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D-80538 München (DE)(54) **Silver halide photographic material and method for processing the same.**

(57) A silver halide photographic material comprising a support having thereon at least one silver halide emulsion layer, wherein the emulsion of the silver halide emulsion layer comprises a silver halide having a silver chloride content of 90 mol% or more containing a transition metal of 1×10^{-6} mol or more per mol of silver; the material has a layer containing a dye subjected to a fine crystalline solid dispersion between the silver halide emulsion layer and the support; the material has an interlayer comprising a hydrophilic colloid and an uppermost layer comprising a hydrophilic colloid and solid grains having a mean grain size of from 1 to 5 μm , above the emulsion layer; and the thickness of the interlayer is at least 0.8 times the thickness of the uppermost layer.

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FIELD OF THE INVENTION

The present invention relates to a silver halide photographic material favorably processable in a so-called "dot-to-dot work" step in a photomechanical process and, more precisely, to a silver halide photographic material having improved photographic properties for daylight dot-to-dot work processing.

BACKGROUND OF THE INVENTION

In the field of printing and duplicating technology, improvements in the processability of photographic materials in the photomechanical process or processing them have been desired for the purpose of satisfactorily dealing with diversified and complicated print forms in these days.

In particular, the efficiency of processing such photographic materials has been planned to be improved by conducting assembly processes and dot-to-dot working operations in the process in lighter environments. For this, developments in silver halide photographic materials for photomechanical process that may be handled in environments substantially comparable to illuminated rooms and also developments in exposure printers have been promoted.

Silver halide photographic materials for illuminated rooms as referred to herein mean photographic materials to which a light having a wavelength of 400 nm or more and containing no ultraviolet light components is applicable as a safelight.

Recently, global interests in environmental problems are increasing, greatly requiring the reduction in the amounts of replenishers to developers and fixers to be used in the systems of processing photographic materials. As one means for reducing the amount of such replenishers, there is known a method of reducing the amount of silver to be coated in the photographic materials, which, however, causes a problem of lowering the maximum density (Dmax) in the processed photographic materials. To obtain a high Dmax, while using a small amount of silver in preparing the photographic materials, there is known a method of reducing the grain size of the grains in photographic silver halide emulsions to thereby increase the covering power of the photographic materials having such emulsions. Since high-silver chloride emulsions for dot-to-dot-working photographic materials for illuminated rooms are not needed to have a high sensitivity, various studies for planning fine silver halide grains for these materials have heretofore been made. For instance, emulsions of fine silver chloride grains are disclosed in JP-A-63-183438 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-63-296034, JP-A-63-306436, JP-A-1-108123 and U.S. Patent 4,659,647.

Photographic emulsions of fine grains are advantageous in increasing their Dmax and also in saving silver in them, but the problem that their tone reproducibility was noticeably worsened when they are subjected to so-called dry-dot work (by over-exposure so as to thicken dots to a desired dot %) which is intrinsic in the dot-to-dot working field has been generated. This is because the transmitted light causes halation in the emulsions. In order to solve the problem, there is known a method of increasing the amount of backing dyes to be incorporated into the photographic materials. However, if backing dyes are added to the photographic materials to such a degree that the added dyes may solve the problem, they cause other problems in that they give many stains in the photographic materials processed by rapid processing and they noticeably lower the lateral reversal sensitivity of the photographic materials. As another method, there is also known a method of introducing an anti-halation (AH) layer having therein fixed dyes into the photographic materials.

To fix dyes in an AH layer, for example, there is known a conventional method of localizing an acidic dye having therein a sulfo group or a carboxyl group in a specific layer with a mordant agent. As the mordant agent for this purpose, there are known polymers of ethylenic unsaturated compounds having a dialkylaminoalkyl ester residue, such as those described in British Patent 685,475; products formed by reacting a polyvinyl alkyl ketone and an aminoguanidine, such as those described in British Patent 850,281; vinyl-pyridine polymers and vinyl-pyridinium cationic polymers, such as those described in U.S. Patents 2,548,564, 2,484,430, 3,148,061 and 3,756,814. These are cationic polymer mordants containing secondary or tertiary amino groups, nitrogen-containing heterocyclic groups or their quaternary cationic groups in their polymer structures so as to effectively mordant the above-mentioned acidic dyes.

When these mordants are used, the mordanted acidic dyes often diffuse to other layers. In order to prevent such diffusion, it has been proposed to use a large amount of a mordant. By the proposed means, however, not only the diffusion could not be completely prevented but also the thickness of the layer, to which a mordant is added, was enlarged to cause another problem. In general, the photographic materials for photoengraving to produce printing plates are subjected to reduction with a reducer so as to adjust their densities and gradations, and the reducer to be used contains a water-soluble iron complex as a reducing

agent. If the above-mentioned cationic mordant agent is applied to such photographic materials for photoengraving, it will bond to the iron complex by electrostatic bonding to disadvantageously give yellow stains in the processed photographic materials.

As still another means for fixing dyes in specific layers of the photographic materials, there are known methods of adding dyes as their solid dispersions to the layers, for example, as described in JP-A-56-12639, JP-A-55-155350, JP-A-52-92716, JP-A-59-193447, JP-A-62-198148, JP-A-63-197943, JP-A-63-27838, JP-A-64-40827, European Patents 0015601B1, 0276566A1, International Patent WO88/04794, JP-A-2-277045 and JP-A-4-204938.

According to the known methods of introducing an AH layer containing dyes fixed therein into a photographic material, however, the dots to be formed were difficult to thicken though the tone reproducibility of the material in the dry-dot working step was improved. As a result, the material needed much exposure in the dry-dot working step and the above-mentioned problem that the tone reproducibility of the material was worsened due to halation was not solved satisfactorily.

A method of providing an interlayer between the emulsion layer and the protective layer in a photographic material so as to easily thicken the dots to be formed in the exposed material is described in U.S. Patent 5,061,595. However, there is a still problem that the method is not compatible with the gradation reproducibility of the material.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a silver halide photographic material for illuminated room, which may have a reduced amount of silver, which may well be subjected to dry-dot work to give improved high-quality images and which has few stains even processed by rapid processing.

