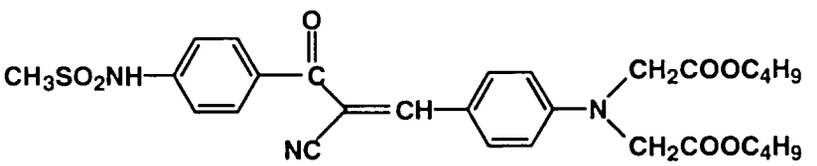

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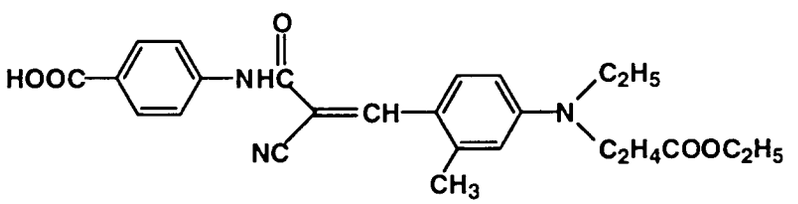

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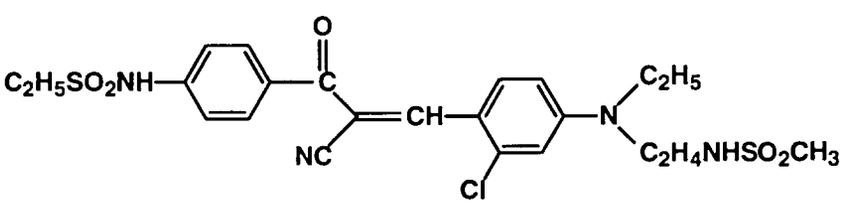

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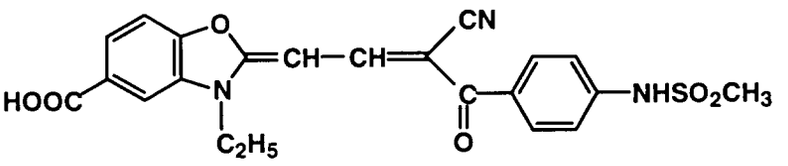

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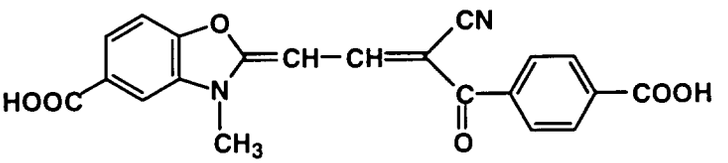

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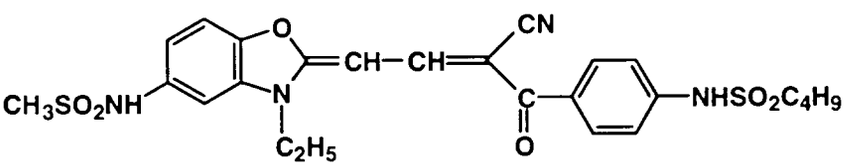

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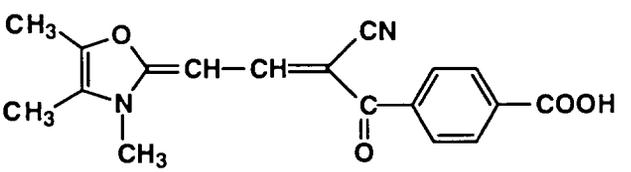

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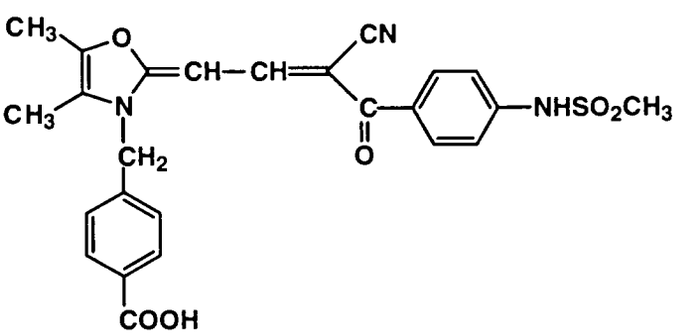

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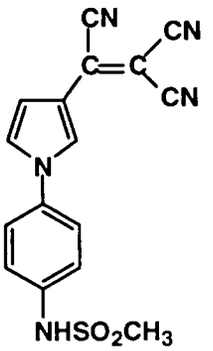

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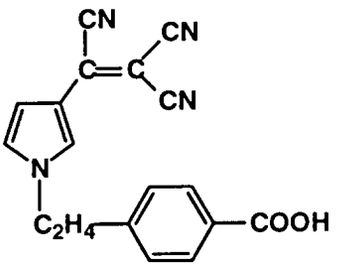

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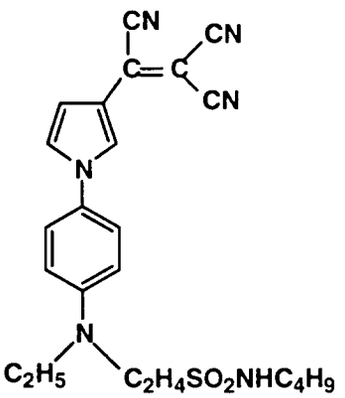

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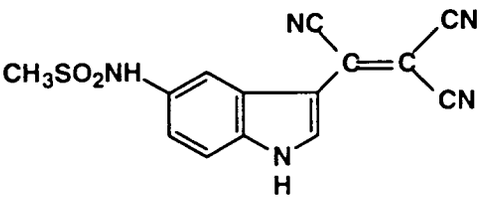

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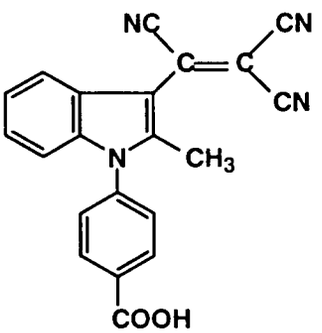


[0081] Other preferable examples of the compounds represented by Formulas (1) - (6) are, for example, described in JP-A No. 7-128793 page 6 - 18, as the compounds which are more concrete, there are given No. I-1 - No. I-30, II-1 - II-12, III-1 - III-8, IV-1 - IV-9, V-1 - V-8, and VI-1 - VI-5.

[0082] As a method for manufacturing solid fine particle dispersion of a dye related to the invention, it is possible to use the methods described in JP-A Nos. 52-92716, 55-155350, 55-155351, 63-197943 and 3-182743 and International

Patent WO88/04794. Concretely, it is possible to manufacture by the use of a fine dispersing machine such as a ball mill, a planetary mill, a vibration mill, a sand mill, a roller mill, a jet mill and a disc-impeller mill. When a compound to be subjected to solid fine particle dispersion is water-insoluble at a relatively low pH and is water-soluble at a relatively high pH, it is possible to obtain the dispersion of the compound through the method wherein the compound is dissolved in an alkaline aqueous solution, then pH is lowered to make the solution to be weakly acidic, and thereby solid fine particles are precipitated, or the method wherein a weakly alkaline solution of the compound and an acidic aqueous solution are mixed simultaneously while adjusting pH and thereby solid fine particles are prepared. Solid fine particle dispersion of the invention can be used either singly or in combination of two kinds or more, and they can further be used together with solid fine particle dispersion other than that of the invention. When using in combination of two kinds or more, they can be mixed after being dispersed independently, or they may be dispersed simultaneously.

[0083] When manufacturing solid fine particle dispersion used in the invention in the presence of aqueous dispersion medium, it is preferable to made a surfactant present in the course of dispersion or after the dispersion. Such surfactant to be used includes an anionic surfactant, a nonionic surfactant, a cationic surfactant and an amphoteric surfactant, and preferable ones are anionic surfactants such as, for example, alkyl sulfonate, alkylbenzenesulfonate, alkylnaphthalenesulfonate, alkyl sulfonates, sulfosuccinate, sulfoalkylpolyoxyethylenealkylphenyl ethers, and N-acyl-N-alkyltaurine, and nonionic surfactant such as, for example, saponin, alkylene oxide derivative and alkylester of sugar. Aforesaid anionic surfactants are especially preferable. Exemplary examples of the surfactant are represented, for example, by 1 - 32 compounds described on pages 26 - 32 of JP-A No. 7-128793 to which the invention is not limited.

[0084] An amount of anionic surfactants and/or nonionic surfactants varies depending on a kind of surfactant or on dispersion conditions of aforesaid dyes, but 0.1 mg - 2000 mg per 1 g of dye is normally preferable, 0.5 mg - 1000 mg is more preferable, and 1 mg - 500 mg is especially preferable.

[0085] As concentration used in a dye dispersion, it is preferable to be used so that 0.01 - 50% by weight may be attained, and 0.1 - 30% by weight is more preferable. With regard to timing for adding surfactants, it is good to add them before the start of dispersion of dyes, and they can also be added to a dye-dispersed solution after completion of dispersion of the dyes, when it is necessary. These anionic surfactants and/or nonionic surfactants can be used either independently or in combination of two or more kinds, and further, both surfactants may be combined.

[0086] It is possible to add hydrophilic colloid used as a binder for a photographic component layer to solid fine particle dispersed products used in the invention, before the start of dispersion or after completion of dispersion. As the hydrophilic colloid, it is advantageous to use gelatin. In addition to this, however, it is possible to use gelatin derivatives such as phenylcarbamated gelatin, acylated gelatin or phthalated gelatin, cellulose derivatives such as graft polymer with monomer having an ethylene group capable of being polymerized with gelatin, carboxymethylcellulose, hydroxymethylcellulose and cellulose sulfate, synthesized hydrophilic polymer such as polyvinyl alcohol, partially oxidized polyvinyl acetate, polyacrylicamide, poly-N,N-dimethylacrylicamide, poly-N-vinylpyrrolidone and polymethacrylic acid, agar, acacia, alginic acid, albumin and casein. These can be used in combination of two or more kinds. As an amount of hydrophilic colloid added to solid fine particle dispersed products, it is preferable to add so that a percentage by weight of 0.1% - 12% may be attained, and 0.5% - 8% is more preferable.

[0087] The average particle diameter of a dye in the form of a solid particle dispersion used in the invention is not more than 0.2 μm, especially preferably 0.05 - 0.15 μm. With regard to the distribution of the particle diameter, it is preferred that the particle diameter of not more than 0.3 μm occupies not less than 70% in the term of scattering strength distribution. A method for measuring the particle diameter and the particle diameter distribution of the dye in the form of the solid particle dispersion is carried out by using ELS-800 produced by Otsuka Denshi Co., Ltd.

[0088] With regard to an added amount of the dye in the form of the solid particle dispersion, though an optimum amount varies depending on an absorption coefficient of the dye in the form of the solid particle dispersion, an amount of not more than 200 mg/m^2 is preferred, and an amount ranging 5 to 50 mg/m^2 is especially preferable. A preferable density of the dye in the form of the solid particle dispersion is preferably associated with a preferable particle diameter range of the dye in the form of the solid particle dispersion.

[0089] An absorption optical density of the dye in the form of the solid particle dispersion is 0.05 to 1.0 at the maximum absorption wave length of the silver halide emulsion, preferably 0.1 to 1.0, especially preferably 0.3 to 1.0.

[0090] In the invention, as a hydrophilic colloid layer which is a layer of the dye in the form of the solid particle dispersion and located at the farther position than the silver halide emulsion layer on the silver halide emulsion layer side to a support, is used a hydrophilic colloid layer consisting of gelatin, polyacrylamide, and synthetic polymer such as hydrophilic high molecular compound and latex.

[0091] A solid fine particle dispersion product of the dye stuff used in the invention is preferably added in a layer locating between a support and an emulsion layer.

[0092] In cases where coating the processing solution, a maximum density of the dye in a hydrophilic layer coated on the support opposite to the emulsion layer is preferably not more than 0.5, more preferably not more than 0.1, and it is especially preferable that said hydrophilic layer does not substantially contain any dye.

[0093] Developing agent incorporated in the light-sensitive material is optionally selected from known ones. In this

invention, the developing agent includes a developing agent precursor which releases a developing agent during development.

[0094] As examples of the developing agents usable in the invention, are cited p-phenylenediamines, p-aminophenols, phosphoramidephenols and sulfonamideanilines described in U.S. Patent No. 3,351,286, 3,761,270, 3,764,328, 3,342,599, 3,719,492, Research Disclosure (hereinafter referred to as RD) 12146, 15108, 15127, and JP-A 56-27132, 53-135628, 57-79035, and hydrazones, phenols, sulfonamidephenols, polyhydroxybenzenes, naphthols, hydroxy bisnaphthyls, methylenebisphenols, ascorbic acid derivatives, 1-aryl-3-pyrazolidones and hydrazones, and precursors of these developing agents.

[0095] Number of carbon atom of the developing agent incorporated in the light-sensitive material of the invention is not more than 20, preferably not more than 15 so that an amount of developing agent is effectively added and it develops the light-sensitive material effectively.

[0096] These developing agents can be used in combination of two kinds or more, especially combined usage of 1-aryl-3-pyrazolidone derivatives and hydroquinone derivatives is preferable.

[0097] With regard to an incorporated amount of the developing agent in the light-sensitive material, the incorporate amount of the developing agent is an amount with which not less than 15% silver halide contributing to forming an image is developable, preferably not less than 50% silver halide is developable, especially preferably not less than 100%. The incorporated amount of the developing agent with which the silver halide is developable means that the developing agent theoretically reduces the silver halide with the incorporated amount of the developing agent.

[0098] These developing agents can be incorporated in the silver halide emulsion layer and other hydrophilic colloidal layers. These developing agents are preferably incorporated in the layers which are coated on the same side as the silver halide emulsion layer to the support, more preferably they are incorporated in the hydrophilic colloidal layers other than the silver halide emulsion layer. They can be incorporated in the optional layers between the support and the silver halide emulsion layer. In cases where the silver halide photographic light-sensitive material contains the developing agent, adding amount of the developing agent is preferably 0.3 to 5.0 g/m^2.

[0099] The developing agents according to the invention is preferably contained in the light-sensitive material in solid dispersion form from the viewpoint of the stability of the light-sensitive material. With respect to the dispersion methods, the following two methods are recommended, (i) a method that the developing agents is mixed with an aqueous solution which does not contain substantially an organic solvent such as ethylacetate, methyl alcohol and methylethylketone etc., but contains one or more kinds of stabilizer(s) or pulverizing agent(s), thereafter the organic solvent is removed by evaporation under a reduced pressure, (ii) a method that solid developing agent is crashed with an inorganic pulverizing medium repeatedly in an aqueous solution containing one or more kinds of stabilizer(s) or pulverizing agent(s). As a hard inorganic pulverizing medium, is cited bead such as sand, silica ball, stainless steel, silicon carbide, glass, zirconium, zirconium oxide, alumina and titanium. The bead size of these mediums is in the range of 0.25 to 3.0 mm. Additionally as a method to decrease the particle size, is cited ball mill, media mill, attriter mill, jet mill and vibration mill etc.

[0100] The average particle diameter of the dispersed product of developing agent obtained by the above mentioned methods is generally 0.05 to 1.5 μm, preferably 0.1 to 1.0 μm.

[0101] In the dispersion of the developing agent used in the invention, a stabilizer or an auxiliary dispersion agent is used. As the stabilizer or the auxiliary dispersion agent, is cited a surfactant or a hydrophilic colloid.

[0102] The light-sensitive material according to the invention comprises the light-sensitive silver halide. As the light-sensitive silver halide, known one is available, such as silver chloride, silver bromide, silver iodobromide and silver chloroiodobromide. It is preferable to use the light-sensitive material containing the silver halide containing 60 mol% or more silver chloride. Concretely, silver chlorobromide or silver chloroiodobromide containing 60 mol% or more silver chloride is preferably used. A silver halide grain may either be uniform in terms of halogen composition from its core to surface or be composed of plural layers, each being different in terms of halogen composition from its core to surface. Such silver grain forms a core/shell form or a grain of which halide composition is stepwise or continuously changed.

[0103] The average grain size of the silver halide is preferably 0.6 μm or less, and, more preferably 0.5 to 0.05 μm. The silver halide grain may be mono-dispersed grain of relatively uniform grain distribution or poly-dispersed grain of relatively wide grain distribution.

[0104] The term "grain size" usually refers to as average diameter of the grain, when the grain is of spherical shape or in the form close thereto. In the case when the grain is a cubic shape, it means as average diameter of a sphere when the cube is converted into a sphere having the equivalent volume. With regard to the method of obtaining the average diameter, one can refer to the disclosure on pages 36 - 43, third edition of "The theory of the photographic process" edited by C.E. Mees and T.H.James and published by Mcmillan Co. in 1966.

[0105] There is no limitation as to the shape of the silver halide grain, and any one of tabular, cubic, spheric, tetradeca hedral or octahedral shape can optionally be used. Concerning grain size distribution, the narrower, the more preferable. Particularly, so-called mono-dispersed emulsion, in which more than 90% (preferably 95%) of the total number of grains fall in the range ±40% around the average grain size, is preferable.

[0106] An emulsion composed of a tabular silver halide grain with ratio of not less than about 5 of a diameter to a

thickness is preferred and an emulsion composed of a tabular grain with not less than 90% of silver chloride having (100) face as the major face is preferred. Such the emulsion can be prepared by referring U.S. Patent Nos. 5,264,337, 5,314,798 and 5,320,958.

[0107] A method for mixing soluble silver halide and soluble halogen salt in the invention may include any of a single-sided mixing method, a simultaneous mixing method a combination thereof. It is also possible to use a method (so-called reverse precipitation method) in which grains are formed under the condition of excessive silver ions. As a type of double-jet methods, it is possible to use a method to keep the pAg constant in a liquid phase in which silver halides are produced, namely the so-called controlled double jet method. Owing to this method, it is possible to obtain a silver halide emulsion in which crystal shapes are regular and grain diameters are almost uniform. The light-sensitive silver halide and the light-sensitive silver halide forming composition used in the light-sensitive material is used in an amount of 0.3 to 3.4 g, preferably 0.9 to 3.0 g per m^2 of the light-sensitive material in term of silver.

[0108] The silver halide emulsion is preferably subjected to a chemical sensitization. As chemical sensitization, sulfur sensitization, selenium sensitization, tellurium sensitization, reduction sensitization and noble metal sensitization are known commonly and can also be used singly or in combination of two kinds or more.

[0109] As a sulfur sensitizing agent, various sulfur compounds such as, for example, thiosulfate, thiourea, rhodanine and polysulfide compounds can be used in addition to sulfur compounds contained in gelatin.

[0110] As a selenium sensitizing agent, known selenium sensitizing agent is used.

[0111] As to the combined usage of these chemical sensitizing agents, the combination of sulfur sensitizing agent with noble metal sensitizing agent, selenium sensitizing agent with noble metal sensitizing agent, and reduction sensitizing agent with noble metal sensitizing agent are employed.

[0112] These chemical sensitizing agents can be added optionally in course of preparing the silver halide emulsion, and preferably during chemical sensitization.

[0113] An added amount of these chemical sensitizing agents is 10^{-9} to 10^{-3} per mol of silver halide, preferably 5×10^{-6} to 5×10^{-4}, more preferably 1×10^{-5} to 2×10^{-4}.

[0114] It is possible to cause light-sensitive materials used in the invention to contain various compounds for the purpose of preventing fog in the course of manufacturing the light-sensitive materials or during storage of photographic processing or stabilizing photographic performances. Namely, it is possible to add many compounds known as antifoggant or stabilizer such as azoles, for example, benzthiazolium salt, nitroindazole, nitrobenzimidazole, chlorobenzimdazole, bromobenzimidazole, mercaptothiazole, mercaptobenzthiazole, mercaptobenzimidazole, mercaptothiadiazole, aminotriazole, benztriazole, nitrobenztriazole, mercaptotetrazole (1-phenyl-5-nercaptotetrazole in particular); mercaptopyrimidine, mercaptotriazine; thioketo compound such as, for example, oxazolinethion; azaindene, for example, triazaindene, tetrazaindene (especially, 4-hydroxy-substituted-1,3,3a,7-tetrazaindene), pentazaindene; benzenthiosulfonic acid, benzenesulfinic acid, benzenesulfonic acid amide and potassium bromide.

[0115] Gelatin is advantageously used as a binder of a photographic emulsion, but another hydrophilic colloid can be used. The examples of the hydrophilic colloid include gelatin derivatives, grafted gelatins with another polymer, proteins such as albumin or casein, cellulose derivatives such as hydroxycellulose, carboxymethylcellulose or cellulose sulfate, starch, agar, acacia, saccharides such as sodium alginate or starch derivatives and synthetic hydrophilic polymers such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinyl pyrrolidone, polyacrylic acid, polymethacrylic acid, polyethyleneglycol (molecular weight of not less than 2000) polyacryl amide, polyvinyl imidazole or polyvinyl pyrazole.

[0116] Gelatin includes limed gelatin, acid processed gelatin, gelatin hydrolysate or enzyme decomposed gelatin.

[0117] An amount of a binder used in each composing layer is usually preferably 0.05 to 8 g per m^2 of a support, more preferably 0.2 to 5 g, especially preferably 0.2 to 1.5 g. A total amount of a binder used in thermal development light-sensitive material is preferably 1 to 30 g per m^2 of a support, more preferably 2 to 15 g.

[0118] The photographic emulsion may contain water insoluble or sparingly soluble synthetic polymer in order to improve dimensional stability. The synthetic polymer includes polymers obtained by polymerization of alkyl-(meth)acrylate, alkoxyacryl(meth)acrylate, glycidyl (meth)acrylate, (meth)acryl amide, vinylester such as vinyl acetate, acrylonitrile, olefin, styrene or a combination thereof, or its combination with acrylic acid, methacrylic acid, α,β-unsaturated dicarboxylic acid, hydroxyalkyl-(meth) acrylate, sulfoalkyl(meth)acrylate or styrene sulfonic acid.

[0119] The photographic emulsion or non-light sensitive hydrophilic colloid in the invention may contain inorganic or organic hardeners. The hardeners include chromium salts (chrome alum, chromium acetate), aldehydes (formaldehyde, glyoxal, glutaraldehyde), a N-methylol compound (dimethylolurea, methyloldimethylhydantoin), dioxane derivatives (2,3-dihydroxydioxane), active vinyl compounds (1,3,5-triacroyl-hexahydro-s-triazine, bis(vinylsulfonyl)methylether, active halogen compounds (2,4-dichloro-6-hydroxy-s-triazine), mucohalogen acids (mucochloric acid, phenoxymucochloric acid), isooxazoles, starch dialdehyde, 2-chloro-6-hydroxy-triazinylated gelatin, isocyanates and active carboxy hardeners. The hardeners may be used singly or in combination of two kinds or more.

[0120] These hardeners are disclosed in Research Disclosure (RD) 176, 17643, (1978, December), page 26, A - C.

[0121] Other various additives are used for light-sensitive materials used in the invention. For example, desensitizer, plasticizer, lubricant, development accelerator and oil are used.

[0122] With regard to s support used in the invention, a transmission type or a non-transmission type can be employed, but the transmission type of plastic support is preferable. The plastic supports include polyethylene compound (e.g., polyethylene terephthalate, polyethylene naphthalate), triacetatecompound (e.g., triacetylcellulose), polystyrene (e.g., syndiotacticspolystyrene).

[0123] Preferable thickness of a support is 50 to 250 μm, especially preferably 70 to 200 μm.

[0124] Techniques described in the following publications are preferably applied to the light-sensitive material according to the invention.

