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- (54) Silver halide photographic light sensitive material.
- 67 A silver halide photographic light-sensitive material is disclosed. The material comprises a support and provided thereon, a silver halide emulsion layer and at least two backing layers on the support opposite to said silver halide emulsion layer. An uppermost layer of said silver halide emulsion layer and/or an uppermost layer of said backing layers contains a lubricant, and a backing layer other than said uppermost backing layer contains a matting agent having an average particle size of more than 10μm.

FIELD OF THE INVENTION

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The present invention relates to a silver halide photographic light-sensitive material, more specifically to a silver halide photographic light-sensitive material which has improved transportability for scanners, facsimile plotters, etc.

BACKGROUND OF THE INVENTION

In recent years, there have been increased demands for use of silver halide photographic light-sensitive materials in the photochemical process. There have also been market demands for shortening product delivery time.

For shortening delivery time, it is desired to save labor in the exposure, processing and other processes to perform these processes in short time. In these processes, scanners and facsimile plotters are used. The use of these scanners and facsimile plotters can pose a problem of light-sensitive material transportation failure therein.

Transportation failure hampers reduction in delivery time.

Photographic light-sensitive materials usually incorporate gelatin as a binder; they become prone to aggregate under humid conditions to cause transportation failure in scanners and facsimile plotters.

To prevent transportation failure in these scanners and facsimile plotters, it has been a practice to add a matting agent to the outermost layer of photographic light-sensitive material, but the obtained effect is insufficient to improve the transportability under humid conditions. Moreover, when the amount of matting agent added is increased to enhance the improving effect, transparency after development deteriorates considerably and sliding quality deteriorates, which in turn poses a problem of deteriorated transportability contrary to the purpose.

Improvements in running property in image taking machines, printers and cameras by adding a lubricant to photographic light-sensitive material are described in US Patent Nos. 3,042,522 and 3,080,317, British Patent Nos. 1,466,304 and 1,143,118 and other publications; however, transportability in scanners and facsimile plotters cannot be improved solely by improving the sliding quality; none of these means offer a sufficient effect to improve the transportability in scanners and facsimile plotters.

In addition, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 42653/1986 describes a combined use of a polymer matting agent of over 3 μ m, preferably 3.5 to 6.0 μ m in average grain size and a silicone lubricant to improve the charge control property and sliding quality, but this method does not offer a sufficient improving effect on the transportability in scanners and facsimile plotters.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a silver halide photographic light-sensitive material having improved transportability in scanners and facsimile plotters.

The object of the present invention described above is accomplished by a silver halide photographic light-sensitive material comprising a support and provided thereon, a silver halide emulsion layer and at least two backing layers on the support opposite to said silver halide emulsion layer, wherein an uppermost layer of said silver halide emulsion layer or an uppermost layer of said backing layers contains a lubricant and a backing layer other than said uppermost backing layer contains a matting agent having an average particle size of more than 10 µm.

When a large sized matting agent is used in photographic light-sensitive material, it is anticipated that the surface roughness increases, the sliding quality deteriorates and the transportability lowers. Contrary to this anticipation, the use of a matting agent exceeding 10 μ m in average grain size in combination with the constitution of the present invention has made it possible to improve the transportability in scanners and facsimile plotters.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is hereinafter described in detail.

Typical examples of lubricants which can be used for the present invention include the silicone lubricants described in US Patent Nos. 3,042,522, 3,080,317, 4,004,927, 4,047,958 and 3,489,567, British Patent Nos. 955,061 and 1,143,118 and Japanese Patent O.P.I. Publication No. 140341/1985, the higher fatty acid, alcohol or acid amide lubricants described in US Patent Nos. 2,454,043, 2,732,305, 2,976,148 and 3,206,311 and Ger-

man Patent Nos. 1,284,295 and 1,284,294, the metallic soaps described in British Patent No. 1,263,722 and US Patent No. 3,933,516, the ester or ether lubricants described in US Patent Nos. 2,588,765 and 3,121,060 and British Patent No. 1,198,387 and the taurine lubricants described in US Patent Nos. 3,502,473 and 3,042,222.

5 Examples of lubricants which can be used for the present invention are exemplified as follows:

10	L-1	C ₁₀ H ₃₃ OSO ₃ Na
	L - 2	C ₁₈ H ₃₇ OSO ₈ Na
15	L-3	C ₁₃ H ₂₇ SO ₃ Na
20	L – 4	C ₁₈ H ₃₃ O (CH ₂) ₄ SO ₃ Na
	L – 5	C ₁₇ H ₃₆ CONCH ₂ CH ₂ SO ₃ Na
25		СН _э
	L-6	C ₁₆ H ₃₅ O (CH ₂ CHO) _n SO ₅ Na CH ₅
30		n = 3
35	L-7	O C ₁₈ H ₃₇ O - P - ONa ONa
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45		$ \begin{array}{c} O \\ \parallel \\ (C_{12}H_{25}O)_2 - P - ONa \end{array} $ $ C_{15}H_{51}COOK $
		016113100011
50	L - 10	C ₁₇ H ₈₅ COONa
55	L-11	C ₁₇ H ₃₅ CONCH ₂ CH ₂ COONa CH ₃

$$CH_{3}$$
 CH_{3}
 CH_{3}
 CH_{3}
 CH_{3}
 CH_{3}
 CH_{3}
 CH_{3}
 CH_{3}
 CH_{3}

$$\begin{array}{c|c} CH_{3} \\ \oplus & | \\ L-14 & C_{16}H_{33} - N - CH_{3} \\ & | \\ CH_{2}COO \end{array}$$

L-15 Sorbitan monolaurate

L-16 Sorbitan monostearate

L-17 Sorbitan dioleate

L-18 $C_{15}H_{31}COOC_{16}H_{33}$

L-19 $C_{17}H_{35}CON(CH_2)_2$

L – 20 (CH₃)₃SiO
$$+$$
 (CH₃)_n Si (CH₃)₃ CH₃

$$n = 30$$

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L -25 HOOC
$$(CH_2)_{H}$$
 $\leftarrow \begin{pmatrix} CH_3 \\ | \\ | \\ | \\ CH_3 \end{pmatrix}_{m}$ $(CH_2)_{10}COOH$

$$m = 30$$

$$L-26 \qquad (CH_{3})_{3}SiO - \left(\begin{array}{c} CH_{3} & CH_{3} \\ | & | \\ SiO - \\ | & m \end{array}\right)_{m} Si \quad (CH_{3})_{5}$$

$$CH_{3} \qquad (CH_{2})_{10}COOH$$

$$m = 30$$
 $n = 2$

These lubricants may previously be added along with the dispersing agent used upon synthesis of an organic matting agent.

The matting agent for the present invention is a powder of an organic or inorganic compound. The organic compound includes water-dispersible vinyl polymers such as polymethyl methacrylate, and cellulose acetate propionate and starch, with preference given to spherical matting agents of water-dispersible vinyl polymers such as homopolymers of acrylates such as methyl methacrylate, glycidyl acrylate and glycidyl methacrylate, or copolymers of these acrylates or copolymers with other vinyl monomer. Examples of inorganic compounds which can be preferably used include silver halide strontium barium sulfate, calcium carbonate, silicon dioxide, magnesium oxide, boron nitride, hollow silica (produced by Japan Fillite Co., Ltd.), ethylene tetrafluoride and titanium oxide. The content of the matting agent is 1 mg/m² to 1000 mg/m², preferably 50 mg/m² to 500 mg/m². Average grain size is greater than 10 μ m, preferably not more than 30 μ m. Average grain sizes exceeding 100 μ m are undesirable because the matting agent becomes liable to detach from the film surface and can cause a plotter failure. Grain size can be determined using an electron micrograph or Coulter counter.

The silver halide photographic light-sensitive material of the invention preferably has a layer containing a water-aoluble dye.

In the present invention, it is preferable to use a water-soluble dye having an absorption maximum at a wavelength of not less than 670 nm selected from the group consisting of compounds represented by the following Formulas Ia. Ib. Ic. II. III and IV.

Of these dyes, those represented by Formulas I, III and IV are suitable for semiconductor laser, while the dye represented by Formula II is suitable for LED light sources.

Formula Ia

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Formula Ib

Formula Ic

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$$Y_{1} \xrightarrow{R_{2} R_{3}} L \leftarrow L - L \xrightarrow{m-1} X_{2} \xrightarrow{R_{5} R_{6}} (X^{\Theta}) n$$

wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_5 independently represent an alkyl group Y_1 and Y_2 independently represent a group of non-metal atoms necessary to form a pyrrolopyridine ring, provided that the ring of Y_1 contains a



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group and the ring of Y2 contains a

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aroun

 R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Y_1 and Y_2 in Formula Ia, R_1 , R_2 , R_3 , R_4 , R_5 , R_5 , Y_1 and Y_2 in Formula Ib and R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Y_1 and Y_2 in Formula Ic independently represent a group which allows the dye molecule to have at least two acid residues or a group which allows the dye molecule to have at least two substituents having one or more -CH₂CH₂OR groups, wherein R represents a hydrogen atom or an alkyl group.

L represents a methine group; X^{\ominus} represents an anion; m represents an integer of 4 or 5; n represents an integer of 1 or 2. When the dye forms an intramolecular salt, n is 1.