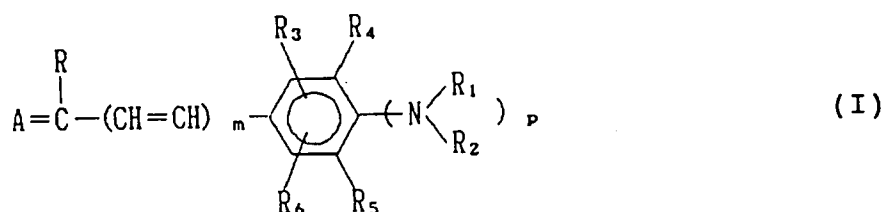
This and other objects of the present invention have been attained by a silver halide photographic material comprising a support having thereon at least one silver halide emulsion layer, wherein the emulsion of the silver halide emulsion layer comprises a silver halide having a silver chloride content of 90 mol% or more containing a transition metal of 1×10^{-6} mol or more per mol of silver; the material has a layer containing a dye subjected to a fine crystalline solid dispersion between the emulsion layer and the support; the material has an interlayer comprising a hydrophilic colloid and an uppermost layer comprising a hydrophilic colloid and solid grains having a mean grain size of from 1 to 5 μm above the emulsion layer; and the thickness of the interlayer is at least 0.8 times the thickness of the uppermost layer.

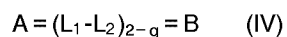
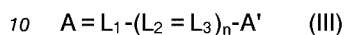
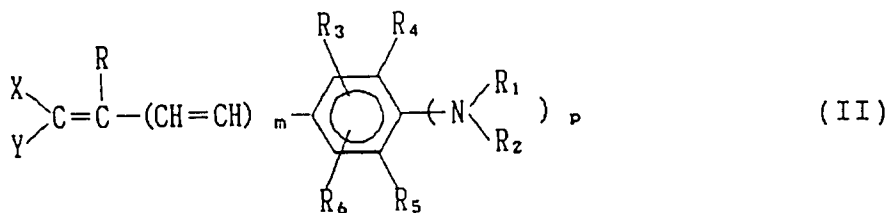
Preferably, the silver halide in the emulsion layer has a mean grain size of 0.2 μm or less and the amount of silver in the emulsion layer is 3.5 g/m² or less.

Further, this and other objects of the present invention has been attained by a method for processing the above-described silver halide photographic material for a total dry-to-dry processing time of from 30 to 60 seconds.

DETAILED DESCRIPTION OF THE INVENTION

As dyes used in the present invention as fine crystalline solid dispersions thereof, mentioned are those described in Table I to Table X in International Patent WO88/04794, those of the following formulae (I) to (VII) and others:





wherein A and A' are the same or different and each represents an acidic nucleus;

B represents a basic nucleus;

X and Y are the same or different and each represents an electron attractive group;

R represents a hydrogen atom or an alkyl group;

R₁ and R₂ are the same or different and each represents an alkyl group, an aryl group, an acyl group or a sulfonyl group, or R₁ and R₂ may be bonded to each other to form a 5-membered or 6-membered ring;

R₃ and R₆ are the same or different and each represents a hydrogen atom, a hydroxyl group, a carboxyl group, an alkyl group, an alkoxy group or a halogen atom;

R₄ and R₅ are the same or different and each represents a hydrogen atom, or a non-metallic atomic group necessary for forming a 5-membered or 6-membered ring along with R₁ bonded to R₄ or along with R₂ bonded to R₅;

L₁, L₂ and L₃ are the same or different and each represents a methine group;

m represents 0 or 1;

n and q are the same or different and each represents 0, 1 or 2;

p represents 0 or 1; provided that when p is 0, then R₃ is a hydroxyl group or a carboxyl group and R₄ and R₅ are each a hydrogen atom;

B' represents a heterocyclic group having a carboxyl group, a sulfamoyl group or a sulfonamido group; and Q represents a heterocyclic group.

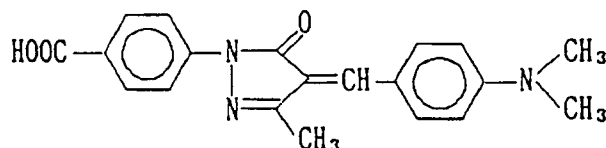
The compounds of formulae (I) to (VII) each has at least one dissociating group having a pKa value of from 4 to 11 in a mixed solution of water and ethanol at a ratio of 1:1 by volume, in one molecule.

As specific examples of dyes to be used in the present invention in the form of their solid dispersions, mentioned are those described in International Patent WO88/04794; European Patents EP-0274723A1, 0276566, 0299435; JP-A-52-92716, JP-A-55-155350, JP-A-55-155351, JP-A-61-205934, JP-A-48-68623; U.S. Patents 2,527,583, 3,486,897, 3,746,539, 3,933,798, 4,130,429, 4,040,841; JP-A-3-7931, JP-A-3-282244, JP-A-3-167546, JP-A-5-113623. Methods of producing solid dispersions of dyes used in the present invention are described in these patent publications. In addition, also usable are a method of mechanically dispersing a solid dye in water along with a suitable dispersing agent, by means of a ball mill, a sand mill or a colloid mill, to form a solid dye dispersion; a method of coating a dissociated salt of a dye

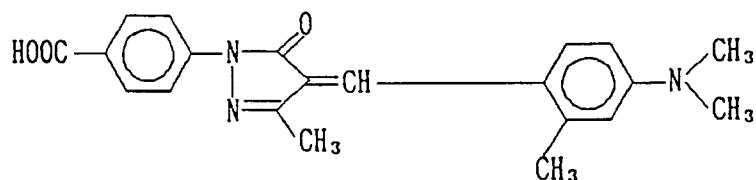
followed by coating gelatin over the coated dye to form a fixed solid dispersion of the dye after coated; a method of dissolving a dye in an aqueous alkali solution at an adjusted pH value, followed by lowering the pH of the solution in the presence of a protective colloid such as gelatin to form fine solid precipitates of the dye; and a method of dissolving a dye in a suitable solvent, followed by adding a poor solvent for the dye to form fine solid precipitates of the dye.

Dyes which are preferably used in the present invention are those having an absorption maximum of from 300 to 500 nm. Specific examples of the dyes preferably used in the present invention are mentioned below, which, however, are not limited thereto.