(1) Compound having an acidic group:

JP O.P.I. No. 62-237445, page(8), line 11 in lower left column, to page 309(25), line 3 in lower right column

(2) Acidic polymer:

JP O.P.I. No. 6-186659, page (10), paragraph [0036] to page (17), paragraph [0062]

(3) Sensitizing dye:

JP O.P.I. No. 5-224330, page (3), paragraph [0017] to page (13), paragraph [0040]
JP O.P.I. No. 6-194771, page (11), paragraph [0042] to page (22), paragraph [0094]
JP O.P.I. No. 6-242533, page (2), paragraph [0015] to page (8), paragraph [0034]
JP O.P.I. No. 6-337492, page (3), paragraph [0012] to page (34), paragraph [0056]
JP O.P.I. No. 6-337494, page (4), paragraph [0013] to page (14), paragraph [0039]

(4) Super sensitizer:

JP O.P.I. No. 6-347938, page (3), paragraph [0011] to page (16), paragraph [0066]

(5) Redox compound:

JP O.P.I. No. 4-245243, page 235(7), to page 250(22)

(6) Syndiotactic polystyrene support:

JP O.P.I. No. 9-80664, page 3 paragraph [0022], to page 8 paragraph [0077]

[0125] As to other conventional additives, compounds disclosed in Research Disclosure Nos. 17643 (December 1978), 18716 (November 19798) and 308119 (December 1989) can be mentioned. Below, compounds disclosed in these three references and locations thereof are given.

	[RD-17643]		[RD-18716]	[RD-308119]	
	Page	Category	Page	Page	Category
Chemical sensitizer	23	III	648 upper right	996	III
Sensitizing dye	23	IV	648-649	996-998	IVA
Desensitizing dye	23	IV		998	IVB
Dye	25-26	VIII	649-650	1003	VIII
Development accelerator	29	XXI	648 upper right		
Anti-foggant, Development inhibitor	24	VI	649 right	998-1000	VI
Brightening agent	24	V	647 right	998	V
Hardener	26	X	651 upper left	1004-1005	X
Surfactant	26-27	XI	650 under right	1005-1006	XI

(continued)

	[RD-17643]		[RD-18716]	[RD-308119]	
	Page	Category	Page	Page	Category
Anti-static agent	27	XIII	650 under right	1006-1007	XIII
Plasticizer	27	XII	650 under right	1006	XII
Lubricant	27	XII	650 under right		
Matting agent	28	XVI	650 right	1008-1009	XVI
Binder	26	IX	651 left	1003-1004	IX
Support	28	XVII		1009	XVII

[0126] A hydrophobic binder preferably used in the invention is transparent or semitransparent, generally coloress, and a synthesized resin derived from natural polymer, polymer, copolymer and a medium which can form film, for example, gelatin, acacia, polyvinylalcohol, hydroxyethylcellulose, celluloseacetate, celluloseacetatebutylate, polyvinylpyrrolidone, casein, starch, polyacrylic acid, poly methylmethacrylic acid, polyvinylchloride, polymethacrylic acid, styrene-maleic acid anhydride copolymer, styrene-acrylonitrile copolymer, styrene-butadiene copolymer, polyvinylacetal derivative (polyvinylformal, poly vinylbutyral etc.), polyester, polyurethane, phenoxy resin, polychlorovinylidene, polyepoxide derivative, polycarbonate derivative, polyvinylacetate, celluloseester derivative and polyamide derivative are cited. Binder may be covered by water, an organic solvent or an emulsion.

[0127] An organic silver salt can be used in the invention. The organic silver salt is relatively stable to light and can form a silver image in the presence of an exposed light catalyst (photographic silver salt etc.) and a reducing agent at 80 °C or more. The organic silver salt is derived from any organic compound which forms reducible silver salt, especially a silver salt of an organic acid having 10 to 30 carbon atoms, preferably 15 to 28 carbon atoms is preferable. A silver complex of an organic or an inorganic salt of which ligands have total stable constant ranging 4.0 to 10.0 is preferably used.

[0128] In forming image according to the invention, as a light source to expose, a tungsten lamp, a halogen lamp, a xenon lamp, a mercury lamp, CRT light source, FO-CRT light source, an emission diode and a laser beam (e.g., a gas laser, dye laser, YAG laser and semi-conductor laser etc.) is used either singly or in combination of two kinds or more. Furthermore, combined usage of a semi-conductor laser and SHG element (second high frequent wave emission element) is also employed. Among them a laser beam source is preferably used, and the laser beam source ranging 600 - 850 nm is preferable, 600 - 700 nm is more preferable.

[0129] The processing process according to the invention, wherein a processing solution is supplied on the surface of the silver halide photographic light-sensitive material which is transferred in a gas phase, may be applicable to not only developing process but also optionally fixing process, stabilizing process and washing process.

(Means for supplying processing solution)

[0130] With respect to means for supplying the processing solution, wherein the processing solution is supplied on the surface of the silver halide photographic light-sensitive material which is transferred in a gas phase, various kinds of coating methods can be employed. A method by supplying the processing solution directly or forming beads from the processing solution supplying outlet such as slit or porous outlet onto the light-sensitive photographic material, and a method by supplying the processing solution onto the light-sensitive photographic material through a gas phase are preferably used.

(In case of slit or porous outlet)

[0131] With respect to supplying the processing solution directly or forming beads from slit or porous outlet, there is no limitation with the form of the solution supplying outlet, as far as it is possible to supply the solution from the solution supplying outlet. In case of the porous nozzle, the diameter of pore is preferably 0.03 to 1.0 mm, more preferably 0.05 to 0.5 mm. The interval between pores is preferably 0.1 to 1.0 mm, more preferably 0.15 to 0.5 mm.

[0132] In case of the slit nozzle, the slit width is preferably 0.03 to 1.0 mm. Too narrow slit width is not preferable for uniformity of coating the processing solution and too wide slit width is not preferable because of the occurrence of solution dripping. The slit width is preferably 0.05 to 0.5 mm, more preferably 0.10 to 0.3 mm. The interval between the solution supplying outlet and the light-sensitive photographic material is 0.03 to 10 mm, preferably 0.05 to 5 mm, more preferably 0.1 to 3 mm from the viewpoint of coating uniformity.

(Supplying the processing solution through a gas phase)

[0133] With respect to a method by supplying the processing solution through a gas phase, is cited a method by coating the processing solution onto the light-sensitive photographic material through a gas phase such as curtain coater.

[0134] In case where the high contrast image of γ of not less than 10 is obtained by supplying the processing solution onto the surface of the light-sensitive material according to the invention, as a preferable supplying method, there is the processing solution supplying method by spraying through a gaseous phase. For example, a method by spraying the solution actively by generating a pressure like the similar structure to ink-jet head portion of ink-jet printer (this is called ink-jet method in the invention) described in JP-A No. 6-324455, and a method by spraying the solution utilizing a liquid pressure like a spray bar are cited. With respect to spraying the solution actively, a method by spraying the solution utilizing the vibration of piezo electricity element or a method by spraying the solution utilizing bumping.

[0135] The method by supplying the processing solution by spraying the solution actively utilizing the similar structure to ink-jet head portion of ink-jet printer is especially preferably used, because it is easy to control the supplied amount of the processing solution and to select the processing position of the light-sensitive photographic material. With respect to the processing solution supplying means, a method by supplying the processing solution through a gaseous phase onto the light-sensitive photographic material from a stripe-like head, or a plane-like head, or a dot-like head etc. is employed. In case where the light-sensitive photographic material is sheet, using the plane-like supplying head in accordance with the size of the light-sensitive photographic material, supplying the processing solution through a gaseous phase onto the light-sensitive photographic material is employed on condition that the position relation between the light-sensitive photographic material and the supplying head being fixed. Shifting the position relation between the light-sensitive photographic material and the supplying head, a method by supplying the processing solution through a gaseous phase onto the light-sensitive photographic material is preferable because it is possible to supply sufficient amount of the processing solution onto the light-sensitive photographic material using the small supplying head. In case of using the stripe-like supplying head, the supplying head may move. To supply the processing solution rapidly, moving the light-sensitive photographic material in the direction other than parallel to the stripe-like supplying head is preferable. Especially, moving the light-sensitive photographic material in the vertical direction to the stripe-like supplying head is preferable to maintain the processing time constant. With respect to the processing solution spraying means, shifting the position relation between the light-sensitive photographic material and the supplying head, spraying the processing solution through a gaseous phase onto the light-sensitive photographic material from the supplying head will be explained in detail below. The number of times per sec. of spraying the processing solution through a gaseous phase onto the light-sensitive photographic material is preferably not less than 1, especially preferably not less than 10. To spray from the supplying head, the number of times per sec. of spraying the processing solution through a gaseous phase onto the light-sensitive photographic material is preferably not more than 1×10^6, especially preferably not more than 1×10^5.

[0136] In case where the processing solution is supplied from the supplying outlet onto the light-sensitive photographic material, the form of the supplying outlet takes any of circle, square, ellipse etc.. The area of each form of the supplying outlet is preferably 1×10^{-11} m^2. especially preferably 1×10^{-10} m^2 to avoid choking caused by drying up. Further, the area of each form of the supplying outlet is preferably 1×10^{-11} m^2. especially preferably 1×10^{-10} m^2 to supply uniformly the processing solution onto the light-sensitive photographic material, The average interval between the margin of the outlet and the margin of the nearest outlet is preferably not less than 5×10^{-6} m from the viewpoint of strength, and to supply sufficient amount of the processing solution, the average interval between the margin of the outlet and the margin of the nearest outlet is preferably not more than 1×10^{-3} m.

[0137] The interval between the solution supplying outlet and the emulsion surface of the light-sensitive photographic material is preferably not less than 50 μm (more preferably not less than 1 mm) to control this interval easily, especially preferably not more than 10 mm (more preferably not more than 5 mm).

[0138] So far as the quality of the obtained image is acceptable, an used amount of the processing solution is preferably less provided from the viewpoint of waste and handling of the processing solution. Concretely, 1 to 200 ml per m^2 of the light-sensitive material is preferable, 10 to 150 ml is more preferable, further 15 to 110 ml is more preferable, especially 20 to 80 ml is most preferable.

[0139] In the invention, only one side layer of the light-sensitive material is preferably contacted with the processing solution. In cases where the layer containing the light-sensitive silver halide on a support is contacted with the processing solution, an opposite side layer on the support to the layer containing the light-sensitive silver halide has preferably sufficiently low UV (ultra violet) and visible density, so that without processing the opposite side layer. any problem occurs. Concretely, UV and visible density are each not more than 0.3, preferably not more than 0.2, more preferably not more than 0.1. The visible spectra absorption does no have preferably specified color. That the UV and visible density of whole layers on the second surface side is not more than 0.3 does not mean the density of each layer on the second surface side, but means that the total UV and visible density of throughout whole layers on the second surface side is not more than 0.3.

[0140] In prior to supplying the processing solution, water is preferably supplied from the viewpoint of rapidity of the processing. In this invention, as occasion demands, water and processing solution cab be contacted with both surface of the light-sensitive photographic material.

[0141] To supply water, water tank may be provided or may be not provided. With respect to supplying water, any of known method and technique is employed. The amount of supplied water is preferably 0.5 to 100 g per m^2 of the light-sensitive photographic material, more preferably 1 to 40 g. As occasion demands, the supplied water can be heated to optional temperature. In this case, absorbed amount of water in the opposite layer to the layer comprising the light-sensitive silver halide emulsion is less than that in the layer comprising the light-sensitive silver halide emulsion. Concretely, the absorbed amount of water in the opposite layer to the layer comprising the light-sensitive silver halide emulsion is preferably not more than 2 g per m^2 of the light-sensitive photographic material, more preferably not more than 1 g. The absorbed amount of water mentioned above can be attained by the technique described in JP-A No. 9-90584 and other technique known to the art. That the absorbed amount of water in whole layers on the second surface side is not more than 2 g does not mean the absorbed amount of water of each layer on the second surface side, but means that the total absorbed amount of water of throughout whole layers on the second surface side is not more than 2 g.

[0142] In the invention, the light-sensitive photographic material supplied and coated with the processing solution is preferably heated. Heating may begin, before the processing solution being supplied, at the same time the processing solution being supplied, and after the processing solution being supplied, but heating preferably begins before the processing solution being supplied. Heating may be carried out at constant temperature continuously during processing or at variable temperature with the passage of time. The temperature of the light-sensitive material is 25 °C to 150 °C, preferably 25 °C to 50 °C, more preferably 35 °C to 46 °C. Heating is carried out so that the temperature before 30% of total processing time after beginning of processing is not more than 40 °C and the temperature after 70% of total processing time is not less than 40 °C. It is more preferable that heating is carried out so that the temperature before 40% of total processing time after processing begins is not more than 40 °C and the temperature after 60% of total processing time is not less than 40 °C. The term "beginning of processing" in the invention means the time when the processing solution (except water supplied prior to the development) was supplied and the term "total processing time" in the invention means time of throughout whole processes after the beginning of processing until completion of drying.

[0143] As to heating means to heat the light-sensitive photographic material, is cited a conductive heating method for contacting the light-sensitive photographic material with heat dram and heat belt, a convective heating method for heating the light-sensitive photographic material by heat convection generated by dryer etc., and a emissive heating method for heating the light-sensitive photographic material by emission of infra redray and high frequent electromagnetic waves.

[0144] Heating means is used in combination with transfer means for the silver halide photographic light-sensitive material and detecting means for the silver halide photographic light-sensitive material. The light-sensitive photographic material is transferred by the transfer means and the existence of the light-sensitive photographic material is detected by the detecting means. When the existence of the light-sensitive photographic material is detected by the detecting means, heating the light-sensitive photographic material begins and the light-sensitive photographic material is heated in predetermined time. In case where coating the processing solution onto the light-sensitive material transferred in a gaseous phase, the surface tension of the solution is preferably 40 dyn/cm, especially preferably 30 dyn/cm. To control the surface tension of the solution, various kinds of surfactants were used. The surfactant containing fluorine atom(s) in it's molecule is more preferable. The method according to the present invention is especially effective in forming high contrast image whose γ is 10 to 100 using later mentioned high contrast increasing agent.

[0145] In this invention, prior to processing the light-sensitive material, it is preferable to maintain the light-sensitive material temporarily on a carrier having gum-containing layer from the viewpoint of planeness, dimensional stability and stability.

[0146] The gum-containing layer has a gum and is a slippage preventing layer utilizing the effect of preventing slippage by gum.

[0147] As a gum, a natural gum is available, but a synthetic gum is preferable. Examples of the synthetic gum are cited styrene-butadiene gum, butadiene gum, isoprene gum, chloroprene gum, urethane gum, polysulfide gum, tetrafluoroethylene-propylene gum, acryl gum, epichlorohydrin gum, ethylene-vinylacetate gum, 1,2-polybutadiene gum, heat plasticity elastomer (styrene derivative, olefin derivative, urethane derivative, polyester derivative, polyamide derivative, fluorine derivative etc.), ethylene-propylene copolymer, ethylene-propylene-diene copolymer, nitrile-butadiene gum, butyl gum, fluoride gum, chlorosulfonatedpolyethylene gum, propyleneoxide gum, ethylene-acryl gum, norbonane gum and silicon gum. Especially silicon gum is preferable. These gums are used in combination of two kinds or more.

[0148] In a slippage preventing layer, (a) pasting resin such as rosin, polyterpene, phenol resin, xylene resin, petroleum hydrogencarbonate, (b) plasticizer such as phthalic acid ester, phosphoric ester, chloride parafine, (c) oil such as animal oil, mineral oil can be added to adjust contact with sheet. Further, age resister, stabilizer, filler, coloring agent can be added.

[0149] As a silicon gum contained in the slippage preventing layer, one having the following repeating unit of line-like organic polysiloxane of which molecular weight is 1000 to 1000000 as a main component is preferable.

$$[\text{-(R)Si(R)-O-}]_n$$

wherein n is an integer of not less than 2, R represents an alkyl group having 1 to 10 carbon atoms, a halogenated alkyl group, a vinyl group or an aryl group. One having R which consists of methyl group of not less than 60% of R is preferable.

[0150] Silicon gum usable in the invention is obtained by condensation reaction of silicon based polymer with the following silicon cross-linking agent.

1. R-Si-(-OR')
2. R-Si-(-OAc)
3. R-Si-(-ON=CR'$_2$)$_2$

[0151] Wherein, R is a synonym of the aforementioned R, R' represents an alkylgroup such as methyl group, ethyl group, Ac is an acetyl group.

[0152] These silicon gums are available in the market, for example, there is YS-3085 produced by Toshiba Silicon CO., Ltd.

[0153] Other usable silicon gums are obtained by reaction of the aforementioned base polymer with H-type silicon oil having the following repeating unit or by addition reaction of the aforementioned base polymer with the silicon base polymer of which about 3% of R consists of vinyl group or by reaction of said H-type silicon oil with the same H-type silicon oil.

$$[\text{-(R)SiH-O-}]_m[\text{-(R)Si(R)-O-}]_n$$

[0154] Wherein, R is a synonym of the aforementioned R, m is an integer of not less than 2, n is 0 or 1.

[0155] To obtain silicon gum by these cross-linking reactions, other than compositions mentioned above, catalysts such as organic carboxylic acid metal salts comprising tin, zinc, cobalt, lead, calcium and manganese, for example, tin dibutyllaurate, tin (II) octoate, cobaltnaphthenate or chloroplatinic acid are added.

[0156] To increase the strength of the silicon gum, a filler can be mixed. The silicon gum mixed with a filler in advance is available in the market as a silicon gum stop or a silicon gum dispersion. If coating a slippage invention layer on silicon gum is preferred, RTV or LTV silicon gum dispersion is preferably used. As examples of these, there are paper coating silicon gum dispersions such as Syl Off-23, SRX-257 and SH-237 produced by Toray Silicon Co., Ltd.

[0157] It is preferable to use a silane coupling agent to improve the contact between the silicon gum layer and a support. As the silane coupling agent, is cited as follows.

a. $H_2NCH_2CH_2N(CH_3)(CH_2)_3Si(OCH_3)_3$
b. $GlyO(CH_2)_3Si(OCH_3)_3$ [Gly = glycidyl group]
c. $HS(CH_2)_3Si(OCH_3)_3$
d. $CH_2=CHSi(OCOCH_3)_3$
e. $CH_2=C(CH_3)COO(CH_2)_3Si(OCH_3)_3$
f. $CH_2=CHSi(OC_2H_5)_3$
g. $H_2NCH_2CH_2NH(CH_2)_3Si(OCH_3)_2CH_3$
h. Chloro silane

[0158] A slippage preventing layer may be singly piled on a dram or completely sticked together (for example, laminating method) with a stick or a primer. A material containing a gum composing the slippage preventing layer is dissolved and dispersed in a solvent, and thus obtained solution may be coated on the dram and dried.

[0159] The dram is made of metal and has stiffness so that the light-sensitive material carried on it is not easily disfigured, and flatness of it's surface is macroscopically maintained. A cylindrical dram, other optional forms (an ellipse form, an equilateral form etc.) of rotational body can be employed. A circulating endless belt can be also employed. Further, a straight moving belt can be also employed.

[0160] The thickness of the slippage preventing layer is not limited thereto, as far as the light-sensitive material can be carried, but from the viewpoint of keeping flatness of the light-sensitive material, it is preferable 0.1 to 500 μm. The slippage preventing layer can be provided on heat dram, but to avoid preventing heat conducdtance, it is preferably 0.1 to 300 μm.

[0161] As a developing agent usable in the invention, dihydroxybenzene (e.g., hydroquinone, hydroquinonemonosul-

fate), 3-pyrazolidone (e.g., 1-phenyl-3-pyrazolidone, 1-phenyl-4-methyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-ethyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone), aminophenol (e.g., o-aminophenol, p-aminophenol, N-methyl-o-aminophenol, N-methyl-p-aminophenol, 2,4-diaminophenol), ascorbic acid derivative (e.g., ascorbic acid sodium arcorbate, erysorbic acid), metal complex (e.g., EDTA-Fe salt, DTPA-Fe salt, DPTA-Ni salt) are used singly or in combination of two kinds or more. Among them, the ascorbic acid and it's derivatives are preferable. The known ascorbic acid are described in U.S. Patent Nos., 2,688,548, 2,688, 549, 3,022,168, 3,512,981, 4,975,354, 5,326,816, and can be used.

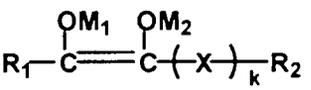
[0162] In the present invention, the combined usage of the developing agent consisting of the ascorbic acid and it's derivative together with the developing agent consisting of 3-pyrazolidone derivative (e.g., 1-phenyl-3-pyrazolidone, 1-phenyl-4-methyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-ethyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone), or aminophenol derivative (e.g., o-aminophenol, p-aminophenol, N-methyl-o-aminophenol, N-methyl-p-aminophenol, 2,4-diaminophenol), or dihydroxybenzene derivative (e.g., hydroquinone, hydroquinonemonosulfate, sodium hydroquinonemonosulfate, potassium 2,5-hydroquinonedisulfate), is preferable. In case of the combined usage, the added amount of the developing agent consisting of 3-pyrazolidone derivative, aminophenol derivative or dihydroxybenzene is usually 0.01 to 0.2 moles per a liter of developing solution. Especially the combination of the ascorbic acid and it's derivative with 3-pyrazolidone derivative, and the combination of the ascorbic acid and it's derivative with 3-pyrazolidone derivative and dihydroxybenzene derivative is preferably used.

[0163] It is possible to add to a developing solution an alkali agent (sodium hydroxide and potassium hydroxide,), a pH buffer agent (e.g., carbonate, phosphate, borate, acetic acid, citric acid and alkanolamine). As the pH buffer agent, carbonate is preferable, and an added amount of it is preferably 0.5 to 2.5 moles per a liter, more preferably 0.75 to 1.5 moles. In case of need, a dissolving aid (e.g., polyethyleneglycol and its ester, alkanolamine), a sensitizing agent (e.g., nonionic surfactant including polyoxyethylene and quaternary ammonium compound), a surfactant, anti-foaming agent and antifoggant (e.g., halogenide such as potassium bromide or sodium bromide, nitrobenzindazole, nitrobenzimidazole, benztriazole, benzthiazole, tetrazole and thiazole), a chelating agent (e.g., ethylenediaminetetraacetic acid or its alkali metal salt, nitrilotriacetate and polyphosphate), a development accelerating agent (e.g., compounds described in U.S. Patent No. 2,304,025 and Japanese Patent Examined Publication No. 45541/1972), a hardening agent (e.g., glutaraldehyde or addition product of its metabisulfite), or an anti-foaming agent.

[0164] The pH of the developing solution is preferably adjusted to 9.0 to 12.0 with alkaline agents, more preferably 9.0 to 11.0.

[0165] The developing solution according to the invention preferably contains the compound presented by the following formula (A). Next, the compound represented by the above mentioned formula (A) used in the present invention will be explained.

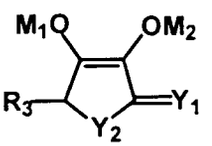
Formula (A)



[0166] In Formula (A), R_1 and R_2 each independently represents a subsituted or an unsubsituted alkyl group, a subsituted or an unsubsituted amino group, a subsituted or an unsubsituted alkoxy group, and a subsituted or an unsubsituted alkylthio group, and R_1 and R_2 may be linked with together to form ring, k is 0 or 1, and X is -CO- or -CS- when k is 1, and M_1 and M_2 are each a hydrogen atom or an alkali metal atom.

[0167] Among the compound represented by the formula (A), the following compound represented by the formula (A-a) in which R_1 and R_2 are linked with together to form ring is especially preferable.

Formula (A-a)



[0168] In Formula (A-a), R_3 represents a hydrogen atom, a substituted or an unsubstituted alkyl group, a substituted or an unsubstituted aryl group, a substituted or an unsubstituted amino group, a substituted or an unsubstituted alkoxy group, a sulfo group, a carboxyl group, an amide group and a sulfonamide group, Y_1 represents O, S or NR_4, R_4 represents a substituted or an unsubstituted alkyl group, and a substituted or an unsubstituted aryl group, and M_1 and M_2 are each a hydrogen atom or an alkali metal atom.