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Formula II

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wherein Q represents an aliphatic group or aromatic group; R represents a hydrogen atom, aliphatic group or aromatic group; M represents a cation; L represents a methine group; n is 0, 1 or 2; p is 1 or 2.

Formula III

$$Z_1$$
 R_3
 R_6
 Z_2
 R_1
 R_2
 R_3
 R_6
 R_5
 R_5
 R_6
 R_7
 R_8
 R_8

wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 , whether identical or not, independently represent a substituted or unsubstituted alkyl group; Z_1 and Z_2 independently represent a group of non-metal atoms necessary to form a substituted or unsubstituted benzo-condensed ring or naphtho-condensed ring. R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Z_1 and Z_2 independently represent a group which allows the dye molecule to have at least four acid residues. L represents a substituted or unsubstituted methine group; X^{\odot} represents an anion; n is 1 or 2. When the dye forms an intramolecular salt, n is 1.

Formula IV

$$\begin{array}{c|c}
 & \text{NH} \\
 & \text{N} \\
 & \text{Fe} \\
 & \text{(V1)}_{n-1} & \text{(V2)}_{m-1} \\
 & \text{3}
\end{array}$$

wherein V_1 and V_2 independently represent a sulfo group or carboxyl group; n represents 1, 2, 3 or 4; m represents 1, 2 or 3; n and m do not represent 1 at the same time.

Formula I is described in detail below.

Formula Ia

Formula Ib

Formula Ic

wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 independently represent an alkyl group; Y_1 and Y_2 independently represent a group of non-metal atoms necessary to form a pyrrolopyridine ring; the ring of Y_1 contains a

N_⊕

group; the ring of Y2 contains a

N ⊕

group.

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 R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Y_1 and Y_2 in Formula Ia, R_1 , R_2 , R_3 , R_4 , R_5 , R_5 , Y_1 and Y_2 in Formula Ib and R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Y_1 and Y_2 in Formula Ic independently represent a group which allows the dye molecule to have at least two acid groups or a group which allows the dye molecule to have at least two substituents having one or more -CH₂CH₂OR groups, wherein R represents a hydrogen atom or alkyl group.

L represents a methine group; X^{\ominus} represents an anion; m represents an integer of 4 or 5; n represents an integer of 1 or 2. When the dye forms an intramolecular salt, n is 1.

Examples of acid groups for Formulas Ia, Ib and Ic include a sulfonic acid group, a carboxylic acid group and a phosphonic acid group, which acid groups include salts thereof. Examples of such salts include salts of alkali metals such as sodium and potassium, ammonium salts and organic ammonium salts such as triethylamine and pyridine.

The alkyl groups represented by R_1 , R_2 , R_3 , R_4 , R_5 and R_5 preferably represent a lower alkyl group having 1 to 8 carbon atoms, such as methyl, ethyl, propyl, i-propyl, butyl and other groups, and may have a substituent other than the acid substituent or -CH₂CH₂OR group described above.

The alkyl group represented by R is preferably a lower alkyl group having 4 or less carbon atoms.

Examples of the substituent containing a -CH₂CH₂OR group include the hydroxyethyl group, hydroxyethoxyethyl group, methoxyethoxyethyl group, hydroxyethylcarbamoylmethyl group,

hydroxyethoxyethylcarbamoylmethyl group,

N,N-dihydroxyethylcarbamoylmethyl group, hydroxyethylsulfamoylethyl group and methoxyethoxyethoxycarbonylmethyl group.

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Examples of other substituents which may be possessed by Y_1 and Y_2 include the sulfo group (including its salt), carboxyl group (including its salt), hydroxy group, cyano group and halogen atoms such as atoms of fluorine, chlorine and bromine.

The methine group represented by L may also have a substituent. Examples of the substituent include substituted or unsubstituted lower alkyl groups having 1 to 5 carbon atoms, such as methyl, ethyl, 3-hydroxypropyl, 2-sulfoethyl and other groups, halogen atoms such as atoms of fluorine, chlorine and bromine, aryl groups such as phenyl group, alkoxy groups such as methoxy and ethoxy groups. The substituents for the methine group may bind to form a 6-membered ring containing three methine groups, such as 4,4-dimethylcyclohexene ring.

The anion represented by X^{\odot} is not subject to limitation. Examples thereof include halogen ions, p-toluenesulfonic acid ions and ethyl sulfate ions.

Examples of the dyes represented by Formulas Ia, Ib and Ic for the present invention (hereinafter referred to as the dye of the present invention) are given below, but the invention is not limited by these examples.

Exemplified Compounds

5 (I - I)CH₃ CH₃ 10 $(\mathring{C}H_2)_3SO_3^{\Theta}$ (CH2)3SO3Na (I - 2)15 20 $(CH_2)_3SO_3^{\Theta}$ (CH₂)₃SO₃Na (I - 3)25 30 (CH₂)₃SO₃ ⁶ (CH₂)₃SO₃Na (I - 4)CH₃ CH₃ 35 CH₃ CH₃ 40 (CH₂),SO₃ Θ (CH₂),SO₃Na (I - 5)CH₃ CH₃ [⊖]0₃S(CH₂)_{1, ⊕} (CH₂)₃SO₃Na 45

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(1 - 6)[⊖]0₃S(CH₂); ⊕ CH₃ CH₃ (CH₂)₃SO₃Na $(CH = CH)_3 - CH$ NaO₃S 10 (I - 7)CH₃ CH₃ CH₃ CH₃ 15 ĊH₂COOH ĊH₂COOH 20 (I - 8)CH₃ CH₃ CH₃ CH₃ 25 $(CH = CH)_3 - CH$ (CH₂)₃PO₃H ^Θ (CH₂)₃PO₃H₂ 30 (I - 9)CH₃ CH₃ CH₃ CH₃ 35 (CH₂)₂PO₃H₂ (CH₂)₂PO₃H₂ (I - I0)40 CH₃ CH₃ 45

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CH 2 COOK

ĊH₂COO [⊖]

$$(I - II)$$

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$$CH_3$$
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 O_3Na
 CH_2COOH
 CH_2COOH

$$(I - 12)$$

CH₃ CH₃ CH₃ CH₃

$$(CH = CH)_3 - CH = CH_2)_4 PO_3 H_2$$

CH₃ CH₃ CH₃ CH₃ CH₃
$$\frac{1}{N}$$
 CH = CH)₃ - CH $\frac{1}{N}$ SO₃Na $\frac{1}{N}$ (CH₂)₃PO₃H₂ (CH₂)₃PO₃H₂

$$(I - 14)$$

$$\Theta$$
 OOCCH 2 Θ CH 3 CH 3 Θ CH 2 COOH Θ CH = CH) 3 Θ CH 2 COOH

$$(1 - 15)$$

$$\Theta$$
HO₃P(CH₂)₂ Θ
 O CH₃ CH₃ CH₃ (CH₂)₂PO₃H₂
 O CH=CH)₃-CH

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(ĊH₂)₃SO₃K

(CH₂)₃SO₃ ^Θ

(I - 21)

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$$CH_3$$
 CH_3 CH_3

CH₂ CH₃ CH₃ CH₃ CH₃ CH₃ CH₃ CH₃ CH₃
$$CH_3$$
 CH₂ CONH(CH₂CH₂O)₂H CH_2 CONH(CH₂CH₂O)₂H

$$(H_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{2} CH_{2}COO(CH_{2}CH_{2}O)_{2}CH_{3} CH_{2}COO(CH_{2}CH_{2}O)_{2}CH_{3}$$

$$(1 - 24)$$

HO(CH₂)₂
$$\xrightarrow{\text{CH}_3}$$
 CH₃ $\xrightarrow{\text{CH}_3}$ CH₂)₂OH
$$\xrightarrow{\text{OD}_3 \text{S}}$$
 $\xrightarrow{\text{CH}_3}$ CH₃ $\xrightarrow{\text{CH}_3}$ CH₂)₂OH

$$40 \quad (I - 25)$$

CH₃ CH₃ CH₃
$$\rightarrow$$
 CH₂CH₂SO₃ \rightarrow CH₃ CH₃ \rightarrow CH₃ CH₃ \rightarrow CH = CH - CH = CH - CH = CH - CH \rightarrow CH₂D₃PO₃H₂ \rightarrow CH₂D₃PO₃H₂

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(CH₂)₃SO₃Na

$$(1 - 31)$$

CH₃ CH₃ CH₃ CH₃
$$CH_3$$
 CH_3 CH_3

NaO₃S
$$\rightarrow$$
 CH₃ CH₃ CH₃ \rightarrow CH₃ CH₃ \rightarrow CH₃ CH₃ \rightarrow CH₃ CH₃ \rightarrow No₃Na (CH₂)₃SO₃Na

(I - 33)

$$\Theta$$
 O₃S(CH₂), Θ CH₃ CH₃ CH₃ (CH₂), SO₃Na SO₃Na

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The dye of the present invention can be synthesized in accordance with the Journal of the Chemical Society, <u>189</u> (1933), US Patent No. 2,895,955 and Japanese Patent O. P. I. Publication No. 123454/1987.