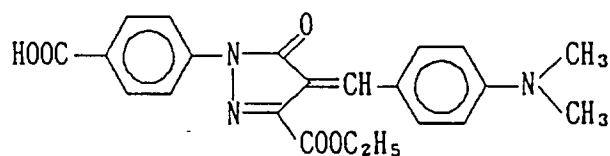
(I-1)



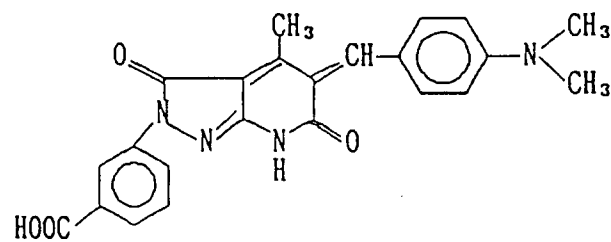
(I-2)



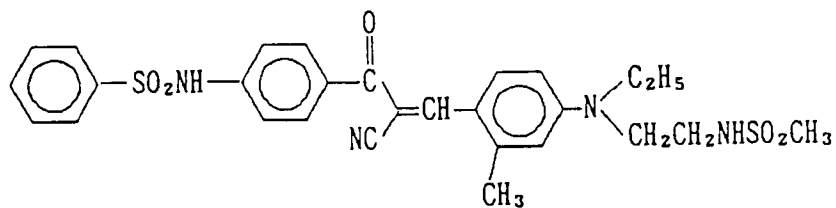
(I-3)



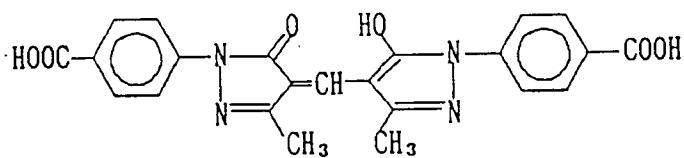
(I-4)



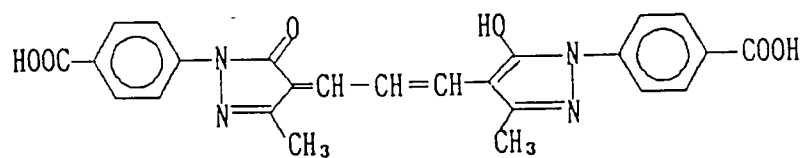
(II-1)



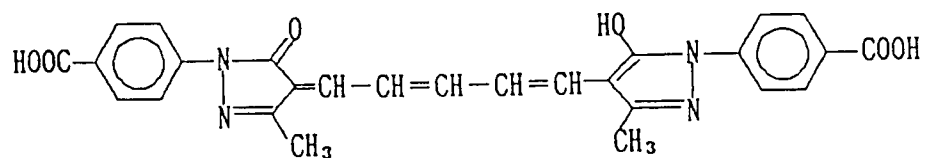
(III-1)



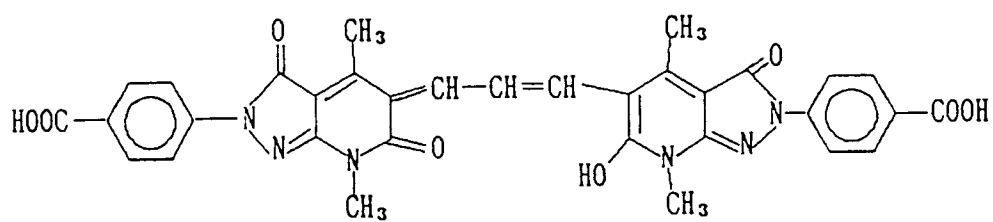
(III-2)



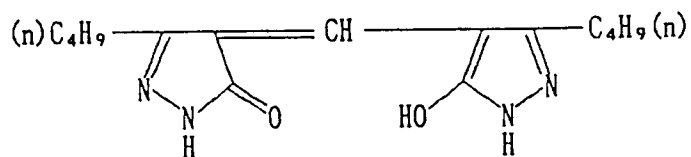
(III-3)



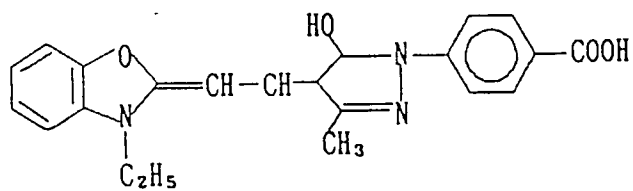
(III-4)



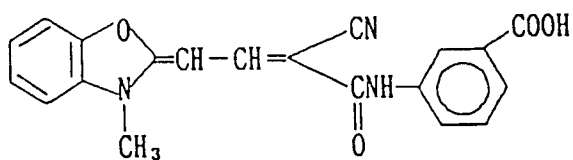
(III-5)



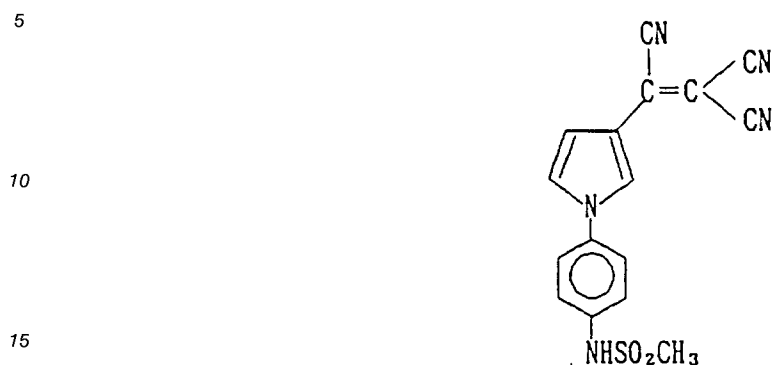
(IV-1)



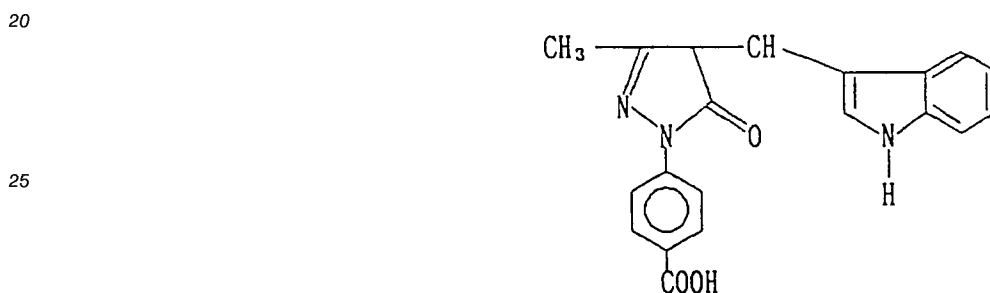
(V-1)