[0169] As an alkyl group in Formula (A) or Formula (A-a), is preferably cited a lower alkyl group having 1 to 5 carbon atoms, as an amino group is preferably cited an unsubstituted amino group or an amino group substituted by a lower alkyl group, as an alkoxy group is preferably cited a lower alkoxy group, as an aryl group is preferably cited a phenyl group or a naphthyl group which may possess substituents such as a hydroxyl group, a hologen atom, an alkoxy group, a sulfo group, a carboxyl group, an amide group and a sulfonamide group.

[0170] Examples of the compound represented by Formula (A) or Formula (A-a) are shown below, but are not limited thereto.

Formula (A)

Compound No.	X	R_1	R_2	M_1	M_2
A−1	— (k=0)	$HOCH_2-CH(OH)-CH(OH)-$	—OH	H	H
A−2	— (k=0)	$CH_3-CH(OH)-CH(OH)-$	—OH	H	H
A−3	— (k=0)	$HOCH_2-CH(OH)-CH(OH)-$	$-CH_3$	H	H
A−4	— (k=0)	$CH_3-CH(OH)-CH(OH)-$	$-CH_3$	H	H
A−5	$-C(=O)-$ (k=1)	$HOCH_2-CH(OH)-CH(OH)-$	—OH	H	H
A−6	$-C(=O)-$ (k=1)	$CH_3-CH(OH)-CH(OH)-$	—OH	H	H
A−7	$-C(=S)-$ (k=1)	$HOCH_2-CH(OH)-CH(OH)-$	—OH	H	H
A−8	$-C(=S)-$ (k=1)	$CH_3-CH(OH)-CH(OH)-$	—OH	H	H
A−9	$-C(=O)-$ (k=1)	$HO-CH_2-$	—OH	Na	H
A−10	$-C(=O)-$ (k=1)	$HO-CH_2-$	$-CH_3$	H	H
A−11	$-C(=O)-$ (k=1)	$HO-CH_2-$	$-C_2H_5$	H	H
A−12	$-C(=O)-$ (k=1)	$HO-CH_2-$	$-C_2H_4OH$	H	Na

Formula (A-a)

Compound No.	Y_1	Y_2	R_3	M_1	M_2
A—13	O	O	H	H	H
A—14	O	O	CH_3	H	H
A—15	O	O	CH_2 | OH	H	H
A—16	O	O	$CH_3—CH—$ | OH	H	H
A—17	O	O	$HOCH_2—CH—$ | OH	H	H
A—18	O	O	$HOCH_2—CH—$ | OH	Na	H
A—19	O	O	$HOOCCH_2—CH—$ | OH	H	Na
A—20	S	O	H	Na	H
A—21	S	O	$CH_3—CH—$ | OH	H	H
A—22	S	O	$HOCH_2—CH—$ | OH	H	H
A—23	O	NCH_3	H	H	H
A—24	O	NH	$HOCH_2—CH—$ | OH	H	K
A—25	O	S	H	H	H
A—26	O	S	$HOCH_2—CH—$ | OH	H	H
A—27	O	S	$CH_3—CH—$ | OH	H	H
A—28	S	S	H	H	H
A—29	S	S	$HOCH_2—CH—$ | OH	H	H
A—30	S	S	H	H	H

[0173] These compounds are representatively ascorbic acid and erythorbic acid, and their salts, or derivatives derived from ascorbic acid and erythorbic acid, and they are commercially available or easily synthesized according to known synthetic method.

[0174] The developer according to the invention is preferably used under the alkaline condition of pH of not less than 9. In case where coating the developing solution, it is preferable that alkaline agent and the developer containing the

compound represented by the formula (A) are separately supplied. The pH of the developer containing the compound represented by the formula (A) is preferably not more than 8, and it is preferable to supply separately an alkaline solution whose pH is not less than 9 to maintain alkaline condition. With respect to the order to coat the alkaline solution and the developer containing the compound represented by the formula (A), simultaneous coating or separate coating is available, it is preferable to coat the alkaline solution after coating the developer containing the compound represented by the formula (A).

[0175] In this invention, as occasion demands, water and processing solution are contacted with both surface of the light-sensitive photographic material. In prior to supplying the processing solution, water is preferably supplied from the viewpoint of rapidity of the processing. To supply water, water tank may be provided or may be not provided. With respect to supplying water, any of known method and technique is employed. The amount of supplied water is preferably 0.5 to 100 g per m^2 of the light-sensitive photographic material, more preferably 1 to 40 g.

[0176] As occasion demands, the supplied water can be heated to optional temperature. In this case, absorbed amount of water in the opposite layer to the layer comprising the light-sensitive silver halide emulsion is less than that in the layer comprising the light-sensitive silver halide emulsion. Concretely, the absorbed amount of water in the opposite layer to the layer comprising the light-sensitive silver halide emulsion is preferably not more than 2 g per m^2 of the light-sensitive photographic material, more preferably not more than 1 g. The absorbed amount of water mentioned above can be attained by the technique described in JP-A No. 9-90584 and other technique known to the art.

[0177] The developing solution preferably contains a silver halide solvent. As the silver halide solvent is cited the compound represented by the formula (I) to (IV) in Japanese Examined Patent Publication No. 7-120023. In the invention, thiosulfate salt (e.g., sodium thiosulfate, ammonium thiosulfate), imide compound (e.g., uracil, 5-methyluracil, 6-methyluracil, 6-butylthiouracil), 4-substituted thiourea compound, organic thioethr compound. thione compound, active methylene compound and mesoion compound are preferably used. More preferably used are sodium thiosulfate, ammonium thiosulfate, uracil, 5-methyluracil, 6-methyluracil and 6-butylthiouracil. Especially preferably used is sodium thiosulfate.

[0178] In the invention, the silver halide solvent added in the developing solution can be used singly or in combination of two kinds or more and combined usage of plural kinds of the silver halide solvents is preferable. Combined usage of an organic silver halide solvent is more preferable.

[0179] As a fixing solution, any one which are popularly known in the art can be used. The pH of the fixing solution is usually between 3.0 and 8.0.

[0180] As the fixing agent, for example, thiosulfates such as sodium thiosulfate, potassium thiosulfate, ammonium thiosulfate, and thiocyanates such as sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate and other organic sulfur compounds which are capable of producing a stable silver complex salts and are known in the art as a fixing agent can be used. The aforesaid fixing agents are preferably used in monobath processing solution, in which is also preferably used uracil or hydantoin described in JP-A 8-179458.

[0181] Into the fixing solution, a compound which functions as a hardening agent, including, for example, water-soluble aluminium salts such as aluminium chloride, aluminium sulfate, potassium alum, aldehyde compounds (such as glutal aldehyde or its sulfite adduct, etc.) may be added.

[0182] The fixing solution may contain, if necessary, preservatives such as sulfites or metasulfites; pH buffers such as acetic acid, citric acid, etc.; pH adjuster such as sulfuric acid, or chelating agents capable of softening hard water, etc.

[0183] The fixing agent contains a salt of citric acid, tartaric acid, malic acid, succinic acid or an optical isomer thereof. As the salt of the citric acid, tartaric acid, malic acid or succinic acid, lithium salt, potassium salt, sodium salt, ammonium salt, etc. can be mentioned. Further, lithium hydrogen salt, potassium hydrogen salt, sodium hydrogen salt, or ammonium hydrogen salt of the tartaric acid; ammonium potassium tartarate; or sodium potassium tartarate, etc. may also be used.

[0184] Developing solution and/or fixing solution may employ a solution which contains a solid processing composition such as a tablet agent or a granule agent which is dissolved in a solvent such as water.

[0185] Each part of granule of developer and fixer used as solid processing composition according to the invention is preferably covered. As examples of sugars and water soluble high molecular compounds to cover the granule, are cited sugar alcohol, monosaccharide (e.g., glucose, galactose), disaccharide (e.g., maltose, sucrose, lactose), polysaccharide, polyalkyleneglycol, polyvinylalcohol, polyvinylpyrrolidone, polyvinylacetal, polyvinylacetate, aminoalkylmethacrylate copolymer, methacrylacid-methacrylacidester copolymer, methacrylacid-acrylacidester copolymer and vinylpolymer containing bataine structure. Among them, sugar alcohol, polysaccharide and polyalkyleneglycol are preferable.

[0186] Preferable examples of sugar alcohol are threitol, erythritol, arabitol, ribitol, xylitol, sorbitol, mannitol, iditol, talitol, galactitol and allodulcitol.

[0187] Preferable examples of polysaccharide are pulran, methylcellulose, ethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, acetic acid phthalic acid cellulose, hydroxypropylmethylcellulosephthalate, hydroxypropylmethylcellulosesuccinate, carboxymethylethylcellulose, dextrin derivative, cyclodextrin derivative and starch decom-

positions. Preferable examples of the starch decompositions are pineflow (produced by Matsugaya Chemical Co., Ltd.) and pine-dex.

[0188] Preferable examples of polyalkyleneglycol are polyethyleneglycol #2000, #4000 and #6000 etc.

[0189] For the granulating method in the invention, a tumbling granulation method, a extrusion granulation method, a jet-layer granulation method, a fluidized layer granulation method, a crush granulation method, a stirring granulation method and a compression granulation method are usable. In the invention, the sugar or water-soluble high molecular weight compound can be coated on the granule prepared by an optional method by a coating method such as a pan coating method, a tumbling coating method, a fluidized layer coating method.

[0190] The granulation and coating can be continuously performed in the same vessel by using a fluidized layer granulation apparatus or a tumbling layer granulation apparatus. Such the method shows a high production efficiency and is preferable from the viewpoint of the effect of the invention.

[0191] A fluid layer granulation apparatus available on the market such as Multiprex series, GPCG series and WST/WSG series manufactured by Pawrex Co., Ltd., New Marumerizer series manufactured by Fuji Powdal Co., Ltd., Mixgrard series manufactured by Ookahara Seisakusyo Co., Ltd., and Spira flow series and Flow coater series manufactured by Freund Co., Ltd., is useful.

[0192] The silver halide light-sensitive photographic material according to the present is usually subjected to process in a washing(or rinsing) bath or in a stabilizing bath. The stabilizing solution usually contains, for the purpose of stabilizing an produced image, an inorganic or organic acid or salt thereof for adjusting pH of the membrane (at pH 3 - 8 after processing), or an alkaline agent or a salt thereof, including, for example, boric acid, metaboric acid, borax, phosphates, carbonates, potassium hydroxide, sodium hydroxide, ammonia water, mono-carboxylic acids, dicarboxylic acids polycarboxylic acids, citric acid, oxalic acid, malic acid acetic acid, etc.; aldehydes such as formalin, glyoxal, glutalalhehyde, etc.; chelating agents such as ethylenediamintetraacetic acid, or an alkali metal salt thereof, nitrilotriacetic acid, polyphosphates, etc.; antimolds such as phenol, 4-chlorophenol, cresol, o-phenylphenol, chlorophenol, dichlorophenol, formaldehyde, p-hydroxybenzoate, 2-(4-thiazoline)-benzimidazole, benzisothiazolin-3-one, dodecyl-benzyl-methylammonium chloride, N-(fluorodichloromethylthio)-phthalimide, 2,4,4'-trichloro-2'-hydroxydiphenyl ether, etc.; toning agents and/or residual color-improving agents such as nitrogen-containing heterocyclic compounds, including, for example, 2-mercapto-5-sodiumsulfonate-benzimidazole, 1-phenyl-5-mercapto tetrazole, 2-mercaptobenzothiazole, 2-mercapto-5-propyl-1,3,4-triazole, 2-mercaptohypoxanthine, etc. Specifically, it is preferable that the stabilizing solution contains an antimold. These compounds may be replenished either in the form of a liquid or a solid.

[0193] In view of a demand for decreasing the amount of waste liquid, the light-sensitive materials according to the invention are processed while being replenished with a given amount of developing solution in proportion to the processed area of the light-sensitive material. The replenishing amount of the fixing solution is not more than 300 ml per square meter of the light-sensitive material. Preferably, it is between 30 to 250 ml.

[0194] In view of a demand for decreasing the amount of waste liquid, the replenishing amount of the developing solution is not more than 250 ml per square meter of the light-sensitive material, preferably, it is between 20 to 200 ml. The temperature of the fixing bath, washing bath and/or stabilizing bath is preferably 30 to 45 °C and the temperature of each bath may be separately controlled.

[0195] The replenishing amount of the fixing solution and developing solution used herein means the amount replenished.

[0196] In the light of a demand for shortening the overall processing time, it is preferable that the overall processing time (Dry-to-Dry) from the time when the front end of a film is put into the automatic processing machine to the time when it comes out of the drying zone is between 10 to 60 seconds. The total processing time mentioned here includes a time period for all steps necessary for processing a black and white light-sensitive material, and it means the time including concretely all time periods for steps of developing, fixing, bleaching, washing, stabilizing and drying, for example, necessary for processing, namely the time of Dry to Dry.

[0197] More preferable overall processing time is 15 to 50 sec.

[0198] To process a large amount of the light-sensitive material of not less than 100 m^2 in running processing, the developing time is preferably not more than 18 sec. and not less than 2 sec.

[0199] In the present invention, a heat conductive member (e.g., a heat roller heated at 60 to 130 °C) or a radiation body (by directly applying electricity to a tungsten, carbon, Nicrome, a mixture of zirconium oxide, yttrium oxide or thorium oxide to heat and emit radiation, or by conducting thermal energy from a resistance pyrogeneous substance to a radiation emissive substance such as copper, stainless, nickel and various types of ceramics to generate heat or radiative infrared rays) can preferably be used to construct the heating zone.

[0200] As the heat conductive substance of 60 °C or higher, a heat roller can be mentioned as an example. The heat roller is preferably made of hollow aluminum cylinder and the peripheral surface thereof is coated with a resin such as silicon rubber, polyurethane or Teflon. Both end portions of this heat roller is preferably arranged inside the drying section in the vicinity of the in-let transport mouth of the processor with shaft bearings made of a heat resistant resin such as "Luron"(trade name) and rotationally supported against side walls of the section.

[0201] Further, it is preferable that one end portion of the heat roller is fixed with a gear, and is rotated in the direction of transport. Inside the roller of the heat roller, a halogen heater has been inserted, and the halogen heater is preferably connected to a heat regulator arranged in the automatic processing machine.

[0202] A thermister, which is arranged in contact with the peripheral surface of the heat roller, is connected to the heat regulator, and the heat regulator has preferably been set up so as to change the switch of the halogen heater, when detected temperature by the thermister is between 60 and 150 °C and more preferably, between 70 and 130 °C.

[0203] As examples of substances capable of emitting radiations with temperature higher than 150 °C (more preferably, higher than 250 °C), the following substances can be mentioned: tungsten, carbon, tantalum, Nichrome, a mixture of zirconium oxide, yttrium oxide and thorium oxide, carbon silicate, molybdenum disilicate. Further, methods of directly applying electricity to a radiating element such as tungsten, carbon, Nicrome, a mixture of zirconium oxide, yttrium oxide and thorium oxide to heat and emit radiation, or conducting thermal energy from a resistance pyrogeneous substance to a radiation emissive substance such as copper, stainless steel, nickel and various types of ceramics, to generate heat or radiate infrared rays may also be used.

[0204] In this invention, the combined usage of the heat conductive substance of 60 °C or higher with the substances capable of emitting radiations with temperature higher than 150 °C can be employed. And warm wind of 60 °C or lower is also used in combination.

[0205] In this invention, the automatic processor having the method and structure as described below can be preferably used.

(1) Deoderization apparatus: JP-A No. 64-37560, 544 page 2 upper left to 545 page 3 upper left.
(2) Regeneration and purification agent and apparatus for washing water: JP-A No. 6-250352, page 3 paragraph [0011] to page 8 paragraph [0058].
(3) Processing method for waste solution: JP-A No. 2-64638, 388 page 2 lower left to 391 page 5 lower left.
(4) Rinsing bath between developing bath and fixing bath: JP-A No. 4-313749, page 18 paragraph [0054] to page 21 paragraph [0065].
(5) Water replenishing method: JP-A No. 1-281446, page 2 lower left to lower right.
(6) Method for controlling drying wind of automatic processor by detecting an external temperature: JP-A No. 1-315745, 496 page 2 lower right to 501 page 7 lower right, JP-A No. 2-108051, 588 page 2 lower left to 589 page 3 lower left.
(7) Silver recovery method from fixer waste solution: JP-A No. 6-27623, page 4 paragraph [0012] to 501 page 7 paragraph [0071].

EXAMPLES

[0206] The invention is described below referring examples, embodiments of the invention are not limited thereto.

Example 1

(Preparation of silver halide emulsion A-1 to A-5)

[0207] To a solution A, were simultaneously added a solution B_1 shown below and an aqueous soluble halide solution C_1 for 15 min. with constant added amount of each solution B_1 and C_1 while keeping at pH 3.0, at the temperature of 35 °C. The resulting emulsion was proved to be an emulsion comprising cubic type silver halide grains having an average diameter of 0.11 μm (comprised of 70 mol% of silver chloride and 30 mol% of silver bromide). In the course of preparing emulsion, pAg was 160 mV before adding and 100 mV when the adding was finished.

[0208] After then, the pH of the emulsion was raised to pH 5.6 by 1N-NaOH aqueous solution, and ripened at 50 °C for 10 min. Thereafter, by ultrafiltration unnecessary salts were removed, then to the resulting solution 15 g of gelatin per mol of silver was added and the pH of the solution was adjusted at pH 5.7 and thus obtained solution was dispersed for 30 min. After dispersion, 4×10^{-4} mol of chloramine T per mol of silver was added. The pAg of thus obtained emulsion was 190 mV (40 °C).

A_1:	Ossein gelatin	25 g
	Nitric acid (5%)	6.5 ml
	Ion-exchanged water	700 ml

(continued)

B_1:	Silver nitrate	6.5 g
	Nitric acid (5%)	4.5 ml
	Ion-exchanged water	700 ml
C_1:	NaCl	47.5 g
	KBr	51.3 g
	Ossein gelatin	6 g
	Transition metal of VI to X groups in a periodic table)	shown in Table 1
	Ion-exchanged water	200 ml

[0209] To the emulsion were added 1.5 x 10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 8.5 x 10^{-4} mol per mol of silver of potassium bromide, and adjusted to be pH 5.6 and EAg 123 mv.

[0210] To the resulting emulsion were added flower of sulfur (2 x 10^{-5} mol of sulfur atom per mol of silver) in a fine solid dispersion and 1.5 x 10^{-5} mol of chloroauric acid per mol of silver and the resulting emulsion was chemically ripened at 60 °C for 80 min. After the ripening, 2 x 10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 3 x 10^{-4} mol per mol of silver of 1-phenyl-5-mercaptotetrazole and 1.5 x 10^{-3} mol per mol of silver of potassium iodide were added. After the emulsion was cooled to 40 °C, to this emulsion was added sensitizing dyes S-1 in an amount of 2 x 10^{-4} mol per mol of silver.

(Preparing light-sensitive material)

[0211] Using thus obtained emulsion, on a subbed support were simultaneously coated [1st layer], [2nd layer] and [3rd layer] containing composition as shown below, so that each layer have a coating amount of composition per m^2 as shown below. After each layer being cooled and set, on a subbed support opposite to the emulsion layer was coated [backing layer] which was cooled and set at -1 °C, and then both side were simultaneously dried. Thus samples Nos. 101 to 110 were obtained.

1st layer (developing agent containing layer)

[0212]

Gelatin	0.50 g
Phenylcarbamoylated gelatin	0.10 g
Polyvinylpyrrolidone (PVP)	0.10 g
Polyethyleneglycol (molecular weight 2000)	0.15 g
1-phenyl-4,4'-dimethyl-3-pyrazolidone	0.07 g
Sodium i-amyl-n-decylsulfosuccinate	0.05 g
Sodium dodecylbenzenesulfonate	0.02 g
2-methylhydroquinone	0.70 g
Na-1 (exemplified compound)	0.05 g
Dye stuff in the form of solid dispersion	amount shown in Table 2

2nd layer (silver halide emulsion layer)

[0213]

Gelatin	0.90 g
Silver halide emulsion	Silver amount 2.75 g equivalent
Organic contrast accelerating agent	amount shown in Table 2
Phenylcarbamoylated gelatin	0.30 g
Suspension polymer of 75 wt.% colloidal silica, 12.5 wt.% vinyl acetate and 12.5 wt.% vinyl pivalinate	1.0 g
Polymer latex L1 (particle diameter 0.10 μm)	0.5 g
Polyvinylpyrrolidone (PVP)	0.15 g
Surfactant (SU-1)	0.09 g
4-mercapto-3,5,6-fluorophthalic acid	0.05 g
Dye stuff (f-1)	0.02 g
Sodium polystyrenesulfonate (average molecular weight 500000)	0.015 g
Coating solution pH was 5.2.	