The parent nucleus for the dye of the present invention is exemplified by the following compounds

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(A) (B)

$$CH_3$$
 CH_3 CH_3 CH_3 CH_3 CH_3

50 (C)

Compound A can be synthesized by the method described in the Journal of the Chemical Society, <u>3202</u> (1959) and British Patent No. 870,753.

Compound B can be synthesized by the method described in the Journal of the Chemical Society, <u>584</u> (1961).

Compound C can be synthesized by the method described in British Patent No. 841,588.

These parent nuclei can be used to obtain quaternary, sulfonic or other derivatives as necessary. It is also possible to synthesize N-alkyl-N-pyridylhydrazine in accordance with the method described in the Journal of the Chemical Society, 3202 (1959) and the Journal of the Chemical Society, 584 (1961) and cyclize it via hydrazone and treat with acid as necessary to yield a 1-alkyl-substituted 3H-pyrrolopyridine derivative, and use it as a starting material.

The dye is dissolved in an appropriate solvent such as water, methanol, ethanol or another alcohol, methyl cellosolve or a mixture thereof and added to a hydrophilic colloid layer coating solution for the present invention.

The dye of the present invention can be used in combination of two or more kinds.

In the present invention, at least one of the compounds represented by Formulas Ia, Ib and Ic is contained in the light-sensitive material to be treated, and may be used in any combination, for example, a combination of two or more kinds of the same compound or a combination of compounds represented by different formulas.

Although the amount of the compound represented by Formulas Ia, Ib and Ic varies depending on the purpose of its use, it is preferably 10^{-3} g/m² to 1.0 g/m², more preferably 10^{-2} g/m² to 0.5 g/m².

Formula II is described in detail below.

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Formula II

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wherein Q represents an aliphatic group or aromatic group; R represents a hydrogen atom, aliphatic group or aromatic group; M represents a cation; L represents a methine group; n is 0.1 or 2; p is 1 or 2.

Examples of the substituents Q, R, M and L in Formula II are given below.

The aliphatic group represented by Q is exemplified by alkyl groups having 1 to 4 carbon atoms, such as methyl group, ethyl group, n-propyl group and n-butyl group. The aromatic group is exemplified by aryl groups such as phenyl group and naphthyl group. These aliphatic groups and aromatic groups may contain an additional substituent other than the sulfo group, such as an atom of a halogen (e.g., fluorine, chlorine), alkyl group (e.g., methyl group, ethyl group), hydroxy group or alkoxy group (e.g., methoxy group).

Examples of the aliphatic group represented by R include alkyl groups having 1 to 4 carbon atoms, such as methyl group, ethyl group and propyl group. Examples of the aromatic group include aryl groups such as phenyl group and naphthyl group. These aliphatic groups and aromatic groups may contain an additional substituent such as an atom of a halogen (e.g., fluorine, chlorine, bromine), alkyl group (e.g., methyl group, ethyl group), aryl group (e.g., phenyl group), carboxyl group, sulfo group, hydroxyl group, alkoxy group (e.g., methoxy group), aryloxy group (e.g., phenoxy group).

The cation represented by M is exemplified by cations of hydrogen atom, alkali metals such as sodium and potassium, alkaline earth metals such as calcium, ammonia and organic bases such as triethylamine, pyridine, piperidine and morpholine.

The methine group represented by L may be substituted by an alkyl group, aryl group or halogen atom. Examples of the alkyl group include methyl group and ethyl group. Examples of the aryl group include phenyl group. Examples of the halogen atom include chlorine atom and bromine atom.

Typical examples of the oxonol dye represented by Formula II are given below, but the oxonol dye relating to the present invention is not limited by these examples.

Exemplified Dyes

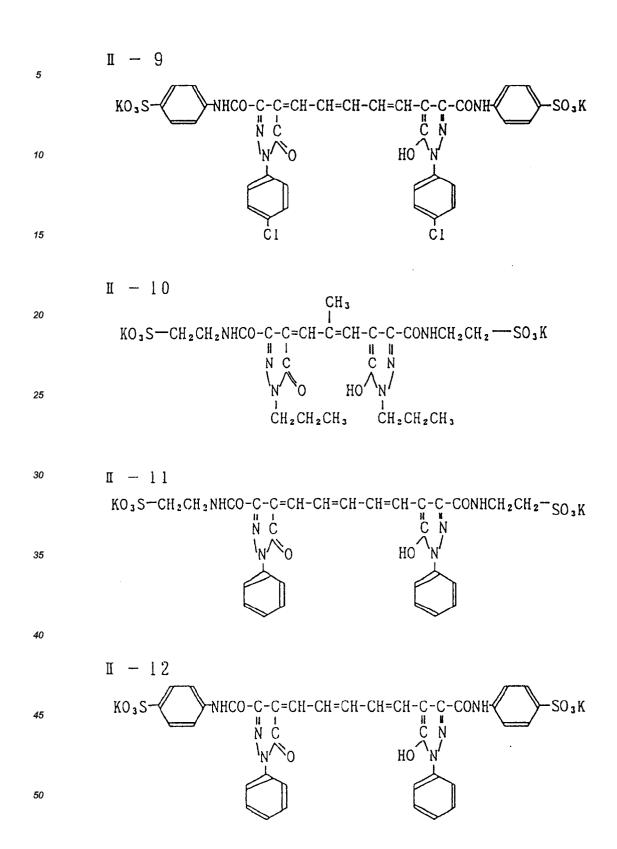
II - 1

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CH2CH2CH2SO3K

CH2CH2CH2SO3K



II - 17-NHCO-C-C=CH-CH=CH-C-C-CONH-N C C N 5 HO 10 II - 18-NHCO-C-C=CH-CH=CH-C-C-CONIII N C C N KO₃S SO,K 15 HO^ 20 ŠO₃K II - 1925 -NHCO-C-C=CH-CH=CH-C-C-CONH II I II II N C C N -SO₃Na NaO₃S HO^ 30 NaO₃S SO₃Na S0₃Na 35 SO₃Na II - 50 $KO_3S-CH_2CH_2NHCO-C-C=CH-C-C-CONHCH_2CH_2-SO_3K$ N C C N40 но

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 SO_3K

SO₃K

II -21KO₃S — NHCO-C-C=CH-CH=CH-C-C-CONH — SO₃K

N C C N

N C C N

CH₂CH₂SO₃K CH₂CH₂SO₃K

II -22NaO₃S — NHCO-C-C=CH-CH=CH-C-C-CONH — SO₃N₃

OCH₃ N C C N

H₂CO C N

H₂CO C C N

CH₂CH₂SO₃K CH₂CH₂SO₃K

35 NaO₃S NHCO-C-C=CH-CH=CH-C-C-CONH SO₃Na
NaO₃S NHCO-C-C=CH-CH=CH-C-C-CONH SO₃Na
NaO₃S NaO₃S NaO₃Na

II - 24

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II
$$-25$$

KO₃S-CH₂NHCO-C-C=CH-C=CH-C-C-CONHCH₂-SO₃K

N C C N

N C C N

N C OCH₃

OCH₃

I - 26

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With respect to the silver halide photographic light-sensitive material of the present invention, the dye represented by Formula II may be used as an anti-irradiation dye in a silver halide photographic light-sensitive emulsion or as a filter dye or anti-halation dye in a non-light-sensitive hydrophilic colloid layer. Two or more kinds of the dye may be used in combination, and the dye may be used in combination with another dye. The dye for the present invention can easily be added to a silver halide photographic light-sensitive emulsion or another hydrophilic colloid layer by an ordinary method. Usually, an aqueous solution of the dye or an organic or inorganic alkali salt thereof is added to the coating solution, and the coating solution is coated to yield a silver halide photographic light-sensitive material containing the dye. Although the content of the dye represented by Formula II varies depending on the purpose of use, the coating solution is coated so that its amount will be 1.0 to 1000 mg per m² of light-sensitive material.

Formula III is described in detail below.

$$Z_{1}$$

$$R_{2}$$

$$R_{3}$$

$$R_{6}$$

$$R_{5}$$

$$R_{1}$$

$$R_{1}$$

$$R_{1}$$

$$R_{2}$$

$$R_{3}$$

$$R_{6}$$

$$R_{5}$$

$$R_{4}$$

$$R_{2}$$

$$R_{3}$$

$$R_{6}$$

$$R_{1}$$

$$R_{4}$$

$$R_{4}$$

wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 , whether identical or not, independently represent a substituted or unsubstituted alkyl group; Z_1 and Z_2 independently represent a group of non-metal atoms necessary to form a substituted or unsubstituted benzo-condensed ring or naphtho-condensed ring. At least four of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 independently represent an acid substituent such as sulfonic acid group or carboxylic acid group, pref-

erably a group which allows the dye molecule to have four sulfonic acid groups.

In the present invention, a sulfonic acid group means a sulfo group or its salt, and a carboxylic acid group means a carboxyl group or its salt.

Examples of such salts include salts of alkali metals such as sodium and potassium, ammonium salts and organic ammonium salts such as triethylamine, tributylamine and pyridine.

L represents a substituted or unsubstituted methine group; X^{\ominus} represents an anion. The anion represented by X^{\ominus} is exemplified by ions of halogens such as chlorine and bromine, p-toluenesulfonic acid ions and ethyl sulfate ions.

n represents 1 or 2; when the dye forms an intramolecular salt, n is 1.