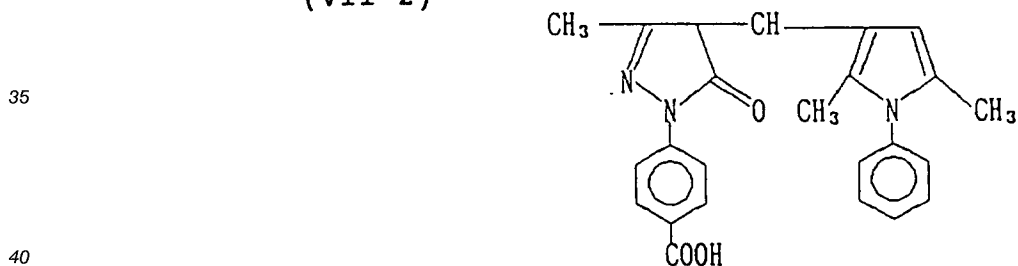
(VI-1)



(VII-1)



(VII-2)



Light that has passed through the light-sensitive emulsion layer during exposure is reflected by the support and the reflected light again passes through the emulsion layer to cause halation which worsens the image to be formed. So as to prevent the halation, according to the present invention, the dye which is subjected to a fine crystalline solid dispersion is added to the non-light-sensitive hydrophilic colloid layer between the emulsion layer and the support. The amount of the dye to be coated is preferably from 10 mg to 80 mg, more preferably from 20 mg to 60 mg, per m² of the photographic material.

Such dyes employable in the present invention can be easily produced by the methods described in International Patent WO88/04794; European Patents EP-0274723A1, 0276566, 0299435; JP-A-52-92716, JP-A-55-155350, JP-A-55-155351, JP-A-61-205934, JP-A-48-68623; U.S. Patents 2,527,583, 3,486,897, 3,746,539, 3,933,798, 4,130,429, 4,040,841; JP-A-3-7931, JP-A-3-282244, JP-A-3-167546 or according to these methods.

The silver halide photographic material of the present invention may contain other dyes so as to ensure its safelight safety and external-light safety. The dyes to be used for this purpose are not limited and the examples thereof include water-soluble dyes and solid disperse dyes.

Other additives which may be added to the photographic material of the present invention are not specifically limited. For instance, the following additives are preferably used in the present invention.

Additives	Examples
5 1) Hydrazine Nucleating Agents	Compounds described in JP-A-2-12236, from page 2, right top column, line 19 to page 7, right top column, line 3; Compounds of Formula (II) and 10 Compounds (II-1) to (II-54) described in JP-A-3-174143, from page 20, right bottom column, line 1 to page 27, right top column, line 20 15
2) Nucleation Accelerators	Compounds of Formulae (II-m) to (II- p) and Compounds (II-1) to (II-22) described in JP-A-2-103536, from page 20 9, right top column, line 13 to page 16, left top column, line 10; Compounds described in JP-A-1-179939
25 3) Silver Halide Emulsions and Methods of Preparing Them	JP-A-2-97937, from page 20, right bottom column, line 12 to page 21, left bottom column, line 14; JP-A-2-12236, from page 7, right top 30 column, line 19 to page 8, left bottom column, line 12; Selenium sensitization described in JP-A-5-11389 35 40 45 50 55

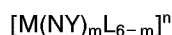
	<u>Additives</u>	<u>Examples</u>
5	4) Spectral Sensitizing Dyes	Spectral sensitizing dyes described in JP-A-2-12236, column 8, from left bottom column, line 13 to right bottom column, line 4; JP-A-2-103536, 10 from page 16, right bottom column, line 3 to page 17, left bottom column, line 20; JP-A-1-112235, JP-A- 2-124560, JP-A-3-7928, JP-A-5-11389
15	5) Surfactant	Compounds described in JP-A-2-12236, page 9, from right top column, line 7 to right bottom column, line 7; 20 Compounds described in JP-A-2-18542, from page 2, left bottom column, line 13 to page 4, right bottom column, line 18
25	6) Antifoggant	Compounds described in JP-A-2-103536, from page 17, right bottom column, line 19 to page 18, right top column, line 4, and page 18, right bottom 30 column, lines 1 to 5; Thiosulfinic acid compound described in JP-A-1-237538
35	7) Polymer latex	Compounds described in JP-A-2-103536, page 18, left bottom column, lines 12 to 20
40	8) Acid group- containing compound	Compounds described in JP-A-2-103536, from page 18, right bottom column, line 6 to page 19, left top column, line 1
45	9) Matting agent; Lubricant; Plasticizer	Compounds described in JP-A-2-103536, page 19, from left top column, line 15 to right top column, line 15

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	<u>Additives</u>	<u>Examples</u>
5	10) Hardening agent	Compounds described in JP-A-2-103536, page 18, right top column, lines 5 to 17
10	11) Dye	Dyes described in JP-A-2-103536, page 17, right bottom column, lines 1 to 18; Solid dyes described in JP-A-2-294638 and JP-A-5-11382
15	12) Binder	Compounds described in JP-A-2-18542, page 3, right bottom column, lines 1 to 20
20	13) Black pepper inhibiting agent	Compounds described in U.S. Patent 4,956,257 Compounds described in JP-A-1-118832
25	14) Redox compound	Compounds of Formula (I) (especially, Compound Nos. 1 to 50) described in JP-A-2-301743; Compounds of Formulae (R-1), (R-2) and (R-3) and Compound Nos. 1 to 75 described in JP-A-3-174143, pages 3 to 20; Compounds described in JP-A-5-257239 and JP-A-4-278939
30		
35	15) Monomethine compound	Compounds of Formula (II) (especially, Compounds II-1 to II-26) described in JP-A-2-287532
40	16) Dihydroxybenzene compound	Compounds described in JP-A-3-39948, from page 11, left top column to page 12, left bottom column; Compounds described in EP-0452772A
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The silver halide grains used in the photographic material of the present invention preferably contain at least one transition metal. Preferred are transition metal coordination complexes, such as hexadentate complexes of the following formula:



wherein M represents a transition metal selected from the elements of the Groups V to VIII in the Periodic Table;

L represents a crosslinked ligand;

N represents a nitrogen atom;

Y represents an oxygen atom or a sulfur atom;

$m = 0, 1$ or 2 ; and

$n = 0, -1, -2$ or -3 .