3rd layer (protective layer)

[0214]

Gelatin	0.90 g
Polyvinylpyrrolidone (PVP)	0.05 g
Colloidal silica	0.20 g
Dimethylsiloxane dispersion (average molecular weight 100000, average particle diameter 0.2 μm)	0.012 g
Surfactant (SU-2)	0.002 g
Sodium dihexylsulfosuccinate	0.010 g
Bactericide Z	0.005 g
Hardener h1	0.07 g
Hardener h2	0.07 g
PMMA latex (particle diameter 3 μm)	0.01 g

Backing layer

[0215]

Gelatin	3.0 g
Sodium hexylsulfosuccinate	0.020 g

(continued)

Polymer latex (L3)	0.30 g
Colloidal solica (average particle diameter 0.05 μm)	0.50 g
Sodium polystyrenesulfonate	0.010 g
Carnaubawax dispersion composition	0.2 g
Polyethyleneglycol (molecular weight 4000) Matting agent (monodispersed polymethylmethacrylate, average particle diameter 3 μm)	0.2 g 0.045 g
Hardener h1	0.05 g
Hardener h2	0.07 g

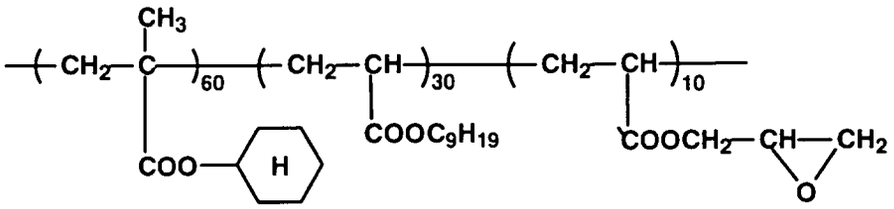
Table 1

Emulsion	Doped metal	Doped amount (mol/1 mol Ag)
A-1	Na_2 [$RhCl_5(H_2O)$]	2 x 10^{-7}
A-2	K_2 [$Ru(NO)Cl_5$]	2 x 10^{-7}
A-3	K_3 [$OsCl_6$]	3 x 10^{-7}
A-4	$(NH_4)_2$ [$Re(NO)Cl_5$]	1.5 x 10^{-7}
A-5	-	-

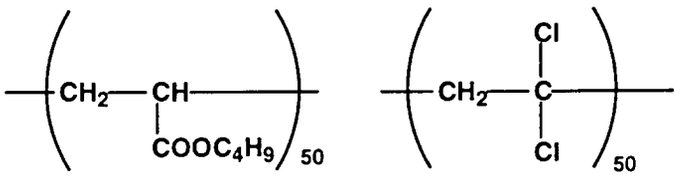
Table 2

Sample No.	Emulsion	Organic contrast accel-erationg agent	Added amount mg/m^2	Dye in solid dispersion (1-25), added amount mg/m^2
101	A-1	H-7	15	50
102	A-1	H-25	20	50
103	A-1	P-23	15	50
104	A-1	P-27	12	50
105	A-1	T-7	40	50
106	A-2	H-25	20	50
107	A-3	H-25	20	50
108	A-4	H-25	20	50
109	A-5	H-25	20	50
110	A-1	H-7	15	-

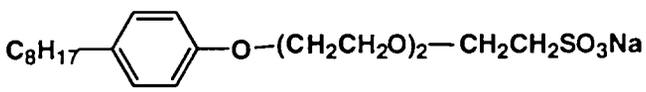
Polymer latex L1



Polymer latex L3

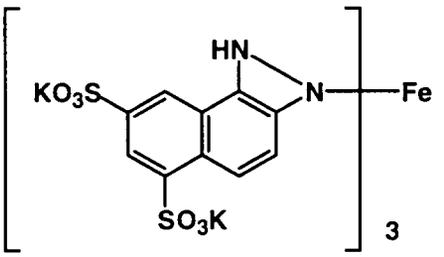


Surfactant Su-1



Surfactant Su-2

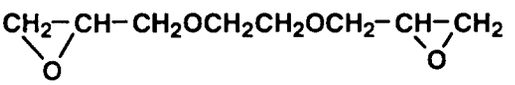
Dye-1



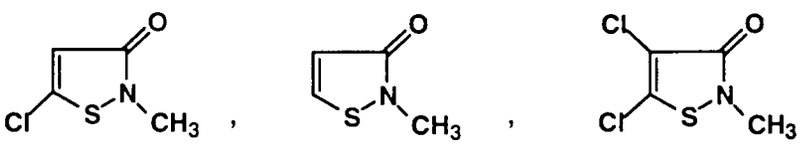
Hardener h1

$(CH_2=CHSO_2CH_2CONHCH_2)_2$—

Hardener h2



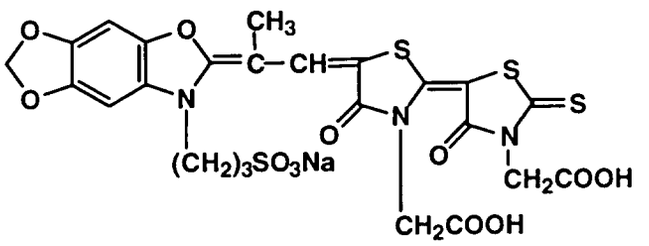
Bactericide Z



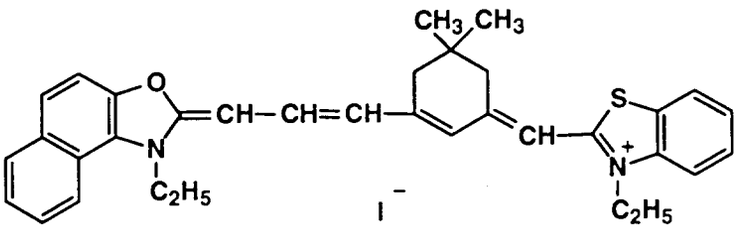
〔A〕 〔B〕 〔C〕

(A):(B):(C) = 50:46:4 (molar ratio)

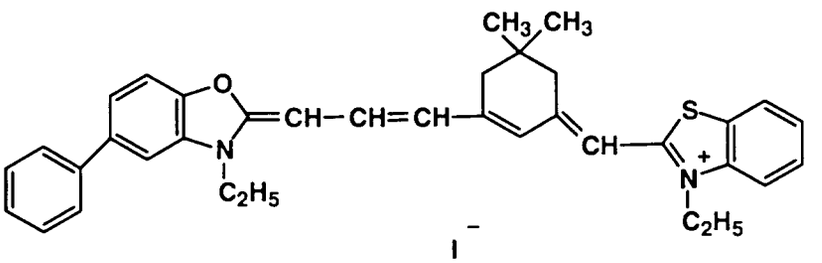
Spectral sensitizing dye S-1



Spectral sensitizing dye S-2



Spectral sensitizing dye S-3



(Evaluation of samples)

[0216] Samples thus obtained were subjected to wedge exposure using He-Ne laser of 633 nm, and then processed using the developing solution and fixing solution prescribed in the following process 1, 2.

Process 1

[0217] The samples were processed by using an automatic processor LD-T1100 (produced by Dainihon Screen Co., Ltd.) under the following condition.

Process	Temperature (°C)	Time (sec.)
Development	35	30
Fixation	35	30
Washing	Ordinary temp.	30
Squeeze, drying	45	30

[0218] The replenishing amount of developer and fixer is each 40 ml/m^2 and 40 ml/m^2 respectively. The light-sensitive material was immersed and processed in developing solution and fixing solution. By using LD-T1100, whole processes including development, washing and fixation are carried out by immersing the light-sensitive material in processing solutions.

Process 2

[0219] The development was carried out using developing solution supplying portion and development apparatus illustrated in Fig. 1 and 2, and the processes after development, namely, fix, washing and drying were carried out in the same way as used in process 1.

[0220] The processing condition of the developing portion is described below.

Temperature of heat roller (4)	50 °C
Time after contacting with heat roller until supplying developing solution	2 sec.
Interval between developing solution supplying outlet and the light-sensitive material (L1)	3 mm
Slit width of extreme point of developing solution supplying outlet	0.01 mm
Time after supplying developing solution until fixation	10 sec.
Temperature after supplying developing solution until fixation	45 °C
Replenishing amount of developer	40 ml/m^2
Replenishing amount of fixer	40 ml/m^2

[0221] Fig.1 is a outline of a cross-sectional view of developing process for forming image according to the invention. In the developing process, the silver halide light-sensitive photographic material is transferred on a transferring track 3 by plural transferring rollers 2, and this transferring track 3 is equipped horizontally. The silver halide photographic light-sensitive material is cut in sheet form before transferred into the developing process and transferred by keeping the image forming side (emulsion layer side) P1 upside. Along by the transferring track 3, a preheat portion, a coating portion and sneeze portion are equipped in this order in the transferring direction.

[0222] In the preheat portion, the transferring roller 2 is equipped on the transferring track 3, the heat roller 4 facing the transferring roller 2 is equipped under the transferring track 3. A heater 5 is incorporated in the heat roller 4 which comprises heat means giving heat required to process the silver halide photographic light-sensitive material. The silver halide light-sensitive photographic material P is heated by the heat roller 4 up to 35 to 90 °C, preferably 40 to 60 °C, thereby developing is accelerated.

[0223] A processing solution supplying means equipped on the transferring track 3 in a coating portion possesses a developing solution supplying portion 8, and the roller 2 facing this developing solution supplying portion 8 is equipped under the transferring track 3. The axis direction of the solution supplying portion 8 is arranged along by the width direction of the silver halide photographic light-sensitive material. The solution supplying portion 8 is equipped at the hind part of the heating means in the transferring direction of the light-sensitive material. A developing solution supplying outlet 9 facing the image forming side P1 of the silver halide light-sensitive photographic material P along by the axis direction is formed in the developing solution supplying portion 8. From this supplying outlet 9, the processing solution was coated on the image forming side P1 of the silver halide light-sensitive photographic material P.

[0224] In a squeeze portion, squeeze roller 12 is equipped on the transferring track 3. At least upside portion of roller which contacts with the image forming side P1 of the silver halide light-sensitive photographic material P is to be the squeeze roller, wherein underside portion is to be the transferring roller 2. The squeeze roller 12 equipped at the hind part of the developing solution supplying portion 8 in the transferring direction of the light-sensitive material, and squeeze the developing solution supplied on the silver halide photographic light-sensitive material P so that the developing solution is coated uniformly.

[0225] The squeeze roller is preferably one which absorbs less water. Preferable ones are metal roller such as SUS, plastic roller, gum roller, woven fiber roller, non-woven fiber roller and sintered roller. As the metal roller, stainless steel (SUS316L, SUS316, SUS304, SUS303), titan (Ti) and brass (Bs) are preferred. As the plastic roller, polyethyleneterephthalate (PET), polyethylene (FE), tetrafluoroethylene perfluoroalkoxyethylene copolymer (PFA), polyacetal (POM), polypropylene (PP), polytetrafluoroethylene (PTFE), polyvinylchloride (PVC), phenol resin (PF), modified polyphenyleneether (PPE), modified polyphenyleneoxide (PPO), polyurethane (PU), polycarbonate (PC), polyphenylenesulfide (PPS), polyfluorovinylidene (PVDF), tetrafluoroethylene hexafluoropropylene copolymer (FEP) and tetrafluoroethylene ethylene copolymer (ETFE) are preferable. As the gum roller, ethylenepropylene gum (EPDM, EPM), silicon gum (Si), nitryl gum (NBR) and chloroprene gum (CR) are preferable. As the material quality of the woven fiber roller and the non-woven fiber roller, polyolefin fiber, polyester fiber, polyacrylnitryl fiber, aliphaticpolyamide fiber, aromatic polyamide fiber and polyphenylenesulfide fiber etc. are preferable. A teflon-coated roller is more preferable.

[0226] Between the developing solution supplying portion 8 and the squeeze rollers 12, and at the hide portion of the squeeze rollers 12, there exist heating means 6, 7 which heat the silver halide photographic light-sensitive material P.

[0227] Next, a structure of the developing solution supplying portion equipped at coating portion will be explained based on Fig. 2.

[0228] In Fig.2, an interval L1 between an extreme point 10 of the developing solution supplying outlet 9 formed in the developing solution supplying portion 8 and the silver halide photographic light-sensitive material P is set to be 0.03 to 10 mm. The processing solution supplied from the developing solution supplying portion 8 is coated uniformly on the image forming side P1 of the silver halide light-sensitive photographic material P in the way in which the processing solution is supplied in curtain-like flow.

[0229] If the interval L1 between an extreme point 10 of the developing solution supplying outlet and the silver halide photographic light-sensitive material P is shorter than predetermined interval, because of the fluctuation of the thickness of the silver halide photographic light-sensitive material P and swelling, the surface of the silver halide photographic light-sensitive material P is easily contact with the developing solution supplying portion 8, thereby transferring the silver halide photographic light-sensitive material P does not work well. On the other hand, if the interval L1 is larger than predetermined interval, bubble and coating non-uniformity occur easily. However, by setting the interval of 0.03 mm to 10 mm, these problems are solved.

(Composition of Developing Solution)

[0230]

Pure water	150 ml
Penta sodium diethylenetriaminepenta acetate	1.0 g
Sodium sulfite	20 g
Potassium bromide	4 g
Potassium carbonate	40 g
Diethyleneglycol	40 g
5-Methybenzotriazole	0.21 g
1-Phenyl-5-mercaptotetrazole	0.03 g
1-Phenyl-4-hydroxy-4-methyl-3-pyrazolidone (Dimezone S)	0.85 g
Sodium erysorbate	30.0 g
Surfactant S-141 (fluoride-containing surfactant, produced by Asahi Glass Co., Ltd.)	0.5 g

(continued)

Potassium hydroxide	18 g
Water was added to make the total volume 400 ml, and the pH was adjusted to 10.4.	

(Composition of Fixing Solution)

[0231]

Pure water	200 ml
Sodium thiosulfate	120 g
Sodium sulfite	20 g
Citric acid	10 g
Di sodium citrate	20 g
Water was added to make the total volume 400 ml, and the pH was adjusted to 5.3.	

(Evaluation of sensitivity)

[0232] Black density of thus developed samples was measured by PDA-65 (Degital densitometer, produced by Konica Co., Ltd.). The sensitivity was defined as a reciprocal of exposure necessary to give a black density of 1.0, wherein sample No. 101 gave black density of 1.0 with an given exposure and a reciprocal of this given exposure was assumed 100. Other sample's sensitivity is a relative value to the reciprocal of exposure of sample 101 (100).

(Evaluation of dot quality (DQ))

[0233] Using image setter Doleve 800 (produced by Cytex Co., Ltd.), square dot of dot 300 L, 50% by appropriate exposure was output and processed by foregoing process. Thus obtained dot quality was evaluated by visual observation. The lowest level available for actual use is evaluated as rank 3 by visual observation. The highest dot quality without any problem in quality is evaluated as rank 5, therefore rank 2 and 1 are not available for actual use.

(Evaluation of γ (gamma))

[0234]

$$\gamma = (3\text{-}1)/[\log(\text{exposure to give } D=3)\text{-}\log(\text{exposure to give } D=1)]$$

(Evaluation of black spot)

[0235] Non-image portion of the processed light-sensitive material was observed under a 40-power magnifier for evaluating black spot. The highest quality without any black spot is evaluated as rank 5. The lowest level available for actual use is evaluated as rank 3 by visual observation under a 40-power magnifier.

(Evaluation of running exhaustion)

[0236] Process 1 and 2 were carried out for all seven days, during these period 30 m^2 per a day was processed, thereafter evaluation of sensitivity, gamma (γ) and black spot was done in the same way as mentioned above.

[0237] Obtained results were shown collectively in Table 3.

Table 3

Sample No.	Process 1								Process 2							
	Fresh				After runnning				Fresh				After runnning			
	S*	γ	DQ	B*	S*	γ	DQ	B*	S*	γ	DQ	B*	S*	γ	DQ	B*
101	100	22	5	5	60	12	1	3	105	22	5	5	103	22	5	5
102	120	24	5	4	60	13	1	2	120	24	5	4	115	24	5	4
103	200	20	4	3	150	14	1	2	200	20	4	3	205	20	4	3
104	170	19	4	4	120	11	1	2	170	19	4	4	175	20	4	4
105	70	18	5	5	40	8	1	5	70	18	5	5	65	18	5	5
106	120	25	4	4	60	15	1	3	120	25	4	4	115	25	4	4
107	100	24	5	5	50	13	1	3	100	24	5	5	95	24	5	5
108	115	23	5	4	60	11	1	3	115	23	5	4	110	23	5	4
109	105	20	4	3	60	11	1	1	105	20	4	3	85	18	4	3
110	100	22	3	5	70	12	1	3	100	22	3	5	100	22	3	5

S*: Sensitivity
B*: Black spot

Example 2

(Preparation of silver halide emulsion B)

[0238] To a solution C_2 were simultaneously added a silver nitrate solution A_2 and a halide solution B_2 containing NaCl and KBr for 7 min. while keeping EAg 120 mV, pH at 3.0, at the temperature of 35 °C and 0.09 μm of silver halide nucleus comprising 70 mol% of silver chloride and 30 mol% of silver bromide was obtained. After then, making the EAg thus obtained solution 100 mV by NaCl, and to the solution were added a silver nitrate solution D_2 and a halide solution E_2 again for 15 min., thereafter 0.20 μm (variation coefficient of 15%) of silver halide emulsion comprising 70 mol% of silver chloride and 30 mol% of silver bromide was obtained.

[0239] After then, the pH of the emulsion was raised to pH 5.6 by 1N-NaOH aqueous solution, and ripened at 50 °C for 10 min.

[0240] Thereafter, adding modified gelatin treated with phenyl isocyanate, and washing blocked emulsion at pH 4.2, then to the resulting solution 15 g of gelatin per mol of silver was added and the pH of the solution was adjusted at pH 5.7 and thus obtained solution was dispersed for 30 min. at 55 °C. After dispersion, 4×10^{-4} mol of chloramine T per mol of silver was added. The pAg of thus obtained emulsion was 190 mV.

A_2:	Silver nitrate	16 g
	Nitric acid (5%)	5.3 ml
	Ion-exchanged water	48 ml
B_2:	NaCl	3.8 g
	KBr	3.5 g
	Ossein gelatin	1.7 g
	Ion-exchanged water	48 ml

(continued)

C_2:	NaCl	1.4 g
	Ossein gelatin	7 g
	Nitric acid (5%)	6.5 ml
	$K_2RhCl_5(H_2O)$	0.06 mg
	Ion-exchanged water	700 ml
D_2:	Silver nitrate	154 g
	Nitric acid (5%)	4.5 ml
	Ion-exchanged water	200 ml
E_2:	NaCl	37 g
	KBr	33 g
	Ossein gelatin	6 g
	$K_2RhCl_5(H_2O)$	0.04 mg
	Ion-exchanged water	200 ml

[0241] To the emulsion were added 1.5 x 10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 8.5 x 10^{-4} mol per mol of silver of potassium bromide, and adjusted to be pH 5.6 and EAg 123mv.

[0242] To the resulting emulsion were added flower of sulfur (2 x 10^{-5} mol of sulfur atom) in a fine solid dispersion and 1.5 x 10^{-5} mol of chloroauric acid and the resulting emulsion was chemically ripened at 60 °C for 80 min. After the ripening, 2 x 10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 3 x 10^{-4} mol per mol of silver of 1-phenyl-5-mercaptotetrazole and 1.5 x 10^{-3} mol per mol of silver of potassium iodide was added. After the emulsion was cooled to 40 °C, to this emulsion were added sensitizing dyes S-2 and S-3 in an amount of 1.0 x 10^{-4} mol and 0.7 x 10^{-4} mol per mol of silver respectively.

(Preparation of silver halide emulsion C)

[0243] To a solution A_3 were simultaneously added a silver nitrate solution B_3 and a halide solution C_3 containing NaCl and KBr for 15 min. with constant added amount of each solution B_3 and C_3 while keeping at pH 3.0, at the temperature of 35 °C. The resulting emulsion was proved to be an emulsion comprising cubic type silver halide grains having an average diameter of 0.09 μm (comprised of 70 mol% of silver chloride and 30 mol% of silver bromide). In the course of preparing emulsion, pAg was 160 mV before adding and 100 mV when the adding was finished.

[0244] After then, the pH of the emulsion was raised to pH 5.6 by 1N-NaOH aqueous solution, and ripened at 50 °C for 10 min.

[0245] Thereafter, by ultrafiltration unnecessary salts were removed, then to the resulting solution 15 g of gelatin per mol of silver was added and the pH of the solution was adjusted at pH 5.7 and thus obtained solution was dispersed for 30 min. at 55 °C. After dispersion, 4 x 10^{-4} mol of chloramine T per mol of silver was added. The pAg of thus obtained emulsion was 190 mV at 40 °C.

A_3:	Ossein gelatin	25 g
	Nitric acid (5%)	6.5 ml
	Ion-exchanged water	700 ml
B_3:	Silver nitrate	170 g
	Nitric acid (5%)	4.5 ml
	Ion-exchanged water	200 ml

(continued)

C_3:	NaCl	47.5 g
	KBr	51.3 g
	Ossein gelatin	6 g
	VI to X transition metal	amount shown in Table 2
	Ion-exchanged water	200 ml

[0246] To the emulsion were added 1.5 x 10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 8.5 x 10^{-4} mol per mol of silver of potassium bromide, and adjusted to be pH 5.6 and EAg 123mv.

[0247] To the resulting emulsion was added flower of sulfur (2 x 10^{-5} mol of sulfur atom) in a fine solid dispersion and 1.5 x 10^{-5} mol of chloroauric acid were added and chemically ripened at 50 °C for 80 min. After the ripening, 2 x 10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 3 x 10^{-4} mol per mol of silver of 1-phenyl-5-mercaptotetrazole and 1.5 x 10^{-3} mol per mol of silver of potassium iodide were added. After the emulsion was cooled to 40 °C, to this emulsion was added hydrazine derivative H-25 in an amount of 3.5 x 10^{-3} mol.

(Preparing a light-sensitive material)

[0248] Using thus obtained emulsion, on a subbed support were simultaneously coated 1st layer, 2nd layer and 3rd containing composition as shown below, so that each layer have a coating amount of composition per m^2 as shown below. After each layer being cooled and set, on a subbed support opposite to the emulsion layer was coated[backing layer which was cooled and set at -1 °C, and then both side were simultaneously dried. Thus sample No. 201 to 211 were obtained.

1st layer (layer containing developing agent)

[0249]

Gelatin	0.50 g
Phenylcarbamoyled gelatin	0.10 g
Polyvinylpyrrolidone (PVP)	0.10 g
Polyethyleneglycol (molecular weight 2000)	0.15 g
Sodium i-amyl-n-decylsulfosuccinate	0.05 g
Sodium dodecylbenzenesulfonate	0.02 g
Developing agent	amount shown in Table 4
Nucleation accelerating agent, exemplified compound Na-21	0.05 g
Dye stuff in a solid dispersion, exemplified compound 2-5	0.05 g

2nd layer (emulsion layer)

[0250]

Gelatin	0.90 g
Silver halide emulsion B	Silver amount 0.30 g equivalent
Silver halide emulsion C	Silver amount 2.40 g equivalent

(continued)

Hydrazine derivative H-7	0.02 g
Phenylcarbamoyled gelatin	0.30 g
Suspension polymer of 75 wt.% colloidal silica, 12.5 wt.% vinyl acetate and 12.5 wt.% vinyl pivalinate	1.0 g
Polymer latex L1 (particle diameter 0.10 μm)	0.5 g
Polyvinylpyrrolidone (PVP)	0.15 g
Surfactant (SU-1)	0.09 g
4-mercapto-3,5,6-fluorophthalic acid	0.05 g
Dye stuff (f-1)	0.02 g
Sodium polystyrenesulfonate (average molecular weight 500000)	0.015 g
Coating solution pH was 5.2.	

3rd layer (protective layer)

[0251]

Gelatin	0.90 g
Polyvinylpyrrolidone (PVP)	0.05 g
Polyacrylic acid	0.20 g
Colloidal silica	0.20 g
Dimethylsiloxane dispersion (average molecular weight 100000, average particle diameter 0.2 μm)	0.012 g
Surfactant (SU-2)	0.002 g
Sodium-dihexylsuccinate	0.010 g
Bactericide Z	0.005 g
Hardener h1	0.07 g
Hardener h2	0.04 g
PMMA latex (particle diameter 3 μm)	0.01 g

Backing layer

[0252]

Gelatin	3.0 g
Sodium hexylsulfosuccinate	0.020 g
Polymer latex L3	0.30 g
Colloidal solica (average particle diameter 0.05 μm)	0.50 g
Sodium polystyrenesulfonate	0.010 g
Carnaubawax dispersion composition	0.2 g
Polyethyleneglycol (molecular weight 4000)	0.2 g

(continued)

Matting agent (monodispersed polymethylmethacrylate, average particle diameter 3 μm)	0.045 g
Hardener h1	0.05 g
Hardener h2	0.07 g

(Evaluation of the light-sensitive material)

[0253] The light-sensitive material thus obtained was subjected to wedge exposure using semi-conductor laser of 780 nm, and then processed using the aforementioned developing solution and fixing solution according to the following process 3.

Process 3

[0254] Using a developing processor made on an experimental basis in Fig. 3, evaluation was carried out. In Fig. 3, the light-sensitive material P with image forming side upside passed the pathway indicated by an arrow and was developed, fixed, washed and dried.

[0255] In Fig. 3, 13 is a transferring roller, 14 is a preheat dram heating in advance, 15 is a dried wind blowing off nozzle, 16 is a washing water puffing out nozzle, 17 is a developing solution puffing out nozzle, 18 is a fixing solution puffing out nozzle.

[0256] 19, 20 is each a developing portion heater, 21 is a fixing portion heater where a panel heaters to heat the light-sensitive material are used. Each of Fig. 4 and 5 illustrates an outline of a cross sectional view of a puffing out nozzle of each 17 and 18.

[0257] Fig. 4 is an outline of a cross sectional view of a structure of solution supplying apparatus.

[0258] The processing solution is introduced from a chamber 23 through a solution inflow pathway 22 of which flow area is narrowed down, thereafter a vibration panel 25 is changed by a driving element 24, thereby abrupt volume change in a chamber occurs. As a result, the processing solution is sprayed from an orifice. The orifice is composed of an orifice channel 28 and an orifice panel 29. A wall above the chamber 23 is composed of the vibration panel 25, and through the vibration panel 25, a change of the driving element 24 is conveyed. An upside of the chamber is preferably composed of the vibration panel 25 so that the driving element 24 and the processing solution do not contact directly. Material quality of the wall of the chamber is preferably composed of vinylidene chloride and the channel of the orifice is preferably also composed of vinylidene chloride. Material quality of the orifice panel is composed of nickel.