The alkyl groups represented by R_1 , R_2 , R_3 , R_4 , R_5 and R_5 preferably represent a lower alkyl group having 1 to 5 carbon atoms, such as methyl group, ethyl group, n-propyl group, n-butyl group, isopropyl group and n-pentyl group, and may have a substituent such as a sulfonic acid group, carboxylic acid group or hydroxyl group.

More preferably, R_1 and R_4 independently represent a lower alkyl group having 1 to 5 carbon atoms and a sulfonic acid group, such as 2-sulfoethyl group, 3-sulfopropyl group or 4-sulfobutyl group.

Examples of the substituent for the benzo-condensed ring or naphtho-condensed ring formed by the group of non-metal atoms represented by Z_1 or Z_2 include sulfonic acid group, carboxylic acid group, hydroxyl group, atoms of halogens such as fluorine, chlorine and bromine, cyano group, substituted amino groups such as dimethylamino group, diethylamino group, ethyl-4-sulfobutyl group and di(3-sulfopropyl)amino group, and substituted or unsubstituted alkyl groups having 1 to 5 carbon atoms bound to the ring directly or via a divalent bonding group, such as methyl group, ethyl group, propyl group and butyl group. Examples of preferable substituents include sulfonic acid group, carboxylic acid group and hydroxyl group. Examples of preferable divalent bonding groups include -O-, -NHCO-, NHSO₂-, -NHCOO-, -NHCONH-, -COO-, -CO- and -SO₂-.

Examples of preferably substituents for the methine group represented by L include substituted or unsubstituted lower alkyl groups having 1 to 5 carbon atoms, such as methyl group, ethyl group, 3-hydroxypropyl group, benzyl group and 2-sulfoethyl group, atoms of halogens such as fluorine, chlorine and bromine, substituted or unsubstituted aryl groups such as phenyl group and 4-chlorophenyl group, and lower alkoxy groups such as methoxy group and ethoxy group.

The substituents for the methine group represented by L may bind to form a 6-membered ring containing three methine groups, such as 4,4-dimethylcyclohexene ring.

Examples of the dye compound represented by Formula III for the present invention are given below, but the invention is not limited by these examples.

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$$(\mathbf{I} - \mathbf{1})$$

KOOC
$$CH_3$$
 CH_3 CH_3 $COOK$
 CH_2), CH_2), $COOK$
 CH_2), CH_2), $COOK$
 CH_3 CH_3 CH_3 $COOK$
 CH_3 CH_3 $COOK$

($\mathbb{m}-2$)

HOOC
$$CH_3$$
 CH_3 CH_3 CH_3 CH_3 CH_2 $COOH$ CH_2 CH_3 CH

 $(\Pi - 3)$

 $(\Pi - 4)$

55

(
$$\mathbb{I} - 5$$
)

5
$$C_2H_5$$
 CH_3 CH_3 CH_3 CH_3 CH_2) CH_3 CH_3 CH_3 CH_4 CH_5 CH

(**II** − 6)

KO₃S
$$CH_3$$
 CH_3 CH_3 CH_3 CH_2)₃ CH_2)₃ CH_2)₃ CH_2)₃ CH_2)₃ CH_3 C

²⁵ (<u>II</u> − 7)

(II — 8)

NaO₃S

$$CH_3$$
 CH_3
 $CH_$

55

(II — 9)

5

NaO₃S

$$CH_3$$
 CH_3
 $CH_$

 $(\Pi - 10)$

CH₃
CH₃
CH₃
CH₃
CH₃
CH₃
CH₃

$$CH_3$$
CH₃
 CH_3
 CH_3
 CH_3
 CH_3
 CH_2
 CH_2
 CH_2
 CH_3
 C

 $(\mathbf{II} - 11)$

SO
$$\frac{CH_3}{CH_3}$$
 $\frac{CH_3}{CH_3}$ $\frac{CH_3}{CH_3}$ $\frac{CH_3}{CO}$ $\frac{CH_3}{CH_2}$ $\frac{CH_3}{CH_2}$ $\frac{CH_3}{CH_2}$ $\frac{CH_3}{CH_3}$ $\frac{CH_3}{CH_$

(11 - 12)

CH₃

$$C_{2}H_{5})_{3}NHO_{3}S$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$C_{2}H_{5}$$

$$CH_{5}CH=CH-CH=C-CH=CH-CH$$

$$CH_{2})_{4}$$

$$CH_{2})_{4}$$

$$SO_{3}\Theta$$

$$SO_{3}H-N(C_{2}H_{5})_{3}$$

50

$$(m - 13)$$

5
$$SO_{3}K CH_{3} CH_{3} CH_{3} CH_{3}$$

$$CH_{2}CH_{3} CH_{3} CH_{3}$$

$$CH_{3}CH_{3} CH_{3}$$

$$CH_{3}CH_{3}$$

$$CH_{3}C$$

 $(\Pi - 14)$

SO₃K CH₃ CH₃ SO₃K

CH₃ CH₃ CH₃

$$CH_3$$
 CH₃
 CH_3 CH₃
 CH_3 CH₃
 CH_3 SO₃K

 CH_2 SO₃K

 CH_2 SO₃K

(III - 15)

(II - 16)

55

$$(III - 17)$$

5

10

 $_{15}$ (III - 18)

(II - 19)

(II - 20)

55

(m - 21)

10

$$(III - 22)$$

(III - 23)

(II - 24)

50

$$(II - 25)$$

5
$$KO_3S$$
 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_4 CH_5 CH_5

 $(\Pi - 26)$

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The dye represented by Formula III has an absorption maximum in the wavelength range of from 730 to 850 nm, and can be synthesized in accordance with the Journal of the Chemical Society, <u>189</u> (1933) and Synthesis Examples for US Patent No. 2,895,955.

The dye can be used in solution in an appropriate solvent such as water, methanol, ethanol or another alcohol, methyl cellosolve or a mixture thereof in a hydrophilic colloid layer coating solution for forming the desired colored layer of light-sensitive material.

The dye of the present invention can be used in combination of two or more kinds.

Although the content of the dye represented by Formula III varies depending on the purpose of its use, it is preferably 10⁻³g/m² to 0.5 g/m², more preferably 10⁻²g/m² to 0.2 g/m².

Formula IV is described in detail below.

Formula IV

$$\begin{array}{c|c}
NH \\
N \\
V_1)_{n-1} & (V_2)_{m-1}
\end{array}$$

wherein V_1 and V_2 independently represent a sulfo group or carboxyl group; n represents 1, 2, 3 or 4; m represents 1, 2 or 3; n and m do not represent 1 at the same time.

Examples of the compound represented by Formula IV are given below, but the compound relating to the invention is not limited by these examples.

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Exemplified Compounds

5 IV - 1 KO₃S NH Fe

5

IM - 3

IV - 4

$$IV - 7$$

These dyes may be used in combination of two or more kinds.

Although the content of the dye represented by Formula IV varies depending on the purpose of its use, it is preferably 10^{-2} g/m² to 2.0 g/m², more preferably 5×10^{-2} g/m² to 1.0 g/m².

The dye of the present invention is preferably contained to a loewer layer of the backing layers.

The silver halide photographic light-sensitive material of the invention may comprise an electroconductive layer containing an electroconductive metal oxide or organic electroconductive polymer coated on at least one side of the support.

The metal oxide in the electroconductive layer for the present invention may be indium oxide, tin oxide or a metal oxide doped with an antimony atom or phosphorus atom, or a combination thereof.

Known indium oxide compounds are primary indium oxide (In_2O) and secondary indium oxide (In_2O_3), with preference given to secondary indium oxide for the present invention.

Known tin oxide compounds are stannous oxide (SnO) and stannic oxide (SnO₂), with preference given to stannic oxide for the present invention. Examples of metal oxides doped with antimony atom or phosphorus atom include tin oxide and indium oxide. To dope antimony or phosphorus to the metal oxide, a halide, alkoxy derivative or nitrate of tin or indium is mixed with a halide, alkoxy derivative or nitrate of antimony or phosphorus, followed by oxidative burning. These metal compounds are easily available. The ratio of antimony or phosphorus doped is 0.5 to 10% by weight of tin or indium. It is preferable to add these inorganic compounds in dispersion in a hydrophilic colloid such as gelatin or in dispersion in a polymer compound such as acrylic acid or maleic acid. The ratio per binder is preferably 1 to 100% by weight.

The organic electroconductive polymer in the electroconductive layer for the present invention is a compound having a molecular weight of 1000 to 1000000, more preferably 1000 to 500000 wherein a sulfonic acid group or its base is bound to an aromatic ring or heterocyclic group directly or via a divalent bonding group. The polymer can easily be synthesized by polymerizing a monomer which is commercially available or can be obtained by a conventional method.

With respect to the electroconductive polymer for the present invention, electroconductivity means that the surface resistivity with an amount of single coating of over 2 g/m² on the polyethylene terephthalate film is not less than $10^{10}\Omega/cm$ (23°C, 20% RH).

The organic electroconductive polymer used in the backing layer for the present invention can be selected out of the examples given above of the organic electroconductive polymer contained in the electroconductive layer.