Preferred examples of L are a halogeno ligand (e.g., fluoride, chloride, bromide, iodide), a cyanido ligand, a cyanato ligand, a thiocyanato ligand, a selenocyanato ligand, a tellurocyanato ligand, an acido ligand and an aquo ligand. For aquo ligands, it is preferred that one or two aquo ligands is/are in one complex.

More preferred examples of M are rhodium, ruthenium, rhenium, osmium and iridium.

Specific examples of transition metal coordination complexes for use in the present invention are mentioned below, which, however, are not limited thereto.

1. $[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]^{-2}$
2. $[\text{RuCl}_6]^{-3}$
3. $[\text{Ru}(\text{NO})\text{Cl}_5]^{-2}$
4. $[\text{RhCl}_6]^{-3}$
5. $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{-2}$
6. $[\text{Ru}(\text{NO})(\text{H}_2\text{O})\text{Cl}_4]^{-1}$
7. $[\text{Re}(\text{NO})\text{Cl}_5]^{-2}$
8. $[\text{Os}(\text{NO})\text{Cl}_5]^{-2}$
9. $[\text{Ir}(\text{NO})\text{Cl}_5]^{-2}$
10. $[\text{Ir}(\text{H}_2\text{O})\text{Cl}_5]^{-2}$
11. $[\text{Re}(\text{H}_2\text{O})\text{Cl}_5]^{-2}$
12. $[\text{RhBr}_6]^{-2}$
13. $[\text{Os}(\text{NS})\text{Cl}(\text{SCN})_4]^{-2}$
14. $[\text{ReCl}_6]^{-3}$
15. $[\text{IrCl}_6]^{-3}$
16. $[\text{Re}(\text{NS})\text{Cl}_4(\text{SeCN})]^{-2}$

To incorporate the above-mentioned metal complex into silver halides, it may be added to them during preparation of their grains.

The content of the transition metal in the silver halide grains of the present invention is 1×10^{-6} mol or more, preferably from 1×10^{-6} to 5×10^{-4} mol, more preferably from 5×10^{-6} to 2×10^{-4} mol, per mol of the silver halide. One silver halide grain may be added in combination with one or more different transition metals.

The transition metal distribution in the silver halide grains of the present invention is not specifically limited, but preferably, more transition metals are in the outside area of one grain.

The silver halide emulsion used in the silver halide photographic material of the present invention is preferably an emulsion of a silver chlorobromide or silver chloriodobromide having a silver chloride content of 90 mol% or more. Increase in the silver bromide or silver iodide content in the silver halide is not preferred, as worsening the safelight safety of the photographic material in daylight rooms or lowering the gamma (γ) value of the material.

The mean grain size of the silver halide in the emulsion layer is $0.2 \mu\text{m}$ or less, preferably from 0.08 to $0.19 \mu\text{m}$, and more preferably from 1.3 to $1.8 \mu\text{m}$. The amount of silver in the emulsion layer is 3.5 g/m^2 or less, preferably from 1.0 to 3.4 g/m^2 , and more preferably from 1.5 to 3.3 g/m^2 .

The photographic material of the present invention preferably contain a matting agent such as silica, magnesium oxide or polymethyl methacrylate in the photographic emulsion layer or other hydrophilic colloid layers so as to increase the adhesiveness of the layers. Preferably, the upper protective layer (uppermost layer) contains the matting agent. Generally, the ratio by weight of the matting agent to the hydrophilic colloid in the layer is from 0.02 to 1 . The matting agent is preferably in the form of grains having a mean grain size of from 1 to $5 \mu\text{m}$, more preferably from 3 to $5 \mu\text{m}$.

The photographic material of the present invention may contain solid grains, such as those of silica, silver halides, magnesium oxide, calcium carboxylates or polymethyl methacrylates, in the photographic emulsion layer or other hydrophilic colloid layers, for the purpose of easily thickening the dots to be formed by exposure. Preferably, the upper protective layer (uppermost layer) contains such grains. Generally, the ratio by weight of the light-scattering agent comprising such grains to the hydrophilic colloid in the layer is from 0.02 to 1 . Preferably, the grains have a mean grain size of from 0.1 to $5 \mu\text{m}$, more preferably from 3 to $5 \mu\text{m}$. The compound of the solid grains may be the same as or different from that of the matting agent.

The thickness of the upper protective layer in the photographic material of the present invention is generally from 0.2 to $1 \mu\text{m}$, preferably from 0.3 to $0.8 \mu\text{m}$. The photographic material of the present invention has an interlayer between the silver halide emulsion layer and the upper protective layer, and the thickness of the interlayer is at least 0.8 times, preferably from 1.0 to 2.0 times, and more preferably from

1.2 to 1.8 times, the thickness of the upper protective layer (uppermost layer) so as to easily thicken the dots to be formed by exposure.

The developing agent used in the developer which is used in processing the photographic material of the present invention is not specifically limited, but the developer is desired to contain dihydroxybenzenes in order to easily form hard images having a good dot quality. As the case may be, a combination of dihydroxybenzenes and 1-phenyl-3-pyrazolidones, or a combination of dihydroxybenzenes and p-aminophenols may also be employed.

Examples of the dihydroxybenzene developing agents usable for processing the photographic materials of the present invention include hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, 2,5-dichlorohydroquinone, 2,3-dibromohydroquinone and 2,5-dimethylhydroquinone. More preferred is hydroquinone.

1-Phenyl-3-pyrazolidone and derivatives thereof may also be used as a developing agent in the present invention. Examples thereof include 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone, 1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone, 1-p-aminophenyl-4,4-dimethyl-3-pyrazolidone, 1-p-tolyl-4,4-dimethyl-3-pyrazolidone and 1-p-tolyl-4-methyl-4-hydroxymethyl-3-pyrazolidone.

Examples of p-aminophenol developing agents also usable in the present invention include N-methyl-p-aminophenol, p-aminophenol, N-(β -hydroxyethyl)-p-aminophenol, N-(4-hydroxyphenyl)glycine, 2-methyl-p-aminophenol and p-benzylaminophenol. More preferred is N-methyl-p-aminophenol.

The amount of the developing agent used in the developer for use in the present invention is preferably from 0.05 mol/liter to 0.8 mol/liter. When a combination of dihydroxybenzenes and 1-phenyl-3-pyrazolidones or p-aminophenols is employed, it is preferred that the content of the former in the developer is from 0.05 mol/liter to 0.5 mol/liter and that of the latter therein is 0.06 mol/liter or less.