[0259] Fig. 5 is an outline of a plane figure of the processing solution supplying apparatus of Fig. 4. A contacting angle of the processing solution on the orifice panel 29 is 20 degrees and the contacting angle of the processing solution on the wall of the chamber is 45 degrees.

[0260] Next, the composition of each of the vibration panel 25 and the driving element 24 will be explained. The vibration panel 25 is, for example, equipped to an exterior material 26 of the processing solution supplying means with epoxy resin stick. The vibration panel is composed of vinylidene chloride resin. The driving element is a piezo electricity element. The piezo electricity element vibrates up and down by stretching and shrinking horizontally, so that it gives the processing solution a pressure. The piezo electricity element is connected by lead lines 31, 32 with an electron pulse emission apparatus which can emit an external pulse voltage.

[0261] A droplet of the processing solution 30 is sprayed from the orifice 27. An extreme point of the orifice channel 28 is to be a fine diameter circle orifice 27 and the diameter of the droplet of the processing solution sprayed from the solution supplying means is controlled. At this time, a pressure of the processing portion is reduced, thereby the processing solution is inflowed from an external processing tank into the chamber 23 through the solution inflow pathway 22.

[0262] In this way, plus and minus voltage switches alternately on two pieces of the piezo electricity elements, so that the processing solution for the light-sensitive material is continuously supplied.

[0263] As a driving condition of the processing solution supplying means, a supplying head of serial type using piezo electricity elements is used. Number of orifice is 64 and zigzag pattern illustrated in Fig. 6 is used. The sprayed volume of the droplet at one time is to be 150 picoliter by adjusting driving voltage, and spraying frequency is set to be 7500 Hz.

[0264] Tying up eight solution supplying portions in a bundle illustrated in Fig. 4, 5 and moving these solution supplying portions in the vertical direction to the light-sensitive material transferred, so that the overall surface of the light-sensitive material is supplied with the processing solution.

[0265] The used processing condition is as follows.

Temperature of preheat dram (14)	40 °C
Time until supplying the developing solution after contacting with preheat dram	2 sec.
Interval between developing solution supplying portion and light-sensitive material	3 mm
Scanning speed of developing solution supplying portion	500 mm/sec.
Supplied amount of developing solution	40 ml/m^2
Time until fixation after supplying developing solution	30 sec.
Temperature until fixation after supplying developing solution	35 °C
Scanning speed of fixing solution supplying portion	500 mm/sec.
Supplied amount of fixing solution	40 ml/m^2
Time until washing after supplying fixing solution	15 sec.
Temperature until washing after supplying fixing solution	35 °C
Time of washing	4 sec.
Temperature of washing	40 °C
Time of drying	10 sec.
Temperature of drying	45 °C

Process 4

[0266] Using the same apparatus as used in process 3, process 4 was carried out in the same way in which process 3 was carried out except the used processing condition being changed as follows.

Temperature of preheat dram (14)	50 °C
Time until fixation after supplying developing solution	10 sec.
Temperature until fixation after supplying developing solution	45 °C
Time until washing after supplying fixing solution	6 sec.
Temperature until washing after supplying fixing solution	45 °C

(Composition of Developing Solution)

[0267]

Pure water	150 ml
Penta sodium diethylenetriaminepenta acetate	1.0 g
Sodium sulfite	20 g
Potassium bromide	4 g
Potassium carbonate	40 g
Diethyleneglycol	40 g
5-Methybenzotriazole	0.21 g

(continued)

1-Phenyl-5-mercaptotetrazole	0.03 g
1-Phenyl-4-hydroxy-4-methyl-3-pyrazolidone (Dimezone S)	0.85 g
Hydroquinone	17.5 g
Surfactant S-141 (fluoride-containing surfactant, produced by Asahi Glass Co., Ltd.)	0.5 g
Potassium hydroxide	18 g
Water was added to make the total volume 400 ml, and the pH was adjusted to 10.8.	

(Composition of Fixing Solution)

[0268]

Pure water	200 ml
Sodium thiosulfate	120 g
Sodium sulfite	20 g
Citric acid	10 g
Di sodium citrate	20 g
Surfactant S-141 (fluoride-containing surfactant, produced by Asahi Glass Co., Ltd.)	0.5 g
Water was added to make the total volume 400 ml, and the pH was adjusted to 5.3.	

(Evaluation of sensitivity)

[0269] Black density of thus developed samples was measured by PDA-65 (Degital densitometer, produced by Konica Co., Ltd.). The sensitivity was defined as a reciprocal of exposure necessary to give a black density of 1.0, wherein sample No. 201 gave black density of 1.0 with an given exposure and a reciprocal of this given exposure was assumed 100. Other sample's sensitivity is a relative value to the reciprocal of exposure of sample 201 (100).

(Evaluation of γ (gamma))

[0270]

$$\gamma = (3\text{-}1)/[\log(\text{exposure to give D=3})\text{-}\log(\text{exposure to give D=1})]$$

(Evaluation of black spot)

[0271] Non-image portion of the processed light-sensitive material was observed under a 40-power magnifier for evaluating black spot. The highest quality without any black spot is evaluated as rank 5. The lowest level available for actual use is evaluated as rank 3 by visual observation under a 40-power magnifier. Obtained results were shown collectively in Table 5.

Table 4

Sample No.	Developing agent	Added amont g/m^2	Process 3			Process 4		
			S*	γ	B*	S*	γ	B*
201	-	-	100	25	4	70	15	4
202	Hydroquinone	0.13	100	25	4	70	17	4
203	Hydroquinone	0.20	100	25	4	90	23	4
204	Hydroquinone	0.50	100	25	4	95	24	4
205	Hydroquinone	1.00	100	25	4	95	24	4
206	Dimezone	1.00	100	25	4	95	24	3
207	Hydroquinone Dimezone	0.5 0.05	100	25	4	100	25	5
208	Hydroquinone Dimezone*	0.5 0.05	100	25	5	100	25	5
209	Methyl-hydroquinone Dimezone	0.5 0.05	110	25	4	115	27	5
210	t-Butyl hydroquinone Dimezone	0.5 0.05	110	25	5	115	27	5
211	Hydroquinone Dimezone S	0.5 0.05	100	25	4	105	25	5

S*: Sensitivity
B*: Black spot
Dimezone*; A solid dispersion compsition dispersed by a ball mill was used.
The average particle diameter was 0.2 μm.

[0272] As can be seen from Table 4, the silver halide-light photographic light-sensitive material according to the invention comprising the dye stuff in a solid dispersion and having the silver halide emulsion layer containing the transition metals of VI to X groups in a periodic table or the organic high contrast accelerating agents exhibited an excellent photographic characteristics with higher sensitivity, higher gamma and no black spot in the processing way in which the processing solution was supplied by coating it on the silver halide-light photographic light-sensitive material.

Example 3

(Preparation of silver halide emulsion A)

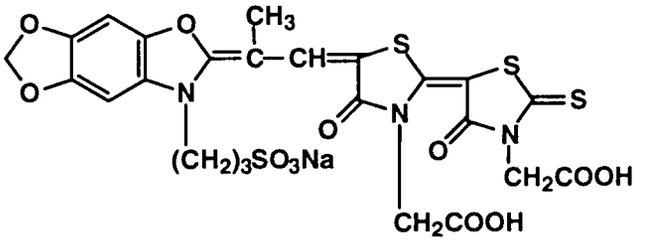
[0273] To a solution A were simultaneously added a silver nitrate solution B and a halide solution C containing NaCl and KBr for 15 min. with constant added amount of each solution B and C while keeping at pH 3.0, at the temperature of 35 °C. The resulting emulsion was proved to be an emulsion comprising cubic type silver halide grains having an average diameter of 0.11 μm (comprised of 70 mol% of silver chloride and 30 mol% of silver bromide). In the course of preparing emulsion, pAg was 160 mV before adding and 100 mV when the adding was finished. After then, the pH of the emulsion was raised to pH 5.6 by 1N-NaOH aqueous solution, and ripened at 50 °C for 10 min. Thereafter, by ultrafiltration unnecessary salts were removed, then to the resulting solution 15 g of gelatin per mol of silver was added and the pH of the solution was adjusted at pH 5.7 and thus obtained solution was dispersed for 30 min. After dispersion, 4 x 10^{-4} mol of chloramine T per mol of silver was added. The pAg of thus obtained emulsion was 190 mV (40 °C).

A:	Ossein gelatin	25 g
	Nitric acid (5%)	6.5 ml
	Ion-exchanged water	700 ml
B:	Silver nitrate	170 g
	Nitric acid (5%)	4.5 ml
	Ion-exchanged water	200 ml
C:	NaCl	47.5 g
	KBr	51.3 g
	Ossein gelatin	6 g
	$Na[RhCl_5(H_2O)]$	0.05 mg
	Ion-exchanged water	200 ml

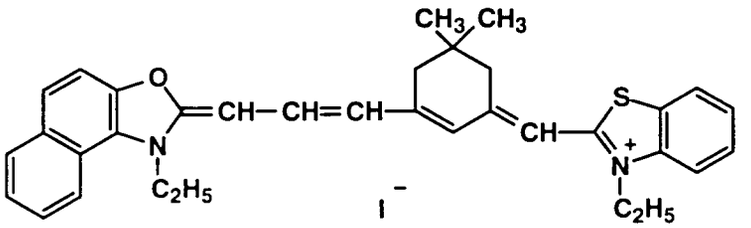
[0274] To the emulsion were added 1.5×10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 8.5×10^{-4} mol per mol of silver of potassium bromide, and adjusted to be pH 5.6 and EAg 123mv. To the resulting emulsion were added flower of sulfur (2×10^{-5} mol of sulfur atom) in a fine solid dispersion and 1.5×10^{-5} mol of chloroauric acid and the resulting emulsion was chemically ripened at 50 °C for 80 min. After the ripening, 2×10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 3×10^{-4} mol per mol of silver of 1-pheny1-5-mercaptotetrazole and 1.5×10^{-3} mol per mol of silver of potassium iodide were added. After the emulsion was cooled to 40 °C, to this emulsion were added sensitizing dyes S-2 and S-3 each in an amount of 1×10^{-4} mol and 1.5×10^{-5} respectively per mol of silver.

[0275] Using thus obtained emulsion, on a subbed support were simultaneously coated [1st layer], [2nd layer] and [3rd layer] containing composition as shown below, so that each layer have a coating amount of composition per m^2 as shown below. After each layer being cooled and set, on a subbed support opposite to the emulsion layer was coated [backing layer] which was cooled and set at -1 °C, and then both side were simultaneously dried. Thus samples Nos. 301 to 303 were obtained.

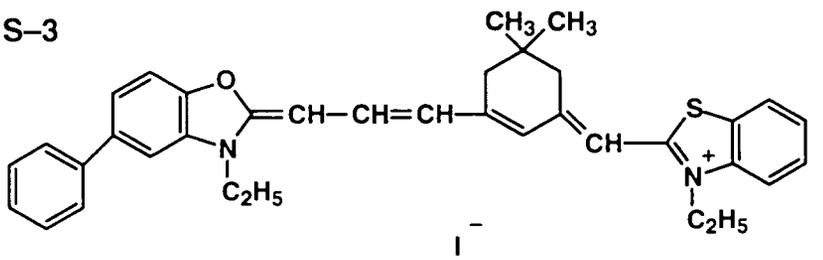
S–1



S–2



S–3



1st layer

[0276]

Gelatin	0.50 g
Phenylcarbamoyled gelatin	0.10 g
Polyvinylpyrrolidone (PVP)	0.10 g
Polyethyleneglycol (molecular weight 2000)	0.15 g
1-phenyl-4,4'-dimethyl-3-pyrazolidine	0.07 g
Sodium i-amyl-n-decylsulfosuccinate	0.05 g
Sodium dodecylbenzenesulfonate	0.02 g

(continued)

2-methylhydroquinone	0.70 g
AM	0.05 g

2nd layer (emulsion layer)

[0277]

Gelatin	0.90 g
Silver halide emulsion A	Silver amount 2.75 g equivalent
Hydrazine derivative H-7	0.12 g
Phenylcarbamoyled gelatin	0.30 g
Suspension polymer of 75 wt.% colloidal silica, 12.5 wt.% vinyl acetate and 12.5 wt.% vinyl pivalinate	1.0 g
Polymer latex L1 (particle diameter 0.10 μm)	0.5 g
Polyvinylpyrrolidone (PVP)	0.15 g
Surfactant (SU-1)	0.09 g
4-mercapto-3,5,6-fluorophthalic acid	0.05 g
Dye stuff (f-1)	0.05 g
Sodium polystyrenesulfonate (average molecular weight 500000)	0.015 g
Coating solution pH was 5.2.	

3rd layer (protective layer)

[0278]

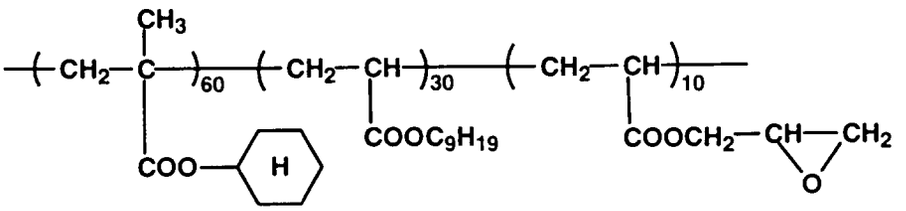
Gelatin	0.90 g
Polyvinylpyrrolidone (PVP)	0.05 g
Ammonium polyacrylate	0.25 g
Colloidal silica	0.20 g
Surfactant	0.02 g
Sodium dihexylsulfosuccinate	0.010 g
Bactericide Z	0.005 g
Hardener (1)	0.07 g
PMMA latex (particle diameter 3 μm)	0.01 g

Backing layer

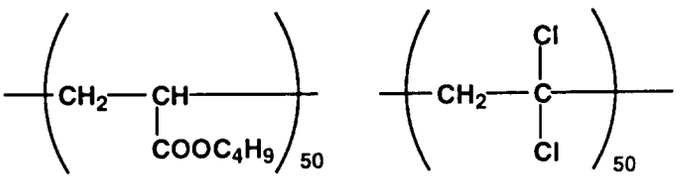
[0279]

Gelatin	3.0 g
Sodium hexylsulfosuccinate	0.020 g
Polymer latex (L3)	0.30 g
Colloidal solica (average particle diameter 0.05 μm)	0.50 g
Sodium polystyrenesulfonate	0.010 g
Carnaubawax dispersion composition	0.2 g
PEG4000 (polyethyleneglycol, molecular weight 4000)	0.2 g
Matting agent (monodispersed polymethylmethacrylate, average particle diameter 3 μm)	0.045 g
Hardener (1)	0.05 g
Hardener (2)	0.07 g

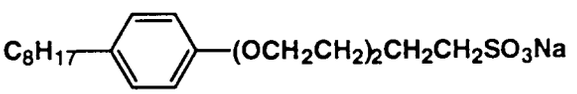
L1



L3

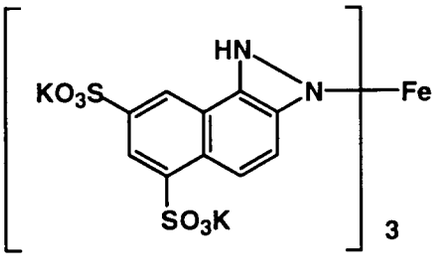


SU–1

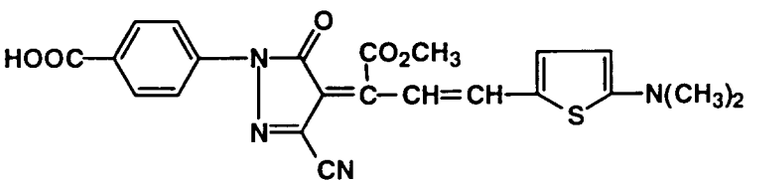


SU–2

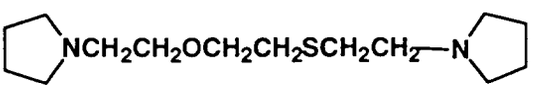
f-1


HN
KO3S
N
Fe
SO3K
3

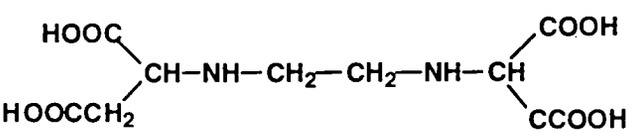
f-2


HOOC
O
N
CO2CH3
C
CH=CH
S
N(CH3)2
N
CN

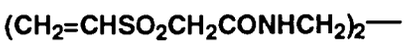
AM


NCH2CH2OCH2CH2SCH2CH2N

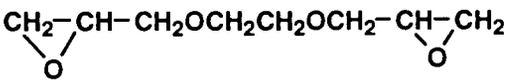
Ch


HOOC
COOH
CH-NH-CH2-CH2-NH-CH
HOOCCH2
CCOOH

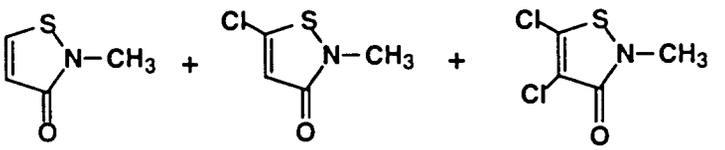
Hardener (1)



Hardener (2)



Bactericide Z



(Evaluation of the light-sensitive material)

[0280] Sample thus obtained was subjected to wedge exposure using semi-conductor laser of 780 nm, and then processed as follows using a monobath developer.

Monobath developer

[0281]

Pure water	200 ml
DTPA • 5Na	1.0 g
Sodium sulfite	20 g
KBr	4 g
Sodium carbonate	40 g
Diethyleneglycol	40 g
5-methylbenzotriazole	0.21 g
8-mercaptoadenine	0.07 g
1-phenyl-5-mercaptotetrazole	0.03 g
Developing agent	amount shown in Table 5
Sodium thiosulfonate	100 g

(continued)

Sodium thiocyanate	20 g
Fluoride-containing surfactant S-141 (produced by Asahi Glass Co., Ltd.)	0.5 g
KOH	18 g
Water was added to make 500 ml in total, and the pH of the working solution was adjusted to 11.0.	

(Processing process)

[0282] Developing was carried out using developing solution supplying portion and development apparatus shown in Fig. 1 and 2, thereafter washing and drying were carried out using the automatic processor for graphic art GR960 (produced by Konica Co., Ltd.).

[0283] Fig.1 is a outline of a cross-sectional view of developing process of automatic developing apparatus. In the developing process 1 of the automatic developing apparatus, a transferring track 3 which transfers the silver halide light-sensitive photographic material by plural transferring rollers 2 is formed, and this transferring track 3 is equipped horizontally. The silver halide photographic light-sensitive material is cut in sheet form before transferred into the developing process 1 and transferred by keeping the image forming side P1 upside. Along by the transferring track 3, a preheat portion 100, a coating portion 200 and squeeze portion 300 are equipped in this order in the transferring direction.

[0284] In the preheat portion 100, the transferring roller 2 is equipped on the transferring track 3, the heat roller 4 facing the transferring roller 2 is equipped under the transferring track 3. A heater 5 is incorporated in the heat roller 4 which comprises heat means giving heat required to process the silver halide photographic light-sensitive material. The silver halide light-sensitive photographic material P is heated by the heat roller 4 up to 35 to 90 °C, preferably 40 to 60 °C, thereby developing is accelerated.

[0285] In a coating portion 200, a processing solution supplying means equipped on the transferring track 3 possesses a solution supplying portion 8, and the roller 2 facing this solution supplying portion 8 is equipped under the transferring track 3. The axis direction of the solution supplying portion 8 is arranged along by the width direction of the silver halide photographic light-sensitive material. The solution supplying portion 8 is equipped at the hind part of the heating means in the transferring direction of the light-sensitive material. A supplying outlet 9 facing the image forming side P1 of the silver halide light-sensitive photographic material P along by the axis direction is formed in the solution supplying portion 8. From this supplying outlet 9, the processing solution was coated on the image forming side P1 of the silver halide light-sensitive photographic material P.

[0286] In a squeeze portion 300, squeeze rollers 12 facing each other are equipped on and under the transferring track 3. At least upside portion of roller which contacts with the image forming side P1 of the silver halide light-sensitive photographic material P is to be the squeeze roller, wherein underside portion is to be the transferring roller 2. The squeeze rollers 12 are equipped at the hind part of the solution supplying portion 8 in the transferring direction of the light-sensitive material, and squeeze the developing solution supplied on the silver halide photographic light-sensitive material P so that the developing solution is coated uniformly.

[0287] The squeeze roller 12 is preferably one which absorbs less water. Preferable ones are metal roller such as SUS, plastic roller, gum roller, woven fiber roller, non-woven fiber roller and sintered roller. As the metal roller, stainless steel (SUS316L, SUS316, SUS304, SUS303) titan (Ti) and brass (Bs) are preferred. As the plastic roller, polyethyleneterephthalate (PET), polyethylene (PE), tetrafluoroethylene • perfluoroalkoxyethylene copolymer (PFA), polyacetal (POM), polypropylene (PP), polytetrafluoroethylene (PTFE), polyvinylchloride (PVC), phenol resin (PF), modified polyphenyleneether (PPE), modified polyphenyleneoxide (PPO), polyurethane (PU), polycarbonate (PC), polyphenylenesulfide (PPS), polyfluorovinylidene (PVDF), tetrafluoroethylene • hexafluoropropylene copolymer (FEP) and tetrafluoroethylene • ethylene copolymer (ETFE) are preferable. As the gum roller, ethylenepropylene gum (EPDM, EPM), silicon gum (Si), nitryl gum (NBR) and chloroprene gum (CR) are preferable. As the material quality of the woven fiber roller and the non-woven fiber roller, polyolefin fiber, polyester fiber, polyacrylnitryl fiber, aliphaticpolyamide fiber, aromatic polyamide fiber and polyphenylenesulfide fiber etc. are preferable. A teflon-coated roller is more preferable.

[0288] Between the solution supplying portion 8 and the squeeze rollers 12, and at the hide portion of the squeeze rollers 12, there exist heating means 6, 7 which heat the silver halide photographic light-sensitive material P.

[0289] Next, a structure of solution supplying portion equipped at coating portion will be explained based on Fig. 2. An interval L1 between an extreme point 10 of a solution supplying outlet 9 formed in a solution supplying portion 8 and the silver halide photographic light-sensitive material P is set to be 0.03 mm to 10 mm. The processing solution supplied from the solution supplying portion 8 is coated uniformly on the image forming side P1 of the silver halide light-sensitive photographic material P in the way in which the processing solution is supplied in curtain-like flow.

[0290] If the interval L1 between an extreme point 10 of a solution supplying outlet 9 and the silver halide photographic light-sensitive material P is shorter than predetermined interval, because of the fluctuation of the thickness of the silver

halide photographic light-sensitive material P and swelling, the surface of the silver halide photographic light-sensitive material P is easily contact with the solution supplying portion 8, thereby transferring the silver halide photographic light-sensitive material P does not work well. On the other hand, if the interval L1 is larger than predetermined interval, bubble and coating non-uniformity occur easily. However, by setting the interval of 0.03 mm to 10 mm, these problems are solved.

[0291] The development was carried out as follows.