The electroconductive layer for the present invention is preferably activated on its surface by corona discharge, glow discharge, ultraviolet irradiation, flaming or other treatment. The particularly preferable activating treatment is corona discharge, preferably at 1 mW to 1 kW/(m²·min). Energy intensity is preferably in the range of from 0.1 W to 1 W/(m²·min).

The electroconductive layer for the present invention is preferably provided with an adhesive layer of gelatin or gelatin derivative thereon. Such an adhesive layer may be layered simultaneously with coating the electroconductive layer or may be coated after drying. The adhesive layer is preferably subjected to heat treatment at 70 to 200°C. Various hardeners can be used in the adhesive layer; from the viewpoint of crosslinking in the lower electroconductive layer and crosslinking in the upper backing layer, any hardener can be selected from the groups comprising acrylamide, aldehyde, aziridine, peptide, epoxy and vinyl sulfone hardeners.

The film thickness of an electroconductive layer is closely related to its electroconductivity. Since the electroconductivity improves with the increase in unit volume, it is better to thicken the film; however, it is preferable to set the film thickness in the range of from 0.1 to 100 μ , more preferably 0.1 to 10 μ for good results because film flexibility lowers when the film is too thick.

The electroconductive polymer is exemplified by the following compounds:

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p-1

p-2

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P - 3

 $CH_{2} - CH \xrightarrow{\chi} CH_{2} - C \xrightarrow{\gamma} X : y = 70:30$ $COOCH_{2}CH_{2}OH \xrightarrow{M} 10000$ $SO_{3}Na$

P - 4

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P-5

$$\begin{array}{c|c}
 & \leftarrow \text{CH}_2 - \text{CH} \xrightarrow{y} \leftarrow \text{CH} - \text{CH} \xrightarrow{y} \\
 & \downarrow & \downarrow & \downarrow \\
 & \downarrow & \downarrow$$

P-6

P - 8

$$\begin{array}{c}
CH_{3} \\
\leftarrow CH_{2} - C \\
\hline
COOCH_{2}CH_{2}OH
\end{array}$$

$$\begin{array}{c}
CH_{3} \\
\leftarrow CH_{2} - CH \\
\hline
COONH_{4} \\
\hline
X: y: z = 40:30:1 \\
\hline
N = 750000$$

$$P-9$$

 $CH_{2}-CH\xrightarrow{}_{X} CH_{2}-CH\xrightarrow{}_{y}$ $COOCH_{2}CH-CH$ $0 \qquad x: y=70:30$ N=20000

P - 10

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25 D 11

P-11

$$CH_{3}$$

$$CH_{2}-CH\xrightarrow{\chi}CH_{2}-CH\xrightarrow{\chi}CH_{2}-C\xrightarrow{\chi}C$$

$$COOC_{2}H_{4}OCCH_{2}COC$$

$$CONHC(CH_{3})_{2}CH_{2}SO_{3}H$$

$$SO_{3}Na$$

$$x:y:z=88:19:3$$

$$N=900000$$

SO₃Na

P - 12

 $CH_{2}-CH\xrightarrow{y}CH_{2}-CH\xrightarrow{y}V$ $COOCH_{2}CH_{2}OH$ x:y=80:20 N=1000000

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P - 18

 $_{15}$ P - 19

 $\frac{-(CH_2 - CH)_X}{N} = 450000$ NaO₃S

P - 20

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 $(CH_2 - CH)_{\overline{X}} (CH_2 - CH)_{\overline{y}}$ $N \qquad COOCH_2 CH_2 OH$ x : y = 60 : 40 $SO_3 Na \qquad \overline{N} = 800000$

P - 21

 $-(CH_2-CH)_{\overline{X}} (CH-CH)_{\overline{Y}}$ $COOCH_2CH_2CH_2OH$ X : y = 70 : $SO_3Na \qquad \overline{N} = 650000$

P - 22

$$(CH_2 - CH)_{\overline{X}} + (CH_2 - CH)_{\overline{Y}} + SO_3 Na + COOCH_2 CH_2 OH = 500000$$

P - 23

$$(CH_2 - CH)_{\overline{X}} (CH_2 - CH)_{\overline{y}} \qquad x : y = 75 : 25$$

$$COOCH_2CH_2OH \overline{N} = 400000$$

$$SO_3Na$$

$$P - 24$$

$$(CH_2 - CH)_{\overline{X}} (CH_2 - CH)_{\overline{y}}$$
 $x : y = 80 : 20$

COONa

 $\overline{N} = 600000$

$$P-25$$

$$(CH_2 - CH)_{\overline{X}} (CH_2 - CH)_{\overline{Y}} \qquad x : y = 90 : 10$$

$$COONa \qquad \overline{N} = 400000$$

$$NaO_3S$$

P - 26

 $(CH_2 - CH)_{\overline{X}} (CH_2 - CH)_{\overline{Y}} \qquad x : y = 55 : 45$ $COONa \qquad \overline{N} = 320000$ NaO₃S

P - 27

P - 28

 $(CH_{z}-CH)_{\overline{x}}(CH_{z}-CH)_{\overline{y}}(CH_{z}-CH)_{\overline{z}}$ $N \quad COONa \quad COONa$ $SO_{3}Na \qquad \qquad x:y:z=80:10:10$ $\overline{x}=800000$

P - 29

 $(CH_2 - CH)_{\overline{X}} + (CH - CH)_{\overline{Y}} + (CH_2 - CH)_{\overline{Z}}$ $N \quad COONa COONa \quad COONa$ x: y = 70:30 $\overline{X} = 10000$

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$$P - 30$$

$$(CH_{2} - CH)_{x} - (CH_{2} - CH)_{y} - (CH_{2} - CH)_{z} - (CH_{2} - CH)_{w} - (COON_{a} - COON_{a} - COON_{a$$

(CH₂),SO₃K

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x:y:z=60:30:10

M = 300000

P - 34
$$(CH_2 - CH)_{\overline{X}} (CH_2 - CH)_{\overline{Y}} (CH_2 - CH)_{\overline{Z}}$$

$$(CH_2)_4 CONHCH_2 CH_2 - O - SO_3 Na$$

x:y:z=40:30:30 $\bar{N} = 500000$

P - 35

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$$\begin{array}{c|c} -\text{CH}_2 - \text{CH}_{\overline{x}} & \text{CH}_2 - \text{CH}_{\overline{y}} & \text{CH}_2 - \text{CH}_{\overline{z}} \\ \hline & & \text{COONa} \\ \hline & & \text{COOCH}_2 - \text{CH} - \text{CH}_2 \\ \hline & & \text{SO}_3 \text{Na} \\ \hline & & \text{X}: \text{y}: \text{z} = 55:35:10} \\ \hline & & \text{N} = 300000 \end{array}$$

P - 36
-(CH₂-CH)
$$\frac{}{x}$$
 (CH - CH) $\frac{}{y}$ (CH₂-CH) $\frac{}{z}$
COONa COONa COONa
COOCH₂-N
SO₃Na $\frac{x:y:z=50:30:20}{N=600000}$

P - 37
$$\frac{(CH_2 - CH)_{\overline{X}} (CH_2 - CH)_{\overline{Y}} (CH_2 - CH)_{\overline{Z}}}{OOONa}$$

$$COOOCH_2 \longrightarrow SO_3Na$$

$$x: y: z = 60:30:10$$

$$\overline{N} = 600000$$

With respect to Exemplified Compounds P-1 through P-37, x, y and z represent the mol % ratios of respective monomer components; M represents the average molecular weight (in the present specification, average molecular weight means number-average molecular weight).

The polymer which serves best for the present invention generally has an average molecular weight of about 1000 to 1000000 as stated above.

The electroconductive polymer content in the electroconductive layer of the silver halide photographic light-sensitive material of the present invention is preferably 0.001 to 10 g, more preferably 0.05 to 5 g per unit m² as solid content.

When an electroconductive polymer is used in a backing layer, backing protective layer or silver halide

emulsion layer, the amount of its addition is preferably 0.01 to 10 g as solid content.

The silver halide emulsion for the light-sensitive material of the present invention may be obtained by any of the acid method, the neutral method and the ammoniacal method, with its grain size preferably ranging from $0.2 \mu m$ to $0.5 \mu m$.

The silver halide grains used in the emulsion of the present invention are prepared by adding a water-soluble rhodium salt and an water-soluble iridium salt to incorporate them therein and/or thereon. The amount of addition is preferably 10⁻⁶ to 10⁻⁹ mol per mol of silver halide.

The silver halide grains may have a uniform silver halide composition distribution therein or be core/shell grains with different silver halide compositions between the core and surface layers, and may be grains wherein latent images are formed mainly on the surface, or grains wherein latent images are formed mainly inside the grains.

The shape of the silver halide grains for the present invention may be any one. A preferred shape is a cube having {100} planes to form the crystal surface. It is also possible to use octahedral, tetradecahedral, dodecahedral or other forms of grains prepared by the methods described in US Patent Nos. 4,183,756 and 4,225,666, Japanese Patent O.P.I. Publication No. 26589/1980, Japanese Patent Examined Publication No. 42737/1980 and the Journal of Photographic Science, <u>21</u>, 39 (1973). Grains having twin crystal planes may also be used.