The developer for use in the present invention may contain, as a preservative, a sulfite such as sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite, potassium metabisulfite and formaldehyde-sodium bisulfite. The content of such a sulfite is preferably 0.3 mol/liter or more, more preferably 0.4 mol/liter or more. The upper limit of the sulfite content is preferably 2.5 mol/liter or less, more preferably up to 1.2 mol/liter or less.

The developer may contain an alkali agent for the purpose of properly adjusting the pH value thereof. As such an alkali agent, usable is a pH adjusting agent or a pH buffer, such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium tertiary phosphate, potassium tertiary phosphate, sodium silicate and potassium silicate.

The developer may further contain additives other than the above-mentioned components. Such additives include, for example, a development inhibitor such as boric acid, borax, sodium bromide, potassium bromide and potassium iodide; an organic solvent such as ethylene glycol, diethylene glycol, triethylene glycol, dimethylformamide, methyl cellosolve, hexylene glycol, ethanol and methanol; an antifog-gant such as mercapto compounds (e.g., 1-phenyl-5-mercaptotetrazole, sodium 2-mercaptobenzimidazole-5-sulfonate), indazole compounds (e.g., 5-nitroindazole) and benzotriazole compounds (e.g., 5-methylbenzotriazole). In addition, it may optionally contain additives such as a color toning agent, a surfactant, a defoaming agent, a water softener and a hardening agent, if desired. In particular, amino compounds such as those described in JP-A-56-106244 and imidazole compounds such as those described in JP-B-48-35493 (the term "JP-B" as used herein means an "examined Japanese patent publication") are preferred, as effective in promoting the developability of the developer and elevating the sensitivity of the photographic material being processed with the developer.

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

The developer may also contain, as a buffer, a boric acid described in JP-A-62-186259, saccharides (e.g., saccharose) described in JP-A-60-93433, oximes (e.g., acetoxime), phenols (e.g., 5-sulfosalicylic acid) and tertiary phosphates (e.g., sodium salts, potassium salts). Preferred is a boric acid.

The fixer used in the present invention is an aqueous solution containing a fixing agent. In addition to the agent, if desired, it may contain a hardening agent (e.g., water-soluble aluminium compounds), an acetic acid and a dibasic acid (e.g., tartaric acid, citric acid, their salts). Preferably, it has a pH value of 3.8 or more, more preferably from 4.0 to 5.5.

As the fixing agent, usable are sodium thiosulfate, ammonium thiosulfate, etc. Especially preferred is ammonium thiosulfate, in view of its fixing rate. The amount of the fixing agent in the fixer may be varied suitably but is, in general, approximately from 0.1 mol/liter to 5 mol/liter.

Water-soluble aluminium salts which acts in the fixer as a hardening agent are compounds that are generally known as hardening agents in acidic film-hardening fixers. Examples thereof include aluminium chloride, aluminium sulfate and potassium alum.

As the above-mentioned dibasic acid, usable are tartaric acid, derivatives thereof, citric acid and derivatives thereof. The dibasic acid may be used singly or in combination. The compound is effectively in the fixer in an amount of 0.005 mol or more per liter of the fixer, more preferably from 0.01 mol/liter to 0.03 mol/liter.

Specific examples of the dibasic acid include tartaric acid, potassium tartarate, sodium tartarate, potassium sodium tartarate, ammonium tartarate and ammonium potassium tartarate.

As examples of usable citric acid and its derivatives, mentioned are citric acid, sodium citrate, potassium citrate, etc.

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

The fixing temperature and the fixing time may follow the developing temperature and the developing time. Preferably, for example, the fixing temperature may be from about 20 °C to about 50 °C and the fixing time may be from 10 seconds to one minute.

Rinsing water to be used for rinsing the processed photographic material of the present invention may contain an anti-fungal agent (e.g., compounds described in Horiguchi, Anti-bacterial and Anti-fungal Chemistry, and JP-A-62-115154), a rinsing accelerating agent (e.g., sulfites), and a chelating agent.

According to the process mentioned above, the photographic material is, after developed and fixed, is rinsed and dried. The rinsing is to remove almost completely the silver salts dissolved by fixation and is effected preferably at about 20 °C to about 50 °C for 10 seconds to 3 minutes. The drying is effected at about 40 °C to about 100 °C. The drying time may be varied appropriately, depending on the ambient conditions, but, in general, may be from about 5 seconds to about 3 minutes and 30 seconds.

The photographic material of the present invention may be processed, using a roller-conveying type automatic developing machine which is described in, for example, U.S. Patents 3,025,779 and 3,545,971. The machine is referred to simply as a roller-conveying type processor. The process by the roller-conveying type processor is composed of four steps of development, fixation, rinsing and drying. Most preferably, the process for processing the photographic material of the present invention follows the four steps, though not excluding other steps (e.g., stopping step). In the rinsing step, employable is a countercurrent rinsing system having two or three rinsing stages so as to save water to be used therein.

The photographic material of the present invention is suitably processed in an automatic developing machine for 30 to 60 seconds for dry-to-dry processing (the time means a total time needed from the start of the processing at which the top of the photographic material to be processed is introduced into the developing zone to the end of the same at which the end of the processed material is taken out from the drying zone).

To store the developer for use in the present invention, it is preferably wrapped with a wrapping material having a low oxygen permeability such as described in JP-A-61-73147. The replenishing system described in JP-A-62-91939 is preferably employed for replenishing the developer in the process of the present invention.

Since the silver halide photographic material gives a high Dmax, it may still maintain its high density even though the dot area formed is reduced when the material is subjected to reduction after processed to form an image.

The reducer usable in the present invention is not specifically limited. For instance, usable are those described in Mees, The Theory of the Photographic Process, pp. 738 to 744 (1954, published by Macmillan), Tetsuo Yano, Theory and Practice of Photographic Processing, pp. 166 to 169 (1978, published by Kyoritsu Publishing, Japan), and in JP-A-50-27543, JP-A-52-68429, JP-A-55-17123, JP-A-55-79444, JP-A-57-10140, JP-A-57-142639 and JP-A-61-61155. Specifically, usable are reducers containing one or more oxidizing agents selected from permanganates, persulfates, ferric salts, cupric salts, ceric salts, red prussiate of potash and bichromates, and optionally containing inorganic acids such as sulfuric acid and alcohols; as well as reducers containing oxidizing agents, such as red prussiate of potash and ferric ethylenediamine-tetraacetates, and silver halide solvents, such as thiosulfates, rhodanides, thioureas and their derivatives, and optionally containing inorganic acids such as sulfuric acid.