Temperature of heat roller (11)	50 °C
Time until supplying developing solution after contacting with heat roller	2 sec.
Interval between developing solution supplying outlet and light-sensitive material (L1)	3 mm
Slit width of developing solution supplying outlet (22)	0.10 mm
Time until washing after supplying developing solution	15 sec.
Temperature of supplying developing solution (for 5 sec. after coating developing solution)	35 °C
Before washing after 5 sec. passing after supplying developing solution	45 °C
Washing condition	20 °C/9 sec.
Drying condition	45 °C/15 sec.
Supplying amount: monobath developer	50 ml/m^2
Washing water	5 l/min.
Sensitivity, Dmax, Dmin	

[0292] Black density of thus developed samples was measured by PDA-65 (Degital densitometer, produced by Konica Co., Ltd.). The sensitivity was defined as a reciprocal of exposure necessary to give a black density of 1.0, wherein sample No. 101 gave black density of 1.0 with an given exposure and a reciprocal of this given exposure was assumed 100. Other sample's sensitivity is a relative value to the reciprocal of exposure of sample 101 (100).

γ (gamma)

[0293]

$$\gamma = (3\text{-}1)/[\log(\text{exposure to give D=3})\text{-}\log(\text{exposure to give D=1})]$$

Non-uniformity

[0294] Using image setter Doleve 800 (produced by Cytex Co., Ltd.), square dot of dot 50% 175 L by appropreate exposure was output and processed by foregoing process. Thus obtained image quality of developing non-uniformity was evaluated by visual observation. The highest dot quality without non-uniformity is evaluated as rank 5 and the lowest level available for actual use is evaluated as rank 3 by visual observation, therefore rank 2 and 1 are not available for actual use.

Table 5

Sample No.	Developing agent	Used amount per 500 ml	S	γ	Development unniformity
301	Soldium erythorbate	30 g	120	20	4
302	Hydroquinone Sodium erythorbate	20 g 10 g	100	20	4
303	Hydroquinone Sodium erythorbate	10 g 20 g	120	24	4

[0295] As can be seen in Table 6, in the coating development method, using developing solution containing the compound represented by Formula (A), less non-uniformity and higher γ can be obtained.

Example 4

Preparation of silver halide

[0296] (Preparation of silver halide emulsion B) To a solution C were simultaneously added a silver nitrate solution A and a halide solution B containing NaCl and KBr for 7 min. while keeping EAg 120 mV, pH at 3.0, at the temperature of 35 °C and 0.09 μm of silver halide nucleus comprising 70 mol% of silver chloride and 30 mol% of silver bromide was obtained. After then, making the EAg thus obtained solution 100 mV by NaCl, and to the solution were added a silver nitrate solution D and a halide solution E again for 15 min., thereafter 0.20 μm (variation coefficient of 15%) of silver halide emulsion comprising 70 mol% of silver chloride and 30 mol% of silver bromide was obtained. After then, the pH of the emulsion was raised to pH 5.6 by 1N-NaOH aqueous solution, and ripened at 50 °C for 10 min. Thereafter, adding modified gelatin treated with phenyl isocyanate, and washing blocked emulsion at pH 4.2, then to the resulting solution 15 g of gelatin per mol of silver was added and the pH of the solution was adjusted at pH 5.7 and thus obtained solution was dispersed for 30 min. at 55 °C. After dispersion, 4×10^{-4} mol of chloramine T per mol of silver was added. The pAg of thus obtained emulsion was 190 mV (40 °C).

A:	Silver nitrate	16 g
	Nitric acid (5%)	5.3 ml
	Ion-exchanged water	48 ml
B:	NaCl	3.8 g
	KBr	3.5 g
	Ossein gelatin	1.7 g
	Ion-exchanged water	48 ml
C:	NaCl	1.4 g
	Ossein gelatin	7 g
	Nitric acid (5%)	6.5 ml
	$K_2RhCl_5(H_2O)$	0.06 mg
	Ion-exchanged water	700 ml
D:	Silver nitrate	154 g
	Nitric acid (5%)	4.5 ml
	Ion-exchanged water	200 ml
E:	NaCl	37 g
	KBr	33 g
	Ossein gelatin	6 g
	$K_2RhCl_5(H_2O)$	0.04 mg
	Ion-exchanged water	200 ml

[0297] To the emulsion were added 1.5×10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 8.5×10^{-4} mol per mol of silver of potassium bromide, and adjusted to be pH 5.6 and EAg 123mv. To the resulting emulsion was added flower of sulfur (2×10^{-5} mol of sulfur atom) in a fine solid dispersion and 1.5×10^{-5} mol of chloroauric acid and the resulting emulsion was chemically ripened at 60 °C for 80 min. After the ripening, 2×10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 3×10^{-4} mol per mol of silver of 1-phenyl-5-mercaptotetrazole and 1.5×10^{-3} mol per mol of silver of potassium iodide was added. After the emulsion was cooled to 40 °C, to this emulsion was added sensitizing dyes S-1 in an amount of 2.0×10^{-4} mol per mol of silver.

(Preparation of silver halide emulsion C)

[0298] To a solution A were simultaneously added a silver nitrate solution B and a halide solution C containing NaCl and KBr for 15 min. with constant added amount of each solution B and C while keeping at pH 3.0, at the temperature of 35 °C. The resulting emulsion was proved to be an emulsion comprising cubic type silver halide grains having an average diameter of 0.09 μm (comprised of 70 mol% of silver chloride and 30 mol% of silver bromide). In the course of preparing emulsion, pAg was 160 mV before adding and 100 mV when the adding was finished. After then, the pH of the emulsion was raised to pH 5.6 by 1N-NaOH aqueous solution, and ripened at 50 °C for 10 min. Thereafter, by ultrafiltration unnecessary salts were removed, then to the resulting solution 15 g of gelatin per mol of silver was added and the pH of the solution was adjusted at pH 5.7 and thus obtained solution was dispersed for 30 min. at 55 °C. After dispersion, 4 x 10^{-4} mol of chloramine T per mol of silver was added. The pAg of thus obtained emulsion was 190 mV (40 °C).

A:	Ossein gelatin	25 g
	Nitric acid (5%)	6.5 ml
	Ion-exchanged water	700 ml
B:	Silver nitrate	170 g
	Nitric acid (5%)	4.5 ml
	Ion-exchanged water	200 ml
C:	NaCl	47.5 g
	KBr	51.3 g
	Ossein gelatin	6 g
	$K_3[RhCl_6]$	0.06 mg
	Ion-exchanged water	200 ml

[0299] To the emulsion were added 1.5 x 10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 8.5 x 10^{-4} mol per mol of silver of potassium bromide, and adjusted to be pH 5.6 and EAg 123mv. To the resulting emulsion was added flower of sulfur (2 x 10^{-5} mol of sulfur atom) in a fine solid dispersion and 1.5 x 10^{-5} mol of chloroauric acid were added and chemically ripened at 50 °C for 80 min. After the ripening, 2 x 10^{-3} mol per mol of silver of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 3 x 10^{-4} mol per mol of silver of 1-phenyl-5-mercaptotetrazole and 1.5 x 10^{-3} mol per mol of silver of potassium iodide were added. After the emulsion was cooled to 40 °C, to this emulsion was added hydrazine derivative H-6 in an amount of 3.5 x 10^{-3} mol.

[0300] Using thus obtained emulsion, on a subbed support were simultaneously coated [1st layer], [2nd layer], [3rd layer] and [4th layer] containing composition as shown below, so that each layer have a coating amount of composition per m^2 as shown below. After each layer being cooled and set, on a subbed support opposite to the emulsion layer was coated [backing layer] which was cooled and set at -1 °C, and then both side were simultaneously dried. Thus sample No. 401 was obtained.

1st layer (layer containing developing agent)

[0301]

Gelatin	0.50 g
Phenylcarbamoyled gelatin	0.10 g
Polyvinylpyrrolidone (PVP)	0.10 g
Polyethyleneglycol (molecular weight 2000)	0.15 g

(continued)

Sodium i-amyl-n-decylsulfosuccinate	0.05 g
Sodium dodecylbenzenesulfonate	0.02 g
Developing agent	amount shown in Table 5
AM	0.05 g
Dye stuff (f-2) in a solid dispersion (average particle diameter 90 nm)	0.05 g

2nd layer (emulsion layer)

[0302]

Gelatin	0.90 g
Silver halide emulsion B	Silver amount 0.30 g equivalent
Silver halide emulsion C	Silver amount 2.40 g equivalent
Hydrazine derivative H-7	0.020 g
Phenylcarbamoyled gelatin	0.30 g
Suspension polymer of 75 wt.% colloidal silica, 12.5 wt.% vinyl acetate and 12.5 wt.% vinyl pivalinate	1.0 g
Polymer latex L1 (particle diameter 0.10 μm)	0.5 g
Polyvinylpyrrolidone (PVP)	0.15 g
Surfactant (SU-1)	0.09 g
4-mercapto-3,5,6-fluorophthalic acid	0.05 g
Dye stuff (f-1)	0.02 g
Sodium polystyrenesulfonate (average molecular weight 500000)	0.015 g
Coating solution pH was 5.2.	

3rd layer (protective layer)

[0303]

Gelatin	0.70 g
Polyvinylpyrrolidone (PVP)	0.04 g
Polyacrylic acid	0.15 g
Colloidal silica	0.15 g
Bactericide Z	0.005 g
Hardener (1)	0.07 g
PMMA latex (particle diameter 3 μm)	0.01 g

4th layer (protective layer)

[0304]

Gelatin	0.20 g
Polyvinylpyrrolidone (PVP)	0.01 g
Polyacrylic acid	0.05 g
Colloidal silica	0.05 g
Dimethylsiloxane (average molecular weight 100000) dispersion (average particle diameter 0.2 μm)	0.03 g
Surfactant (SU-2)	0.01 g
Sodium hexylsulfosuccinate	0.005 g
Bactericide Z	0.001 g

Backing layer

[0305]

Gelatin	3.0 g
Sodium hexylsulfosuccinate	0.020 g
Polymer latex (L3)	0.30 g
Colloidal solica (average particle diameter 0.05 μm)	0.50 g
Sodium polystyrenesulfonate	0.010 g
Carnaubawax dispersion composition	0.2 g
PEG4000	0.2 g
Matting agent (monodispersed polymethylmethacrylate, average particle diameter 3 μm)	0.045 g
Hardener (1)	0.05 g
Hardener (2)	0.07 g

(Evaluation of the light-sensitive material)

[0306] Sample thus obtained was subjected to wedge exposure using He-Ne laser of 633 nm, and then processed using the developing solution and fixing solution prescribed in the following process 2, 3, then washed and dried.

Process 1

Developing solution

[0307]

Pure water	150 ml
Penta sodium diethylenetriaminepenta acetate	1.0 g

(continued)

Sodium sulfite	20 g
Potassium bromide	4 g
Potassium carbonate	40 g
Diethyleneglycol	20 g
5-Methybenzotriazole	0.21 g
1-Phenyl-5-mercaptotetrazole	0.03 g
1-Phenyl-4-hydroxy-4-methyl-3-pyrazolidone (Dimezone S)	0.85 g
Sodium erysorbate	30.0 g
Surfactant S-141 (fluoride-containing surfactant, produced by Asahi Glass Co., Ltd.)	0.5 g
Potassium hydroxide	18 g
Water was added to make the total volume 400 ml, and the pH was adjusted to 11.0.	

Fixing Solution

[0308]

Pure water	200 ml
Sodium thiosulfate	120 g
Sodium sulfite	20 g
Di sodium citrate	20 g
Surfactant S-141 (fluoride-containing surfactant, produced by Asahi Glass Co., Ltd.)	0.5 g
Water was added to make the total volume 400 ml, and the pH was adjusted to 5.3 by adding citric acid.	

Stabilizing solution

[0309]

Biodegradable chelating agent (Ch)	40 g
Potassium sulfite	35 g
Potassium carbonate	25 g
8-Mercaptoadenine	0.1 g
Sanbag-P (produced by Sanai Sekyu Co., Ltd)	20 g

[0310] Using a developing processor made on an experimental basis in Fig. 3, evaluation was carried out. In Fig. 3, the light-sensitive material P with the emulsion layer side upside passed the pathway indicated by an arrow and was developed, fixed, stabilized and dried. In Fig. 3, 13 is a driving roller which transfer the light-sensitive material, 14 is a preheat dram heating in advance, 15 is a dried wind blowing off outlet, 16 is a stabilizing solution puffing out nozzle, 17 is a developing solution puffing out nozzle, 18 is a fixing solution puffing out nozzle.

[0311] The solution puffing out nozzle of 17, 18 is illustrated in Fig. 4.

[0312] In Fig. 4, 24 is a piezo electricity element, 22 is a solution inlet pathway, 25 is a vibration panel, 23 is a chamber, 28 is an orifice channel, 27 is an orifice and 30 is a droplet.

[0313] Tieing up eight solution supplying portions in a bundle illustrated in Fig. 4 and moving these solution supplying

portions in the vertical direction to the light-sensitive material transferred, so that the overall surface of the light-sensitive material is supplied with the processing solution.

[0314] The used processing condition is as follows.

Temperature of heat dram	40 °C
Time until supplying the developing solution after contacting with heat dram	2 sec.
Interval between developing solution supplying portion and light-sensitive material	3 mm
Scanning speed of developing solution supplying portion	500 mm/sec.
Supplied amount of developing solution	40 ml/m^2
Time until fixation after supplying developing solution	10 sec.
Temperature until fixation after supplying developing solution	50 °C
Scanning speed of fixing solution supplying portion	500 mm/sec.
Supplied amount of fixing solution	40 ml/m^2
Time until washing after supplying fixing solution	10 sec.
Temperature until washing after supplying fixing solution	45 °C
Time of washing	4 sec.
Temperature of washing	40 °C
Time of drying	10 sec.
Temperature of drying	45 °C

Process 2

Developing solution A

[0315]

Pure water	120 ml
Penta sodium diethylenetriaminepenta acetate	1.0 g
Sodium sulfite	20 g
Potassium bromide	4 g
Diethyleneglycol	20 g
1-Phenyl-4-hydroxy-4-methyl-3-pyrazolidone (Dimezone S)	0.85 g
Sodium erysorbate	30.0 g
Surfactant S-141 (fluoride-containing surfactant, produced by Asahi Glass Co., Ltd.)	0.5 g
Water was added to make the total volume 200 ml, and the pH was adjusted to 6.3.	

Developing solution B

[0316]

Pure water	120 ml
Potassium carbonate	40 g
5-Methybenzotriazole	0.21 g
1-Phenyl-5-mercaptotetrazole	0.03 g
Potassium hydroxide	18 g
Water was added to make the total volume 200 ml, and the pH was adjusted to 11.8.	

[0317] The same fixing solution and stabilizing solution as used in process 1 were used.

Developing machine

[0318] The processing solution supplying portions were combined shown in Fig. 7. The same processing way was employed as process 1 except supplying the developing solution A from the portion represented by a and the developing solution B from the portion represented by b.

Replenished amount of the developing solution A	20 ml/m^2
Replenished amount of the fixing solution B	20 ml/m^2

Process 3

[0319] Using the same developing, fixing and stabilizing solution as used in process 2, the process 3 was carried out with the developing machine whose developing solution supplying portion illustrated in Fig. 3 was reformed as illustrated in Fig. 8. Process 3 was carried out in the same way as process 1 except supplying the developing solution A from the portion 5c and the developing solution B from the portion 5d.

[0320] 5c and 5d is each composed of five nozzles illustrated in Fig. 4 tied up in a bundle.

Replenished amount of the developing solution A	20 ml/m^2
Replenished amount of the developing solution B	20 ml/m^2
Supplying time of supplying the developing solution B after supplying the developing solution A	2 sec.
Time until supplying the fixing solution after supplying the developing solution B	10 sec.

Process 4

[0321] Using the same developing, fixing and stabilizing solution as used in process 3, the process 4 was carried out in the same way as process 1 except supplying the developing solution B from the portion 5c and the developing solution A from the portion 5d.

Replenished amount of the developing solution A	20 ml/m^2

(continued)

Replenished amount of the developing solution B	20 ml/m^2
Supplying time of supplying the developing solution A after supplying the developing solution B	2 sec.
Time until supplying the fixing solution after supplying the developing solution A	10 sec.

Sensitivity, gamma, development uniformity were evaluated in the same way as in example 1, and black spot was evaluated as follows.

[0322] Non-image portion of the processed light-sensitive material was observed under a 40-power magnifier for evaluating black spot. The highest quality without any black spot is evaluated as rank 5. The lowest level available for actual use is evaluated as rank 3 by visual observation under a 40-power magnifier. Obtained results were shown collectively in Table 6.

Table 6

Sample No.	Process	S	γ	Black Spot	Development unniformity
401	1	100	20	3	4
402	2	120	22	4	5
403	3	120	24	5	5
404	4	100	20	4	5

[0323] As can be seen from Table 6, dividing the developing solution into the developing agent represented general formula (A) containing solution and the alkaline solution, the development uniformity was improved. Especially, by supplying the alkaline solution after coating the developing agent represented general formula (A) containing solution, were obtained excellent sensitivity, γ (gamma), development uniformity.

Example 5

(Preparation of silver halide emulsion A_1)

[0324] Employing a double-jet method, silver bromochloride core grains having an average grain diameter of 0.09 μm composed of 70 mol% of silver chloride and silver bromide. When forming core grains, an aqueous solution of silver nitrate and a water-soluble halide solution were mixed simultaneously in the presence of $7x10^{-8}$ mol of $K_3Rh(NO)_4(H_2O)$ per mol of silver in completion of grain formation and $8x10^{-6}$ mol of K_3OsCl_6 added. While keeping 40 °C pH 3.0 silver potential (EAg) 165 mV. Then, this core grain was covered with a shell through a double-jet method wherein EAg was lowered to 125 mV by sodium chloride. In that case, $3x10^{-7}$ mol of K_2IrCl_6 and $9x10^{-8}$ mol of K_3RhCl_6 respectively per mol of silver were added to the halide solution. Further, silver iodide grains were further added, and an emulsion thus obtained proved to be one which was cube-shaped silver bromochloride (composed of 70 mol% of silver chloride, 0.2 mol% of silver iodide and silver bromide) of a core/shell monodispersed type (variation coefficient of 10%) having an average grain diameter of 0.15 μm. Then, the emulsion was desalted by modified gelatin described in Japanese Patent O.P.I. Publication No. 280139/1990 (e.g., exemplified compound G-8 on page (3) of No. 287 of Japanese Patent O.P.I. Publication No. 280139/1990 wherein an amino group in gelatin is substituted with phenylcarbamyl). EAg observed after the desalting was 190 mV at 50 °C.

[0325] To the emulsion thus obtained were added $8.5x10^{-4}$ mol of per mol of silver of potassium bromide and citric acid, and the emulsion was adjusted to a pH of 5.6 and EAg of 123 mV. After $1x10^{-3}$ mol of sodium p-toluenesulfonylchloroamide trihydrate (chloramine T) was added for reaction thereof, elemental sulfur (S_8) compound dispersed in the form of solid particles (Seishin Kigyo Co.: those dispersed to an average size of 0.5 μm by adding saponin by the use of PM-1200) and $1.5x10^{-5}$ mol of chloroauric acid were added to the emulsion to conduct chemical sensitization until the maximum sensitivity can be obtained at 55 °C.

[0326] Then, after the temperature was lowered to 40 °C, 2×10^{-3} mol of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene per mol of silver, 3×10^{-4} mol of 1-phenyl-5-mercaptotetrazole and $5x10^{-3}$ of potassium iodide were added, and the pH was adjusted to 5.1 by citric acid. After that, 100 mg of sensitizing dye d-1 was added.

(Preparation of silver halide emulsion B_1)

[0327] Silver halide emulsion B_1 was prepared in the same manner as in silver halide emulsion A_1, except that $6x10^{-8}$ of K_3RhCl_6 in the shell was used. When chemical sensitization was similarly applied to the emulsion B_1, its sensitivity is higher than that of the emulsion A_1 by 40%.

(Preparation of silver halide photographic light-sensitive material 1)

[0328] On a support was made simultaneous multi-layer coating wherein a gelatin-subbing layer having the following composition 1 was coated so as to have an amount of gelatin of 0.55 g/m^2, silver halide emulsion layer 1 having composition 2 was coated on the gelatin-subbing layer so as to have an amount of silver of 1.73 g/m^2 and an amount of gelatin of 0.66 g/m^2, silver halide emulsion layer 2 having composition 3 was coated on the silver halide emulsion layer 1 so as to have an amount of silver of 1.5 g/m^2 and an amount of gelatin of 0.65 g/m^2, and a protective layer coating solution having the following composition 4 was further coated so as to have an amount of gelatin of 1.3 g/m^2. A subbing layer on the side of the support opposite to aforesaid layer side was subjected to simultaneous multi-layer coating wherein a backing layer having the following composition 5 was coated so as to have an amount of gelatin of 2.3 g/m^2, and a backing protective layer having the following composition 6 was coated so as to have an amount of gelatin of 0.7 g/m^2.

Composition 1 (Gelatin-subbing layer composition)

[0329]

Gelatin	0.55 g/m^2
Saponin	56.5 mg/m^2
Dye AD-8 (in a solid dispersion)	10 mg/m^2
Dye SF (in a solid dispersion)	20 mg/m^2
Dye f1	65 mg/m^2
Dye f2	15 mg/m^2
Dye f3	100 mg/m^2
Sodium polystyrenesulfonate (average molecular weight 500000)	10 mg/m^2
Bacteriocide z	0.5 mg/m^2

Composition 2 (Silver halide emulsion layer 1 composition)

[0330]

Silver halide emulsion A_1	Silver amount 1.45 g/m^2 equivalent
Hydrazine derivative (exemplified compound H-15)	2 x 10^{-3} mol/Ag mol
Compound a	100 mg/m^2
2-pyrydinol	1 mg/m^2
Polymer latex L1 (grain diameter 0.25 μm)	0.25 g/m^2
Saponin	20 mg/m^2
2-mercapto-6-hydroxypurine	2 mg/m^2
2-mercaptopyrimidine	1 mg/m^2

(continued)

n-propyl gallate	25 mg/m^2
Ascorbic acid	20 mg/m^2
EDTA	25 mg/m^2
Sodium polystyrenesulfonic acid	15 mg/m^2
Coating solution pH was 5.2.	

Composition 3 (Silver halide emulsion layer 2 composition)

[0331]

Silver halide emulsion B_1	Silver amount 1.45 g/m^2 equivalent
Hydrazine derivative (exemplified compound H-15)	4 x 10^{-3} mol/Ag mol
Amino compound AM-1	7 mg/m^2
4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	4 x 10^{-3} mol/Ag mol
Saponin	20 mg/m^2
2-mercapto-6-hydroxypurine	1 mg/m^2
Nicotinicacidamide	1 mg/m^2
n-propyl gallate	25 mg/m^2
2-mercaptopyrimidine	1 mg/m^2
EDTA	50 mg/m^2
Dye f5	15 mg/m^2
Polymer latex L3	0.25 g/m^2
Colloidal silica (average grain diameter 0.05 μm)	150 mg/m^2
Reduced dextrin (weight average molecular weight 1000, 0.2% of reduced glucose composition)	0.3 g/m^2
Phthalated gelatin was used as gelatin, and coating solution pH was 4.8.	