The silver halide grains for the present invention may be of a single shape or a mixture of various shapes. Any grain size distribution may be used. Emulsions with wide grain size distribution (referred to as polydispersed emulsion) may be used, and emulsions with narrow grain size distribution (referred to as monodispersed emulsion) may be used singly or in combination of two or more kinds. Furthermore, a polydispersed emulsion and a monodispersed emulsion may be used in combination.

The silver halide emulsion may be used in combination of two or more separately formed silver halide emulsions.

The silver halide emulsion for the present invention is preferably a monodispersed silver halide emulsion. With respect to the monodispersed silver halide grains in the monodispersed emulsion, the weight of silver halide grains which fall in the grain size range of \pm 20% of the average grain size r preferably accounts for not less than 60% of the total weight of silver halide grains, more preferably not less than 70%, and still more preferably not less than 80%.

Here, the average grain size r is defined as the grain diameter ri which gives a maximum value for ni x ri³, wherein ri denotes the grain diameter and ni denotes the number of grains having a diameter of ri (significant up to three digits, rounded off at the last digit).

The grain diameter stated here is the diameter of the silver halide grain when the grain is spherical or the diameter of a circle converted from a grain projection image with the same area when the grain is not spherical.

Grain size can be obtained by measuring the diameter of the grain or the area of projected circle on an electron micrograph taken at x 10000 to 50000 (the number of subject grains should be not less than 1000 randomly).

A highly monodispersed emulsion preferred for the present invention has a degree of monodispersion of not more than 20, more preferably not more than 15 as calculated using the following equation 1.

Equation 1

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$\frac{\text{Grain size standard deviation}}{\text{average grain size}} \times 100 = \text{degree of monodispersion}$

Here, average grain size and grain size standard deviation are calculated from ri defined above. A monodispersed emulsion can be prepared in accordance with Japanese Patent O.P.I. Publication Nos. 48521/1979, 49938/1983 and 122935/1985.

The light-sensitive silver halide emulsion may be used as a primitive emulsion without chemical sensitization, but it is the common practice to subject it to chemical sensitization.

Chemical sensitization can be achieved by the methods described in publications by Glafkides or Zelikman et al., or Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden, Akademische Verlagsgesellschaft, 1968, edited by H. Frieser.

Accordingly, it is possible to use the sulfur sensitization method using a sulfur-containing compound capable of reacting with silver ions or active gelatin, the reduction sensitization method using a reducing agent, and other methods using gold or another noble metal compound singly or in combination. Examples of sulfur sensitizers which can be used include thiosulfates, thioureas, thiazoles, rhodanines and other compounds, exemplified in US Patent Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668 and 3,656,955. Examples of reduction sensitizers which can be used include stannous salts, amines, hydrazine derivatives, formamidosulfininc

acid and silane compounds, exemplified by US Patent Nos. 2,487,850, 2,419,974, 2,518,698, 2,983,609, 2,983,610 and 2,694,637.

For noble metal sensitization, complex salts of metals in Group VII in the periodic table of elements such as platinum, iridium and palladium can be used in addition to complex salt of gold, exemplified in US Patent Nos. 2,399,083 and 2,448,060 and British Patent No. 618,061.

Although there is no limitation on chemical sensitization conditions such as pH, pAg or temperature, pH is preferably 4 to 9, more preferably 5 to 8; pAg is preferably 5 to 11, more preferably 7 to 9. Temperature is preferably 40 to 90°C, more preferably 45 to 75°C.

The photographic emulsion for the present invention may be subjected to the reduction sensitization method using a reducing agent, the noble metal sensitization method using a noble metal compound and other methods in combination with the sulfur sensitization method and gold-sulfur sensitization method described above.

The light-sensitive emulsion may be used singly or in combination of two or more kinds.

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In the embodiment of the present invention, after completion of chemical sensitization as described above, various stabilizers can be used, such as 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 5-mercapto-1-phenyltetrazole and 2-mercaptobenzothiazole. A silver halide solvent such as thioether or a crystal habit control agent such as a mercapto-containing compound or sensitizing dye may be used as necessary.

The emulsion for the present invention allows the unnecessary soluble salts to be removed or remain contained after completion of growing silver halide grains. The salts can be removed in accordance with the method described in Research Disclosure No. 17643.

The photographic emulsion may contain various compounds for preventing sensitivity reduction and fogging during preparation, storage or processing of the silver halide photographic light-sensitive material.

An example of usable compound is given in the Theory of the Photographic Process, 3rd edition, 1966, edited by K. Mees, with reference to the original source.

For more specific examples and other methods of use, US Patent Nos. 3,954,474, 3,982,947 and 4,021,248 and Japanese Patent Examined Publication No. 28660/1977 serve as references.

Also, the silver halide photographic light-sensitive material of the present invention may contain in its photographic structural layer an alkyl acrylate latex as described in US Patent Nos. 3,411,911 and 3,411,912 and Japanese Patent Examined Publication No. 5331/1970.

The silver halide photographic light-sensitive material of the present invention may contain various additives. Specifically, there can be used the thickening agents or plasticizers described in US Patent Nos. 2,960,404 and 3,767,410, Japanese Patent Examined Publication No. 4939/1968, West German Patent Publication No. 1,904,604, Japanese Patent O.P.I. Publication No. 63715/1973 and Belgian Patent Nos. 762,833 and 588,143 such as styrene-sodium maleate copolymer and dextran sulfate, hardeners such as those based on aldehyde, epoxy, ethylene imine, active halogen, vinyl sulfone, isocyanate, sulfonate, carbodiimide, mucochloric acid and acyloyl, the ultraviolet absorbents described in US Patent No. 3,253,921 and British Patent No. 1,309,349 specifically 2-(2'-hydroxy-5-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-t-butylphenyl)benzotriazole, 2-(2-hydroxy-3'-t-butyl-5'-butylphenyl)-5-chlorobenzotriazole and 2-(2'-hydroxy-3',5'-dit-butylphenyl)-5-chlorobenzotriazole. Examples of additives for improving the permeability against coating aids, emulsifiers, processing solutions and others, defoaming agents, surfactants for controlling various physical properties of light-sensitive material include the anionic, cationic, nonionic or amphoteric compounds described in British Patent Nos. 548,532 and 1,216,389, US Patent Nos. 2,026,202 and 3,514,293, Japanese Patent Examined Publication Nos. 26580/1969, 17922/1968, 17926/1968, 3166/1968 and 20785/1973, French Patent No. 202,588, Belgian Patent No. 773,459 and Japanese Patent O.P.I. Publication No. 101118/1973, with preference given to anionic surfactants having a sulfone group such as sulfonated succinates and alkylbenzenesulfonates. Examples of antistatic agents include the compounds described in Japanese Patent Examined Publication Nos. 24159/1971, 39312/1971 and 43809/1973, Japanese Patent O.P.I. Publication Nos. 89979/1973, 20785/1973, 43130/1973, 90391/1973 and 33627/1972 and US Patent Nos. 2,882,157 and 2,972,535.

The pH of the photographic emulsion coating solution preferably ranges from 5.3 to 7.5. In the case of multiple-layer coating, the coating solution mixture of the coating solutions for the layers in the ratio of the amount of coating preferably has a pH in the above-mentioned range of from 5.3 to 7.5. pH values out of this range are undesirable because hardening is retarded if the pH is lower than 5.3 and because the photographic performance is adversely affected if the pH exceeds 7.5.

The light-sensitive material of the present invention may contain various other additives as desired. More specifically, these additives are described in Research Disclosure (RD), Vol. 176, Item 17643 (December 1978) and Vol. 187, Item 18716 (November 1979).

Table 1 below shows where the additives are described.

Table 1

	Add	itive	RD17643	RD18716
5	1.	Chemical sensitizer	p. 23	p. 648. right column
	2.	Sensitizer		the same as above
10	3.	Spectral sensitizer and supersensitizer	pp. 23-24	p. 648, right column - p. 649, right column
15	4.	Brightening agent	p. 24	
20	5.	Antifogging agent and stabilizer	pp. 24-25	p. 649, right column
25	6.	Light absorbent, filter dye and ultraviolet absorbent	pp. 25-26	p. 649 right column - p. 650, left column
	7.	Antistaining agent	p. 25, right column	p. 650, left to right columns
30	8.	Dye image stabilizer	p. 25	
	9.	Hardener	p. 26	p. 651, left column
35	10.	Binder	p. 26	the same as above
	11.	Plasticizer and lubricant	p. 27	p. 650, right column
40	12.	Coating aid, surfactant	pp. 26-27,	the same as above
	13.	Antistatic agent	p. 27,	the same as above

Various methods can be used without limitation for photographic processing of the silver halide photographic light-sensitive material of the present invention. Processing temperature is selected from the range from 18 to 50°C, but may be lower than 18°C or higher than 50°C.

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The developing agent for the black-and-white developer for the present invention may contain singly or in combination dihydroxybenzenes such as hydroquinone, 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, aminophenols such as N-methyl-p-aminophenol for facilitating the obtainment of better performance.

The silver halide photographic light-sensitive material of the present invention can be processed with a developer containing an imidazole as a silver halide solvent. In addition to this additive, the developer may contain various additives such as preservatives, alkalis, pH buffers and antifogging agent, and as necessary dissolution aids, tone adjusters, development accelerators, surfactants, defoaming agents, water softening agents, hardeners and tackifiers.