Typical examples of the reducer usable in the present invention include so-called Farmer's reducer, ferric ethylenediamine-tetraacetates, potassium permanganate, ammonium persulfate reducer (Kodak R-5)

and ceric salt reducers.

In general, it is preferred that the reduction of the photographic material of the present invention is effected at from 10 °C to 40 °C, preferably at from 15 °C to 30 °C, to be completed within several seconds to several ten minutes, preferably within several minutes. Using the photographic material for photomechanical process of the present invention, one may have a lot of latitude in the reduction of the material under this condition.

The reducer is made to act on the silver image formed in the emulsion layer, via the non-light-sensitive upper layer containing the compound of the present invention.

Concretely, various methods may be employable for the reduction. For instance, the photographic material for photomechanical process of the present invention is dipped in a reducer while stirring, or a reducer may be applied to the surface of the photographic material with a brush or roller.

The present invention will be explained in more detail with reference to the following example, however, it should be understood that the present invention is not to be deemed to be limited thereto.

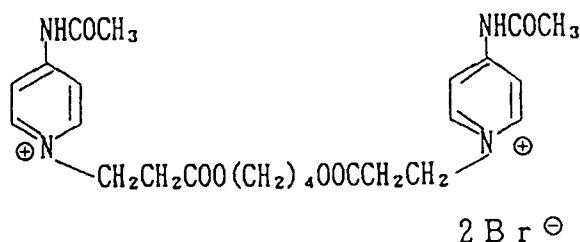
EXAMPLE

Preparation of Emulsion:

An aqueous solution of silver nitrate and an aqueous solution of sodium chloride containing 4×10^{-5} mol, per mol of silver, of $(\text{NH}_4)_2\text{Rh}(\text{H}_2\text{O})\text{Cl}_5$ were simultaneously added to an aqueous solution of gelatin containing 5,6-cyclopentane-4-hydroxy-1,3,3a,7-tetrazaindene (5×10^{-3} mol per mol of silver) kept at 40 °C, over a period of 7 minutes, while the potential of the reaction system was controlled at 95 mV, to prepare core grains (grain size: 0.12 μm). Afterwards, an aqueous solution of silver nitrate and an aqueous solution of sodium chloride containing 1.2×10^{-4} mol, per mol of silver, of $(\text{NH}_4)_2\text{Rh}(\text{H}_2\text{O})\text{Cl}_5$ were simultaneously added thereto over a period of 14 minutes, while the potential of the reaction system was controlled at 95 mV, to prepare cubic silver chloride grains having a mean grain size of 0.15 μm .

Preparation of Coated Samples:

To the emulsion prepared above, added were 50 mg/m² of a compound having a structural formula of $\text{C}_{16}\text{H}_{33}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{25}\text{H}$, 24 mg/m² of 5,6-cyclopentane-4-hydroxy-1,3,3a,7-tetrazaindene, 5 mg/m² of 5-methylbenzotriazole, 770 mg/m² of polyethyl acrylate latex (mean grain size: 0.05 μm), 3 mg/m² of the following compound:



and, as a hardening agent, 126 mg/m² of 2-bis(vinylsulfonylacetamido)ethane. The resulting mixture was coated on a polyester support in an amount of 3.0 g/m² in terms of silver. Gelatin coated was 1.1 g/m².

Over the thus-coated emulsion layer, simultaneously coated were a lower protective layer (interlayer) containing 5 mg/m² of 5-nitroindazole, 8 mg/m² of lipoic acid, 6 mg/m² of $\text{C}_2\text{H}_5\text{SO}_2\text{SNa}$, 50 mg/m² of hydroquinone, 15 mg/m² of 1-hydroxy-2-benzaldoxime and 230 mg/m² of polyethyl acrylate latex (mean grain size: 0.05 μm), its thickness being determined by adjusting the amount of gelatin therein as shown in Table 1 below; and an upper protective layer (uppermost layer) containing 55 mg/m² of a matting agent (silicon dioxide; mean grain size: 3.5 μm), 135 mg/m² of methanol silica (mean grain size: 0.02 μm), 25 mg/m² of sodium dodecylbenzenesulfonate as a coating aid, 20 mg/m² of sodium salt of sulfate ester of polyoxyethylene nonylphenyl ether (polymerization degree: 5) and 3 mg/m² of potassium salt of N-perfluorooctanesulfonyl-N-propylglycinerits thickness being determined by adjusting the amount of gelatin therein as shown in Table 1 below; while coating an AH layer containing 0.5 g/m² of gelatin, 50 mg/m² of potassium polystyrenesulfonate, 50 mg/m² of polyethyl acrylate latex and a dispersion of solid dye (III-1) of

the invention (see Table 1 for its amount) between the emulsion layer and the support. Accordingly, coated samples were prepared.

The support used herein had the following backing layer and back-protecting layer. The swelling degree of the back surface of the support was 110 %.

Backing Layer:	
Gelatin	170 mg/m ²
Sodium Dodecylbenzenesulfonate	32 mg/m ²
Sodium Dihexyl- α -sulfosuccinate	35 mg/m ²
SnO ₂ /Sb (9/1, by weight; mean grain size: 0.25 μ m)	318 mg/m ²

Back-Protecting Layer:

Gelatin 7 g/m²

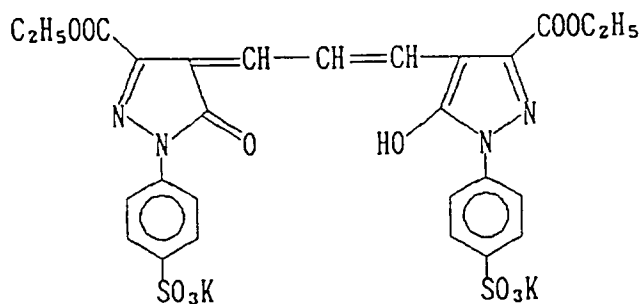
Silicon Dioxide Matting Agent 26 mg/m²
(mean grain size: 3.5 μ m)