Composition 4 (Emulsion-protective layer composition)

[0332]

Gelatin	1.0 g/m^2
Amino compound AM-1	14 mg/m^2
Matting agent: Spherical polymethylmethacrylate with average grain size of 2.8 μm	30 mg/m^2
Surfactant S1	20 mg/m^2
Lubricant W1	75 mg/m^2
Compound a	50 mg/m^2
Polymer latex L3 (grain size 0.10 μm)	0.25 g/m^2
Colloidal silica (average grain size 0.05 μm)	150 mg/m^2

(continued)

Hardener h2	150 mg/m^2
Sodium polystyrenesulfonate	10 mg/m^2
Bactericide z	0.5 mg/m^2

Composition 5 (Backing layer composition)

[0333]

Gelatin	0.5 g/m^2
Sodium iso-amyl-n-decyysulfosuccinate	5 mg/m^2
Polymer latex L4	0.4 g/m^2
Colloidal silica (average grain size 0.05 μm)	100 mg/m^2
Sodium polystyrenesulfonate	10 mg/m^2
1-phenyl-5-mercaptotetrazole	10 mg/m^2
Hardener h3	100 mg/m^2
Zinc hydroxide	50 mg/m^2
Compound D	10 mg/m^2
EDTA	50 mg/m^2

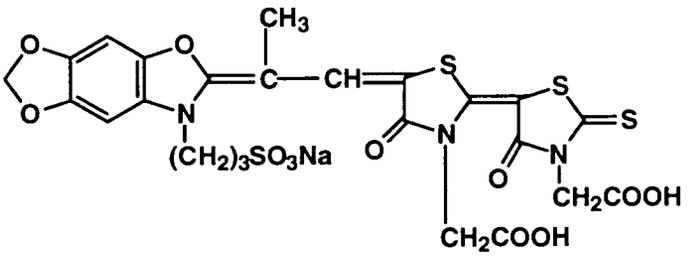
Composition 6 (Backing protective layer composition)

[0334]

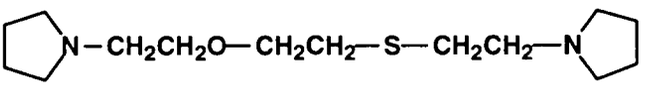
Gelatin	0.05 g/m^2
Matting agent: monodispersed polymethylmethacrylate with average grain size of 5 μm	400 mg/m^2
Polymer latex L4	1 g/m^2
Amorphous silica with average grain size of 3 μm	350 mg/m^2
Sodium-di-(2-ethylhexyl)-sulfosuccinate)	10 mg/m^2
Surfactant S1	18 mg/m^2
Compound a	50 mg/m^2
Hardener h1	20 mg/m^2
Sodium polytyrenesulfonate	10 mg/m^2

[0335] UV (ultra violet) density and visual density of the backing layer is each 0.09 and 0.06 respectively.

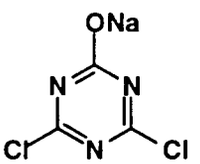
Sensitizing dye d-1



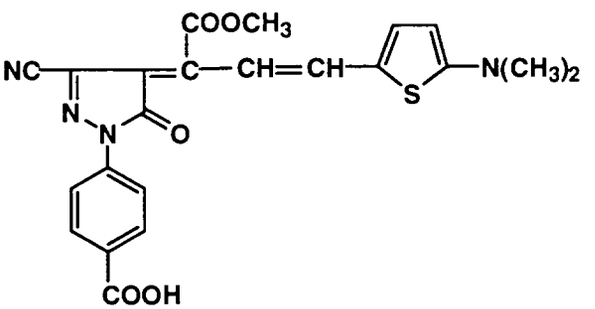
Amino compound AM-1



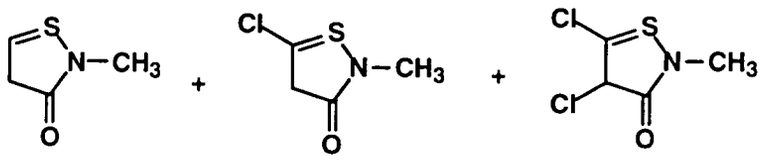
Hardener h1



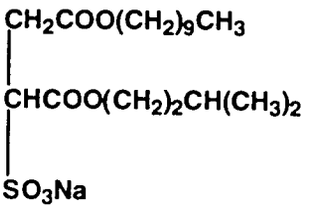
Dye AD-8



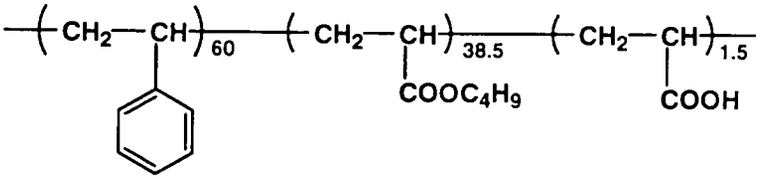
Bactericide Z



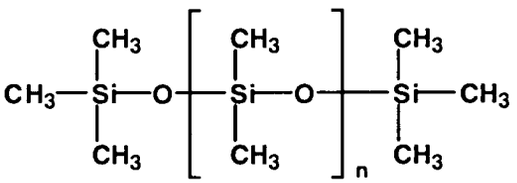
Compound a



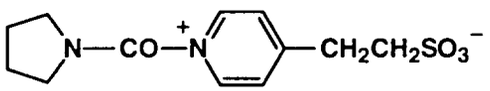
Polymer latex L1



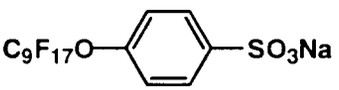
Lubricant W1



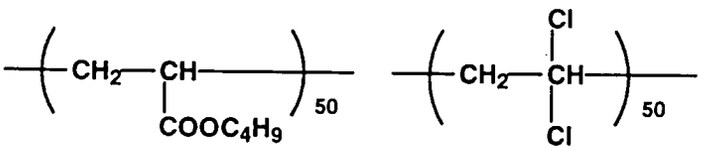
Hardener h2



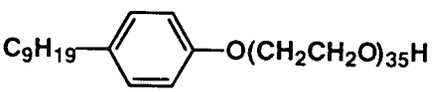
Surfactant S1



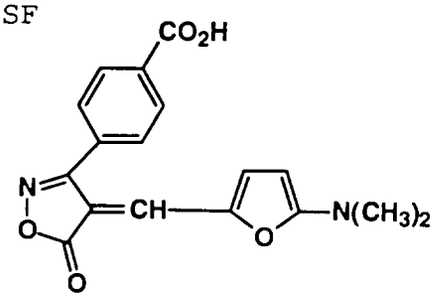
Polymer latex L4



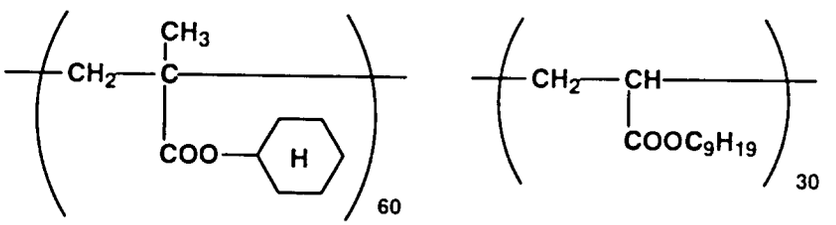
Compound D

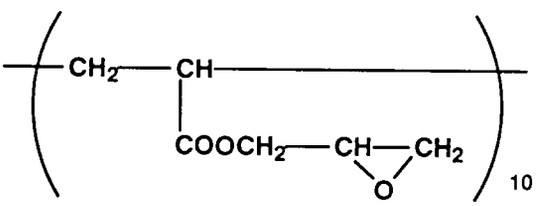


Dye SF

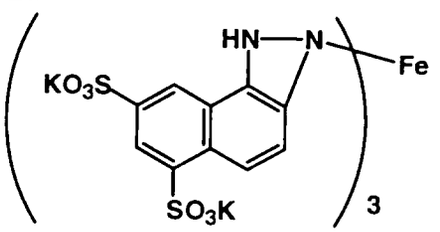


Polymer latex L3

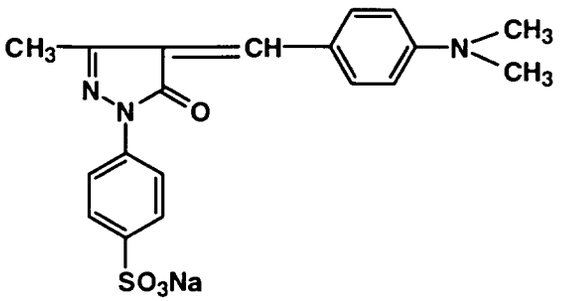




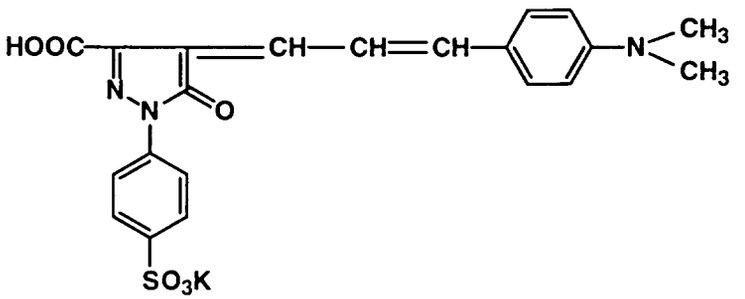
Dye 15



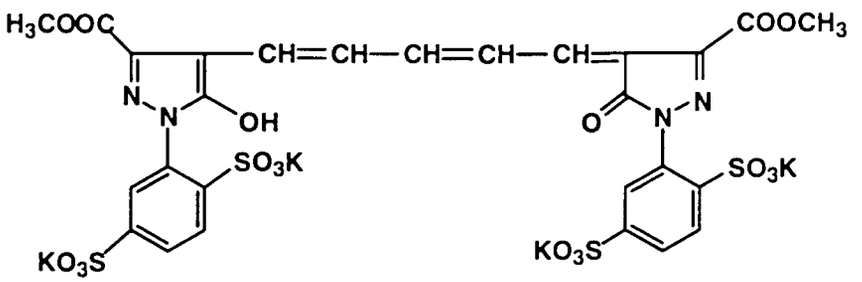
Dye f1



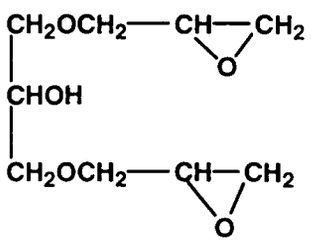
Dye f2



Dye f3



Hardener h3



Preparation of Light-sensitive material 1b

[0336] The light-sensitive material 1b was prepared in the same way in which the light-sensitive material 1 was prepared except adding dye f1, f2 and f3 in the backing layer each in an amount of 30, 120 and 150 mg/m^2 respectively. The UV density and the visual density of the backing layer is each 0.32 and 0.96 respectively.

(Preparation of developing solution A)

[0337] The developing solution A was prepared as follows.

Working solution of 1 liter

[0338]

Penta sodium diethylenetriaminepenta acetate	1.0 g
Sodium sulfite	42.5 g
Potassium sulfite	17.5 g
Potassium carbonate	55 g
Sodium erysorbate	5 g
Hydroquinone	20 g
1-Phenyl-4-hydroxymethyl-4-methyl-3-pyrazolidone (Dimezone S)	0.85 g
Potassium bromide	4 g
5-Methybenzotriazole	0.2 g
Boric acid	8 g
Diethyleneglycol	40 g
8-mercaptoadenine	0.3 g
Sodium thiosulfate	50 g
KOH was added so that the pH of the working solution was adjusted to 10.4.	

(Preparation of developing solution B)

[0339] Developing solution B was prepared in the same way in which the developing solution A was prepared except adding uracil in an amount of 0.5 g/l of the working solution.

(Preparation of developing solution C)

[0340] Developing solution C was prepared in the same way in which the developing solution A was prepared except removing sodium thiosulfate.

(Preparation of fixing solution)

[0341] The fixing solution was prepared as follows.

Working solution of 1 liter

[0342]

Ammonium thiosulfate (70% aqueous solution)	200 ml
Sodium sulfite	22 g
Boric acid	9.8 g
Sodium acetate • $3H_2O$	34 g

(continued)

Acetic acid (90% aqueous solution)	14.5 g
Tartaric acid	3.0 g
Aluminum sulfate (27% aqueous solution)	25 ml
Sulfuric acid was added so that the pH of the working solution was adjusted to 4.9.	

[0343] By changing an amount of light at 1.5 x 10^{-7} sec. step exposure was carried out using a laser sensitometer employing He-Ne laser beam of 633 nm as a light source.

[0344] Using a developing processor made on an experimental basis illustrated in Fig. 3, development was carried out. In Fig. 3, the light-sensitive material P with image forming side upside passed the pathway indicated by an arrow and was developed, fixed, washed and dried.

[0345] In Fig. 3, 12 is a squeeze roller, 13 is a transferring roller, 14 is a preheat dram heating in advance, 15 is a dried wind blowing off nozzle, 16 is a washing water puffing out nozzle, 17 is a developing solution puffing out nozzle, 18 is a fixing solution puffing out nozzle. 19, 20 is each a developing portion heater, 21 is a fixing portion heater where panel heaters to heat the light-sensitive material are used. The surface of each roller is coated with YS-3085 (produced by Toshiba Silicon Co., Ltd.) in a shickness of 300 μm.

[0346] Fig. 4 is an outline of a cross sectional view of the structure of the processing solution supplying apparatus.

[0347] The processing solution is introduced from a chamber 23 through a solution inflow pathway 22 of which flow area is narrowed down, thereafter a vibration panel 25 is changed by a driving element 24, thereby abrupt volume change in a chamber occurs. As a result, the processing solution is sprayed from an orifice 27. The orifice is composed of an orifice channel 28 and an orifice panel 29. A wall above the chamber 23 is composed of the vibration panel 25, and through the vibration panel 25, a change of the driving element 24 is conveyed. An upside of the chamber is preferably composed of the vibration panel 25 so that the driving element 24 and the processing solution do not contact directly. Material quality of the wall of the chamber is preferably composed of vinylidene chloride and the channel of the orifice is preferably also composed of vinylidene chloride. Material quality of the orifice panel is composed of nickel.

[0348] Fig. 5 is an outline of a plan view of the processing solution supplying apparatus of Fig. 4. A contacting angle of the processing solution on the orifice panel 29 is 20 degrees and the contacting angle of the processing solution on the wall of the chamber is 45 degrees.

[0349] Next, the composition of each of the vibration panel 25 and the driving element 24 will be explained. The vibration panel 25 is, for example, equipped to an exterior material 26 of the processing solution supplying means with epoxy resin stick. The vibration panel is composed of vinylidene chloride resin. The driving element is a piezo electricity element. The piezo electricity element vibrates up and down by stretching and shrinking horizontally, so that it gives the processing solution a pressure. The piezo electricity element is connected by lead lines 31, 32 with an electron pulse emission apparatus which can emit an external pulse voltage.

[0350] A droplet of the processing solution 30 is sprayed from the orifice 27. An extreme point of the orifice channel 28 is to be a fine diameter circle orifice 27 and the diameter of the droplet of the processing solution sprayed from the solution supplying means is controlled. At this time, a pressure of the processing portion is reduced, thereby the processing solution is inflowed from an external processing tank into the chamber 23 through the solution inflow pathway 22.

[0351] In this way, plus and minus voltage falls alternately on two pieces of the piezo electricity elements, so that the processing solution for the light-sensitive material is continuously supplied.

[0352] As a driving condition of the processing solution supplying means, a supplying head of serial type using piezo electricity elements is used. Number of orifice is 64 and zigzag pattern illustrated in Fig. 6 is used. A sprayed volume of the droplet at one time is to be 150 picoliter by adjusting driving voltage, and spraying frequency is set to be 7500 Hz.

[0353] Tying up eight solution supplying portions in a bundle illustrated in Fig. 4, 5 and moving these solution supplying portions in the vertical direction to the light-sensitive material transferred, so that the overall surface of the light-sensitive material is supplied with the processing solution.

[0354] The used processing condition is as follows. But a supplied amount of developing solution and, temperature and time of development, fixation, washing and drying are variable.

Temperature of heat roller (1)	40 °C
Time after contacting with heat roller until supplying developing solution	2 sec.

(continued)

Interval between developing solution supplying outlet and the light-sensitive material	3 mm
Scanning speed of developing solution supplying portion	500 mm/sec.
Scanning speed of fixing solution supplying portion	500 mm/sec.
Supplied amount of fixing solution	60 ml/m^2

Processing solution

[0355]

Process	Temperature (°C)	Time (sec.)
Development	38	15
Fixation	-	-
Washing	Ordinary temp.	15
Squeeze, drying	50	15

[0356] Under the above mentioned processing condition, samples Nos., 501 to 506 were obtained by processing in the way as described in Table 7. A coated amount of the developing solution is 60 ml per m^2 of the light-sensitive material.

(Evaluation of photographic characteristics)

[0357] Sensitivity, Dmax and Dmin of thus developed samples were measured by PDA-65 (Degital densitometer, produced by Konica Co., Ltd.). The sensitivity was defined as a reciprocal of exposure necessary to give a black density of 1.0, wherein sample No. 501 gave black density of 1.0 with an given exposure and a reciprocal of this given exposure was assumed to be 100. Other sample's sensitivity is a relative value to the reciprocal of exposure of sample 501 (100). Sharpness and fixability (clearness) were evaluated by visual observation. The lowest level available for actual use is evaluated as level 3 by visual observation. The highest quality without any problem in quality was evaluated as level 5, therefore level 2 and 1 were not available for actual use. After processing 20 m^2 of the light-sensitive material, deterioration of image caused by the running process was evaluated by processing line image shown in Table 8. The evaluation was done by visual observation and classified into 5 levels. Level 5 is the highest without any deterioration of image and level less than level 2 is not available for actual use.

[0358] Obtained results are shown in Fig. 8.

Table 7

Sample No.	Light-sensitive material	Developing solution	Fixation		Processing apparatus	Remarks
			Temperature (°C)	Time (Sec.)		
501	1	A	38	15	Inv.	Inv.
502	1	B	38	15	Inv.	Inv.
503	1	C	38	15	Inv.	Inv.
504	1	A	38	15	LD-T1080	Comp.
505	1	B	38	15	LD-T1080	Comp
506	1	C	38	15	LD-T1080	Comp.

Inv.;Invention
Comp.;Comparison
LD-T1080; Automatic developing processor produced by Dainihon Screen Co.,Ltd.

Table 8

Sample No.	S	Dmax	Dmin	Sharpness (Definition)	Fixability (Clearness)	Running resistance	Remarks
501	100	4.41	0.01	4	5	5	Inv.
502	98	4.30	0.01	4	5	5	Inv.
503	105	4.92	0.02	4	5	5	Inv.
504	100	3.90	0.01	4	5	1	Comp.
505	98	3.61	0.01	4	5	1	Comp.
506	104	4.91	0.02	4	5	1	Comp.

[0359] As can be seen in Table 8, according to the image forming method of the invention, the sharp black-white image with an excellent discrimination was obtained in a very short time.

Example 6

(Preparation of silver halide photographic light-sensitive material 2)

[0360] The silver halide photographic light-sensitive material 2 was prepared in the same way as in example 5 except an each amount of silver of silver halide emulsion A_1 and B_1 of silver halide emulsion 1 and 2 to be 1.6 g/m^2 in example 5.

(Preparation of silver halide photographic light-sensitive material 3)

[0361] The silver halide photographic light-sensitive material 3 was prepared in the same way as in Example 5 except an each amount of silver of silver halide emulsion A_1 and B_1 of silver halide emulsion 1 and 2 to be 1.85 g/m^2 in example 5.

Processing condition

[0362] An coated amount of the developing solution is shown in Table 9.

Process	Temperature (°C)	Time (sec.)
Development	38	15
Washing	Ordinary temp.	15
Squeeze, drying	50	15

[0363] Under the above mentioned processing condition, samples Nos., 601 to 612 were obtained by using the developing solution B and processing in the way as described in Table 9. Thus obtained samples were evaluated in the same way as in Example 5. The obtained results were shown in table 10.

Table 9

Sample No.	Light-sensitive material	Coated amount of developing solution (ml/m^2)
601	1	180

Table 9 (continued)

Sample No.	Light-sensitive material	Coated amount of developing solution (ml/m^2)
602	2	180
603	3	180
604	1	120
605	2	120
606	3	120
607	1	90
608	2	90
609	3	90
610	1	60
611	2	60
612	3	60

Table 10

Sample No.	S	Dmax	Dmin	Sharpness (Definition)	Fixability (Clearness)	Apparatus stain by dripping solution	Remarks
601	100	4.5	0.02	4	5	Stain is observed	Inv.
602	102	4.9	0.03	4	5	Stain is observed	Inv.
603	104	5.6	0.05	4	4	Stain is observed	Inv.
604	100	4.4	0.02	4	5	Stain is observed sometimes	Inv.
605	102	4.8	0.03	4	5	Stain is observed sometimes	Inv.
606	103	5.6	0.05	4	4	Stain is observed sometimes	Inv.
607	98	4.4	0.02	4	4	Stain is not observed	Inv.
608	100	4.7	0.04	4	4	Stain is not observed	Inv.
609	102	5.5	0.06	4	4	Stain is not observed	Inv.
610	98	4.3	0.02	4	4	Stain is not observed	Inv.
611	101	4.7	0.04	4	4	Stain is not observed	Inv.
612	103	5.5	0.06	4	3	Stain is not observed	Inv.

Inv.; Invention

[0364] As can be seen in Table 10, according to the image forming method of the invention, the sharp black-white

image with an excellent discrimination was obtained in a very short time.

Example 7

(Preparation of silver halide photographic light-sensitive material 4)

[0365] The silver halide photographic light-sensitive material 4 was prepared in the same way as in example 5 except an each amount of gelatin and polymer latex L 4 of the backing layer to be 0.6 g/m^2 and 0.4 g/m^2 respectively in example 5. An absorbing amount of water of the backing layer was 3.5 g/m^2.

Processing condition

[0366]

Process	Temperature (°C)	Time (sec.)
Immersion in water	shown in Table 11	
Development	shown in Table 11	
Washing	Ordinary temp.	15
Squeeze, drying	50	15

[0367] Under the above mentioned processing condition, samples Nos., 701 to 704 were obtained by using the developing solution B and processing in the way as described in Table 11. Thus obtained samples were evaluated in the same way as in example 5. The obtained results were shown in table 12.

Table 11

Sample No.	Light-sensitive material	Temperature of water immersion (°C)	Time of water immersion (sec.)
701	1	35	2
702	4	35	2
703	1	No water immersion	-
704	4	No water immersion	-

Table 12

Sample No.	S	Dmax	Dmin	Sharpness (Definition)	Fixability (Clearness)	Drying ability	Remarks
701	99	4.4	0.01	4	5	Good	Invention
702	99	4.4	0.01	4	5	Not good	Invention
703	98	4.3	0.02	4	4	Good	Invention
704	98	4.3	0.02	4	4	Not good	Invention

[0368] As can be seen in Table 12, according to the image forming method of the invention, the sharp black-white image with an excellent discrimination was obtained in a very short time.

Example 8

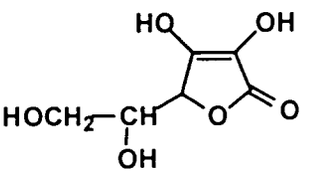
(Preparation of developing solution D)

Preparation of granule A (1 liter equivalent)

[0369]

Sodium sulfite	23 g
Sodium carbonate	12 g
1-Phenyl-4-hydroxymethyl-4-methyl-3-pyrazolidone (Dimezone S)	0.7 g
Potassium bromide	5 g
Penta sodium diethylenetriaminepenta acetate	3 g
Benzotriazole	0.26 g
Hydroquinone	10 g
Mannitol	10 g
Compound A	70 g

Formula A



[0370] Above mentioned raw materials were mixed and pulverized for 3 min. in a stirring granulator which is available in the market. 5% of water of total weight was gradually added to the obtained mixture, thereafter thus obtained granulated composition was transferred to a fluidized layer dryer and dried for 2 hours by supplying warm air of 60 °C. Thus obtained granule was dressed with 5 mm mesh in a granulation dresser which is available in the market.