The silver halide photographic light-sensitive material of the present invention may also be developed by so-called the lith type process. As a special method of development, the light-sensitive material may contain the developing agent in its emulsion, for instance, and may be developed with an aqueous solution of alkali. If

the developing agent is hydrophobic, it may be contained in an emulsin layer by the method described in Research Disclosure No. 169 and other publications. This method of development may be used in combination with a silver salt stabilizing process using thiocyanate.

The fixer used has a commonly used composition and may contain a water-soluble aluminum salt as a hardener.

For exposure of the photographic emulsion for the present invention, various light sources can be used as appropriate, such as tungsten lamps, fluorescent lamps, arc lamps, mercury lamps, xenon sun light lamps, xenon flash lamps, cathode ray tube flying spots, laser beams, electron beams, X-ray and fluorescent screens for radiography, selected according to chemical sensitization conditions, purpose of use and other factors.

Exposure time is normally 1/1000 to 100 seconds, but short exposure time of 10^{-4} to 10^{-9} second is possible when using a xenon flash lamp, cathode ray tube or laser beam.

The present invention makes it possible to provide a silver halide photographic light-sensitive material having improved transportability in scanners and facsimile plotters.

15 EXAMPLES

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The present invention is hereinafter described in more detail by means of the following examples, but the invention is not limited by these examples.

Example 1

Preparation of backing layer coating solution

500 g of gelatin was dissolved in 8 l of water. To this solution were added 1 g of the following dye compound 5 and then 20 g of saponin as a surfactant, 20 g of a butyl acrylate-vinylidene chloride copolymer as a polymer latex and 2.5 g of a styrene-maleic anhydride copolymer as a thickening agent, after which a matting agent listed in Table 3 was added to yield a backing layer coating solution.

Compound 5

CH₃ CH₉

$$(CH = CH) = CH$$

$$(CH2)3SO3\Theta$$

$$(CH2)3SO3K$$

Preparation of backing protective layer coating solution

40 g of gelatin was dissolved in 1000 ml of water. To this solution were added a matting agent listed in Table 3, 30 g of a 1% aqueous solution of 1-decyl-2-(3-isopentyl)succinate-2-sodium sulfonate and a lubricant listed in Tables 2 through 4 to yield a backing protective layer coating solution.

Preparation of emulsion layer coating solution

To an aqueous solution containing gelatin and sodium chloride being kept at 40° C, an aqueous solution of silver nitrate and a mixed aqueous solution containing potassium bromide and sodium chloride prepared by adding potassium hexachloroiridate at 6×10^{-7} mol per mol of silver halide and hexabromorhodium salt at 4×10^{-8} mol per mol of silver halide were added by the double jet method to yield silver chlorobromide grains containing 35% silver bromide (distribution width 9%, cube, grain size 0.25 μ m) while maintaining a pH of 3.0 and a pAg of 7.7. After returning the pH to 5.9, the mixture was desalted by a conventional method, and a mixture represented by the following formula 6 was added at 5 mg per mol of silver halide.

The resulting emulsion was sensitized with sulfur, and the sensitizing dye represented by the following formula 7 was added at 60 mg per mol of silver halide. To this mixture were added 70 mg of 1-phenyl-5-mercaptotetrazole and 1.2 g of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene per mol of silver halide. After ripening was

stopped by adding gelatin, 4 g of hydroquinone, 3 g of potassium bromide, 5 g of saponin and 2 g of a styre-ne-maleic acid copolymer as a thickening agent and 3 g of an ethyl acrylate polymer latex were added to yield an emulsion layer coating solution.

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Formula 6

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

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Formula 7

CH₃ CH₃

$$CH = CH - CH - CH$$

$$C_2H_5$$

$$C_2H_5$$

$$C_2H_5$$

Preparation of emulsion protective layer coating solution

50 g of gelatin was dissolued in 1000 ml of water.

To this solution were added 1 g of potassium bromide and 40 g of a 1% aqueous solution of 1-decyl-2-(3-isopentyl)succinate-2-sodium sulfonate as an extender, followed by addition of a matting agent listed in Tables 2 through 4 to yield an emulsion protective layer coating solution.

Using the coating solutions thus obtained, a backing layer and a backing protective layer were simultaneously coated on one face of a subbed polyethylene terephthalate base of $100 \, \mu m$ in thickness to be a gelatin amount of $2 \, g/m^2$ and $1 \, g/m^2$, respectively. Subsequently, the other face was coated with an emulsion layer and an emulsion protective layer at the same time so that the amount of silver coated on the emulsion layer became $3.8 \, g/m^2$, the amount of gelatin coated on the emulsion layer became $1.5 \, g/m^2$ and the amount of gelatin coated on the emulsion protective layer became $1.0 \, g/m^2$.

For a subbing layer for the backing layer, a polyethyleneterephthalate base was subjected to corona discharge treatment and coated with a coating solution containing a compound shown in Table 2 and hexamethyleneaziridine, and then the base was subjected to hot drying at 50°C for 60 minutes.

The emulsion protective layer contained formaldehyde added at 8 mg per gram of the gelatin on the emulsion layer side. A hardener listed in Table 4 was added to the backing protective layer.

The samples thus obtained were prepared as sheet products and automatically transported in an atmosphere of 23°C and 80% RH using the facsimile plotter PT-503 (produced by Matsushita Graphic Communications Systems, Inc.) to evaluate their transportability.

Transportability was evaluated on the basis of failure rate. Failure rates exceeding 1.0% hamper practical use.

The degree of hardening is expressed in the degree of swelling as calculated using the following equation 2.

Equation 2

5	$\label{eq:Degree} Degree of swelling = \frac{(amount of water absordes per m^2)}{(amount of gelatin per m^2)}$ (value obtained after water immersion at 23°C for 10 seconds) According to the invention, degree of swelling is preferably not less than 2. The results are shown in Tables 2 through 4.
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Table 2

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İ		Subbin	g layer	er Emulsion layer							
Sample No.		of backing layer		Matting agent						Lubricant	
		Kind	Amount	Kind	Grain size	Amount	Kind	Grain size	Amount	Kind	Amount
			g/m ²		μm	mg/m ²		μm	mg/m ²		mg/m ²
1	Comparative			РММА	3.8	50	Silica	3.2	200	_	
2	Comparative	_		PMMA	3.8	50	Silica	3.2	200		
3	Comparative			РММА	3.8	50	Silica	3.2	200		
4	Inventive			РММА	3.8	50	Silica	3.2	200	_	
5	Inventive	_	_	РММА	3.8	50	Silica	3.2	200	_	
6	Inventive	_		РММА	3.8	50	Silica	3.2	200		
7	Inventive	1	_	РММА	3.8	50	Silica	3.2	200	_	_
8	Inventive	_	_	РММА	3.8	50	Silica	3.2	200	_	_
9	Inventive	-		РММА	3.8	50	Silica	3.2	200		_
10	Inventive			РММА	3.8	50	Silica	3.2	200	_	_
11	Inventive	_	_	РММА	3.8	50	Silica	3.2	200	_	_
12	Inventive		_	РММА	3.8	50	Silica	3.2	200	_	_
13	Inventive	_	_	РММА	3.8	50	Silica	3.2	200	_	_
14	Inventive	_	_	РММА	3.8	50	Silica	3.2	200	_	_
15	Inventive	_	_	PMMA	3.8	50	Silica	3.2	200	_	_
16	Inventive	_	_	РММА	3.8	50	Silica	3.2	200	_	_
17	Inventive	_	_	РММА	3.8	50	Silica	3.2	200	_	_
18	Inventive	_	_	PMMA	3.8	50	Silica	3.2	200	L-21	2.0
19	Inventive	_	_	РММА	3.8	50	Silica	3.2	200	L-21	2.0
20	Inventive	_	_		-	_	Silica	3.2	200	L-21	2.0
21	Inventive	_	_	_	-	_	Silica	3.2	200	L-21	2.0
22	Inventive			РММА	4.8	50	Silica	3.2	200		
23	Inventive	*ZnO ₂	0.5	РММА	3.8	50	Silica	3.2	200	L-21	2.0
24	Inventive	P-4	0.5	РММА	3.8	50	Silica	3.2	200	L-21	2.0
25	Inventive	P-21	0.5	PMMA	3.8	50	Silica	3.2	200	L-21	2.0
26	Inventive	P-22	0.5	РММА	3.8	50	Silica	3.2	200	L-21	2.0

^{*} A very small amount of Sb is doped in ${\rm ZnO_2}$

Table 3

Amount mg/m^2 2.0 2.0 2.0 2.0 2.0 2.0 20.0 2.0 2.0 2.0 2.0 2.0 20.0 160.0 2.0 2.0 2.0