Sodium Dihexyl- α -sulfosuccinate 20 mg/m²

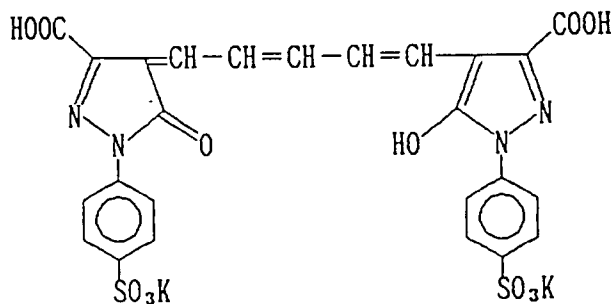
Sodium Dodecylbenzenesulfonate 67 mg/m²

$\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_3\text{H}_7)(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}_2)_4\text{SO}_3\text{Li}$ 5 mg/m²

Dye B 32 mg/m²



Dye C 59 mg/m²



Polyethyl Acrylate Latex (mean
grain size: 0.05 μm)

260 mg/m^2

1,3-Divinylsulfonyl-2-propanol

149 mg/m^2

Evaluation of Photographic Properties:

Using P-627 FM Printer (with a mercury lamp; made by DAINIPPON SCREEN MFG. CO., LTD.), each of these samples thus prepared was exposed through a dot original for dot-to-dot work and through an optical wedge by the following developer. The exposed samples were developed at 38°C for 20 seconds, then fixed, rinsed and dried, using an automatic developing machine FG800 RA Model (manufactured by Fuji Photo Film Co., Ltd.). The thus-processed samples were evaluated with respect to the following test items.

1) Dmax: A film having a halftone dot image formed on an adhesive base (halftone dot original) that had been fixed on an adhesive tape was kept in face-to-face contact with each sample with the protective layer of each sample facing to the halftone dot original, and the thus-combined sample was exposed to have 50% halftone dot area in the original film, whereupon the maximum black density (Dmax) was obtained.

2) Gradation: This is represented by the following equation:

$$\text{Gradation} = (1.5 - 0.1) / \{-\log (\text{amount of exposure for giving density of } 0.1) - \log (\text{amount of exposure for giving density of } 1.5)\}$$

3) Sensitivity: Using the same original film as that used in determining Dmax in 1), obtained was the time for exposure needed to form 70% dots in the exposed sample from 50% halftone dots in the original film by dot-to-dot working. The sensitivity was represented by the time thus obtained.

4) Dry-Dot Property: For each sample, 50% halftone dots in UGRA Offset Test Kail (1982; made by KOHAN DENSITOGRAPH TRADING CO., LTD.) were thickened to 70% halftone dots, whereupon the image quality was evaluated and the exposure time was measured. The image quality was evaluated by measuring whether nonimage area of 95% halftone dot area was clearly formed, and the results were shown by five ranks. "5" means the best quality, while "1" means the worst quality. "3" and higher ranks indicate practical samples.

The developer used for processing the exposed samples had the following composition:

Composition of Developer:

Potassium Hydroxide	35.0 g
Diethylenetriamine-pentaacetic Acid	2.0 g
Potassium Carbonate	12.0 g
Sodium Metabisulfite	40.0 g
Potassium Bromide	3.0 g
Hydroquinone	25.0 g
5-Methylbenzotriazole	0.08 g
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	0.45 g
2,3,5,6,7,8-Hexahydro-2-thioxo-4-(1H)-quinazolinone	0.04 g
Sodium 2-Mercaptobenzimidazole-5-sulfonate	0.15 g
Sodium Eryorbate	3.0 g
Water to make	1 liter
Potassium Hydroxide to make	pH of 10.5

As will be noted from the results in Table 1 below, Sample Nos. 6 and 7 of the present invention were good in that the exposure time for dry-dot work was short and the quality of the images formed was good.

Table 1

Sample No.	Amount of Dispersion of Solid Dye Added (mg/m ²)	Thickness of Layer (μm)		Photographic Properties			Dry-Dot Properties	
		Lower Protective Layer	Upper Protective Layer	Dmax	Grada- tion	Sensi- tivity	Image Quality (sec)	Time for Exposure (sec)
1	-	-	1.2	5.8	8.7	7	1	60
2	30	-	1.2	5.8	8.7	7	3	120
3	60	-	1.2	5.8	8.7	7	4	130
4	-	0.6	0.6	6.0	8.9	7	1	60
5	30	0.4	0.6	6.0	8.9	7	3	110
6	30	0.6	0.6	6.0	8.9	7	5	70
7	30	0.8	0.6	6.0	8.9	7	5	80

Nos. 6 and 7 are samples of the present invention.

Claims

1. A silver halide photographic material comprising a support having thereon at least one silver halide emulsion layer,
wherein the emulsion of the silver halide emulsion layer comprises a silver halide having a silver

chloride content of 90 mol% or more containing a transition metal of 1×10^{-6} mol or more per mol of silver;

the material has a layer containing a dye subjected to a fine crystalline solid dispersion between the silver halide emulsion layer and the support;

5 the material has an interlayer comprising a hydrophilic colloid and an uppermost layer comprising a hydrophilic colloid and solid grains having a mean grain size of from 1 to 5 μm above the emulsion layer; and

the thickness of the interlayer is at least 0.8 times the thickness of the uppermost layer.

10 2. The silver halide photographic material as claimed in claim 1, wherein the silver halide in the emulsion layer have a mean grain size of 0.2 μm or less and the coated amount of silver in the emulsion layer is 3.5 g/m² or less.

15 3. A method for processing a silver halide photographic material of claims 1 or 2 for a total dry-to-dry processing time of from 30 to 60 seconds.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 11 5396

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)
Y	EP-A-0 490 302 (FUJI) * page 3, line 3 - line 5 * * page 30, line 7 - line 11 * * page 30, line 29 - line 34 * * page 33, line 55 - page 34, line 1 * * page 35, line 2 - line 4 * * page 35, line 9 - line 29 * ----	1-3	G03C1/76 G03C1/825 G03C1/035
Y	EP-A-0 317 247 (KONICA) * page 3, line 28 - line 36 * * page 6, line 24 - line 32 * * page 35, line 11 - line 17 * ----	1-3	
Y	US-A-4 777 113 (INOUE ET AL.) * column 1, line 11 - line 16 * * column 3, line 3 - line 11 * * column 9, line 63 - column 10, line 22 * * column 14, line 55 - line 58; claims 1,2 * ----	1-3	
Y	US-A-4 904 565 (SCHMIDT ET AL.) * column 1, line 5 - line 7 * * column 4, line 16 - column 5, line 43; claim 1; examples 1-6 * -----	1-3	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 December 1994	Examiner Magrizos, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	