Preparation of granule B (1 liter equivalent)

[0371]

Sodium sulfite	20 g
Sodium carbonate	10 g
Sodium thiosulfate	58 g
Sodium acetate	15 g
Mannitol	10 g
Powdery sorbitol	5 g

(continued)

Uracil	0.5 g

[0372] Above mentioned raw materials were mixed and pulverized for 3 min. in a stirring granulator which is available in the market. 5% of water of total weight was gradually added to the obtained mixture, thereafter thus obtained granulated composition was transferred to a fluidized layer dryer and dried for 2 hours by supplying warm air of 60 °C. Thus obtained granule was dressed with 5 mm mesh in a granulation dresser which is available in the market.

[0373] Each of 5 liter equivalent of the granule A and B was put in a fluidized granulator GPCG-5 type (produced by Powlex CO., Ltd.) and fluidized by supplying warm air of airflow of 8 m^3/min. at 60 °C.

[0374] By spraying 20 g of 30% sorbitol aqueous solution per 1 liter equivalent of each of the granule A and B by two-streamed spray on the surface of each of the granule A and B, the surface of each of the granule A and B was coated. Thus coated granule was each called a and b respectively.

[0375] 15 liter equivalent of each a and b of two kinds of granules obtained above was prepared. a, b and 2 wt.% sodium 1-octanesulfonate of total weight of a plus b were added and mixed for 10 min. in a cross rotary mixer. The mixture was tabletted in an amount of 10 g with diameter of 30 mm per piece at a tabletting pressure of 1 ton/cm^2 by an oil press.

[0376] Using of 35 liter equivalent of thus obtained solid processing composition, developing solution D was prepared.

Processing

[0377]

Process	Temperature (°C)	Time (sec.)
Development	shown in table 13	15
Washing	Ordinary temp.	15
Squeeze, drying	50	15

[0378] Under the above mentioned processing condition, samples Nos., 801 to 804 were obtained by using the light-sensitive material 1 and processed as described in Table 13. Thus obtained samples were evaluated in the same way as in example 5. The obtained results were shown in table 14.

Table 13

Sample No.	Developing Solution	Development (Temperature, time after coated)			
		Until 3 sec.	Until 6 sec.	Until 9 sec.	Until 15 sec.
801	B	36°C	38°C	41°C	42°C
802	D	36°C	38°C	41°C	42°C
803	B	38°C	38°C	38°C	38°C
804	D	38°C	38°C	38°C	38°C

Table 14

Sample No.	S	Dmax	Dmin	Sharpness (Definition)	Fixability (Clearness)	Remarks
801	101	4.5	0.01	4	5	Invention
802	101	4.5	0.02	4	5	Invention
803	98	4.3	0.02	4	4	Invention

Table 14 (continued)

Sample No.	S	Dmax	Dmin	Sharpness (Definition)	Fixability (Clearness)	Remarks
804	98	4.3	0.02	4	4	Invention

[0379] As can be seen in Table 14, according to the image forming method of the invention, the sharp black-white image with an excellent discrimination was obtained in a very short time and the same result was obtained by using the solid processing composition.

[0380] Disclosed embodiment can be varied by a skilled person without departing from the spirit and scope of the invention.

Claims

1. A method for processing a silver halide photographic light-sensitive material with a processing solution, wherein said processing solution is supplied on a surface of said silver halide photographic light-sensitive material which is transferred in a gaseous phase to be processed and said silver halide photographic light-sensitive material comprises a support having a first surface and a second surface opposite to said first surface, component layers including a silver halide emulsion layer and hydrophilic colloidal layer which are coated on the same side as said first surface of said support, wherein said silver halide emulsion layer contains a light-sensitive silver halide and at least one of said component layers contains an organic contrast accelerating agent.

2. In a method for processing of claim 1, said silver halide photographic light-sensitive material forms an image of which gamma is from 10 to 100 by said processing.

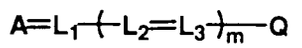
3. In a method for processing of claim 1, said processing solution is supplied by spraying through a gaseous phase on said silver halide photographic light-sensitive material which is transferred in said gaseous phase.

4. In a method for processing of claim 1, said silver halide emulsion layer of said silver halide photographic light-sensitive material contains transition metal of VI to X groups in a periodic table.

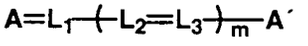
5. In a method for processing of claim 1, said organic contrast accelerating agent is a hydrazine derivative or a 5,6-membered nitrogen containing heterocyclic derivative or a tetrazolium salt.

6. In a method for processing of claim 1, at least one of said component layers contains the compound represented by the following formulae (1) - (6),

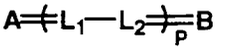
Formula (1)



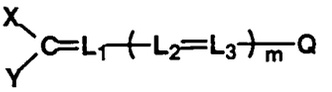
Formula (2)



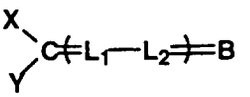
Formula (3)



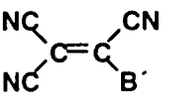
Formula (4)



Formula (5)



Formula (6)



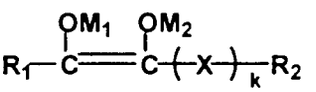
(In the formulae (1) - (6), A and A' may be either the same with or different from each other, and each of them represents an acidic nucleus, B represents a basic nucleus, Q represents an aryl group or a heterocyclic group, B' represents a heterocyclic group, X and Y may be either the same with or different from each other and each of them represents an electron withdrawing group, and each of L_1, L_2 and L_3 represents a methine group, m represents 0 or 1, n represents 0, 1 or 2, p represents 0 or 1.)

7. In a method for processing of claim 1, said silver halide photographic light-sensitive material contains a developing agent of 0.3 to 5.0 g/m^2.

8. In a method for processing of claim 1, said silver halide photographic light-sensitive material contains a developing agent of which amount can make not less than 15% of silver halide in said silver halide photographic light-sensitive material developable.

9. In a method for processing of claim 1, said processing solution is a processing solution for development, wherein said developing solution contains the compound represented by the following formula (A),

Formula (A)



(In the formula (A), R_1 and R_2 each independently represents a substituted or an unsubstituted alkyl group, a substituted or an unsubstituted amino group, a substituted or an unsubstituted alkoxy group, and a substituted or an unsubstituted alkylthio group, and R_1 and R_2 may be linked with together to form ring, k is 0 or 1, and X is -CO- or -CS- when k is 1, and M_1 and M_2 are each a hydrogen atom or an alkali metal atom.)

10. In a method for processing of claim 9, a processing solution containing the compound represented by the formula (A) and an alkaline aqueous solution of which pH is not less than 9 were supplied on the surface of said silver halide photographic light-sensitive material which is transferred in said gaseous phase.

11. In a method for processing of claim 10, a processing solution containing the compound represented by the formula (A) is supplied on the surface of said silver halide photographic light-sensitive material which is transferred in said gaseous phase, thereafter said alkaline aqueous solution is supplied on the surface of said silver halide photo-

graphic light-sensitive material.

12. In a method for processing of claim 1, ultra violet density of all layers coated on said second surface side of said support of said silver halide photographic light-sensitive material is not more than 0.3 and visual density of said all layers is not more than 0.3.

13. In a method for processing of claim 12, said processing solution is a processing solution for development, wherein said processing solution for development contains at least one silver halide solvent of which amount is not less than a mol of developing agent.

14. In a method for processing of claim 13, at least one of said silver halide solvent is an organic fixing agent.

15. In a method for processing of claim 12, said processing solution is a processing solution for development, wherein said processing solution for development consists of only one kind of solution.

16. In a method for processing of claim 12, said processing solution is a processing solution for development, wherein spraying said processing solution for development through a gaseous phase to supply said processing solution for development on the surface of said silver halide photographic light-sensitive material which is transferred in a gaseous phase, and supplied amount of said processing solution for development is 10 to 150 ml per 1 m^2 of said silver halide photographic light-sensitive material.

17. In a method for processing of claim 12, an amount of silver contained in said silver halide photographic light-sensitive material is 0.3 to 3.4 g per 1 m^2 of said silver halide photographic light-sensitive material.

18. In a method for processing of claim 12, an amount of absorbed water of all layers coated on said second surface side of said support of said silver halide photographic light-sensitive material is not more than 2 g/m^2.

19. In a method for processing of claim 12, said processing solution is a processing solution for development, wherein water is supplied to said silver halide photographic light-sensitive material before said processing solution for development is supplied to said silver halide photographic light-sensitive material.

20. In a method for processing of claim 12, said silver halide photographic light-sensitive material is carried with a carrier comprised of a gum containing layer before supplying said processing solution for development.

21. In a method for processing of claim 1, the temperature of said silver halide photographic light-sensitive material is 25 to 50 °C when processing it with said processing solution.

22. In a method for processing of claim 1, after beginning of the processing said silver halide photographic light-sensitive material, the temperature of said silver halide photographic light-sensitive material before 30% of total processing time is not more than 40 °C, and the temperature of said silver halide photographic light-sensitive material after 70% of total processing time is not less than 40 °C.

23. In a method for processing of claim 1, said silver halide photographic light-sensitive material is exposed imagewise by laser beam.

24. In a method for processing of claim 1, said silver halide photographic light-sensitive material is exposed imagewise by a light of which wave length is 600 to 850 nm.

25. In a method for processing of claim 1, said processing solution is provided by dissolving a solid processing composition.

26. In a method for processing of claim 1, said processing solution contains developing agent.

FIG. 1

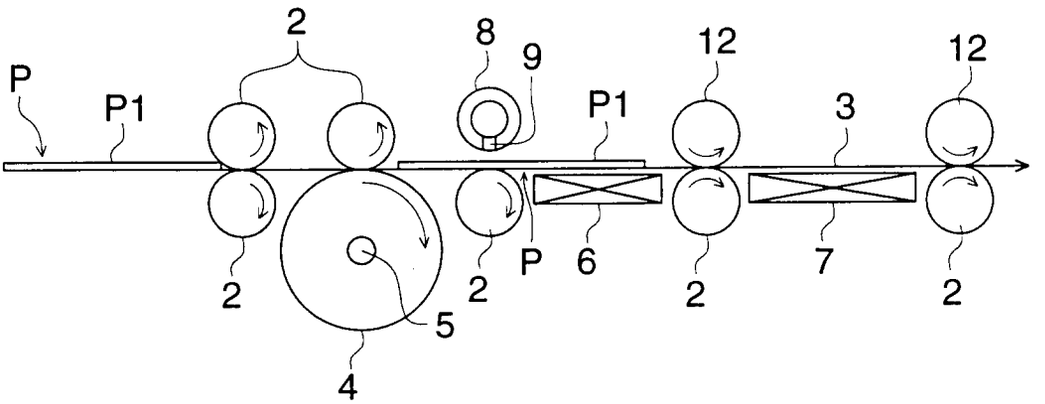


FIG. 2

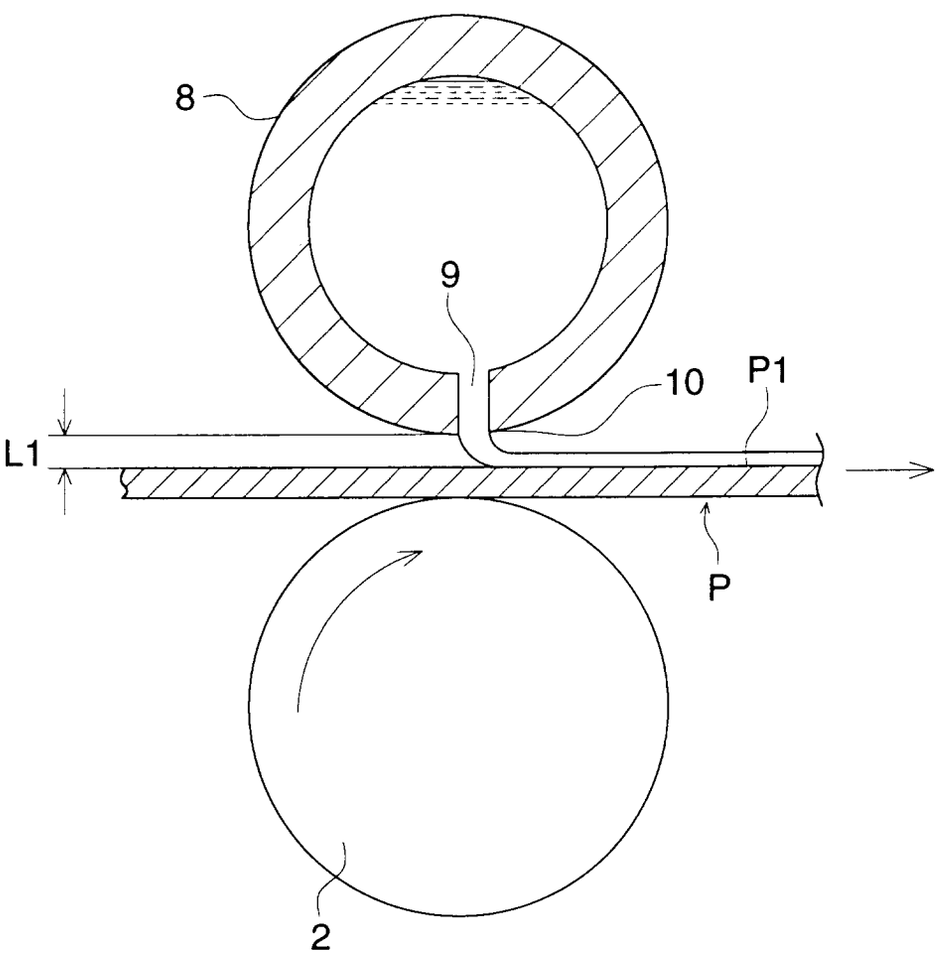


FIG. 3

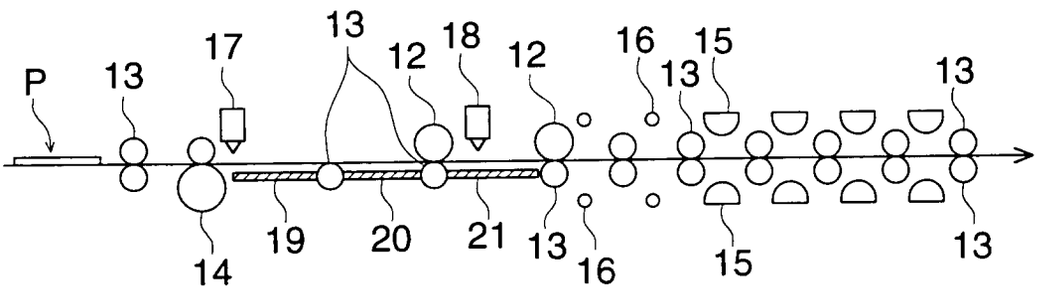

P
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FIG. 4

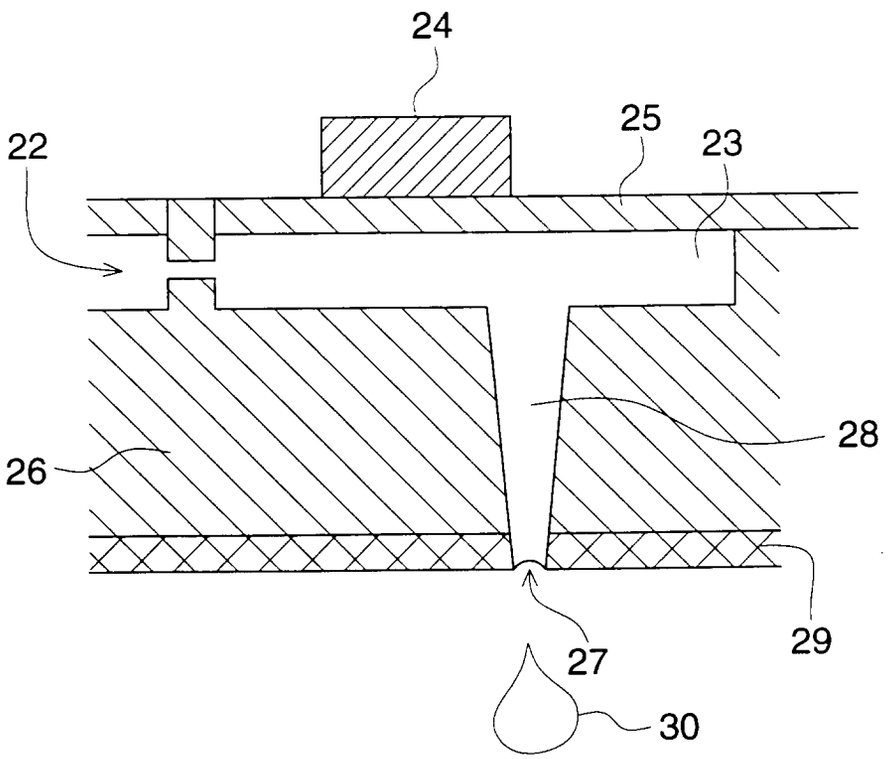
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FIG. 5

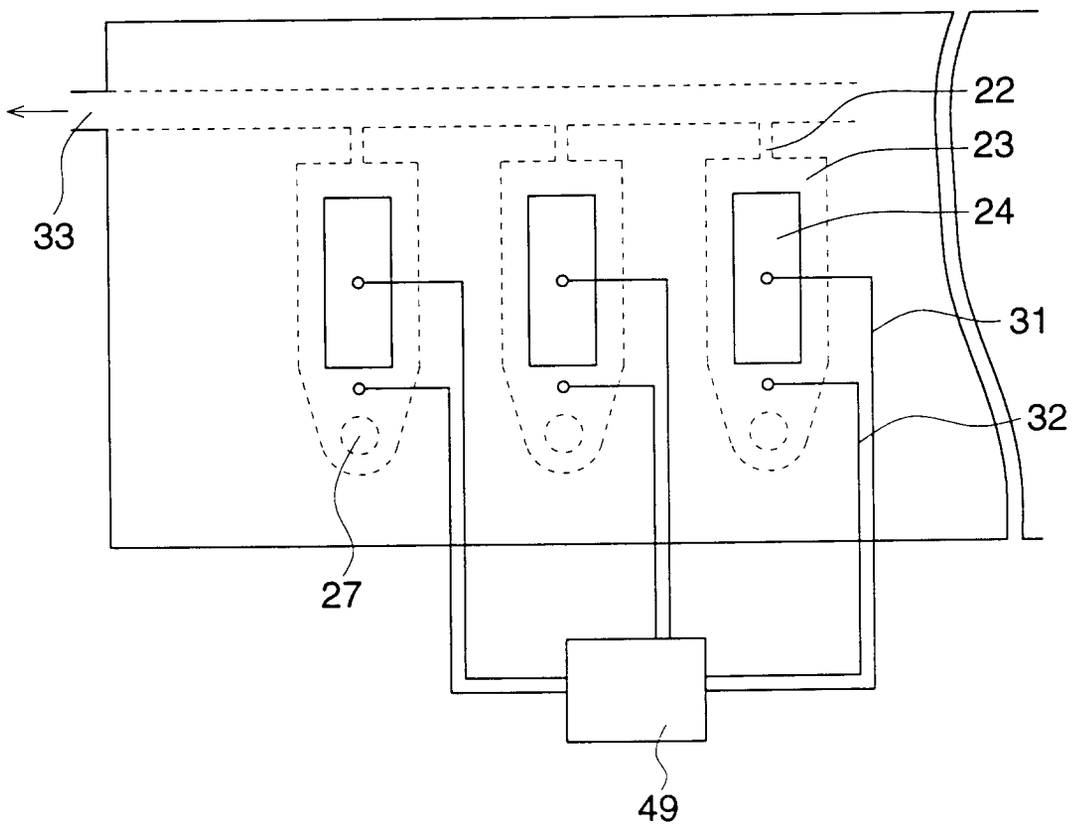


FIG. 6

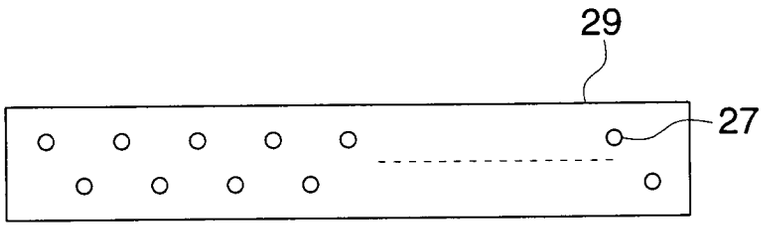


FIG. 7

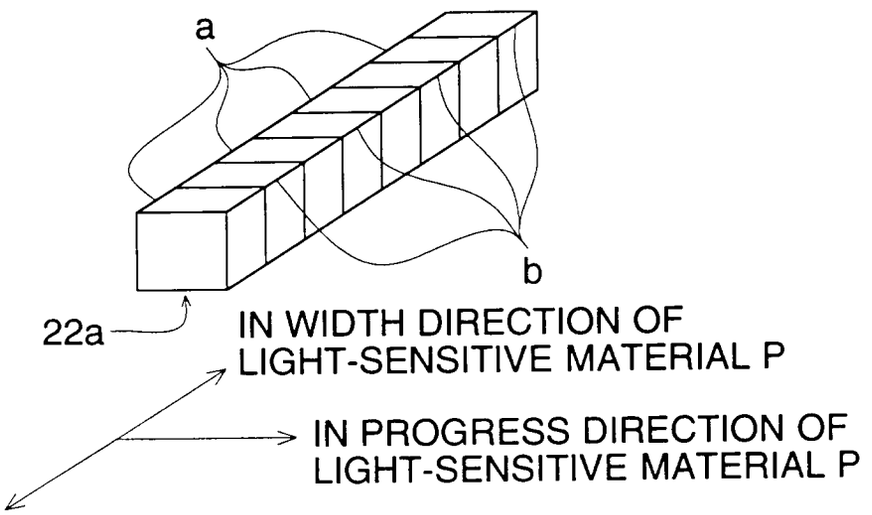
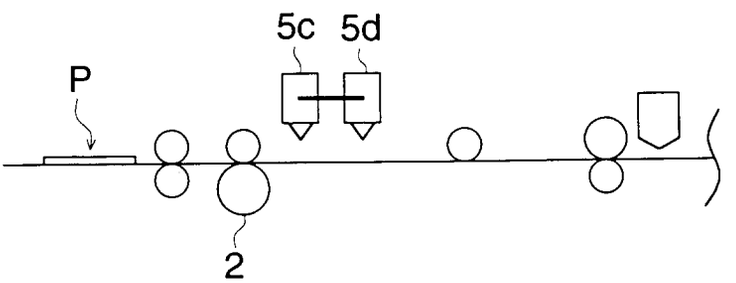

a
b
22a
IN WIDTH DIRECTION OF
LIGHT-SENSITIVE MATERIAL P
IN PROGRESS DIRECTION OF
LIGHT-SENSITIVE MATERIAL P

FIG. 8


5c
5d
P
2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 0370

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	GB 1 281 696 A (DOUGLAS JOHNSON) 12 July 1972 * page 1, line 50 - line 70; claims 1-11; figure 1 *	1,3	G03C5/26 G03C1/06 G03C5/29
A	US 2 178 896 A (G N PIFER) 7 November 1939 * page 1, left-hand column, line 1 - line 10; claim 2; figure 1 *	1,3	
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 369 (P-1090) '4312!, 9 August 1990 & JP 02 136850 A (KONICA CORPORATION), 25 May 1990 * abstract *	1,3	
A	R S POMEROY ET AL: "Liquid-sealed gas processing apparatus" RESEARCH DISCLOSURE., no. 122, June 1974, page 16 XP002103259 HAVANT GB * the whole document *	1,3	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C
D,A	DATABASE WPI Section PQ, Week 9723 Derwent Publications Ltd., London, GB; Class P83, AN 97-249438 XP002103280 & JP 09 080720 A (KONICA CORP) , 28 March 1997 * abstract *	1,3	
P,A	EP 0 831 367 A (EASTMAN KODAK CO) 25 March 1998 * claim 1; figure 1 *	1,2,5,7, 8	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 May 1999	Bolger, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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25-05-1999

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