2.0

L-21

			•		Backin	σ lave:	r		
Sample No.			ing ag	ent in ayer	Matti	ng age		Lubr	cicant
		Kind	Grain size	Amount	Kind	Grain size	Amount		Amount
			μm	mg/m ²		μm	mg/m ²	mg/m ²	mg/m ²
1	Comparative				PMMA	12.5	200	L-21	2.0
2	Comparative		_	_	PMMA	16.2	200	L-21	2.0
3	Comparative		_	_	PMMA	22.0	200	L-21	2.0
4	Inventive	PMMA	12.5	200	_	_		L-21	2.0
5	Inventive	PMMA	12.5	200	_			L-21	2.0
6	Inventive	PMMA	12.5	200			_	L-22	2.0
7	Inventive	PMMA	12.5	200			_	L-22	20.0
8	Inventive	PMMA	12.5	200		_	_	L-10	2.0
9	Inventive	PMMA	16.2	200	_	-		L-21	2.0
10	Inventive	PMMA	16.2	200			_	L-22	2.0
11	Inventive	PMMA	22.0	200	_		_	L-21	2.0
12	Inventive	PMMA	22.0	200	_		_	L-21	2.0
13	Inventive	PMMA	12.5	200	_	_	_	L-21	20.0
14	Inventive	PMMA	12.5	200	_	_	_	L-21	160.0
15	Inventive	РММА	12.5	200	PMMA	3.5	50	L-21	2.0
16	Inventive	РММА	16.2	200	РММА	3.5	50	L-21	2.0
17	Inventive	PMMA	22.0	200	PMMA	3.5	50	L-21	2.0
18	Inventive	PMMA	12.5	200		_		_	_
19	Inventive	PMMA	12.5	200		_	_	L-21	2.0
20	Inventive	PMMA	12.5	_	_	_		_	_
21	Inventive	PMMA	12.5	_	_	_	_	L-21	2.0
22	Inventive	PMMA	12.5	200	_	_	_	L-21	2.0
23	Inventive	PMMA	12.5	200	_	-	_	L-21	2.0
24	Inventive	РММА	12.5	200	_	_	_	L-21	2.0
25	Inventive	PMMA	12.5	200	<u> </u>	_	_	L-21	2.0
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Inventive

PMMA

12.5

200

Table 4

5			n	king lay		
				Transpor-		
	Sample		Degree of hardening			tation
	No			Amount	Degree	failure
10	-		Hardener	mg/gG	of swelling	rate (%)
	1	Comparative	Formalin	8.0	1.2	2.7
	2	Comparative	Formalin	8.0	1.2	2.8
15	3	Comparative	Formalin	8.0	1.2	1.9
	4	Inventive	Formalin	8.0	1.2	0.5
	5	Inventive	Formalin	8.0	2.6	0.9
	6	Inventive	Formalin	8.0	1.2	0.7
20	7	Inventive	Formalin	8.0	1.2	0.3
	8	Inventive	Formalin	8.0	1.2	0.8
	9	Inventive	Formalin	8.0	1.2	0.4
25	10	Inventive	Formalin	8.0	1.2	0.7
25	11	Inventive	Formalin	8.0	1.2	0.2
	12	Inventive	Formalin	8.0	2.5	0.7
	13	Inventive	Formalin	8.0	1.2	0.6
30	14	Inventive	Formalin	8.0	1.2	0.8
	15	Inventive	Formalin	8.0	1.2	0.2
	16	Inventive	Formalin	8.0	1.2	0.2
	17	Inventive	Formalin	8.0	1.2	0.0
35	18	Inventive	Formalin	8.0	1.2	0.2
	19	Inventive	Formalin	8.0	1.2	0.3
	20	Inventive	Formalin	8.0	1.2	0.4
40	21	Inventive	Formalin	8.0	1.2	0.3
	22	Inventive	Formalin	8.0	1.2	0.3
	23	Inventive	Formalin	8.0	1.2	0.1
	24	Inventive	Formalin	8.0	1.2	0.0
45	25	Inventive	Formalin	8.0	1.2	0.1
	26	Inventive	Formalin	8.0	1.2	0.0

50 Grain size of matting agent: Volume-average grain diameter determined using the Coulter counter PMMA: Polymethyl methacrylate

Amount of hardener: Figures in mg/gG are mg numbers per gram of the gelatin in backing layer.

55 Claims

1. A silver halide photographic light-sensitive material comprising a support and provided thereon, a silver

halide emulsion layer and at least two backing layers on the support opposite to said silver halide emulsion layer, wherein an uppermost layer of said silver halide emulsion layer or an uppermost layer of said backing layers contains a lubricant, and a backing layer other than said uppermost backing layer contains a matting agent having an average particle size of more than $10\mu m$.

- 2. The material of claim 1, wherein an uppermost layer of said silver halide emulsion layer and an uppermost layer of said backing layers.contains a lubricant, and a backing layer other than said uppermost backing layer contains a matting agent having an average particle size of more than 10μm.
- 10 3. The material of claim 1, wherein the content of the matting agent is 1 mg/m² to 1000 mg/m².
 - 4. The material of claim 1, wherein the matting agent has an average particle size of not more than 30μm.
- 5. The material of claim 1, wherein said material further contains a water-soluble dye having an absorption maximum at a wavelength of not less than 670 nm.
 - 6. The material of claim 5, wherein said dye is selected from the group consisting of compounds represented by the following Formulas Ia, Ib, Ic, II, III and IV,

Formula Ia

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Formula Ib

Formula Ic

wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 independently represent an alkyl group, Y_1 and Y_2 independently represent a group of non-metal atoms necessary to form a pyrrolopyridine ring, provided that the ring of Y_1 contains a

$$\geqslant$$
N⁺-R₁

group and the ring of Y2 contains a

$$N^{+}-R_{4}$$

group, at least two of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Y_1 and Y_2 represent acid residues or groups having -CH₂CH₂OR wherein R represents a hydrogen atom or an alkyl group, L represents a methine group, X^- represents an anion, m represents an integer of 4 or 5, and n represents an integer of 1 or 2.

Formula II

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$$(MO_3S)_{\overline{p}}Q - NHCO - C - C = L - (L = L)_{\overline{n}}C - C - CONH - Q + (SO_3M)_{\overline{p}}$$

$$N C C N$$

$$N C C N$$

$$N C N$$

$$N C N$$

$$N C R$$

$$N C R$$

wherein Q represents an aliphatic group or an aromatic group, R represents a hydrogen atom, an aliphatic group or an aromatic group, M represents a cation, L represents a methine group, n is 0,1 or 2, and p is 1 or 2.

Formula III

$$Z_{1}$$

$$R_{2}$$

$$R_{3}$$

$$R_{6}$$

$$R_{5}$$

$$R_{6}$$

$$R_{1}$$

$$R_{1}$$

$$R_{1}$$

$$R_{2}$$

$$R_{3}$$

$$R_{6}$$

$$R_{5}$$

$$R_{5}$$

$$R_{2}$$

$$R_{4}$$

$$R_{4}$$

$$R_{4}$$

$$R_{4}$$

$$R_{5}$$

$$R_{7}$$

$$R_{1}$$

wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_5 independently represent an alkyl group, Z_1 and Z_2 independently represent a group of non-metal atoms necessary to form a benzo-condensed ring or a naphtho-condensed ring, at least four of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Z_1 and Z_2 represent acid residues, L represents a methine group, X^- represents an anion, and n is 1 or 2.

Formula IV

$$(V_1)_{n-1} \qquad (V_2)_{m-1} \qquad 3$$

wherein V_1 and V_2 independently represent a sulfo group or a carboxyl group, n represents an integer of 1 to 4, m represents an integer of 1 to 3, provided that m and n is not simultaneously 1.

- 7. The material of claim 5, wherein said water-soluble dye is contained a lower layer of said backing layers.
- **8.** The material of claim 1, wherein said material further comprises a layer containing an electroconductive metal oxide or an organic electroconductive polymer.



EUROPEAN SEARCH REPORT

Application Number

EP 92 30 0086

Category	Citation of document with ind	ication, where appropriate,	Relevant	CLASSIFICATION OF THE	
	of relevant pass	ages	to claim	APPLICATION (Int. Cl.5)	
Y	GB-A-2 039 072 (FWI)		1-8	G03C1/76	
	* abstract *			G03C1/83	
	* page 2, line 13 - line	16 *		G03C1/95	
	* page 3, line 58 - line	61 *		-	
	* page 4, line 2 - line	18; claims 1-3 *			
Y	US-A-4 857 443 (AONO ET /	AL.)	1-8		
	* column 11, line 17 - 1	ine 38 *			
Y	EP-A-0 341 958 (KONICA)		5-7		
	* page 3, line 25 - page	13, line 47 *			
	* page 14, line 52 - line				
,	EP-A-0 303 176 (KONICA)		5-7		
ļ	* page 14, line 21 - page	24, line 56; claims			
	1,3 *				
γ	EP-A-0 388 908 (KONICA)		5-7		
	* page 8; example 24 *				
	* page 15, line 3 - line	5 *			
				TECHNICAL FIELDS	
		-		SEARCHED (Int. Cl.5)	
}					
				G03C	
	The present search report has bee	n drawn up for all claims			
	Place of search	Date of completion of the search	<u> </u>	Examiner	
	THE HAGUE	12 FEBRUARY 1992			
	CATEGORY OF CITED DOCUMENT	S T: theory or princip E: earlier patent do	ple underlying the	invention	
Y : part	icularly relevant if taken alone icularly relevant if combined with anoth	after the filing d	iste	•	
doc: A : tech	ament of the same category mological background	L: document cited			
O: non	-written disclosure rmediate document	& : member of the s	ame patent famil	v. corresponding	